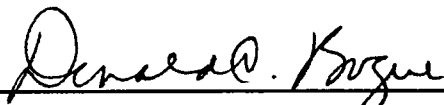
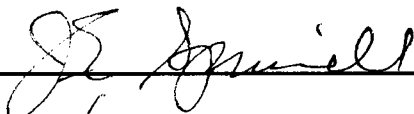


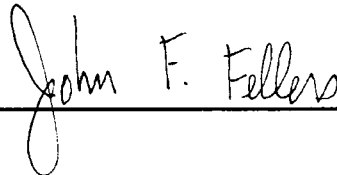
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I am submitting herewith a dissertation written by Wen-Chien Ko entitled "Time-Dependent Volume Effects in Polymers: Theory and Applications." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Polymer Engineering.

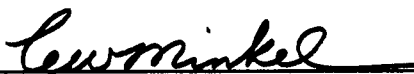

Donald C. Bogue, Major Professor

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and recommend its acceptance:





Accepted for the Council:


Vice Provost
and Dean of The Graduate School

**TIME-DEPENDENT VOLUME EFFECTS IN POLYMERS:
THEORY AND APPLICATIONS**

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Wen-Chien Ko

August 1989

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ABSTRACT

Time-dependent volume changes are important in polymer processing because the material almost always cools rapidly from a rubbery melt into a nonequilibrium solid. The present work is part of a continuing study on the development and use a new constitutive equation which includes volume (compressibility) effects in amorphous polymers. Experiments and analysis involving simultaneous pulling and cooling were done for testing the theory and for specifying the parameters in the equations. Applications of the theory to certain practical volume-related problems were then carried out: first, the cooling step in injection molding and, second, the development of residual stresses in free, quenched samples.

The theoretical framework for coupling volume changes with stress changes (prior work at the University of Tennessee) has been restated in a more tractable and slightly modified form in the present work. The new theory reduces naturally to the existing theories of linear elasticity, large-deformation viscoelasticity, and to equilibrium and rate-dependent PVT equations.

The data of the present work came from measuring the force build-up in fiber-like polystyrene samples, which were subjected to simultaneous pulling and cooling, with cooling rates up to $3.3\text{ }^{\circ}\text{C}/\text{sec}$. In the analysis a set of two moduli and two time constants (with accompanying shift factors) are needed for the volume changes and stress changes, respectively. The time constants and associated shift factors were obtained from fitting the dilatometry data

of Greiner and Schwarzl and melt shear data of Racin. The modulus $G(T)$ as a function of temperature was estimated from literature data. Satisfactory fits with reasonable parameters were obtained, although the results depended strongly on the choice of the $G(T)$ function. The experiments were not definitive because the volume change data were not measured. Further testing on the theory is being continued in separate work.

The cooling step in injection molding was simulated by using the simple geometry of a thin slab and assuming that there were no temperature and pressure gradients in the plane along the flow direction. Before the cooling step, the gapwise temperature profile at the end of mold filling was approximated from the C-FLOW mold filling program, while the build-up of packing pressure was introduced as a forcing function, similar to the data of the Cornell group. Two cases were studied as regards the compressibility (PVT) behavior: an equilibrium case, and a time-dependent case. While both could be fit to the data, the time-dependent case allowed one to use a more reasonable PVT equation.

The problem of inducing residual stresses in rapidly quenched slabs is a classical one, with the basic theory being that of Lee, Rogers and Woo (LRW), and special cases of it. The result of the LRW theory is an integral, which is not easily modified to change the inherent rheological assumptions. In the present work the problem is reformulated on a layer-by-layer basis, such that the computer simulation is directly connected to the physical problem. In the cases studied the PVT behavior was taken as time-dependent (unlike the equilibrium assumption of the LRW theory), with a discontinuous assumption for

the modulus (like the special case of the LRW theory due to Aggarwala and Saibel). In this latter case the modulus is taken to be either zero (completely “fluid”) or finite (completely “solid” with a modulus G_g), depending on the temperature relative to the glass transition. With the modulus G_g as an adjustable parameter, good fits to residual stress data from the literature can be made, but the numerical value of G_g is more reasonable when the PVT behavior is time-dependent. There are also literature data for the density profile across the slab and these are in qualitative agreement with the analysis. The inability to measure densities *in situ* precludes a direct quantitative comparison.

The complexity of the problems, involving time-dependent behavior in the rubbery, transition and glassy states, means that a large amount of independent data are needed. In the absence of such data simplified cases with adjustable parameters must be treated. These cases illustrate, however, the usefulness and tractability of the generalized theory in problems of practical interest.

CHAPTER 1

INTRODUCTION

Most polymer processing operations involve a flow step in the molten state and a cooling step to produce a solid state. During cooling volume contraction occurs, typically not uniformly through the part, affecting the dimensions and also the properties. Packing the mold (to pre-compensate the later contraction) and cooling the melt rapidly in injection molding are good examples of practical processes involving volume changes. In addition to these complications one almost always “freezes in” molecular orientation produced by the prior flow — intentionally in the case of fiber spinning, but often unintentionally, as in the case of injection molding. No matter whether it is intentional or not, frozen-in orientation (and frozen-in nonequilibrium volume) can have a significant effect on the final properties [166,151]. Also, of course, the occurrence and later development of crystal structure is important [151,164,198]. In the present study, however, attention is limited to amorphous polymers.

To solve polymer processing problems involving rapid cooling, one must deal with compressibility effects, both those imposed directly by the temperature changes and those imposed indirectly through the build-up of stresses. Unfortunately, existing rheological theory can deal with melt deformations and also with solid deformations, but little of it bridges the gap [161,97]. That

is, at temperatures above the glass transition T_g , a viscoelasticity model is used to describe polymer stress-strain behavior [57,10], while at temperatures below T_g , the equations are usually linear elasticity theory [194,175]. Since temperature ranges of interest typically include T_g , it would be useful to have a constitutive equation applicable both above and below T_g . However, viscoelasticity theory, as it is actually applied, is limited to incompressible materials [10]. While classical linear elasticity theory is not restricted to incompressible materials, it is, like all theories of elasticity, a theory for equilibrium stress-strain response and cannot deal with time effects [194]. Consequently, if one wishes to describe time-dependent aging behavior of amorphous glasses, an elastic equation is not adequate. For such cases a time-dependent equation of state (a PVT relation with time constants and shift factors) must be employed [166,37,173,157,27,168,139,181].

Although there is now a large literature on volume changes (aging) in the glassy state [166,168,90,91,138,19,140,139,181], work on rate effects in PVT equations has not been done extensively. In introducing compressibility effects in rheological theory, one might define the compressibility in terms of the second and/or third invariants of stress [133,132]. But with the complicated viscoelastic theories now being used, no simple relationship like this is obvious. This is an area that needs further study. However, here at the University of Tennessee the compressibility problem has been attacked by Bogue and coworkers [161,87] as a long-range study. In particular, Snow and Bogue [161] set down a generalized integral equation including compressibility in the rubbery and

glassy states, which allows one in principle to deal with volume and orientation effects in general, both as they occur at the present time and also as they are “remembered” from some prior history. The integral statement there is quite complicated, however, and is difficult to execute except in the simplest deformations. It was then one of the objectives of this work to continue the theoretical development in this area. Fortunately, it has been possible to restate the prior integral formulation in a more tractable form, as will be presented subsequently in this dissertation (and as was published recently by Ko and Bogue [87]). Experiments, started as a part of the author’s MS thesis, were continued in the present work and analyzed with the Ko-Bogue equations; these experiments involve the stress-time response of fiber-like samples which are subjected to rapid cooling at the same time as they are pulled.

Examples of volume-related problems of practical interest are the cooling step in injection molding and the related problem of residual stresses. In prior literature work on the cooling step in injection molding [191,192,80,77], equilibrium PVT relationships have been assumed. One of the objectives of this work was to re-do such analyses with a time-dependent PVT equation and to make comparisons with literature data [191,77]. There is a considerable literature on the residual stresses in rapidly quenched samples (coming from thermal gradients) [162,149,155,167,75] and in injection molded products (coming from thermal gradients and the flow history) [30,74,75,152,199,174,67,176]. Some of it came from work done here at the University of Tennessee by Bogue and coworkers [207,100,206,186]. The classical theories on residual stresses cre-

ated by thermal gradients (the so-called volume-induced residual stresses) have assumed instantaneous PVT response [99,1], the only time-dependence being that associated with the stress term. On the basis of prior studies of Bogue and his students [207,100,206,186] it was concluded that the reverse assumption is probably more reasonable: time-dependence in the PVT response with instantaneous response in the stress behavior (at least after the material has cooled below T_g). A final objective, then, was to recast residual stress theory in a more tractable form than has been done classically — in such a way that time-dependent PVT response can be incorporated.

CHAPTER 2

BACKGROUND

The literature which is relevant to the present work will now be reviewed. The subjects of elasticity and viscoelasticity theories will first be discussed. The review will then be extended to the rate-dependent volume equations and followed by the analyses of filling, packing and cooling steps in injection molding. Finally a brief survey of the studies on various kinds of residual stresses will be presented.

2.1 Elasticity and Viscoelasticity Theories

The stress-strain behavior of polymers is generally considered to be elastic or viscoelastic, depending on the particular polymer and the experimental conditions, such as the temperature relative to the glass transition and the experimental time scales. A perfectly elastic solid responds instantaneously to the applied stresses by producing equilibrium strains [175]. If there are time effects in the response, then one must use viscoelasticity theory [37]. Stress relaxation and elastic recovery are two well-known time dependent phenomena that illustrate the viscoelastic nature of polymers [166,37]. Various forms of elasticity and viscoelasticity theories will now be discussed.

2.1.1 Linear Elasticity Theory

Linear elasticity theory, derived from continuum mechanics, is usually used to describe the small deformation of glassy polymers. Such materials exhibit volume changes upon deformation, even at constant temperature [175]. In contrast, large-deformation (or nonlinear) elasticity theory, based on strain energy functions, is applied to rubbers subjected to large strains, which will not be included in this discussion.

The linear elasticity theory assumes that stress and strain are linearly proportional in the form

$$\sigma_{ij} = C_{ijkl} \tilde{\epsilon}_{kl} \quad (2.1)$$

where C_{ijkl} is an array of elastic moduli and $\tilde{\epsilon}_{kl}$ is the linear strain tensor [194]. Eqn. (2.1) is a generalized form of Hooke's law and is applicable to anisotropic materials. There are 81 components of C_{ijkl} . Due to the symmetry of the stress and strain tensors, only 36 of these moduli are independent [194]. Most real materials have some inherent symmetry which reduces the number of independent moduli further. Ultimately, for a completely isotropic material, there are only two moduli as shown in the classical linear theory of elasticity (i.e. simple Hooke's law) [194]:

$$\sigma_{ij} = \lambda \tilde{\epsilon}_{kk} \delta_{ij} + 2G\tilde{\epsilon}_{ij} \quad (2.2)$$

where λ and G are the so-called Lamé constants. Eqn. (2.2) may be written in other equivalent forms in terms of Poisson's ratio [175]. The quantity $\tilde{\epsilon}_{kk}$ in

Eqn. (2.2) is related to the volume change through the relationship [175]

$$\tilde{\epsilon}_{kk} = \frac{\Delta V}{V_o} \quad (2.3)$$

For an incompressible material the Poisson's ratio is $1/2$ and $\tilde{\epsilon}_{kk} \rightarrow 0$; these two restrictions are possible only if $\lambda \rightarrow \infty$ and thus $\lambda\tilde{\epsilon}_{kk}$ is indeterminate. Eqn. (2.2) then takes the form [34]

$$\sigma_{ij} = -\mathcal{P}\delta_{ij} + 2G\tilde{\epsilon}_{ij} \quad (2.4)$$

where $\mathcal{P}$ is an indeterminate scalar.

When temperature is not constant, thermal stresses from volume changes should be considered. This effect was treated by Timoshenko and Goodier [175] and written in the following equation

$$\sigma_{ij} = \left[\lambda\tilde{\epsilon}_{kk} - \alpha\left(\frac{2}{3}G + \lambda\right)(T - T_o) \right] \delta_{ij} + 2G\tilde{\epsilon}_{ij} \quad (2.5)$$

where α is the coefficient of thermal expansion, T_o is the reference temperature. Eqn. (2.5) may be motivated by linearizing the volume change with temperature

$$V = V_o - \alpha(T - T_o)V_o \quad (2.6)$$

where one assumes $\alpha(T - T_o)$ is small. If there is no applied stress Eqn. (2.5) gives

$$\sigma_{kk} = 0 = 3\lambda\tilde{\epsilon}_{kk} - \alpha(2G + 3\lambda)(T - T_o) + 2G\tilde{\epsilon}_{kk} \quad (2.7)$$

which, using Eqn. (2.3), reduces to Eqn. (2.6). By comparing this equation with Eqn. (2.2) for the isothermal case, one sees that volume changes in glassy polymers may come from either varying the temperature or applying stresses.

2.1.2 Incompressible Viscoelasticity Theory

The theory for describing viscoelastic stress-strain behavior during isothermal deformation is well-developed and has been presented in many forms. Basically these models are of two types: differential-type models and integral-type models. Considerable details can be found in the books of Bird, Armstrong, and Hassager [10], Tanner [172], and Larson [98]. However, most of the existing viscoelasticity theories are incompressible in the sense of Poisson's ratio — that is, no deformation-induced volume changes occur at constant temperature.

The classical differential-type viscoelastic equation, due to Maxwell [111], may be written as

$$\tau_{ij} + \lambda \dot{\tau}_{ij} = G \lambda \dot{\gamma}_{ij} \quad (2.8)$$

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

$$\sigma_{ij} = -P\delta_{ij} + \tau_{ij} \quad (2.9)$$

Eqn. (2.8) is most readily motivated by a mechanical model consisting of a spring (elastic element) and a dashpot (viscous element) in series. Such a differential model can be generalized to multiple time constants by setting up simultaneous differential equations. But they cannot deal easily with discontinuous histories, such as the change from shear to elongational flow at the exit of a die in melt spinning.

If λ is constant, Eqn. (2.8) may be integrated to give

$$\tau_{ij} = \int_{-\infty}^t G \exp\left(\frac{-(t-t')}{\lambda}\right) \dot{\gamma}(t, t') dt' \quad (2.10)$$

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

$$\tau_{ij} = \int_{-\infty}^t \sum_n G_n \exp\left(\frac{-(t-t')}{\lambda_n}\right) \dot{\gamma}(t, t') dt' \quad (2.11)$$

where the sum is over the number of Maxwell elements. The Boltzmann superposition principle [13] assumes that the stresses may be obtained by adding small step strains over past time, and leads to the following constitutive equation:

$$\tau_{ij} = \int_{-\infty}^t G(t, t') \dot{\gamma}(t, t') dt' \quad (2.12)$$

Linear viscoelasticity theory is restricted to describing phenomena associated with small strains and strain rates. To describe more general deformations nonlinear viscoelasticity theory is required.

Nonlinear viscoelastic equations of the differential type are of the same general form as Eqn. (2.8). However, the dot, which denotes ordinary time derivative for the linear viscoelasticity, represents one of several kinds of more complicated time derivatives in the nonlinear equations [208,128,129,123,195,44], as reviewed by Bird, Armstrong, and Hassager [10]. An embedded coordinate system which translates and rotates with the material was first considered

by Zaremba [208], which is referred to as a corotational coordinate system. Such a coordinate system describes deformations which are independent of the translation and rigid rotation of material. Oldroyd [128] considered a coordinate system which translates, rotates and deforms with the material, which he termed a convected coordinate system. Other generalizations were described by Noll [123], White and Metzner [195], Goddard and Miller [44], and Williams and Bird [203]. When these complicated time derivatives are adopted in the constitutive equations, one encounters a number of material constants. However, the White and Metzner model [195] is comparatively simple and describes important features of nonlinear viscoelasticity [68,69]. It may be written as

$$\tau_{ij} + \lambda \frac{\delta \tau_{ij}}{\delta t} = G \lambda d_{ij} \quad (2.13)$$

where

$$d_{ij} = V_{i|j} + V_{j|i} \quad (2.14)$$

$$\frac{\delta \tau_{ij}}{\delta t} = \frac{D \tau_{ij}}{Dt} - V_{i|k} \tau_{kj} - V_{j|k} \tau_{ik} \quad (2.15)$$

where $D()/Dt$ is the substantial time derivative. The Cartesian coordinate system is understood throughout this dissertation. White and Metzner [195] proposed that the modulus G is constant and the relaxation time λ is a function of the second invariant of d_{ij} , that is,

$$\lambda = \lambda(II_d) = \lambda(tr d_{ij}^2) \quad (2.16)$$

The analogous integral forms of these nonlinear differential models are not easily obtained; however, Bird, Armstrong, and Hassager [10] have presented several

of the corresponding pairs. A general method for generalizing the viscoelastic equations is based on the assumption that the stress may be expressed as a functional over the strain history. An integral expansion of the functional gives the result that the stress may be expressed as a series of multiple integrals [49,26]. If only a few terms are retained, this general expansion may be reduced to many of the existing models [10].

Another method of generalizing a viscoelastic equation is introducing time effects into the nonlinear elasticity theory. This was first done by Bernstein, Kearsley, and Zapas [8,9] and gives the following form

$$\sigma_{ij} = -P\delta_{ij} + 2 \int_{-\infty}^t \left[\frac{\partial U}{\partial I} C_{ij}^{-1} - \frac{\partial U}{\partial II} C_{ij} \right] dt' \quad (2.17)$$

where U denotes a time-dependent strain energy function, C_{ij}^{-1} and C_{ij} are the Finger and Cauchy relative strain tensors, I and II are the first and second invariants of C_{ij}^{-1} , and δ_{ij} is the Kronecker delta.

The above equation and most other integral viscoelastic theory may be summarized by [10,58,172,12,196]

$$\sigma_{ij} = -P\delta_{ij} + \int_{-\infty}^t \left[M_1(t-t') C_{ij}^{-1}(t,t') - M_2(t-t') C_{ij}(t,t') \right] dt' \quad (2.18)$$

where M_1 and M_2 are memory functions. Generally, the memory functions depend on the past time t' , the present time t , and various invariants of the strain and deformation rate tensors [10,58,17,18,187]. For many problems, M_2 may be taken equal to zero which reduces equation (2-11) to Lodge's fluid [10,58]. A simple form for M_1 may be expressed in terms of either discrete or

continuous relaxation spectra

$$M_1(t - t') = \sum_n \frac{G_n}{\tau_n} \exp\left(\frac{-(t - t')}{\tau_n}\right) \quad (2.19)$$

or

$$M_1(t - t') = \int_{-\infty}^{\infty} \frac{H(\tau)}{\tau} \exp\left(\frac{-(t - t')}{\tau}\right) d \ln \tau \quad (2.20)$$

where G_n (or $H(\tau)$) are the elastic moduli (or the continuous spectra), and τ_n (or τ) are the relaxation time.

Another important form of $M_1(t - t')$ has been suggested by Bogue [11] and later modified by Bogue and White [12]. Their equation has been found to correlate data on bulk polymers successfully [68,115,70,170], and is of the form

$$M_1(t - t') = \sum_{i=1}^n \frac{G_i}{\tau_{i,eff}} \exp\left(\frac{-(t - t')}{\tau_{i,eff}}\right) \quad (2.21)$$

where

$$\tau_{i,eff} = \frac{\tau_i}{1 + a \tau_i \langle II_d^{1/2} \rangle} \quad (2.22)$$

$$\langle II_d^{1/2} \rangle = \frac{1}{s} \int_0^s |II_d|^{1/2} ds \quad (2.23)$$

where $s = t - t'$ is the elapsed time from “now” to “then” (some time in the past).

The previous formulations are for isothermal behavior. If the temperature during any one experiment is held constant, the time-temperature superposition principle can be used to normalize together experiments done at different deformation rates or different temperatures [36,204]. A master curve may be obtained through a reference time constant with a shift factor $a_T(T)$ given by

$$\tau(T) = \tau_0 a_T(T) \quad (2.24)$$

where

$$\log a_T(T) = \frac{-C_1(T - T_o)}{C_2 + T - T_o} \quad (2.25)$$

where τ_o is the relaxation time at a reference temperature T_o , and $a_T(T)$ is a shift factor for the temperature T . Eqn. (2.25), referred to as the Williams-Landel-Ferry (WLF) equation, is one of the explicit forms of the shift factors which expresses the temperature-dependence of the relaxation time [37]. However, if the temperature changes with time during an experiment, some type of integration must be done to deal with the nonisothermal history.

The nonisothermal treatment was first formalized by Morland and Lee [121], who generalized the linear Maxwell model to include nonisothermal effects. A nonlinear, nonisothermal differential model was derived by Marrucci [104] and applied to the melt spinning process by Fisher and Denn [39]. Matsui and Bogue [105,106], after carrying out systematic experimental studies [107,108], proposed a nonlinear, nonisothermal integral model

$$\sigma_{ij} = -P\delta_{ij} + \int_{-\infty}^t \sum_n \frac{G_n(t')}{\tau_n(t')} \exp\left[-\int_{t'}^t \frac{dt''}{\tau_n(t'')}\right] C_{ij}^{-1}(t, t') dt' \quad (2.26)$$

where $\tau_n(\bullet)$ was introduced to predict non-Newtonian viscosities and other non-linear effects and takes the form

$$\tau_n(\bullet) = \frac{\tau_n^o a_T[T(\bullet)]}{1 + b \langle II_d^{1/2} \rangle \tau_n^o a_T[T(\bullet)]} \quad (2.27)$$

where II_d is the second invariant of the deformation rate tensor and b is an empirical parameter. Analogous to the relation between the simple integral viscoelasticity (Eqn. (2.10)) and the differential Maxwell model (Eqn. (2.8)),

the Matsui and Bogue model (Eqn. (2.26)) should be a solution to Fisher and Denn's nonisothermal convected differential model [16].

All of the viscoelasticity theories discussed so far are restricted to polymer melts which are incompressible, as mentioned earlier. But when the temperature is lowered below T_g , this assumption is no longer satisfactory and thus a viscoelasticity theory including volume (compressibility) effects is necessary.

2.1.3 Compressible Viscoelasticity Theory

Classical viscoelasticity theory, as discussed above, does not include compressibility effects and therefore is not compatible with linear elasticity theory. Since the Poisson's ratio of rubbery materials is typically near 0.5, volume changes accompanying deformation can be safely neglected at temperatures significantly above T_g [58]. When the temperature goes through T_g and down into the glassy state, compressibility effects increasingly become more important. First, glassy polymers have a Poisson's ratio of about 0.3 and therefore significant volume changes are associated with the deformation [194]. Also, nonequilibrium volume changes owing to rapid cooling are often frozen-in, and time-dependent volume aging occurs in the glass [166]. A review of compressibility effects in the various forms discussed above has been given by Snow and Bogue [161], by Landel and Peng [97], and more recently by Ko and Bogue [87]. However, there is very little theoretical work on constitutive equations including compressibility and most of it has been done here at the University of Tennessee [161,87].

In introducing compressibility effects into rheological theory, one might re-

late the compressibility to the second and/or third invariants of stress [133,132]. But with the complicated viscoelasticity theories presently in use, no simple relationship like this is possible. Therefore, as the first effort, Snow and Bogue [161] set down a generalized integral equation which includes compressibility in the rubbery and glassy states. This generalized model is stated in terms of an isotropic volume term and an anisotropic deformation term as follows

$$\sigma_{ij} = \sigma_{ij}^v + \sigma_{ij}^s \quad (2.28)$$

where σ_{ij}^v is the stress from isotropic volume changes, and σ_{ij}^s is the stress from anisotropic deformations. The isotropic term is expressed by

$$\sigma_{ij}^v = -(P_o + \pi)\delta_{ij} + \delta_{ij} \int_{-\infty}^t \lambda^*(t') \exp\left[-\int_{t'}^t \frac{dt''}{\tau_\lambda(t'')}\right] \frac{d\phi_f(t')}{dt'} dt' \quad (2.29)$$

and the anisotropic term is given by

$$\sigma_{ij}^s = \int_{-\infty}^t \frac{G(t')}{\tau_G(t')} \exp\left[-\int_{t'}^t \frac{dt''}{\tau_G(t'')}\right] C_{ij}^{-1*}(t, t') dt' \quad (2.30)$$

where

$$\begin{aligned} \pi &= \bar{\lambda}^* \left[\left(\frac{V_o - V}{V_o} \right) - \bar{\alpha} (T - T_o) \right] \\ \phi_f &= \Delta\alpha (T - T_{ge}) - \Delta\kappa (P - P_{ge}) \\ P &= -\frac{1}{3} \sigma_{kk} \\ C_{ij}^{-1*} &= C_{ij}^{-1} - \delta_{ij} - \frac{2}{3} \left(\frac{V(t) - V(t')}{V(t')} \right) \delta_{ij} \end{aligned}$$

where $\bar{\lambda}^*$ and $\bar{\alpha}$ are a "suitably averaged" bulk modulus and coefficient of thermal expansion, respectively; and $\Delta\alpha = \alpha_r(t') - \alpha_g(t')$; $\Delta\kappa = \kappa_r(t') - \kappa_g(t')$; α and κ are, respectively, the coefficients of thermal expansion and pressure compressibility in the rubbery (r) and glassy (g) states; and $\tau_\lambda(\bullet)$ and $\tau_G(\bullet)$ are the

relaxation times associated with the local and long-range motions of polymer molecules [161].

This generalized equation allows one in principle to deal with volume and orientation effects, both as they occur at the present time and also as they are “remembered” from prior history. In particular, it was shown to reduce to several special cases: (1) linear elasticity theory, (2) existing (incompressible) viscoelasticity theory, (3) a one-parameter volume rate equation, and (4) an equilibrium PVT equation. However, the integral statement there is quite complicated and difficult to execute on a computer except in the simplest deformations.

Recently the prior formulation was simplified by Ko and Bogue [87] to a more tractable and slightly modified form. The new formulation consists of a set of simultaneous equations: a generalized $\wp$ VT rate equation, a generalized stress-strain (constitutive) equation, and a constraint of kinematics. By introducing a scalar stress ($\wp$) to couple the volume changes with stress changes, the compressibility effects can easily be calculated and applied to volume-related problems. The details of the new theory are shown in Chapter 3 and in the paper of Ko and Bogue [87] (Appendix A).

2.2 Rate-Dependent Volume Equations

The nonequilibrium volume behavior of amorphous polymers has been extensively studied [138,20,143,90,91,92,19,21]. Experimental work has been re-

viewed by Struik [166] and Tant and Wilkes [173], Hutchinson and Ruddy [66], and Tribone et al. [181]. Rate equations with accompanying shift factors have been summarized by Kovacs et al. [138,90,92], Ramos et al. [139], Tribone et al. [181], and also treated in some detail at a recent symposium of the Society of Rheology [168]. In the discussion here volume recovery along with the shift factors for the relaxation times will be emphasized.

2.2.1 Free Volume Theory

The idea of free volume (or fractional “holes”) was originally used to describe the viscous behavior of low molecular weight liquids and latter applied to polymers, especially in regard to glass transition phenomena [35,2]. The free volume theory is intuitively simple and also useful in describing many aspects of the vitrification of amorphous polymers [166].

According to Fox and Flory [40], the free volume, V_f , is defined as the difference in the occupied volume, V_g , and the total volume, V , as follows:

$$V_f = V - V_g \quad (2.31)$$

The occupied volume (denoted above as V_g to imply the glassy volume) may be thought of as that portion of the total volume taken up by the molecules when they are “completely packed”. There are several different definitions of free volume [156,183], for example, from a microscopic viewpoint by Turnbull and Cohen [183]. But the basic principles are the same and have been summarized by Rusch [146]. As illustrated in Figure 2.1, the free volume is comprised of an

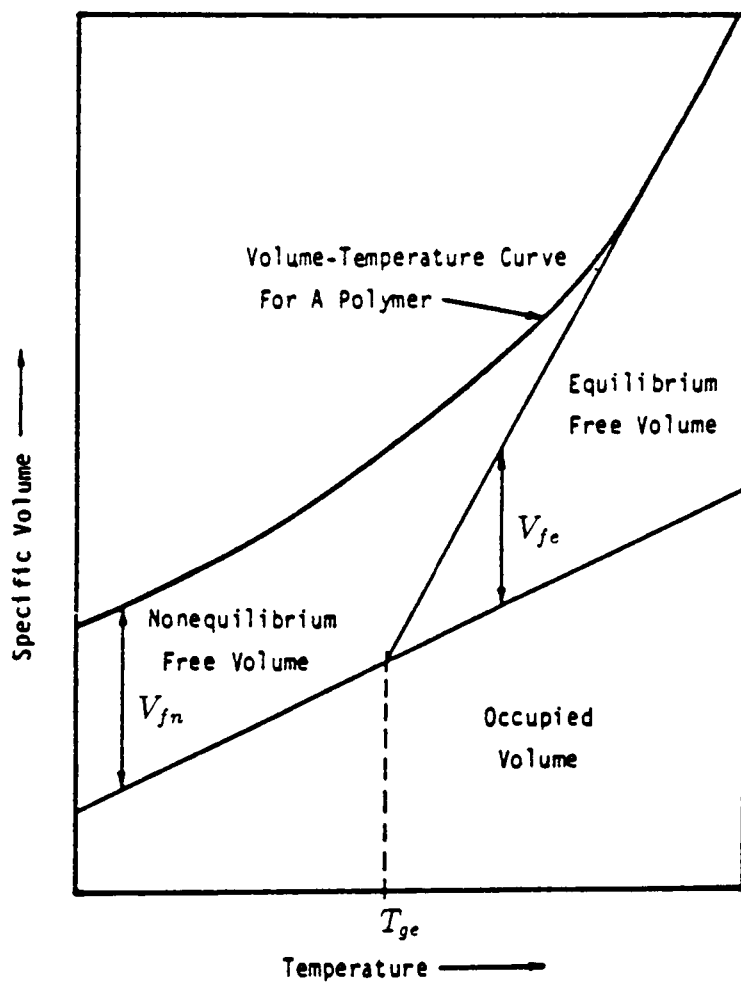


Figure 2.1: Volume-temperature plot showing the free volume concept.

equilibrium portion, V_{fe} , and a nonequilibrium portion, V_{fn} . [146]

$$V_f = V_{fe} + V_{fn} \quad (2.32)$$

The temperature denoted by T_{ge} in Figure 2.1 represents the equilibrium T_g , which would be observed at an infinitely slow cooling rate. In such a case, there will be no free volume at temperatures below T_{ge} . While at temperatures above 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 .

The equilibrium volumes V_r and V_g may be defined in terms of an equilibrium reference volume V_o chosen at a reference temperature T_o , well above the glass transition. The equations for V_r and V_g lines, and for the equilibrium free volume V_{fe} are

$$V_r = V_o - \alpha_r (T_o - T) V_o \quad (2.33)$$

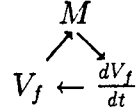
$$V_g = V_o - \alpha_r (T_o - T_{ge}) V_o - \alpha_g (T_{ge} - T) V_o \quad (2.34)$$

$$V_{fe} = V_r - V_g = V_o \Delta\alpha (T - T_{ge}) \quad (2.35)$$

where $\Delta\alpha = \alpha_r - \alpha_g$ is the effective coefficient of thermal expansion of the free volume.

If a polymer is cooled through its glass transition at a finite cooling rate, it will contain frozen-in (nonequilibrium) volume which provides a driving force for change. The rate of the approach to equilibrium depends on the molecular mobility. Following Struik [166], the free volume concept states that the molecular mobility primarily depends on the extent of packing, or in other words, on

the free volume. With increased packing, the mobility and the free volume both decrease. The rate of change of free volume, dV_f/dt , determines the free volume, V_f . The amount of free volume in turn determines the molecular mobility, M . The mobility then determines the rate of change of free volume. This cyclic interrelation may be represented symbolically as [166]



This closed loop scheme, which implies that volume recovery process is nonlinear, is an essential principle for understanding physical aging.

2.2.2 Volume Rate Equations

The free volume concept described above was used in developing many of the rate-dependent volume equations [138,90,91,19,20] to describe the nonequilibrium behavior of amorphous glasses. Tant and Wilkes [173] and Kovacs [90,91] have reviewed some of the theories, which may be classified into single- and multi-parameter models [90].

The simple, first-order rate equations proposed by Tool [178], Saito et al. [150], Davies and Jones [28], and Goldbach and Rehage [45,46] are of the following form at constant pressure:

$$\frac{d(V - V_\infty)}{dt} = -\frac{(V - V_\infty)}{\tau} \quad (2.36)$$

where V is the total volume, V_∞ is the equilibrium volume at infinite time, and τ is the relaxation time of the material. Kovacs [89] extended this equation to

include the effect of cooling on the occupied (glassy) volume as follows:

$$\frac{dV}{dt} = -\frac{(V - V_{\infty})}{\tau} - \alpha_g R V_{\infty} \quad (2.37)$$

Eqn. (2.37) may be restated in terms of the recoverable free volume, δ , as shown by Kovacs et al. [92].

$$\frac{d\delta}{dt} = -\frac{\delta}{\tau} - \Delta\alpha q \quad (2.38)$$

where q is the temperature gradient, $q = dT/dt$, and δ , a measure of the departure of the system from its equilibrium state, is defined by

$$\delta = \frac{(V - V_{\infty})}{V_{\infty}} = \frac{V}{V_{\infty}} - 1 \quad (2.39)$$

Equations in the form of Eqn. (2.37) or (2.38) are referred to by Kovacs et al. [90,92] as single-parameter models. The single relaxation mechanism in such equations is usually modeled after the WLF equation or some modification of it. The single-parameter model is simple and also quite useful qualitatively in describing many characteristics of the nonequilibrium behavior of glassy polymers. But it fails to describe memory effects in multiple temperature jumps involving cooling and reheating [90,91]. These discrepancies may arise in part from the different relaxation mechanisms for various hole sizes and the need for a distribution of relaxation times [138,91].

Turnbull and Cohen [183,25] suggested that the free volume may be distributed over holes of various sizes. There would thus be a distribution of holes larger than a critical size which allows mobility (the local motion of molecules). The mobility is therefore determined not only by the total free volume, but also

by the distribution of free volume; these cannot be described by a single relaxation time. During the past decade several multi-parameter models were advanced which utilize a distribution of relaxation times to accommodate memory effects in the nonequilibrium behavior of glassy polymers [138,91,19,20,122,29]. The spectrum of relaxation time depends not only on temperature but also on the instantaneous state of the system. Although the basic assumptions involved with all of the models are similar to those in the original models of Narayanaswamy [122] and Moynihan [29], we will here focus on the more recent approaches used by Kovacs and coworkers [138,91] and by Chow et al. [19,20].

Kovacs et al. [138,91] have found that by utilizing a distribution of relaxation time, the discrepancies seen in the single-parameter models are overcome. They assumed that there is a particular mode of molecular motion which controls a specific fraction δ_i of the total recoverable free volume δ . With this assumption they proposed the following equation for the volume recovery rate under constant pressure [91]

$$\frac{d\delta_i}{dt} = -\frac{\delta_i}{\tau_i} - \Delta\alpha_i q \quad (1 \leq i \leq N) \quad (2.40)$$

where

$$\delta = \sum_{i=1}^N \delta_i$$

$$\Delta\alpha = \alpha_r - \alpha_g = \sum_{i=1}^N \Delta\alpha_i = \Delta\alpha \sum_{i=1}^N g_i$$

where g_i , associated with τ_i , is defined by the “structural” relaxation spectrum $G(\tau_i)$, and τ_i is the relaxation time of element i :

$$\tau_i(T, \delta) = \tau_{i,r} \exp[-\theta(T - T_r)] \exp[-(1-x)\theta \delta / \Delta\alpha] \equiv \tau_{i,r} \mathbf{a}_T \mathbf{a}_\delta \quad (2.41)$$

where θ is a material constant which determines the contribution of temperature and x is an adjustable parameter which determines the relative contribution of "structure" to the τ_i ; that is, the effects from temperature and from the instantaneous state (the "structure") on the relaxation mechanism are introduced by the temperature shift factor a_T and by the "structure" shift factor a_δ . Experimental evaluation of the structure parameter x were shown by Hutchinson and Ruddy [66] and others [65,180].

Based on the Williams-Watts function [201], Chow et al. [19,20] proposed an integral model corresponding to Eqn. (2.40) as follows:

$$\delta(t) = \delta_o \varphi(t, t_o) - \Delta\alpha \int_{t_o}^t q \varphi(t, t') dt' \quad (2.42)$$

where $\varphi(t, t')$ is the Williams-Watts function [29]:

$$\varphi(t, t') = \exp \left[- \left(\int_{t'}^t \frac{dt''}{\tau(t'')} \right)^\beta \right] \quad (2.43)$$

where β is a measure of the width of relaxation time distribution and $0 < \beta \leq 1$. Such integral volume rate equations are readily adopted for discontinuous thermal histories, such as cooling followed by abrupt reheating in a complete process. But on the other hand, double integrals are involved, such that calculation becomes more complicated than for differential models, especially when structural effects (such as shown in Eqn. (2.41)) are considered for the shift factor. In all of these equations mentioned so far, including both the differential and integral types, the volume recovery is considered to take place under constant pressure.

The effect of pressure on volume recovery behavior has not so extensively studied as that of temperature. Most of the early studies of pressure effects are limited to polymer melts [113,112,130,109,127,134,158,126]. Review articles of experimental work are given by Parry and Tabor [130], Goldblatt and Porter [47], Tschoegl and coworkers [38,118,119,120], and Tribone et al. [181]. In analyses involving pressure, one must have pressure-volume-temperature (PVT) equations and there is an extensive literature on them. These include the empirical Tait equation [134,158,169], the extension of the WLF equation [38,118,120], the theoretical Simha-Somcynsky equation [157] and its simplified forms proposed by Hartmann and Haque [60,61], Zoller [210], Utracki [184,185], and more recently by Driscoll [32]. One notes that these PVT equations work well for polymer melts only; although some of them are stated to work as well for glasses, it is still questionable whether this is true or not.

Similar to the situation for PVT state equations, most existing pressure shift factors are concerned with polymer melts and more studies are needed for glasses. These pressure shift factors usually use the concept of free volume theory and take the same form as the temperature-dependent WLF equation [37]. McKinney and coworkers [113,112] proposed a WLF-like shift factor equation after systematic experiments on dynamic bulk compressibility (which is associated with the local motion of molecules) under high hydrostatic pressures. Tschoegl and coworkers [38,118,119,120] have also done much work on such equations for polymer melts by experiments of shearing and torsion (which are concerned with the long-range motion of molecules), although they produced

finally a quite complicated form (involving six constants). A general review of pressure effects is given by Driscoll [32].

More recently, the volume rate equation of Kovacs et al. (i.e., Eqn. (2.40) has been extended to combine the effects of pressure and temperature [139]. Following the original framework, Ramos et al. [139] includes the pressure effect on the compressibility of free volumes and shows the following equation:

$$\frac{d\delta_i}{dt} = -\frac{\delta_i}{\tau_i} - \Delta\alpha_i q + \Delta\kappa_i p \quad (1 \leq i \leq N) \quad (2.44)$$

where $q = dT/dt$ and $p = dP/dt$ are the heating/cooling and compression/decompression rates, respectively. The excess compressibility of the liquid with respect to the glass is defined as

$$\Delta\kappa = \kappa_r - \kappa_g = \sum_{i=1}^N \Delta\alpha_i$$

The other terms are similar to that in Eqn. (2.40). The relaxation time of element i , τ_i , is then written as a product of shift factors:

$$\tau_i(T, P, \delta) \equiv \tau_{i,r} \mathbf{a}_T \mathbf{a}_P \mathbf{a}_\delta \quad (2.45)$$

where $\tau_{i,r}$ is the i th relaxation time at a reference temperature and pressure (T_r , P_r), whereas $\mathbf{a}_T$, $\mathbf{a}_P$, and $\mathbf{a}_\delta$ are the shift factors that describe the temperature, pressure, and instantaneous state (δ) dependencies of the relaxation times. Several forms of $\mathbf{a}_P$ are proposed, including the WLF form, the exponential, and one following the Tait equation of state [139]. Such an equation for combining the temperature and pressure effects can readily be reduced from the Ko-Bogue equations [87], as will be shown in Chapter 3.

Based on Eqn. (2.44), Tribone et al. [181] analyzed the pressure-dependent volume relaxation at constant temperature. The observations are analogous to that obtained under atmospheric pressure by rapid changes in temperature. Finally, the corresponding integral form of Eqn. (2.44) is given as [139]

$$\delta(t) = \int_0^t (-\Delta\alpha q + \Delta\kappa p) \exp \left[- \left(\int_{t'}^t \frac{dt''}{\tau(t'')} \right)^\beta \right] dt' \quad (2.46)$$

where β is a measure of the width of relaxation time distribution and $0 < \beta \leq 1$. When β equals to unity, Eqn. (2.46) reduces to the single-element model, as previously discussed in Eqn. (2.42) [139].

2.3 Analysis of Injection Molding

The general features of the injection molding process are shown in Figure 2.2. During part A (the mold filling step) the molten polymer flows into the mold until it is filled. At that point the plunger of the injection machine continues to move forward (during the packing step, part B), “over-filling” the mold to a high pressure in order to pre-compensate for the subsequent thermal contraction. Finally during part C (the cooling step) the molded part contracts as it cools, leading to a decrease of the pressure. The general mechanisms for orientation (or birefringence) development in injection molding have been recognized for some time [163,4,188,74,171] and recently reviewed by Isayev [74,77] and Greener et al. [53]. The associated phenomena were firstly analyzed by Dietz, White, and Clark [30], and later by Isayev and Hieber [73], Greener and Pearson [50] among others. Skin-core structure and mechanical properties in the injection-molded

samples were also extensively studied by Dietz et al. [30,31,197], Russell and Beaumont [147], Katti and Schultz [86], Guo and Bowman [56], Trotignon and Verdu [182], and Fujiyama et al. [41]. Various steps in injection molding will now be reviewed.

2.3.1 Filling Step in Injection Molding

The mold filling step has been studied in some detail and there are several commercial computer programs available for describing it (for example: C-FLOW, Ithaca, New York [193]; MOLDFILL, Chicago [145]; MOLDFLOW-4, Australia [3]; and CADMOLD, West Germany [114].) Some general reviews are provided by Kamal and co-workers [84,48,80], Hieber [64], Mavridis [110], Richardson [142], and the Cornell University injection molding group [190].

After the first systematic studies by Spencer and Gilmore [43,163], various incompressible, Newtonian or power-law models combined with finite difference or finite element methods have been developed for theoretical analyses. One-dimensional radial filling of a center-gated disc was studied by Kamal and Kenig [80], Gogos et al. [6,205], and Stevenson [165]. One-dimensional flow in rectangular cavities has been analyzed by Harry and Parrott [59] and Lord and Williams [102]; whereas Williams and Lord [202] and Nunn and Fenner [124] considered flow in a circular tube. Recently Hieber et al. [63] analyzed the polymer flow in a non-circular tube under non-isothermal conditions. Oda, White, and Clark [125] related the steady filling and the jetting of the melt to the magnitude of melt swelling at the gate. Based on a Hele-Shaw type of flow

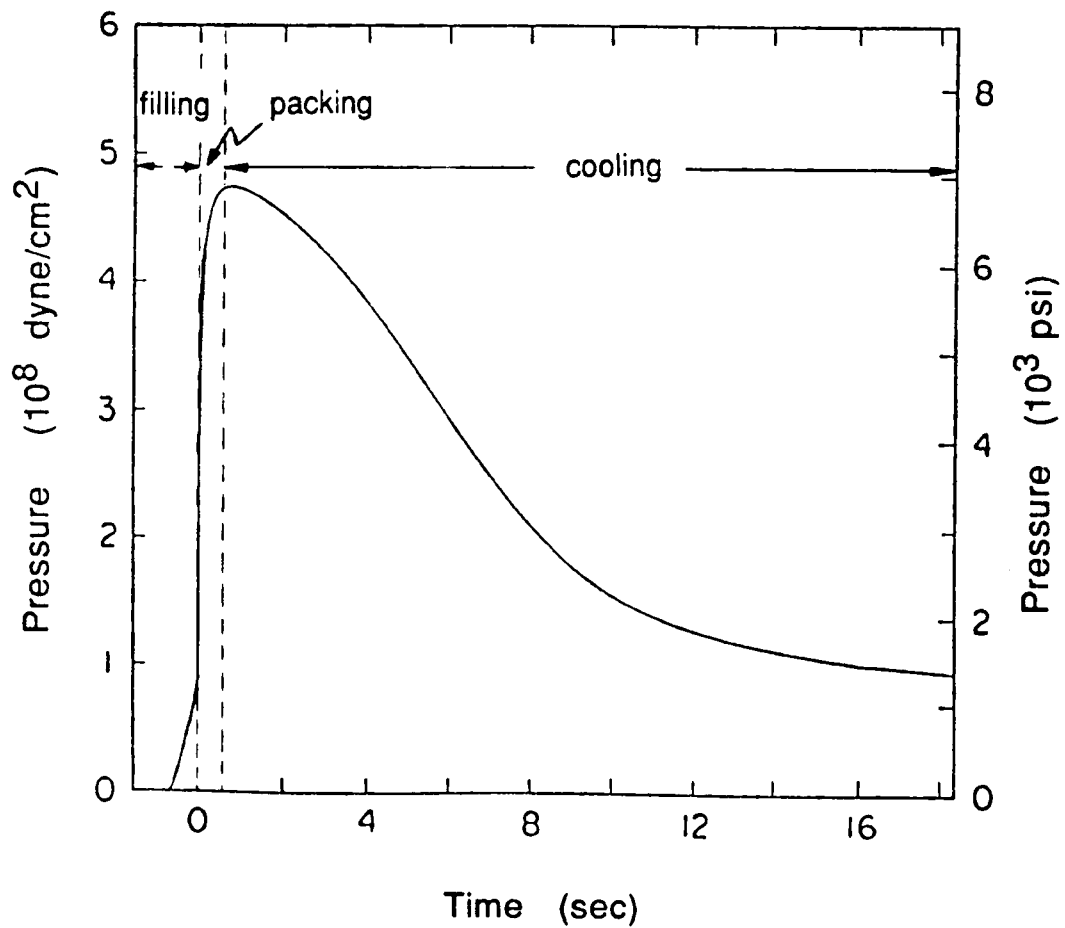


Figure 2.2: Pressure-time diagram in injection molding with typical pressure value in each step. (Taken from Cornell's data [191])

[141,62], studies of two-dimensional filling flow in a thin cavity have been given by Richardson [141], Kamal and coworkers [81,95], Broyer et al. [15], Krueger and Tadmor [94], and Wang et al. [190,191]. Hieber and Shen [62] presented a combined finite element/finite difference method to solved a similar problem (also see Shen [153]), whereas a conformal mapping technique was used by Ryan and Chung [148]. The planar flow in thin cavities of variable gap thickness was shown by Hieber et al. [63].

The viscoelastic nature of polymers was introduced by Dietz, White, and Clark [30] for stress relaxation in the calculation of residual stresses. Similar approaches were later shown by Isayev and Hieber [73], using the Leonov model [101], and by Kamal and co-workers [96,48,84], using the White-Metzner model [195], to calculate the shear and normal stresses in the cavity. Fountain flow, wall slip, and crystallization effects were also considered by Kamal and co-workers [83,48,84].

In the existing commercial programs for the filling step [193,145,3,114], the underlying physical assumptions are similar: temperature and stress gradients are supposed to be dominant in the gapwise (z) direction compared with the lateral (x and y) directions (see Figure 2.3). The basic mathematical structure has been shown by the Cornell project on injection molding (see Hieber and Shen [62] and Wang, Hieber, and Wang [193]). Four balances (a mass or continuity balance, two force balances, and an energy balance) are then written down with the appropriate dimensional assumptions for the two-dimensional (planar) flow. The rheological equation is taken to be of the form of an in-

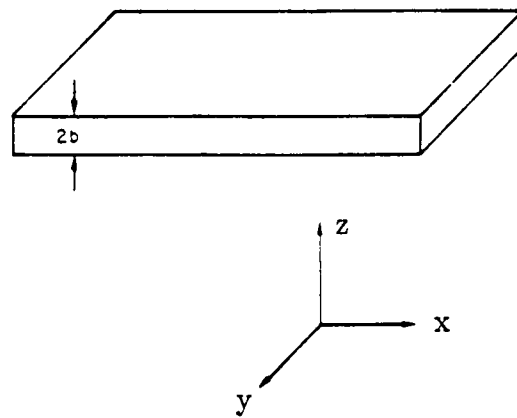


Figure 2.3: Orientation of axes for a rectangular thin cavity in injection molding.

compressible viscous (but not viscoelastic) fluid, showing Newtonian behavior at low shear rates and power law behavior at high shear rates. The governing equations are solved simultaneously over the flow field, using a finite element method in the x-y plane and a finite difference method in the z-direction [62].

2.3.2 Packing and Cooling Steps in Injection Molding

The assumptions of incompressible behavior are appropriate up to the time the mold fills (during part A in Figure 2.2), but are not adequate for the later steps. During the packing and cooling steps the compressible (PVT) behavior of the material must obviously be introduced. However, relatively little work has been done as compared to the studies on the mold filling step. Moreover, the compressible behavior was always assumed to obey some empirical, equilibrium PVT equations.

The Spencer-Gilmore equation of state [163] has been the most widely used, as, for example, by Spencer and Gilmore [163], Kamal et al. [81], Chung et al. [24,23,22], and Wang et al. [191,192]. The Tait equation [134] was employed by Greener [51] and Wang et al. [192]. Some simpler relationship between density and pressure was also assumed: a linear proportion was used by Kamal and Kenig [80] and Greener [52], while an exponential relation was employed by Titomanlio et al. [177]. Kamal and Lafleur [96] measured the density changes from the PVT program and directly used such experimental PVT data to simplify their analyses; simplifications were necessary because a viscoelastic constitutive equation (the White-Metzner model) and crystallization effects were included

in the model. General features of the packing and cooling steps have been discussed and reviewed by Kamal et al. [80,96], Greener [51], Grmela [55], Hieber [64], and Wang et al. [190,191,192].

For the planar flow in a thin slab during the packing and cooling steps, the four basic balances for viscous fluids, as described in a recent Cornell project report [191,64], are as follows:

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho v_x)}{\partial x} + \frac{\partial(\rho v_y)}{\partial y} = 0 \quad (2.47)$$

$$0 = -\frac{\partial P}{\partial x} + \frac{\partial}{\partial z} \left(\eta \frac{\partial v_x}{\partial z} \right) \quad (2.48)$$

$$0 = -\frac{\partial P}{\partial y} + \frac{\partial}{\partial z} \left(\eta \frac{\partial v_y}{\partial z} \right) \quad (2.49)$$

$$\rho C_p \left(\frac{\partial T}{\partial t} + v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y} \right) = k \frac{\partial^2 T}{\partial z^2} + \eta \dot{\gamma}^2 \quad (2.50)$$

where $\dot{\gamma}$, a generalized deformation rate, and η , a non-Newtonian viscosity, are defined by

$$\dot{\gamma} = \sqrt{\left(\frac{\partial v_x}{\partial z} \right)^2 + \left(\frac{\partial v_y}{\partial z} \right)^2}$$

$$\eta = \eta(\dot{\gamma}, T, P)$$

An averaging of the rheological response across the z direction (through half-gap thickness, b) results in the following equation:

$$\frac{\partial \bar{\rho}}{\partial t} = \frac{1}{b} \left[\frac{\partial}{\partial x} \left(S \frac{\partial P}{\partial x} \right) + \frac{\partial}{\partial y} \left(S \frac{\partial P}{\partial y} \right) \right] \quad (2.51)$$

where

$$S = \int_0^b \frac{z^2}{\eta} dz \quad (2.52)$$

and $\bar{\rho}$ is the gapwise average density, treated as some representative constant value.

To complete the description one must introduce a PVT equation, those due to Spencer and Gilmore [163] and Tait [134] having been considered by the Cornell group [191,192]. The equation of Spencer and Gilmore, which is mathematically more convenient, is given by:

$$(P + \hat{P}) \left(\frac{1}{\rho} - \frac{1}{\hat{\rho}} \right) = \hat{R}T \quad (2.53)$$

where $\hat{P}$, $\hat{\rho}$, and $\hat{R}$ are constants.

From the heat transfer theory the temperature field can be rigorously analyzed as a time-dependent three-dimensional function, $T = T(x, y, z, t)$. However, pressure and density were usually assumed to be independent of the z -direction and treated as some gapwise-averaged values: $P = P(x, y, t)$ and $\rho = \rho(x, y, t)$. Thus, the Spencer-Gilmore equation, Eqn. (2.53), may be rewritten in terms of $\bar{\rho}$:

$$\frac{\partial \ln \bar{\rho}}{\partial t} = G(x, y, t) \frac{\partial P}{\partial t} + F(x, y, t) \quad (2.54)$$

where

$$G(x, y, t) \equiv \frac{1}{b} \left(\frac{1}{P + \hat{P}} \right) \int_0^b \left(1 - \frac{\rho}{\hat{\rho}} \right) dz \quad (2.55)$$

$$F(x, y, t) \equiv -\frac{1}{b} \int_0^b \left(1 - \frac{\rho}{\hat{\rho}} \right) \frac{\partial \ln T}{\partial t} dz \quad (2.56)$$

Combining Eqn. (2.51) with Eqn. (2.54) gives finally

$$G(x, y, t) \frac{\partial P}{\partial t} + F(x, y, t) = \frac{1}{b} \left[\frac{\partial}{\partial x} \left(S \frac{\partial P}{\partial x} \right) + \frac{\partial}{\partial y} \left(S \frac{\partial P}{\partial y} \right) \right] \quad (2.57)$$

The mathematical problem is finally one of solving Equations (2.50) and (2.57) simultaneously with the associated viscosity model. Wang et al. [191,192] used a

kind of pressure and temperature dependent power-law model. In addition, the viscosity was taken to be infinite below the glass transition temperature or below a crystallization temperature so that the solidification and crystallization effects were implicitly included. When the left-hand side of Eqn. (2.57) is negligible because the density is almost constant, as in the mold filling step, Eqn. (2.57) can then be reduced to the Hele-Shaw equations [64] for the planar flow in thin slabs, as used in the C-FLOW program [193,62]. During the packing step, the G term in Eqn. (2.57) becomes important while the F term is still negligible, due to the temperature being almost constant in the short time of packing (about 0.1 second). Finally during the cooling step, both G and F terms become important, with the F term being the driving force for pressure change.

In the context of this work one important assumption is that the PVT response is instantaneous (see Equation 2.53 or the Tait equation mentioned above.) In view of the rapid cooling times involved in injection molding, that assumption is not likely to be satisfactory, a conclusion reached by the Cornell group as well [192]. In order to obtain satisfactory fits to the pressure-time data during the packing and cooling steps, they found it necessary to empirically adjust some of the parameters in the equilibrium (Spencer-Gilmore) equation [192]. In the present work a time-dependent PVT equation is introduced (as presented in Chapter 5). For mathematical tractability, however, the simplification of homogeneity in the x - y plane will be made; thus the consequences of a non-equilibrium PVT behavior will be explored, but in a simplified manner as regards the practical (necessarily non-homogeneous) problem of injection

molding.

2.4 Residual Stresses in Rapidly Cooled Samples

In a typical polymer process, the melt is being deformed before it is cooled rapidly to the solid state. If the deformation is homogeneous, one obtains a stress-free, but oriented sample. If it is not, the frozen-in non-homogeneous orientation may relax non-uniformly, finally resulting in actual stresses. Separate from this non-homogeneity, the rapidly cooled sample almost always has thermal gradients. It produces non-uniform volume contraction, also resulting in the classical "residual stresses." The general features of residual stresses have been discussed by Struik [167], White [199,200], Isayev and Crouthamel [75], and Miyano et al. [117]. It is now well-known that residual stresses in rapidly cooled samples can strongly affect the properties, such as impact strength, softening temperature, and failure behavior [162,67,14,154,137].

Residual stresses is obviously a good example of a practical problem in which a highly coupled volume-temperature-time-stress history is involved. However, terms like "residual stresses" or "internal stresses" are often used differently by different authors. Discussion of the various mechanisms involved is given by Struik [167], Isayev and Crouthamel [75], and White [199]. According to the mechanism involved, the stresses may be termed as "volume-induced residual stresses" for those caused by uneven volume contraction from thermal gradients; and "orientation-induced residual stresses" for those caused by shrinkage

from frozen-in orientation relaxation. The common cause is the nonhomogeneity of the thermal history (in both cases) and possibly the nonhomogeneity of the strain history as well (in the case of orientation-induced residual stresses). However, the frozen-in orientation (also termed as "residual orientation") may not give rise to actual stresses unless the sample is later reheated under constraint. A brief review of residual stresses induced by various mechanisms will now be presented.

2.4.1 Volume-Induced and Orientation-Induced Residual Stresses

Volume-induced residual stresses are observed in rapidly cooled samples which should be free of initial residual orientation [167,75]. Figure 2.4 shows the schematic diagram of its occurrence. Initially there is a stress-free body at a uniform high temperature (time a). As the outside of the body cools, the "skin" begins to contract (time b). The center (or the "core") is still hot and not going to contract thermally, so that it opposes the contraction of the skin resulting in a tensile stress in the skin and a compressive stress in the core. Also because the core is still hot it flows (or contracts) plastically under compression (with almost no extra stress increase.) As cooling continues (time c), the core now begins to contract thermally, pulling on the frozen skin. Since the skin has been frozen as like a "solid cage", it becomes under compression when it is pulled in by the contracting core. As the core continues to cool, the entire body finally reaches a uniform temperature (time d). Due to its total thermal plus plastic contraction exceeds that of the skin, the core has a frozen-in tensile

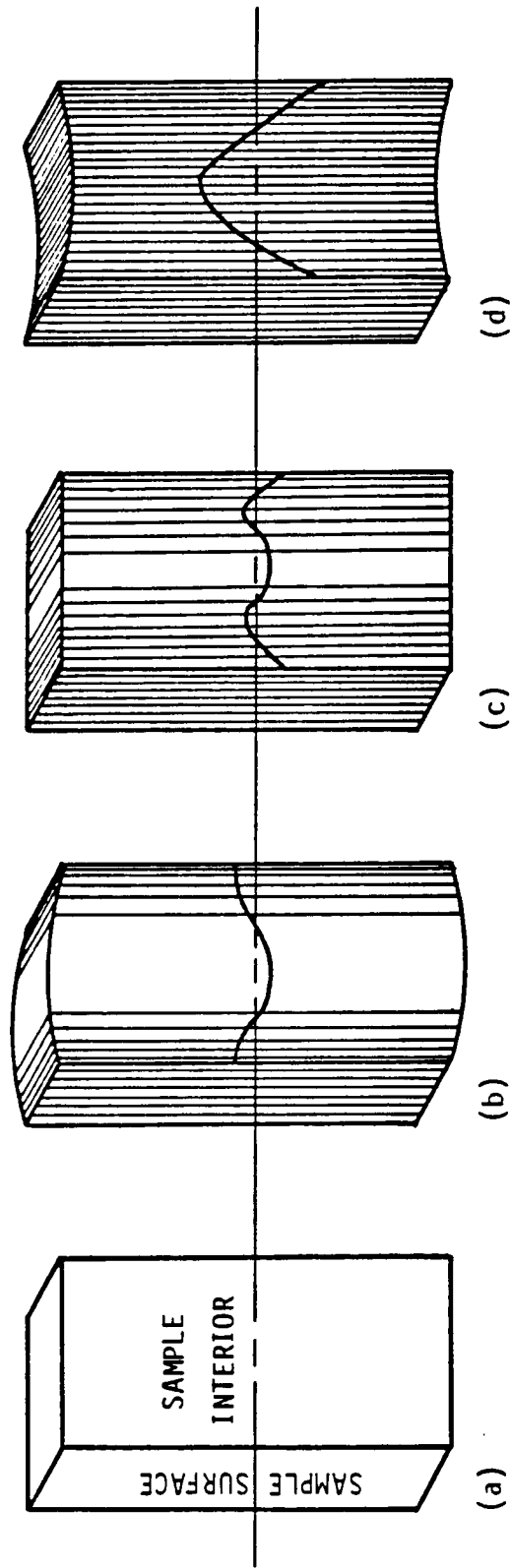


Figure 2.4: Schematic diagram of volume-induced residual stresses. (Light areas are hot; shaded areas are cold (taken from Wust [206])).

stress, whereas the skin has a compressive stress because of its opposition to the contraction of the core. In other words, the core “wants to be shorter” (but was opposed by the frozen skin) and is being held under tension. The skin “wants to be longer” (but was pulled in to some extent by the contracting core) and is being held under compression.

The theories developed for the volume-induced residual stresses have been reviewed by Gardon [42] and recently by Wust [206] and Isayev [77]. The most general treatment is that of Lee, Rogers, and Woo (LRW) [99], which is based on nonisothermal linear viscoelasticity for the quenching of a slab. In that theory temperature-dependent relaxation of the residual stresses is allowed, but the volume response is taken as instantaneous. The final result is presented as

$$\sigma(x_2, t) = 3 \int_0^t R[\xi(x_2, t) - \xi(x_2, t')] \frac{\partial [\epsilon_1(t') - \alpha T(x_2, t')]}{\partial t'} dt' \quad (2.58)$$

with the constraint

$$\int_0^b \sigma(x_2, t) dx_2 = 0 \quad (2.59)$$

where $\epsilon_1(t')$ is the isotropic strain in the x_1x_3 plane, ξ is the reduced time defined by

$$\xi(x_2, t) = \int_0^t \frac{dt'}{\tau_G(T)} \quad (2.60)$$

in which $\tau_G(T)$ is a temperature-dependent relaxation time, and $R(\xi - \xi')$ is an auxiliary modulus function satisfying

$$\frac{4}{3\kappa} \int_0^\xi G(\xi - \xi') \frac{\partial R(\xi')}{\partial \xi'} d\xi' + R(\xi) = 2G(\xi) \quad (2.61)$$

where κ is the bulk modulus and G is the relaxation shear modulus. This theory is quite complicated but has been used to predict both transient and final residual stress profiles of glasses during quenching.

More recently, Markovsky et al. [103] wrote a set of differential equations which are corresponding to the integral LRW theory. The stresses have been separated into shear and bulk (dilatational) components, each having its own relaxation function. These two stress components, with the accompanying relaxation functions, are assumed to be independent of each other. Although coupling effects have been neglected in these equations, the relaxation functions are very complicated even in the simplest uniaxial deformations.

A special case of the LRW theory is that of Aggarwala and Saibel (AS) [1], in which the material is assumed to have no memory or complete memory (depending on whether it is above or below T_g). Using the notation of Aggarwala and Saibel [1], the LRW and AS theories are connected by

$$R_c = 2\beta = \frac{2E}{6(1 - \nu)} \quad (2.62)$$

where R_c a characteristic auxiliary modulus in the glassy state, ν is Poisson's ratio and E is Young's modulus. After a number of steps Equation (2.58) reduces to the final form of AS theory:

$$\sigma(x_2, t) = \int_{\bar{t}(x_2)}^t 6\beta \left\{ \left(\frac{1}{b - \bar{x}_2(t)} \int_{\bar{x}_2(t)}^b \frac{\partial[\alpha T(x'_2, t')]}{\partial t'} dx'_2 \right) - \frac{\partial[\alpha T(x_2, t')]}{\partial t'} \right\} dt' \quad (2.63)$$

where $\bar{t}(x_2)$ is the time at which a particular position x_2 passes through T_g , $\bar{x}_2(t)$ is the position of the solidification line at any time t , and 6β is an elastic

modulus related to Young's modulus. By integrating the strain over the solid portion the stresses in the glass can be calculated.

When the thermal coefficient of expansion in the above equation is treated as some temperature-independent constant value, the AS theory will be equivalent to the Indenbom theory [71,72,77]. Although the Indenbom theory can predict the final residual stress profile for some special cases (in particular, slow cooling), it is not capable of describing transient stresses [77]. A brief summary of these theories is presented in Appendix B. More detailed descriptions are given by Wust [206] and by Isayev [77].

Measurements of volume-induced residual stresses were given by So and Broutmann [162], Saffell and Windle [149], Siegmann et al. [155], Struik [166], and Isayev and Crouthamel [75]. These residual stresses will induce non-uniform birefringence, which resulting from the non-uniform volume contraction (the residual stress itself), but not from prior flow history. Such birefringences typically have positive and negative values with nonequal areas. The birefringence component in the plane along the thickness direction has a parabolic shape, while other components are zero. Experimental data of these birefringences have been measured by Isayev [74], Broutmann and Krishnakumar [14], Saffell and Windle [149], Bogue et al. [207,100], and Mills [116].

Theoretical analyses on the volume-induced residual stresses and the related birefringence distribution have been done by Bogue et al. [207,100]. The LRW theory and its simplified form of AS theory were employed to calculate the residual stresses. Both temperature-dependent and independent strain optical

coefficients were used in the strain-optical law for converting stress to birefringence. Satisfactory fits to the data for PS, PMMA, and PC were obtained when values of the strain optical coefficient just above the glass transition temperature were used. For materials where the sign of the coefficient changed, the sign was that of the rubbery state. Similar approaches were shown by Isayev and Crouthamel [75] and by Mills [116]. One important assumption in these analyses is the instantaneous volume response accompanying with the time-dependent stress relaxation. In the present work, the reverse assumption was used to explore the volume-induced residual stresses in rapidly cooled samples.

Theoretical study on orientation-induced residual stresses is much less extensive. Analysis of residual stresses in a glass fiber induced by the draw force was given by Rongved [144], which is based on linear viscoelasticity with simplifying assumptions: a steady-state for fiber drawing and no effects of lateral normal stresses or the thermal strain on the fiber-axial stress. The analysis is thus limited to an incompressible material. Theoretical analysis of the capture and release of orientation in elongated fibers of polystyrene was done by Snow, Potnis and Bogue [160]. While it dealt with homogeneous relaxation of orientation throughout the sample, volume effects were, again, not included in that analysis. However, the small volume change can have an enormous effect on the free volume (and the shift factors) and thus need to be considered in the general case.

2.4.2 Residual Stresses in Injection Molding

Both kinds of residual stresses are typically found in injection-molded samples, in which the nonhomogeneity comes from both the thermal history and the prior flow history. Considering the shear stresses involved in the melt flow, it is obvious that orientation in the layers next to the mold wall is much higher than the center layers [30,74,197]. Besides the orientation gradient, injection molding also involves rapid cooling and the thermal gradients thus produced. Therefore, both kinds of residual stresses are created. However, that is not to say that both residual stress mechanisms are equally important and it may be so that volume-induced residual stresses predominate in some cases. For example, injection-molded optical disk substrates have a very thin thickness and need low birefringences. One may raise the melt temperature or prolong the filling time to minimize the flow rates and thus the birefringences [53]. When the flow effects are reduced, the cooling effects become dominant, particularly on the transverse birefringence (in the plane across the thickness) [53]. Certainly the flow and thermal histories are also coupled and a detailed analysis will be necessary before a clear distinction can be made.

There is now a considerable literature data on residual stresses in injection molding, notably in the recent work of Sandilands and White [152], Thompson and White [174], Isayev and Crouthamel [75], Iacopi and White [67], Titomanlio et al. [176], and Takeshima and Funakoshi [171], which can be used to check against theoretical studies. A good review is given by Isayev [77]. It was found

that residual stresses in injection-molded parts are entirely tensile and much smaller (about ten times) than the volume-induced residual stresses (compressive on the surface layers and tensile the center layers) in rapidly cooled samples of similar size. Variations in space are also observed: stresses are higher near the gate and gradually decreasing from there. Birefringence distributions in the gapwise-direction are usually lower in the frozen-in zone on the surface (due to the frozen-in fountain flow effects), a high shear zone is next (due to the shearing effects), and finally a low core zone occurs in the center (due to the relaxation effects). Processing conditions may affect the magnitudes: a higher melt temperature or mold temperature will lower the residual stresses, for example. High residual stresses in injection molding may not give a higher birefringence. It depends mainly on the stress optical coefficient and the relaxation time of different materials [77,53].

Since complex interactions always exist in injection-molded samples, a clear distinction between orientation and volume-induced residual stresses is difficult to make. Little of existing theory can deal with these highly coupled residual stresses. Therefore, analyses were always restricted to the orientation-induced (or flow-induced) residual stresses and thus birefringences in injection-molded samples, such as the works by Janeschitz-Kriegl [78] Dietz, White, and Clark [30], Kamal and Tan [82], Isayev et al. [73,74], Wang et al. [190], and Greener et al. [50,53].

Dietz et al. [30,31] extended the approach of Janeschitz-Kriegl by using an isothermal, power-law model for the one-dimensional steady-state shear flow in

the filling step. The non-isothermal cooling was then included by calculating the frozen skin thickness. They employed an empirical equation to correlate the shear stress and the first normal stress difference, which is required by the stress optical law. After the mold is filled, nonisothermal stress relaxation was estimated by using a one-element Maxwellian model, in which the relaxation time is independent of shear rate. Good fits to the data of Wales [189] were shown. The same approach was followed by Greener and Pearson [50], except that a viscoelastic constitutive equation (the Marucci model) was used for the non-isothermal stress relaxation. Isayev and Hieber [73] later employed the Leonov viscoelastic equation in both the filling and cooling steps. Three components of birefringence could be calculated.

More recently, Greener, Kesel, and Contestable [53] analyzed the residual stresses in injection-molded optical disk substrates. They followed Dietz et al. [30,31] in using the isothermal power-law model and calculated the skin layer thickness during the mold filling, but then employed a viscoelastic, integral Wagner model for stress relaxation after the filling step. The general approach of Matsui and Bogue [106] was adapted for the nonisothermal effects on the relaxation times. As soon as the material vitrifies, the unrelaxed stresses freeze in the glassy state. The frozen-in stresses were diagonalized for the stress-optical law and then integrated across the disk thickness to obtain the gapwise-averaged residual birefringences. Good fits were found for the birefringence in the surface plane, while the prediction for the other component (transverse birefringence) in the plane along the thickness direction was too low. They

attributed this discrepancy to the fact that the transverse retardation is induced by cooling history and thus cannot be predicted from the prior flow mechanism in the analysis [53]. In the above-mentioned works, the packing step was always skipped and coupling effects were also neglected. We believe the Ko-Bogue theory (see Appendix A) provides, in principle at least, a framework for dealing with these complicated problems. However, the present work will focused on the volume-induced residual stresses in rapidly cooled samples.

Recently residual stresses in other processes have been studied as well. Kang and White [85] have studied the birefringence distribution in thick fibers of PS and PMMA and calculated the volume-induced residual stresses. Related studies on melt spun fibers of PS and of glass have been reported by Bell and Edie [5]. Residual stress distribution in polyimide coated films has been shown by Elsner [33].

2.4.3 Determination of Residual Stresses

Experimental methods related to the determination of the residual stress distribution in the molded, or rapidly cooled samples include the layer-removal technique or the photoelastic (birefringence) method. More detail on these methods are given by White [199,200], Isayev et al. [75,77], and Wust [206].

The layer-removal technique [179] involves removing layers of the material and measuring the small bending that occurs as the stresses are thus relieved. Based on linear elasticity theory, the residual stress profile prior to layer removal is expressed as a function of depth of material removed. For the special case of a

homogeneous surface plane ($\rho(y) = \rho_x(y) = \rho_z(y)$), the stresses from quenching are isotropic in the plane:

$$\sigma_x(y_1) = \sigma_z(y_1) = \frac{-E}{6(1-\nu)} \left\{ (b+y_1)^2 \frac{d\rho(y_1)}{dy_1} + 4(b+y_1)\rho(y_1) - 2 \int_{y_1}^b \rho(y') dy' \right\} \quad (2.64)$$

where b is initial upper surface, y_1 is the new upper surface after each layer removal, E is the elastic modulus, ν is Poisson's ratio, and $\rho(y)$ is the curvature parallel to the x (or z) direction. From measuring the height of the arc and the length of the chord, one obtains the radius of curvature, r . The curvature ρ equals the reciprocal of r .

Application of the above procedure to polymers needs to consider the creep behavior, because Eqn. (2.64) is based on linear elasticity theory. Contradictory experimental procedures, concerning the time of measurement, are found in the literature. Good reviews have been given by Isayev [75,77] and by Wust [206]. Since the creep phenomenon occurs slowly at room temperature, the measurement of the curvature immediately following machining may safely be assumed to be due to the elastic response. If the specimen is allowed to warp to its equilibrium curvature, higher residual stresses are observed as compared to the results by measuring the curvature in few minutes after machining [154,162]. Relaxation of the residual stresses has also been observed [67,75]. Higher values are found for the specimen tested immediately after quenching or injection molding. After aging for several weeks lower values are observed. Thus the stress profiles depend on the elapsed time between introducing the stresses and

carrying out the layer removal. Even though experimental difficulties are involved, the layer removal method provides a direct measurement of the stresses.

Photoelasticity or birefringence is also used to determine stresses in transparent samples, which are subjected to a strain or stress [75,77,100,206]. In the photoelastic method the isochromatic patterns (the color fringes) are assumed to be corresponding to a constant principal stress difference. By finding the order and location of fringes, the stress distribution can be specified if the stress-optical law is applicable. The stress-optical rules assume a linear relation between the difference in principal refractive indices Δn (the birefringence) and the difference in principal stress. However, the stress-optical coefficient can become highly temperature dependent near the glass transition. Thus the frozen-in birefringence distribution may be quite different from that for a material with a constant stress-optical coefficient. Such a memory effect, due to quenching from the rubbery state through the transition to the glassy state, leads to a situation in which the simple stress-optical relation is not satisfied [77,100,206,207]. Therefore the photoelastic method or the birefringence method should carefully be applied to polymers having complicated thermal histories. These methods provide indirect measurements of residual stresses, as compared to the layer-removal procedure.

CHAPTER 3

A NEW CONSTITUTIVE EQUATION INVOLVING COMPRESSIBILITY EFFECTS

Rheological theory including volume (compressibility) effects is important in a practical sense in that many polymer processes involve rapid cooling to a final, typically nonequilibrium, glassy state. In such processes nonequilibrium specific volume and also nonequilibrium orientation can affect the mechanical properties and may also change (age) with time [166]. Crystallization behavior is also, of course, of considerable importance but the complex mechanisms involved there are not included in the present work, which is limited to amorphous polymers.

Volume effects may result from a change in temperature or hydrostatic pressure, which has been considered in the context of equations of state (PVT relations). There are also compressibility effects in the sense of Poisson's ratio — that is, deformation-induced volume changes occur even at constant temperature. In most of existing viscoelasticity theory (the rheological constitutive equations) one assumes incompressible behavior for rubbery melts, which means that the volume does not change during deformation (for example, in uniaxial pulling Poisson's ratio is taken to be $1/2$). Such an assumption cannot be made in the glassy state, however, since the increase of volume upon pulling

(or the decrease upon contraction) is an important characteristic of that state. Classical viscoelasticity theory is therefore not compatible with linear elasticity theory, which would be appropriate for small deformations in the equilibrium glassy state.

Considering rate-dependent effects in PVT equations, or equivalently, introducing compressibility effects into rheological theory, has not been done extensively, although there is now a growing literature on volume changes (aging) in the glassy state [168]. In introducing compressibility effects into rheological theory, one might relate the compressibility to the second/or third invariants of stress [133,132]. But with the complicated viscoelasticity theories presently in use, no simple relationship like this is possible. Therefore, as the first effort, Snow and Bogue [161] set down a unified equation from the phenomenological viewpoint, which includes all the effects mentioned above. This generalized equation includes an integral rate equation for isotropic volume changes and combines it with existing integral constitutive theory for nonisotropic stresses. It allows one, in principle, to deal with volume and orientation effects in general, both as they occur at the present time and also as they are "remembered" from prior history. However, the general integral statement is quite complicated and difficult to execute except in the simplest deformations. Recently a restatement of the prior formulation has been made (see Ko and Bogue [87]) in more tractable and slightly modified form.

The details of the Ko-Bogue formulation are shown by means a reprint (Appendix A). The essential idea can be understood by considering the generalized

PVT rate equation, the generalized stress-strain (constitutive) equation, and a constraint on the kinematics (an equation of continuity); those are Equations (1) (or (2)), (9), and (10) in the paper, respectively. In the generalized stress-strain equation, which is similar to classical integral viscoelasticity theory, volume effects on stress build-up are brought into the normalized relative Finger strain tensor, C_{ij}^{-1*} . Such a coupling effect is shown in the definition of C_{ij}^{-1*} , in which the strain due to volume change has been subtracted off (i.e., $C_{ij}^{-1*} = C_{ij}^{-1} - \delta_{ij} - (2/3)(\Delta V/V(t'))\delta_{ij}$, where C_{ij}^{-1} is the conventional, unnormalized form of that tensor). During the deformation the strains must satisfy the requirement of continuity, which is imposed by the kinematical restraint (Eqn. (10) in Appendix A). If the deformation induces a significant "Poisson's ratio effect" (i.e., a volume change with stress), this effect will be accounted naturally in the theory by means of the scalar stress $\wp$, which enters into the definition of θ and thus into the generalized $\wp$ VT rate equation (Eqn. (1) or (2) in Appendix A).

The scalar stress $\wp$ is the hydrostatic pressure in isotropic deformations but has a more general meaning in anisotropic deformations (i.e., those with unequal normal stresses). More descriptions of the physical meaning of $\wp$ are given in the paper (see the discussion of the special cases and the concluding remarks there). Finally, the time-dependent behavior of stresses can be included in the modulus $G(t')$ and the time constant $\tau_G(t')$, in that they depend on temperature, pressure, and possibly other parameters (such as free volume) which depend on time.

For homogeneous deformations, the generalized ϕ VT rate equation (Eqn. (1) in Appendix A) reduces to

$$\frac{d(\theta + \phi_f)}{dt} = \frac{-\Delta\theta}{\tau_\lambda} \quad (3.1)$$

This is actually Eqn. (2) in Appendix A, which is repeated here for showing the reduction to a special case below. The quantity θ is a state variable characterizing the instantaneous ϕ VT state of the material; $\Delta\theta$ is the difference between the instantaneous state and an arbitrary initial state (P_0, V_0, T_0); θ_f is the driving force for creating free volume, as described in the paper [87]; and τ_λ is the time constant governing volume changes with accompanying shift factors. This is a generalized ϕ VT rate equation in the sense that the time-dependent volume changes can be a function of temperature, or of pressure, or of both.

The most common problem of this kind is one in which the pressure is held constant and the temperature is changed. In such a case, as already shown in the original paper [87], Eqn. (3.1) reduces to a volume rate equation similar to Kovacs' one parameter rate equation; also shown there is the corresponding model of multiple element (see Eqns. (14) and (17) in Appendix A). Following these derivations, a more general case involving temperature change as well as pressure change will now be presented.

Considering both temperature and pressure being changed, the definition functions of θ , $\Delta\theta$ and ϕ_f are exactly the Eqns. (3), (4) and (8) in Appendix A. Here one follows the assumption in the paper that the imposed scalar stresses ϕ will not have a large effect on the glass transition. These functions are shown

as follows:

$$\theta(t) = \kappa(t)\varphi(t) + V(t)/V_0 - \alpha(t)T(t) \quad (3.2)$$

$$\Delta\theta(t) = \bar{\kappa}[\varphi(t) - P_0] + [V(t) - V_0]/V_0 - \bar{\alpha}(t)[T(t) - T_0] \quad (3.3)$$

$$\phi_f(t) = \Delta\alpha(t)[T(t) - T_{ge}] - \Delta\kappa(t)[\varphi(t) - P_0] \quad (\text{moderate } \varphi, T > T_{ge}) \quad (3.4)$$

In these expressions $\kappa [= 1/\lambda^*]$ is the pressure coefficient of expansion (or compressibility coefficient); the overbars on $\bar{\kappa}$ and $\bar{\alpha}$ denote averages between the initial time and the time of consideration t ; and $\phi_f = 0$ for $T < T_{ge}$ as discussed in the paper. Similar restriction on material constants is also adopted here. That is, above T_{ge} , one has $\alpha = \alpha_r$, $\kappa = \kappa_r$ and $\Delta\alpha = \alpha_r - \alpha_g$, $\Delta\kappa = \kappa_r - \kappa_g$; and below T_{ge} , one has $\alpha = \alpha_g$, $\kappa = \kappa_g$ and $\Delta\alpha = 0$, $\Delta\kappa = 0$.

After taking the time derivatives of both θ and ϕ_f , and inserting into Eqn. (3.1), the generalized equation reduces finally to

$$\frac{dV}{dt} = - \left(\frac{V - V_e}{\tau_\lambda} \right) + V_0\alpha_g \frac{dT}{dt} - V_0\kappa_g \frac{d\varphi}{dt} \quad (3.5)$$

where $V_e [= V_0 + V_0\bar{\alpha}(T - T_0) - V_0\bar{\kappa}(\varphi - P_0)]$ is the volume which would exist at the instantaneous state if equilibrium were allowed to occur. This is essentially the single-element, generalized rate equation of Kovacs et al. [139,181] (see Eqn. (2.44) in Chapter 2), except that we have linearized around V_0 and not V_∞ , as before. The time constant $\tau_\lambda(t) [= a_{PVT}(t) \tau_{\lambda 0}]$ is a function of time in that it depends, by accompanying shift factors, on some combination of φ , T , and V , or quantities such as free volume which is equivalently determined by $\Delta\theta$. The specific form of the factor a_{PVT} will be shown in the following chapters for particular problems.

The parallel development for the corresponding model of multiple element can be easily obtained in a manner analogous to that shown in Appendix A, which leads to the final result as:

$$\frac{dV}{dt} = - \sum_i \frac{[v_i - v_{ei}]}{\tau_{\lambda,i}} + V_0 \alpha_g \frac{dT}{dt} - V_0 \kappa_g \frac{d\wp}{dt} \quad (3.6)$$

where $\sum_i v_i = V$, $\sum_i v_{0i} = V_0$, and $v_{ei} [= v_{0i} + v_{0i} \bar{\alpha}(T - T_0) - v_{0i} \bar{\kappa}(\wp - P_0)]$. Similarly in the associated definition functions of θ_i and $\Delta\theta_i$, V and V_0 may be replaced with v_i and v_{0i} . Such a multi-element model is actually a set of simultaneous differential equations, as noted before.

In addition to the rate-dependent $\wp$ VT equations, the Ko-Bogue equations reduce naturally to the existing theories of linear elasticity, large-deformation viscoelasticity, and also the equilibrium $\wp$ VT equation, as shown in Appendix A. The theory can, in principle at least, be applied to problems involving temperature-volume-time behavior, or pressure-volume-time behavior, or any two of the three (temperature, pressure, volume) as the independent variables. Several examples will be illustrated in the following chapters.

CHAPTER 4

EXPERIMENTS AND ANALYSIS INVOLVING SIMULTANEOUS PULLING AND COOLING

The basic experiments of the present work and of the author's MS thesis [88] involved the measurements of stress build-up in uniaxially constrained samples as they are cooled at various constant rates. Small fiber-like samples of polystyrene, contained in an air oven, are held in an Instron tensile tester, with either stationary clamps (the MS research) or with moving clamps (the present work), and the force build-up is measured as the samples are cooled. No further work on stationary clamps will be reported here although work of this kind continues in a separate project [79]. Both of these experiments involve a "coupling" of the volume change and the anisotropic (tensile) stress build-up, thereby providing a test of the Ko-Bogue equations [87].

An analysis of such experiments needs two sets of independent parameters (or functions): the parameters in the volume rate equation (a time constant, an equation for the shift factor, and thermal expansion coefficients and compressibility coefficients for the rubbery and glassy states); and the parameters in the anisotropic stress equation (a time constant, an equation for the shift factor, and the modulus as a function of temperature). In this chapter the experimen-

tal procedure will now be described, followed by the theoretical development for the analysis, and finally, a comparison of the equations with the data of the present work.

4.1 Experiments Involving Simultaneous Pulling and Cooling

The raw material and sample preparation for the simultaneous pulling and cooling experiments are summarized first. Then, the equipment and experimental procedure for making the stress measurements are described.

4.1.1 Material and Sample Preparation

The material investigated was an atactic and noncrystallizable polystyrene (Shell TC3-30) from the Shell Chemical Company. The molecular weights are $M_w = 2.8 \times 10^5$ and $M_n = 6.1 \times 10^4$, giving $M_w/M_n = 4.6$ [170,136]. The rheological properties of this polymer have extensively characterized under wide ranges of temperature and time scale by Bogue and coworkers [161,170,105,106,107,108,32,136].

The samples were made by extruding the polystyrene at a temperature of 200 °C from an Instron capillary rheometer at a low cross-head speed of 0.5 *cm/min* through a capillary die of 0.074 *cm* diameter and $L/D=20$. The fiber-like samples were then annealed in an air-oven for 24 hours at 130 °C prior to use. The samples after annealing had diameters of approximately 0.12 *cm* and lengths of about 20 *cm*.

4.1.2 Equipment and Experimental Procedure

A schematic diagram of the experimental equipment is shown in Figure 4.1. It is a modification of that reported in more detail in earlier work [207,106,107,108]. The fiber-like samples were held between the clamps of an Instron tensile tester in an air oven through which air was passed. The clamps were located outside the cooling chamber. A heater/blower system mixed hot air and room air, which was in turn incorporated into the control system so as to create linear cooling rates ranging from 0.08 to 3.7 °C/sec, with an upper temperature limit of about 160 °C and a lower limit of about 70 °C. Small diameters of the samples (about 0.12 cm) were used to minimize heat transfer effects — that is, the temperature of the sample was assumed to track that of the cooling air.

The top end of sample was first clamped by an air-clamp at about 60 °C. A small weight (0.68 gram of mass) was put on the bottom end of the sample before heating up to 125 °C in order to align and to remove the initial slack from the sample. The sample was held at 125 °C to allow equilibration for 5 minutes, then the bottom air-clamp was closed. The gauge length before pulling (or the initial sample length between the clamps) is 16.9 cm. Air pressure used for the air clamps is 50 psi. At the initial temperature the sample was slightly pulled — at a cross-head speed of 0.5 cm/min for 6 seconds to remove any slack from closing the air-clamps; then the experiments were started for simultaneous pulling and cooling immediately. The experiments include the cooling rates of 1.15, 2.50 and 3.30 °C/sec and the pulling rates of 0.5, 2.0 and 5.0 cm/min.

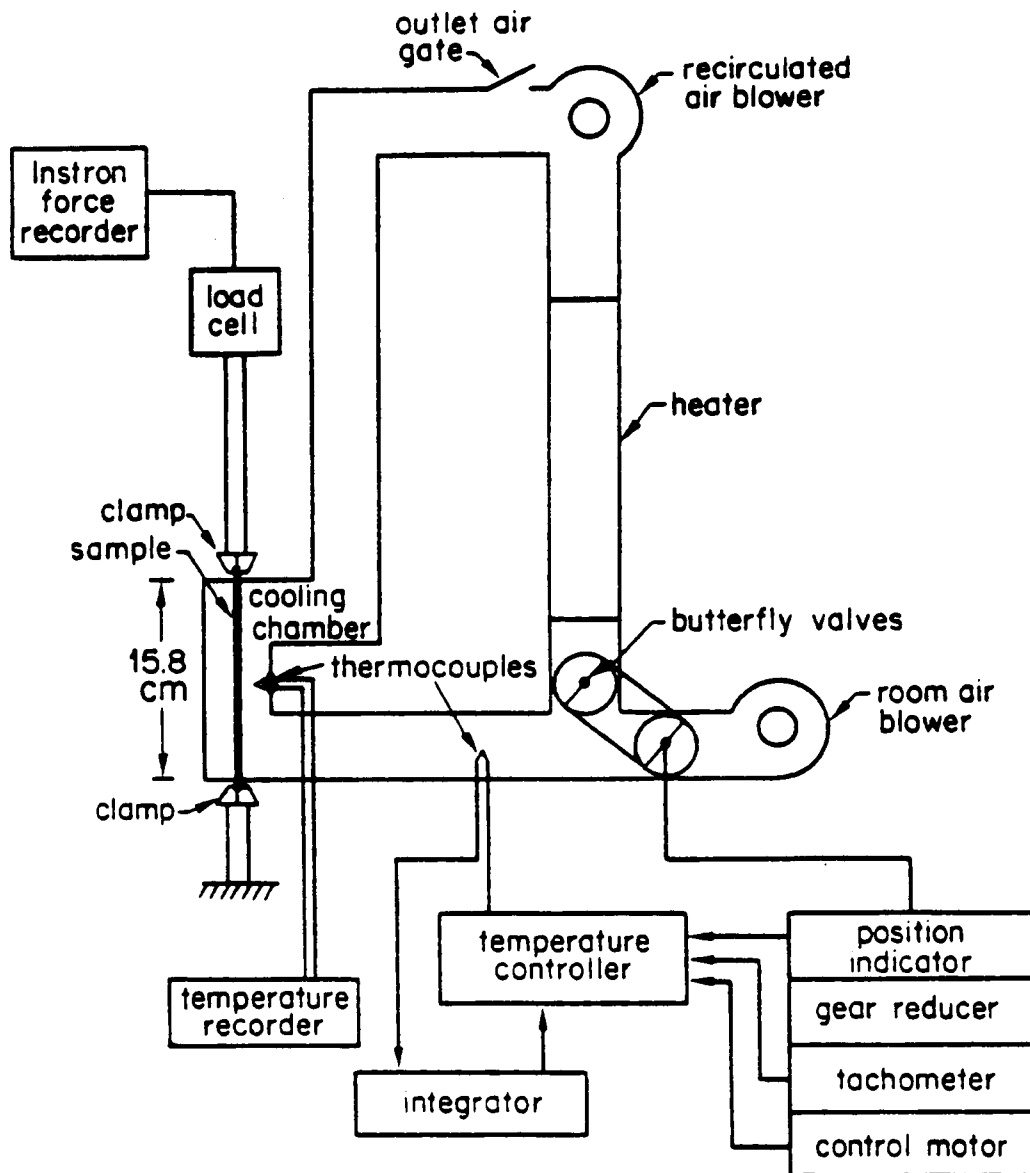


Figure 4.1: Schematic diagram of the equipment of the present work.

While temperature was linearly cooled down from 125 °C, the build-up of force was simultaneously recorded. An automatic "event-marker" was used to make marks on the force curve at the instantaneous temperatures of 110 °C and 90 °C. From these marks precise reference temperatures on the force curve could be obtained. Using these reference points one can extrapolate back to a "time zero", corresponding to the initial temperature 125 °C. Therefore, the problem of initial transients in the cooling and pulling systems could be eliminated in the force measurements.

The air-actuated clamps were mounted external to the cooling chamber in order not to subject the clamps themselves to the changing temperature. This arrangement caused some of the samples to be pulled out of the chamber and exposed to room air during the cooling. At a pulling rate of 2.0 *cm/min*, 0.66 *cm* of the original length of 16.9 *cm* was exposed to room air in a typical run lasting 20 seconds (the time required to cool from 125 °C to 75 °C at the rate of 2.5 °C/*sec*). In the worst case (pulling at 5 *cm/min* and cooling at 1.15 °C/*sec*) the run was terminated sooner, leading to about 2.5 *cm* of exposed sample. While this is not insignificant, the error was nonetheless felt to be within the scatter and was not corrected for.

The Instron tensile tester runs at a constant cross-head speed, with an actually decreasing elongation rates. But because of the small percent elongations, the experiment can be treated as one of nearly constant elongation rate; that is, $\dot{E} = (1/L)(dL/dt) \approx (1/L_0)(dL/dt) = \text{constant}$, where $L_0 = 16.9$ *cm* is the original sample length and dL/dt is the cross-head speed in *cm/sec*. However,

volume changes during the pulling and cooling were not measured because of experimental difficulties. The data of force build-up were converted into stresses, which will be compared with the theoretical predictions in the following section.

4.2 Analysis of Simultaneous Pulling and Cooling Experiments

The theoretical development of necessary equations will be presented first, followed by the comparison of predicted stress build-up with data of the present work.

4.2.1 Theoretical Development

Since the coupling of volume changes and stress changes is involved, the analysis needs the three equations in the Ko-Bogue formulation: the generalized ϕ VT equation, the generalized stress-strain (constitutive) equation, and a constraint on the kinematics (an equation of continuity). For a fiber-like sample exposed to a constant pulling rate and cooling rate ($R = -dT/dt$) at atmospheric pressure, the generalized ϕ VT equation (Eqn. (2) in Appendix A) reduces, as shown in Chapter 3, to

$$\frac{dV}{dt} = - \left(\frac{V - V_e}{\tau_\lambda} \right) + V_0 \alpha_g \frac{dT}{dt} - V_0 \kappa_g \frac{d\phi}{dt} \quad (4.1)$$

where $V(t)$ is the specific volume at time t and the associated functions are specified by

$$V_e(t) = V_0 - \alpha_r(T_0 - T_{ge})V_0 - \alpha_g(T_{ge} - T)V_0 - \bar{\kappa}\phi V_0 \quad (\text{at } T < T_{ge})$$

$$V_e(t) = V_0 - \alpha_r(T_0 - T)V_0 - \kappa_r\phi V_0 \quad (\text{at } T \geq T_{ge})$$

$$\Delta\theta(t) = \bar{\kappa}\varphi + \frac{V-V_0}{V_0} - \bar{\alpha}(T - T_0) = \frac{V-V_*}{V_0}$$

$$\tau_\lambda(t) = \tau_{\lambda 0} \exp[-\beta_T(T - T_0)] \exp[-\beta_v \Delta\theta]$$

where T_{ge} is the equilibrium glass transition temperature, $\tau_{\lambda 0}$ is the time constant at the initial temperature, β_T and β_v are shift factor parameters related to temperature change and nonequilibrium volume, respectively. The other symbols have previously been defined (see Appendix A). Here the effect of φ (a scalar stress) on volume relaxation is assumed to be comparatively small and not included in the relaxation function. Although this function can be readily expanded into multiple elements, a single-element is adopted in the analysis for simplicity in showing the essential characteristics of relaxation. The determination of the time constant for volume changes $\tau_{\lambda 0}$ and the related shift factors will be discussed later.

Considering the starting equilibrium state at time zero, the generalized stress-strain equation (Eqn. (9) in Appendix A) reduces to

$$\sigma_{ij} = -\varphi\delta_{ij} + \int_0^t G(t') \exp\left[-\int_{t'}^t \frac{dt''}{\tau_G(t'')}\right] \frac{dC_{ij}^{-1*}}{dt'} dt' \quad (4.2)$$

where $\sigma_{ij}(t)$ is the total stress, $G(t')$ is the modulus (the Lamé's constant), $\tau_G(t'')$ is the time constant for stress changes (also requiring a shift factor), and C_{ij}^{-1*} is the normalized relative Finger strain tensor, in which the strain due to volume change has been subtracted off. This strain tensor, the "pressure-like" scalar φ , and other details of notation are discussed further in the paper [87].

For the uniaxially pulling, the kinematical equation is

$$C_{11}^{-1}(t, t') = \left(\frac{L(t)}{L(t')} \right)^2 = \exp[2\dot{E}(t - t')] \quad (4.3)$$

where $\dot{E}$ is the nearly constant elongation rate, as discussed in the section of experimental procedure. Because of the symmetry of the fiber-like samples, the deformation in the 2- and 3- directions (perpendicular to the fiber axis) should be equal. Using Eqn. (4.3) and the constraint of kinematics (Eqn. (10) in Appendix A), these lateral deformations are given by

$$C_{22}^{-1}(t, t') = C_{33}^{-1}(t, t') = \frac{V(t)}{V(t')} \left(\frac{1}{\exp[\dot{E}(t - t')]} \right) \quad (4.4)$$

where $V(t)$ and $V(t')$ are the volumes at the moment of consideration and at some arbitrary past time, respectively. The corresponding normalized strain tensors are obtained by the definition $C_{ij}^{-1*} = C_{ij}^{-1} - \delta_{ij} - (2/3)(\Delta V/V(t'))\delta_{ij}$, as follows:

$$C_{11}^{-1*} = C_{11}^{-1} - 1 - (2/3)(\Delta V/V(t')) \quad (4.5)$$

and

$$C_{22}^{-1*} = C_{33}^{-1*} = C_{22}^{-1} - 1 - (2/3)(\Delta V/V(t')) \quad (4.6)$$

where $\Delta V = V(t) - V(t')$. Noting that $\sigma_{22} = 0$, one now inserts these kinematical relations into Eqn. (4.2), which yields two equations:

$$\wp(t) = - \int_0^t G(t') \exp(A) \frac{dC_{22}^{-1*}}{dt'} dt' \quad (4.7)$$

and the stress build-up σ_{11}

$$\sigma_{11}(t) = \int_0^t G(t') \exp(A) \frac{d(C_{22}^{-1} - C_{11}^{-1})}{dt'} dt' \quad (4.8)$$

where

$$A = \frac{\exp(-c_3 R t) - \exp(-c_3 R t')}{c_3 \tau_{G0} R} \quad (4.9)$$

in which τ_{G0} is the time constant at the initial temperature (125 °C) and c_3 is the constant in a linearized shift factor equation for $\tau_G = a_T \tau_{G0}$, namely $a_T = \exp[-c_3(T(t) - T_0)]$. The linearization of the shift factor equation is made in order to avoid the inner integral in Eqn. (4.2). The determination of the constants τ_{G0} , c_3 and the modulus $G(t')$ will be discussed later.

These two equations (Eqns. (4.1) and (4.7)) must be solved simultaneously to obtain the two unknowns $V(t)$ and $\phi(t)$. This can be done numerically by guessing the volume changes so as to satisfy the boundary condition of $\sigma_{22} = 0$ (i.e., Eqn. (4.7)). Substituting the volume changes into Eqn. (4.8), the stress build-up σ_{11} can now be determined and compared with the experimental data. The computer program for the analysis is presented in Appendix B.

Before solving these equations, one notes that the derivatives of strain tensors in Eqns. (4.7) and (4.8) as well as the derivative $d\phi/dt$ in Eqn. (4.1) may be expressed in terms of the volume change. After some manipulations, one obtains

$$\frac{dC_{22}^{-1*}}{dt'} = V(t) \left[\frac{\dot{E}V(t') - \dot{V}(t')}{V^2(t') \exp[\dot{E}(t - t')]} + \frac{2}{3} \frac{\dot{V}(t')}{V^2(t')} \right] \quad (4.10)$$

and

$$\frac{d(C_{22}^{-1} - C_{11}^{-1})}{dt'} = V(t) \left[\frac{\dot{E}V(t') - \dot{V}(t')}{V^2(t') \exp[\dot{E}(t - t')]} + 2\dot{E} \exp[2\dot{E}(t - t')] \right] \quad (4.11)$$

Using the Leibnitz's rule for taking derivative of the integral in Eqn. (4.7) gives

the result, which is in turn used in Eqn. (4.1), as follows:

$$\begin{aligned} \frac{d\wp}{dt} = & G(t) \left(\frac{1}{3} \frac{\dot{V}(t)}{V(t)} - \dot{E} \right) + \left(\frac{\dot{V}(t)}{V(t)} - \frac{1}{\tau_{G0} \exp(c_3 R t)} \right) \wp \\ & + \dot{E} V(t) \int_0^t G(t') \exp(A) \left(\frac{\dot{E} V(t') - \dot{V}(t')}{V^2(t') \exp[\dot{E}(t - t')]} \right) dt' \end{aligned} \quad (4.12)$$

where t is the time at consideration, t' is the prior time, $\dot{V}(t') = dV(t')/dt'$, $\dot{V}(t) = dV(t)/dt$, and A is the same as Eqn. (4.9).

4.2.2 Comparisons with Data of the Present Work

In the analysis two sets of parameters need to be specified: one for the volume rate equation and the other for the anisotropic stress equation. The first set of parameters were obtained by fitting the dilatometry data of Greiner and Schwarzl [54], as shown in Figure 4.2. The literature data were measured at atmospheric pressure with constant cooling rates ranging from 0.042 to 120 °C/hr, of which two curves are omitted to avoid crowding. The equation for this fitting were reduced from Eqn. (4.1) by neglecting the terms of $\wp$, as shown below:

$$\frac{dV}{dt} = - \left(\frac{V - V_e}{\tau_\lambda} \right) + V_0 \alpha_g \frac{dT}{dt} \quad (4.13)$$

where the associated functions are specified by

$$V_e(t) = V_0 - \alpha_r(T_0 - T_{ge})V_0 - \alpha_g(T_{ge} - T)V_0 \quad (\text{at } T < T_{ge})$$

$$V_e(t) = V_0 - \alpha_r(T_0 - T)V_0 \quad (\text{at } T \geq T_{ge})$$

$$\Delta\theta(t) = \frac{V - V_0}{V_0} - \bar{\alpha}(T - T_0) = \frac{V - V_e}{V_0}$$

$$\tau_\lambda(t) = \tau_{\lambda 0} \exp[-\beta_T(T - T_0)] \exp[-\beta_v \Delta\theta]$$

where $\tau_{\lambda 0}$ is the time constant at an equilibrium reference state T_0 , V_0 is an initial (equilibrium) volume at the temperature $T_0=125\text{ }^\circ\text{C}$, and α_r and α_g are the rubbery and glassy thermal coefficient of expansion, respectively. As noted previously (see Appendix A), Eqn. (4.13) is essentially Kovacs' one parameter rate equation. The adjustable shift factors β_T and β_v are similar to that suggested by Kovacs et al. [90,92,138]; while β_v is a lumped constant which incorporates Kovacs' structure x and the factor $\Delta\alpha$. The time constant $\tau_{\lambda 0}$ is similar to that obtained by Greiner and Schwarzl, who used a WLF equation with a reference temperature at $T_r = 105\text{ }^\circ\text{C}$ to analyze their volume relaxation data for polystyrene; that is

$$\log a_T = \frac{-c_1(T - T_r)}{c_2 + T - T_r} \quad (4.14)$$

where $c_1 = 10.37$, $c_2 = 44.3\text{ }^\circ\text{C}$ [54]. In the present analysis their time constant ($\tau_r = 0.3\text{ sec}$ at $105\text{ }^\circ\text{C}$) was adjusted to a new reference time constant $\tau_{\lambda 0}$ at the initial temperature $125\text{ }^\circ\text{C}$, using Eqn. (4.14).

$$\tau_{\lambda 0}(125\text{ }^\circ\text{C}) = \tau_r a_T(125\text{ }^\circ\text{C}) = 1.77 \times 10^{-4}\text{ sec} \quad (4.15)$$

The values of α_r and α_g were directly taken from the measurements of Greiner and Schwarzl [54]. Values for the equilibrium glass transition temperature (T_{ge}) will be discussed below. The fitting parameters and the values of the compressibility coefficients (taken from Ferry's book [37]) were brought into Eqn. (4.1) for the present analysis.

The second set of parameters needed in the analysis includes a time constant for stress relaxation (τ_{G0}), a linearized shift factor equation, and the modulus

as a function of temperature. The time constant τ_{G0} was obtained by fitting the shear rate and shear viscosity data (also the normal stress data) of Racin [135], using the Bogue-White model (Eqn. (2-15)). Since the data was measured at a high temperature (160 °C), the time constant need to be adjusted to the starting temperature of this work (125 °C), giving finally $\tau_{G0} = 324 \text{ sec}$ at 125 °C. The shift factor equation used by Racin is analogous to Eqn. (4.14) but with a somewhat different parameters. A linearization of the shift factor equation was made between 125 to 70 °C to avoid the double integration in Eqn. (4.2), as previously discussed. Although the corresponding shift factor from Racin's data is not out-of-line with the present linearized form, the constant $c_3 = 0.22 \text{ }^\circ\text{C}^{-1}$ must finally be taken as "semi-empirical" in the sense that the linearization and the large extrapolation are made. However, it does not have much effect on the result because of the very large values of τ_G at the lower temperature.

Values for the equilibrium glass transition temperature (T_{ge}) have been given in the literature. A value as low as 70 °C has been quoted in Isayev and Har-
 iharan [76]. But Snow [159] has reviewed a great deal of the literature on
 volume-temperature data at slow cooling rates (for example, [146,93]), which
 one hopes will show the "equilibrium" T_{ge} , and concluded that 85 °C is prob-
 ably a reasonable mid-range value for the transition. Generally T_{ge} of 85 °C
 was used in most of the analyses (see Chapters 5 and 6). But in the present
 chapter a lower effective T_{ge} of 75 °C was selected for convenience, because the
 experiments were stopped at about 75 °C. This selection does not make any
 practical difference in the final analysis.

Finally the modulus $G(T)$ was taken to be that given by the continuous curve in Figure 4.3, the vertical cross-hatching summarizing the range of values from eight literature sources, as reviewed by Wust and Bogue [207]. The final function of $G(T)$ was empirically chosen so as to obtain a reasonable fit to the stress build-up data of Figures 4.4 – 4.6. There is obviously considerable latitude in placing the curve in Figure 4.3, but it is within the bounds established by the prior literature. The material constants (except the function $G(T)$ of Figure 4.3) and parameters used in the analysis are summarized in Table 4.1.

The theoretical predictions were obtained by simultaneously solving Eqs. (4.1) and (4.7). The numerical algorithm involved a trial-and-error procedure to guess the volume changes so as to satisfy the boundary condition $\sigma_{22} = 0$. The volumes so obtained were inserted into Eqn. (4.8) to calculate the stress build-up. As shown in Figures 4.4 – 4.6 at various cooling rates, reasonable fits were obtained. The range of stresses covered in the log scale in these figures is large, which means that there are significant differences between theory and experiment at individual points, but the overall fit does nonetheless pick up the essential features of the data over a considerable range of pulling rates.

The predicted coupling effect is shown in Figure 4.7. At low pulling rates the volume decreases with decreasing temperature, as one would expect from a straightforward argument based on a thermal coefficient of expansion. At high pulling rates, however, the tensile stress is high enough to induce a significant “Poisson’s ratio effect” (i.e., an increase of volume with tensile stress),

large enough in fact to override the contraction with temperature. This effect occurs naturally in the theory by means of the scalar stress $\wp$ (as calculated by Eqn. (4.7), which in turn enters into the generalized volume rate equation (Eqn. (4.1)). However, in the present work force data were measured, but not volume data, and thus the effect of volume changes is being seen only indirectly.

One notes that the result of stress build-up is strongly dependent on the choice of the modulus. The function $G(T)$ is obviously not the most basic way to introduce the modulus. Even though we allow the modulus G to depend on temperature, the model is “one-element”, in the sense that each choice of G is not allowed to be coupled with a particular time constant and an accompanying shift factor. Further study on these aspects is being continued in a separate project [79].

Finally it was concluded that the essential features can be picked up by the theory with a set of two moduli and two time constants (and accompanying shift factors), with all values being in plausible agreement with prior literature. Applications of the theory to practical processes involving volume changes (the cooling step in injection molding and the related residual stress problem) will be done in the following chapters.

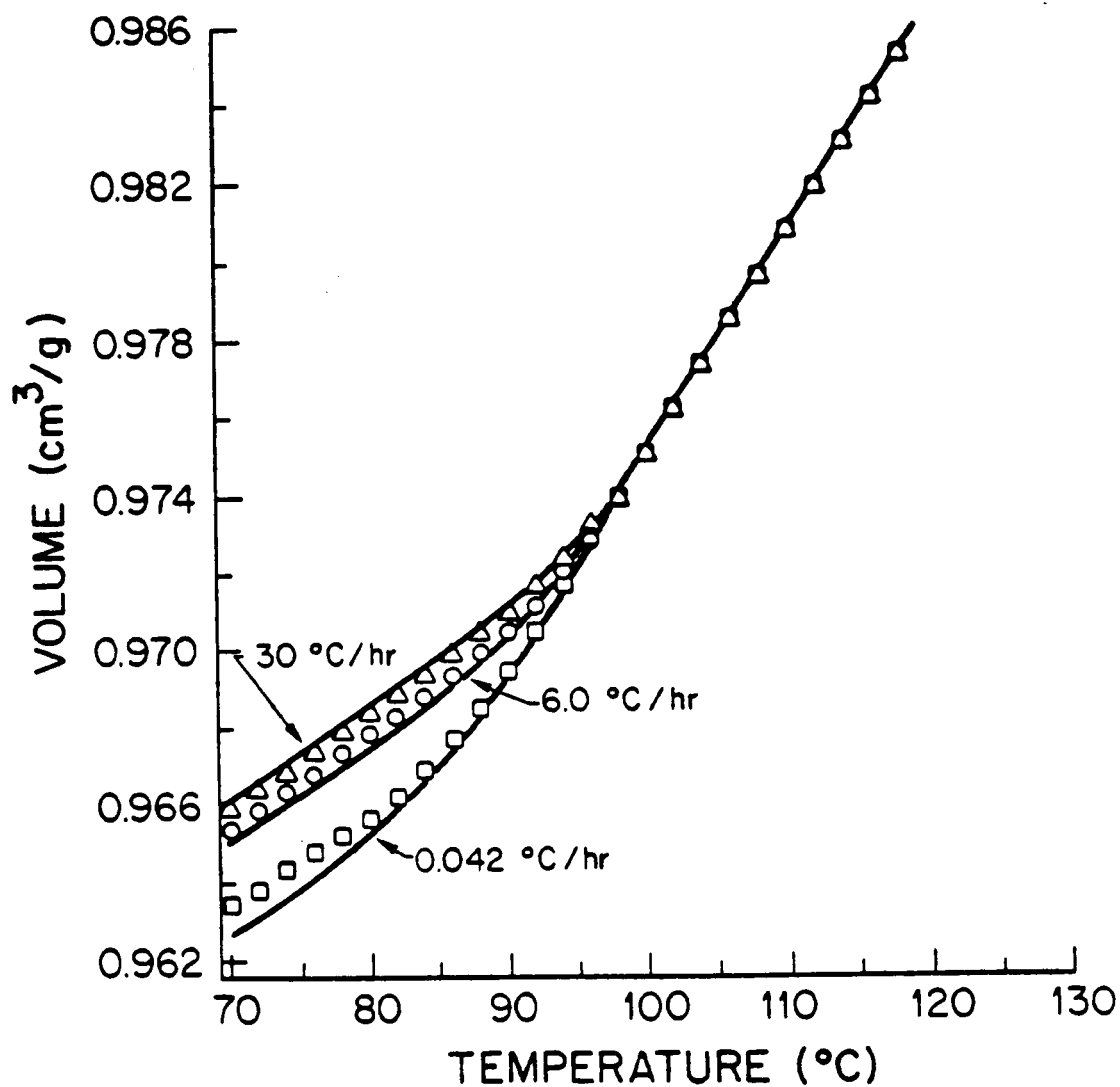


Figure 4.2: Comparison of theory with the cooling rate-dependent volume data of Greiner and Schwarzl [54], for PS. (Lines for theory; symbols for data, rates as shown.)

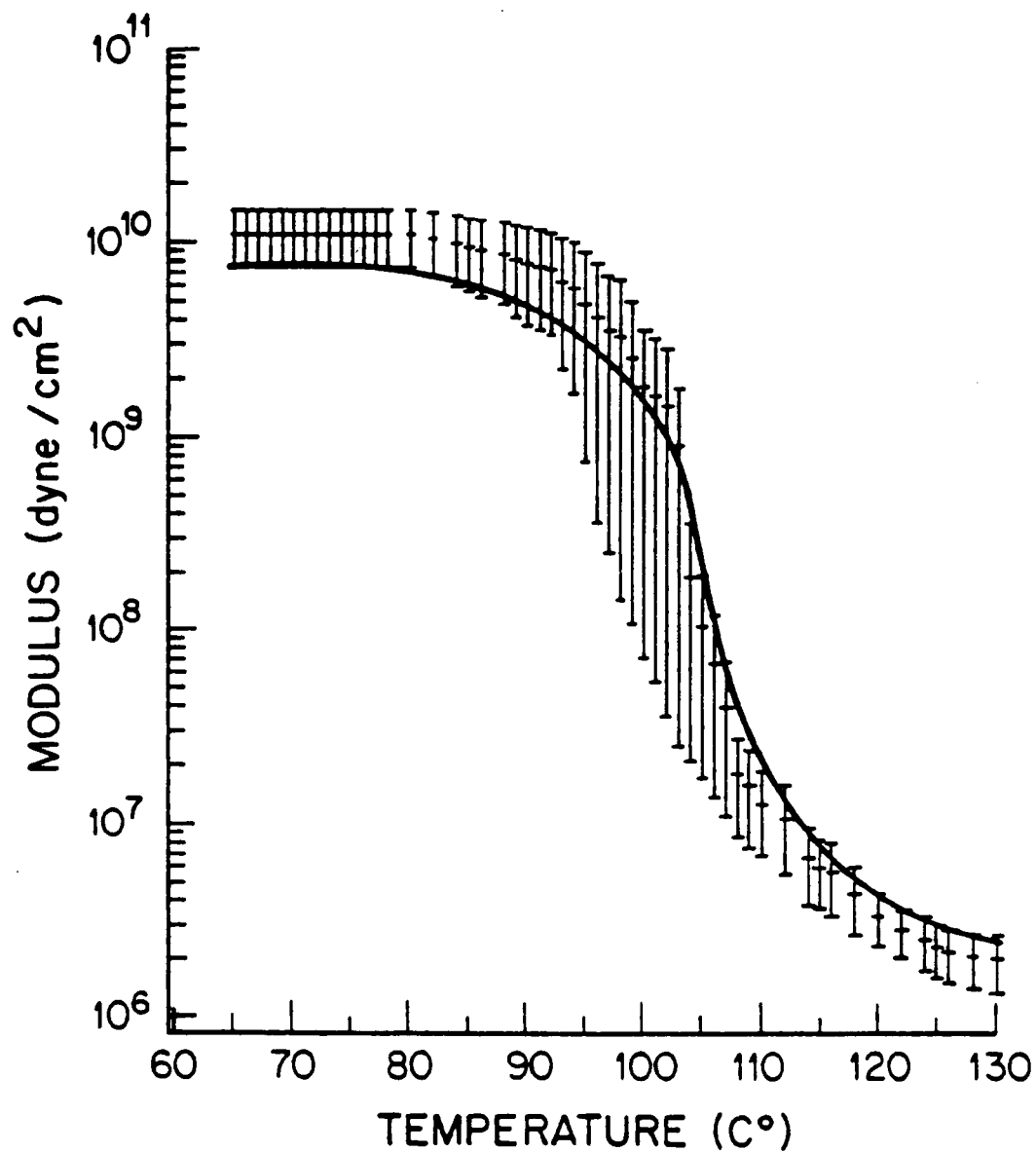


Figure 4.3: Elastic modulus G as a function of temperature. (Continuous curve for values used in modelling Figures 4.4 – 4.6. Vertical cross-hatching for the range of literature values as summarized by Wust and Bogue [207].)

Table 4.1: Summary of material constants and parameters used in the analysis of simultaneous pulling and cooling experiments.

Material constants (values in reasonable agreement with prior literature):	
V_0	$= 0.9893 \text{ cm}^3/g \quad (\text{at } 125 \text{ }^\circ\text{C})$
$\tau_{\lambda 0}$	$= 1.77 \times 10^{-4} \text{ sec} \quad (\text{at } 125 \text{ }^\circ\text{C})$
τ_{G0}	$= 3.24 \times 10^2 \text{ sec} \quad (\text{at } 125 \text{ }^\circ\text{C})$
α_r	$= 5.68 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$
α_g	$= 2.48 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$
κ_r	$= 9.10 \times 10^{-11} \text{ cm}^2/\text{dyne}$
$\bar{\kappa}$	$= 6.20 \times 10^{-11} \text{ cm}^2/\text{dyne}$
$T_{g\epsilon}$	$= 75 \text{ }^\circ\text{C}$
Adjustable parameters (values adjusted empirically in the present work):	
$G(T)$	: see Figure 4.3 and Appendix C
β_T	$= 0.47 \text{ }^\circ\text{C}^{-1}$
β_v	$= 4.0 \times 10^2$
c_3	$= 0.22 \text{ }^\circ\text{C}^{-1}$

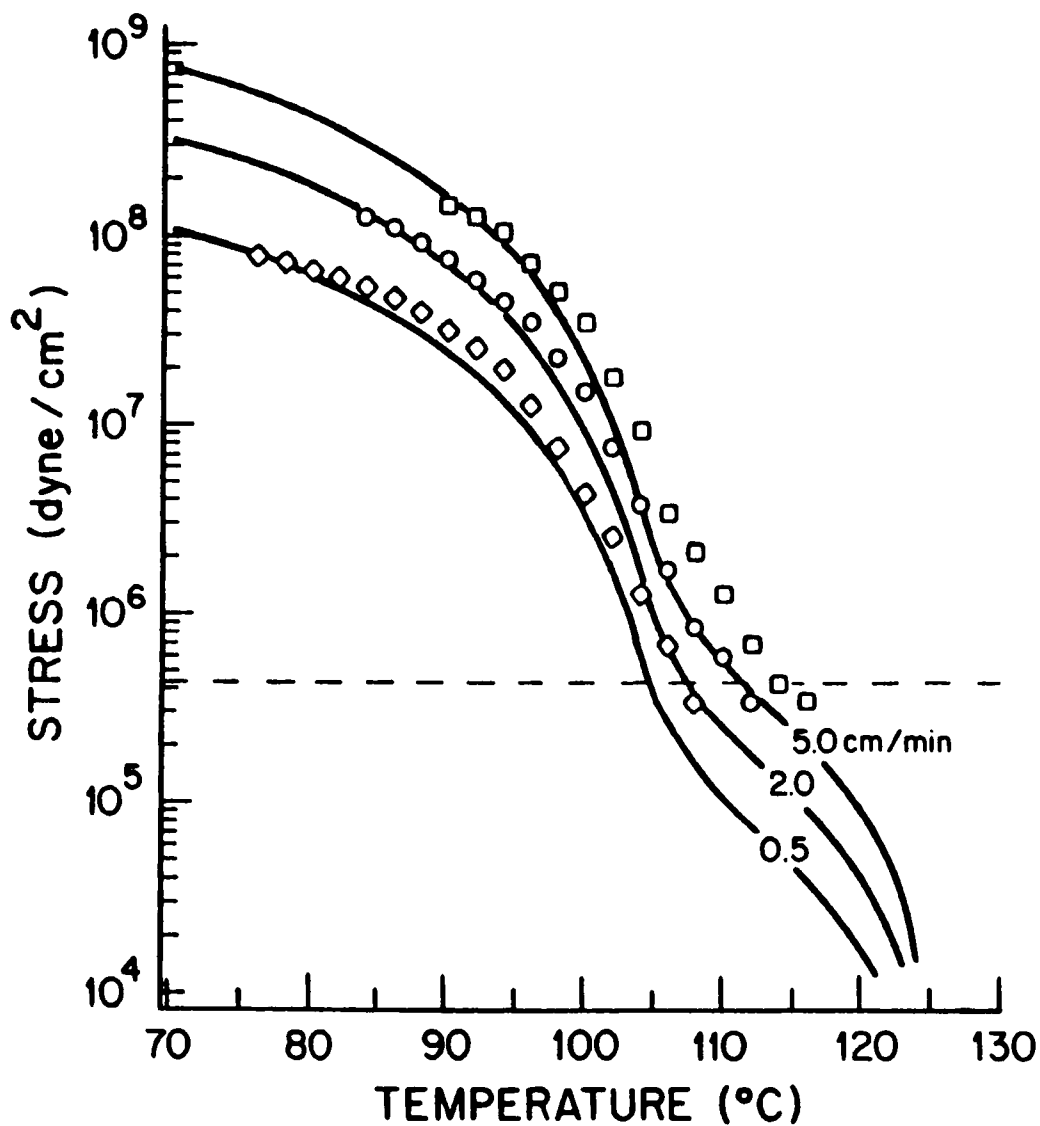


Figure 4.4: Comparison of theory with the stress build-up data of the present work, for PS ($R = 1.15\text{ }^{\circ}\text{C}/\text{sec}$). (Lines for theory; symbols for data, pulling rates as shown. Horizontal broken line for the stress level above which forces could be measured accurately.)

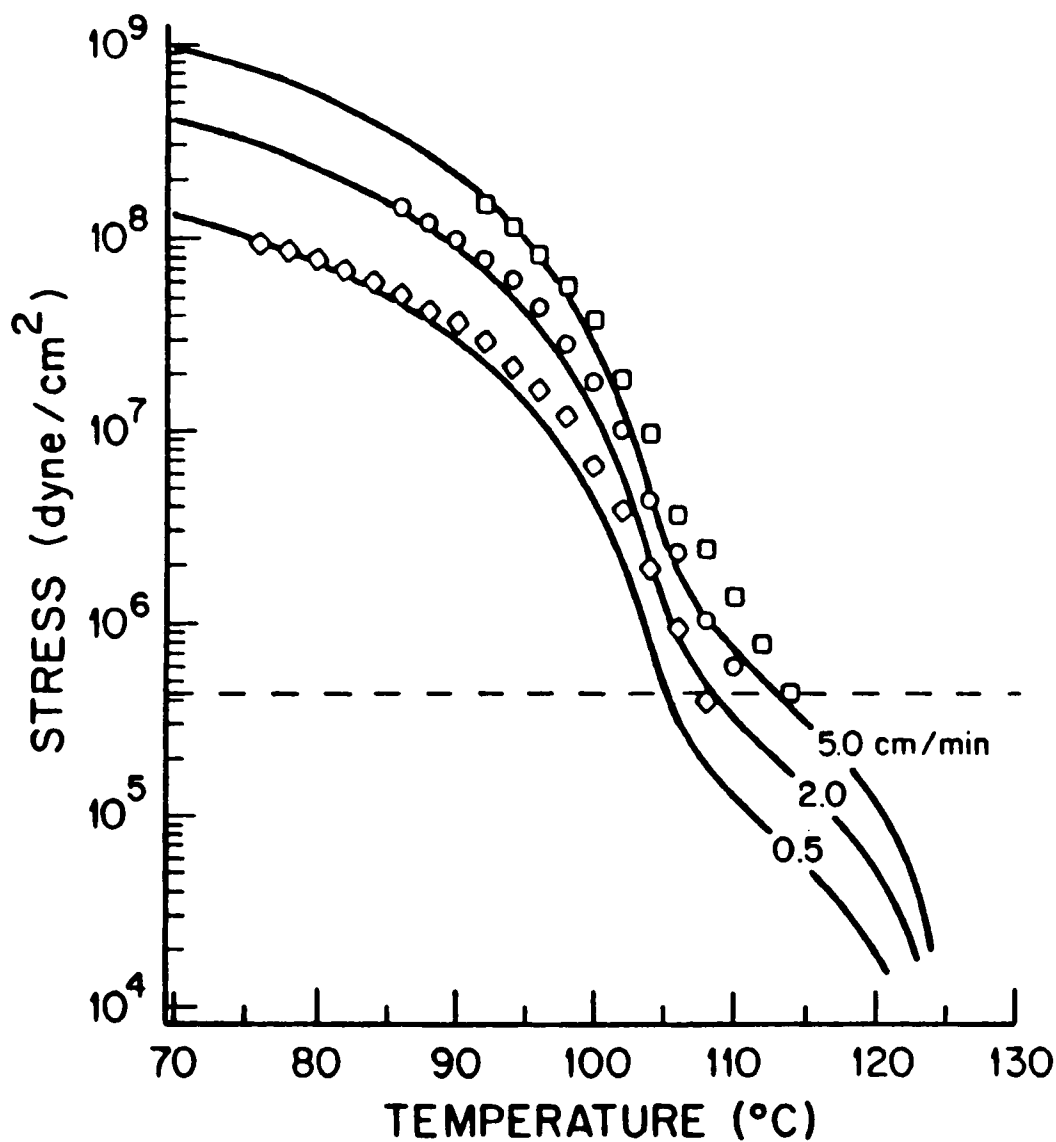


Figure 4.5: Comparison of theory with the stress build-up data of the present work, for PS ($R = 2.50^\circ\text{C}/\text{sec}$). (Lines for theory; symbols for data, pulling rates as shown. Horizontal broken line for the stress level above which forces could be measured accurately.)

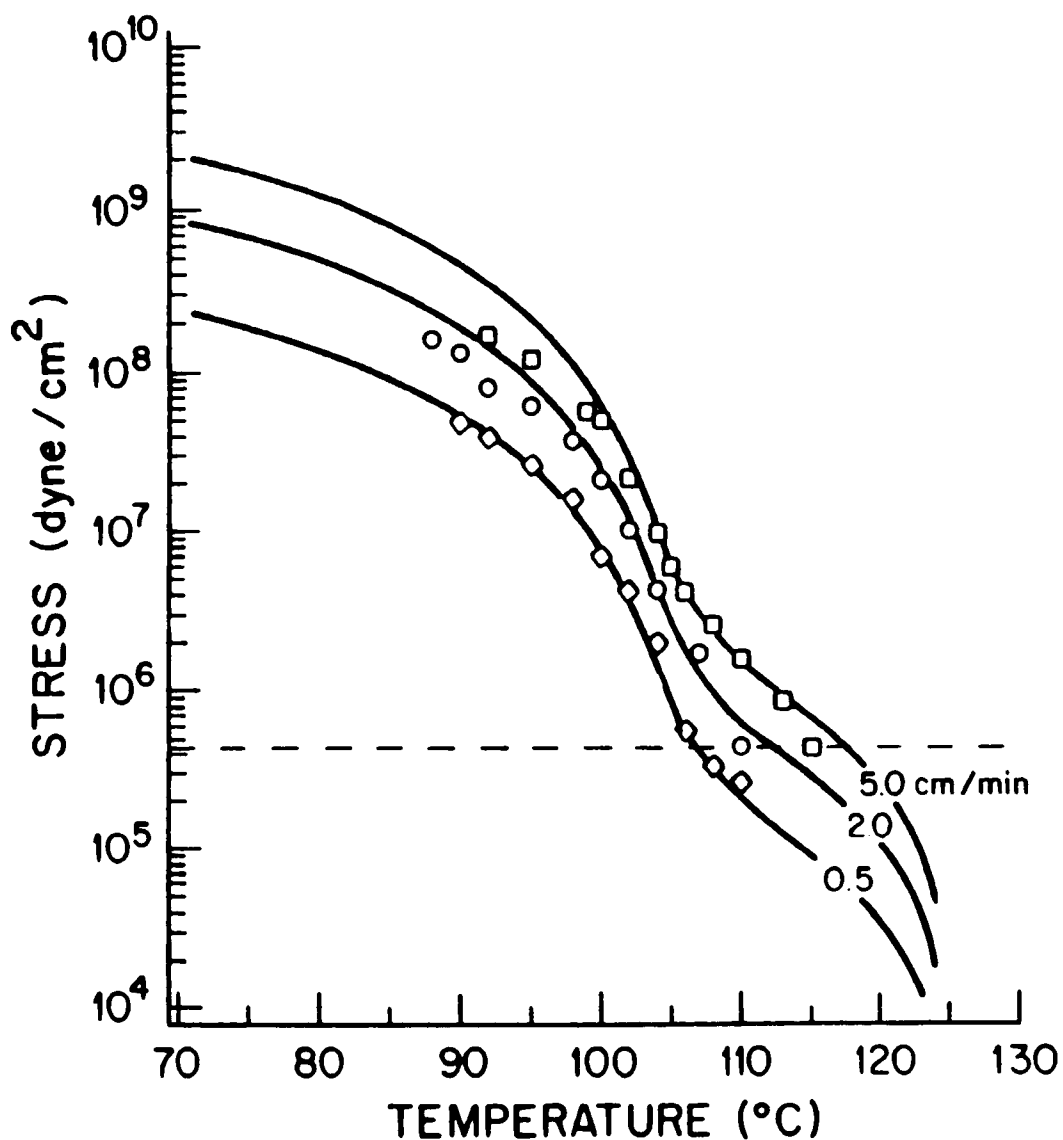


Figure 4.6: Comparison of theory with the stress build-up data of the present work, for PS ($R = 3.30\text{ }^{\circ}\text{C/sec}$). (Lines for theory; symbols for data, pulling rates as shown. Horizontal broken line for the stress level above which forces could be measured accurately.)

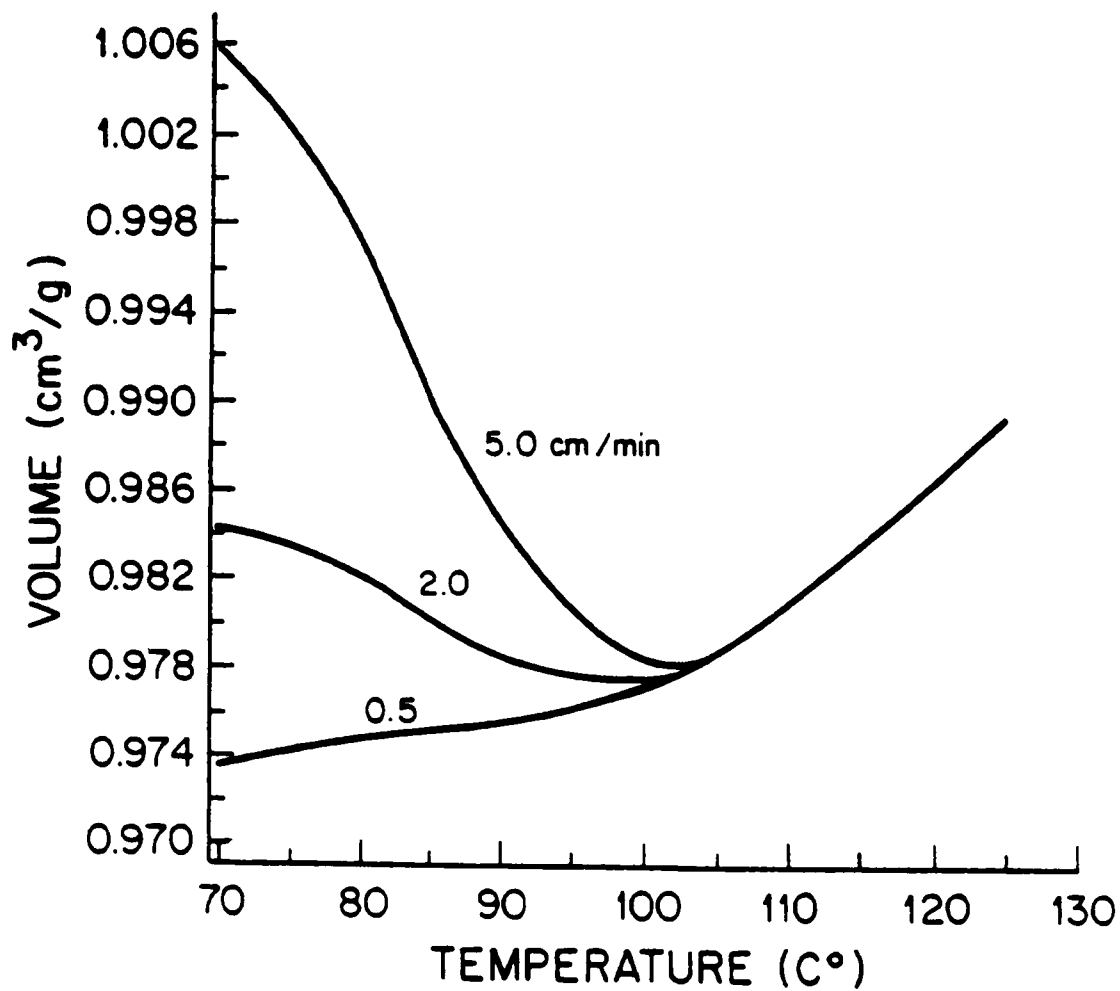


Figure 4.7: Predicted volume changes as a function of temperature, at various pulling rates and a typical cooling rate ($1.15^{\circ}\text{C}/\text{sec}$).

CHAPTER 5

SIMULATION OF THE COOLING STEP IN INJECTION MOLDING

As a polymer melt is introduced into an injection mold and solidified there, several steps can be identified, as shown schematically in Figure 2.2. In prior literature work on the cooling step in injection molding, equilibrium PVT relationships have been assumed, as reviewed in Chapter 2. In view of the rapid cooling always involved, that assumption is not likely to be satisfactory, a conclusion reached by the Cornell group as well [192]. In this chapter we will present two cases to simulate the cooling step, both using the Ko-Bogue equations. Similar to the prior literature work an equilibrium PVT equation will be used in the first case. Then a time-dependent PVT equation is introduced in the second case to account for non-equilibrium behavior. For mathematical tractability, a simple rectangular cavity is adopted, as in the Cornell report [191]. The theoretical development for both cases will be discussed first, followed by the comparisons with the literature data [191].

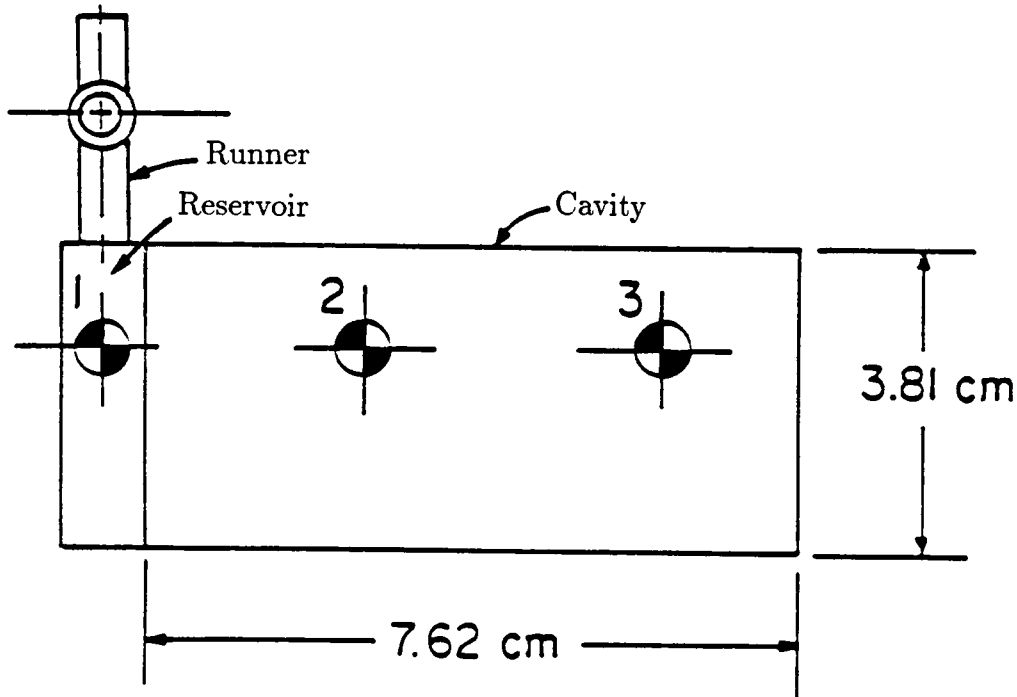
5.1 Theoretical Development

The present work involves a simulation of the cooling step, but in order to do that one must consider the prior steps as well. The analysis is a "simulation" in that the complicated pressure and temperature distributions which are present in an actual injection-molded part are simplified somewhat. That is, during the cooling step we assume there is no pressure and temperature gradients in the plane along the flow directions (a temperature gradient is presumed to exist only in the gapwise direction).

Data for comparison with the analyses are taken from the work of the Cornell group [191]. In that work a polystyrene melt at 200 °C was packed into a rectangular (slab-shaped) cavity with the long dimensions being the directions of flow, as shown schematically in Figure 5.1. The pressure was measured at three positions along the x_1 direction, one of the flow directions, see Figure 5.1. At the end of the packing step the pressure was somewhat higher at point 1 than point 2, which in turn was somewhat higher than point 3. In the present work, however, we imagine that in the x_1x_3 plane of the slab the pressure and also the temperature are uniform and similar to that at point 3. The pressure prior to the cooling step will be imposed as a known function and the computer analysis will predict the decrease of pressure during the cooling step.

While there is no pressure gradient in the gapwise direction (as can be proved by considering a differential force balance with negligible inertial terms), there is, of course, a sharp and rapidly changing temperature distribution in that

Geometry of the cavity (taken from the experiments of the Cornell group):



Cavity thickness = 0.254 cm

Melt temperature = 200 °C

Mold temperature = 32 °C

Material : Polystyrene (Styron 678U/Dow)

The pressure trace at point 3 is simulated in the present work.

Figure 5.1: Schematic diagram of the cavity and the processing conditions in injection molding (summarized from experiments of the Cornell group [191]).

direction (see Figure 5.1). During the cooling step this gapwise distribution can be calculated from standard theory for transient heat transfer in a solid slab (see the computer program in Appendix C). However, "time zero" in the heat transfer theory cannot be taken as the time at the beginning of the cooling step, because the temperature is not uniform (in the gapwise direction) then, some cooling having already taken place during the mold filling and packing steps.

The extent of cooling in the filling step was estimated by running the C-FLOW mold filling program (see Chapter 2) under the conditions given in the Cornell work [191]. At the moment the mold filled, the gapwise temperature profile at point 3 was read out of the C-FLOW program. It was found that this profile could be reasonably approximated by running the transient heat transfer program for 0.16 sec, starting with a slab at an initial uniform temperature of 200 °C, exposed to a surface temperature of 32 °C at time zero. A comparison of the C-FLOW temperature profile and that from transient heat transfer theory is shown in Figure 5.2. One notes that point 3 is close to the end of the flow direction in Figure 5.1. Thus the time after the melt passes point 3 until the mold filled is quite short. It is the same short time for heat conduction in the gapwise direction. That explains why the heat transfer program runs only 0.16 sec to simulate the temperature distribution at the end of the filling step at point 3. In the the final analysis, then, the thermal history was traced by running the heat transfer program for 16.26 sec — that is, 0.16 sec for the filling simulation, 0.1 sec for the packing simulation (as will be explained below), and

then 16 sec for the cooling step itself.

When the problem was first considered, it was felt that the packing step could be approximated by a step change in pressure, since this step takes place very rapidly (in about 0.1 sec as estimated from the Cornell work [191]). A step change in pressure causes mathematical difficulties, however, because differential equations are involved. To avoid a step change, a continuous (but steeply changing) function was taken as an approximation to the experimental pressure at point 3 prior to the cooling step:

$$\wp(t) = 7.7 \times 10^7 \exp(12.3t) - 7.7 \times 10^7 \quad (5.1)$$

where t is the time in seconds and $\wp(t)$ is the pressure in dyne/cm^2 . This is imposed from time zero up to the point of the end of the packing step, at which point the pressure reaches $4.74 \times 10^8 \text{ dyne/cm}^2$. From that point onward the computer program calculates the pressure $\wp(t)$ (as well as the temperature $T(x_2, t)$, as previously described). The algorithm for this calculation is essentially based on imagining a slab of constant mass and constant overall volume (i.e., the volume of the cavity). One also imagines the slab to be divided into thin layers (along the x_1x_3 plane) for calculating the gapwise temperature distribution and the specific volume. This function $\wp(t)$ is thus obtained numerically by a trial-and-error procedure such that the overall mass in the cavity is constant during the cooling step. That is, one fits the following boundary condition:

$$\int_{-b}^b \frac{1}{V(x_2, t)} (L_1 L_3 dx_2) = M \quad (5.2)$$

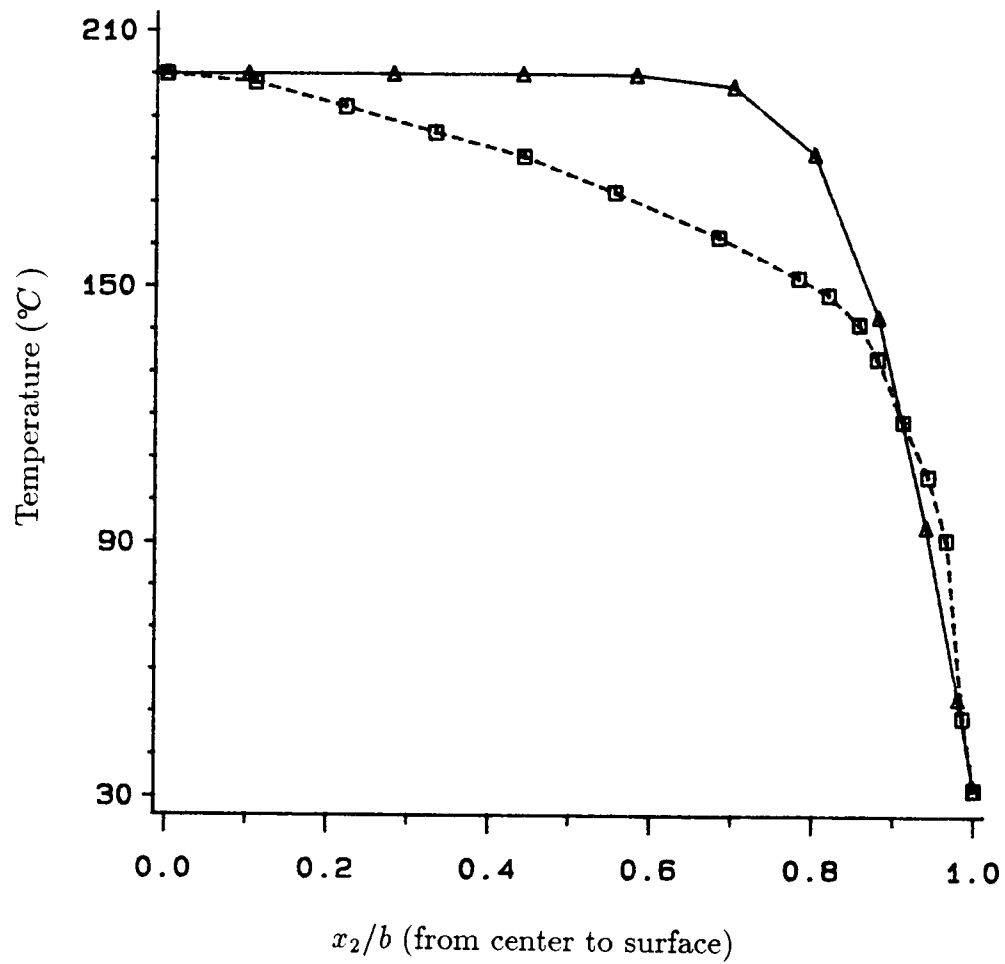


Figure 5.2: Comparison of simulated gapwise temperature profiles at the end of mold filling. (Solid line for the transient heat transfer theory (Eqn. (5.3)), broken line for the C-FLOW mold filling program.)

where b is half of the gap thickness; L_1 and L_3 are the long dimensions of the cavity; $V(x_2, t)$ is the specific volume of each layer at time t . The constant overall mass M can be obtained from the weight of the molded part (or estimated from the cavity volume and the specific volume at the temperature of mold wall).

The equation of transient heat transfer with an infinite heat transfer coefficient for a solid slab can be written as

$$\frac{T - T_w}{T_0 - T_w} = 2 \sum_{n=0}^{\infty} \left[\frac{(-1)^n}{(n + \frac{1}{2})\pi} \cos \left((n + \frac{1}{2})\pi \frac{x_2}{b} \right) \exp \left(-(n + \frac{1}{2})^2 \pi^2 \frac{\alpha t}{b^2} \right) \right] \quad (5.3)$$

where $T(x_2, t)$ is the temperature at x_2 (the midpoint of each layer) at time t ; T_0 is the melt temperature; T_w is the wall temperature of the mold; α is the thermal diffusivity. The boundary conditions are imposed by imagining that a slab at an initial uniform temperature of T_0 is exposed to a constant surface temperature of T_w at time zero.

As the temperature drops, so does the pressure. The changes of specific volume depend on some combined effects of temperature and pressure. Although the overall volume in the cavity is constant, the specific volumes of the individual layers are not, because of the gapwise temperature distribution. The changes of specific volume may be described by equilibrium PVT equations as in the prior literature work as reviewed in Chapter 2. However, a more rigorous analysis should consider the time effects since the rapid cooling involved. Therefore, two cases are included in this study: one using an equilibrium PVT equation, and the other, using a time-dependent PVT equation, both derived

from Eqn. (2) in Appendix A. The layout of the governing equations during the cooling step will now be presented for each of these two cases.

5.1.1 Equilibrium PVT Case for the Cooling Step

The starting temperature distribution and pressure at the beginning of the cooling step can be simulated as described above. The gapwise temperature distribution is calculated by Eqn. (5.3). If one neglects the time effects, as in prior work in the literature, the changes of specific volume of each layer may be traced by an equilibrium PVT equation. Such an equation is taken from Eqn. (4) in Appendix A for the cooling step. To impose an equilibrium state one lets $\Delta\theta = 0$, as discussed in the paper [87], and obtains finally

$$\frac{\Delta V}{V_0} = -\alpha_r(T_0 - T_{ge}) - \alpha_g(T_{ge} - T) - \bar{\kappa}\wp \quad (5.4)$$

where $\Delta V/V_0 = (V - V_0)/V_0$ and the symbols have been defined in Appendix A. One notes that P_0 , the atmospheric pressure, has been taken as zero by thinking of $\wp$ as “gauge pressure”. The subscript “zero” stands for the initial equilibrium state at time zero. At temperatures above T_{ge} Eqn. (5.4) obviously reduces to

$$\frac{\Delta V}{V_0} = -\alpha_r(T_0 - T) - \bar{\kappa}\wp \quad (5.5)$$

Although the total volume (or mass) in the cavity is constant during the cooling step, the specific volume of each layer is not, due to the temperature distribution. As the temperature drops, the pressure $\wp(t)$ decreases as a function of time. The function $\wp(t)$ is obtained numerically by trial-and-error such

that the boundary condition (Eqn. (5.2)) is satisfied during the cooling step, as previously discussed. The iteration continues until the center layers have been cooled down below T_{ge} ; that is, for about 16 sec of cooling, at which time the mold is opened. The computer program for the equilibrium PVT case is presented in Appendix B. A more rigorous simulation including the time effects for the cooling step now follows.

5.1.2 Time-dependent PVT Case for the Cooling Step

Because of the rapid cooling in injection molding, the thermal history and thus volume effects should be traced from the beginning of the filling step. This time-dependent non-equilibrium behavior becomes more complicated because of the high pressure that is involved. A time-dependent PVT equation is therefore needed to describe the influences of both thermal and pressure histories on the volume changes. Such an equation can be derived from our generalized PVT equation (Eqn. (2) in Appendix A), as shown in Chapter 3; that is

$$\frac{dV}{dt} = - \left(\frac{V - V_e}{\tau_\lambda} \right) + V_0 \alpha_g \frac{dT}{dt} - V_0 \kappa_g \frac{d\wp}{dt} \quad (5.6)$$

where $V(x_2, t)$ is the specific volume of each layer at time t . The associated functions are specified by

$$V_e(x_2, t) = V_0 - \alpha_r(T_0 - T_{ge})V_0 - \alpha_g(T_{ge} - T)V_0 - \bar{\kappa}\wp V_0 \quad (\text{at } T < T_{ge})$$

$$V_e(x_2, t) = V_0 - \alpha_r(T_0 - T)V_0 - \bar{\kappa}\wp V_0 \quad (\text{at } T \geq T_{ge})$$

$$\Delta\theta = \bar{\kappa}\wp + \frac{V-V_0}{V_0} - \bar{\alpha}(T - T_0) = \frac{V-V_e}{V_0}$$

$$\tau_\lambda(x_2, t) = \tau_{\lambda 0} \exp[-\beta_T(T - T_0)] \exp[\beta_p \wp] \exp[-\beta_v \Delta\theta]$$

The symbols have been defined in the paper (see Appendix A). One notes that the combined effects of temperature, pressure and non-equilibrium free volume can easily be built into the relaxation function to describe the time-dependent behavior. A single-element relaxation function is used for simplicity in showing the characteristics of relaxation.

The same assumption of temperature and pressure uniformity in the x_1x_3 plane continues to be used in the time-dependent PVT case. Similar to the equilibrium case, the temperature distribution prior to the cooling step (that is, during the "simulated" filling and packing steps) was simulated by running the transient heat transfer program (Eqn. (5.3)) for 0.26 sec; while the pressure $\varphi(t)$ was imposed for the packing step by Eqn. (5.1). In the present case derivatives of T and φ are also needed in Eqn. (5.6). By taking the time derivative of Eqn. (5.3), $dT(x_2, t)/dt$ at the midpoint x_2 of each layer is obtained for all steps. This temperature derivative can be written as

$$\begin{aligned} \frac{dT}{dt} = 2(T_0 - T_w) \sum_{n=0}^{\infty} & \left[\frac{(-1)^n}{(n + \frac{1}{2})\pi} \cos \left((n + \frac{1}{2})\pi \frac{x_2}{b} \right) \right. \\ & \left. \exp \left(-(n + \frac{1}{2})^2 \pi^2 \frac{\alpha t}{b^2} \right) \left(-(n + \frac{1}{2})^2 \pi^2 \frac{\alpha}{b^2} \right) \right] \end{aligned} \quad (5.7)$$

Following a comparatively small pressure (and thus the pressure derivative) in the filling step, the imposed pressure derivative in the packing step $d\varphi(t)/dt$ is obtained from the time derivative of Eqn. (5.1), as follows:

$$\frac{d\varphi}{dt} = 9.47 \times 10^8 \exp(12.3 t) \quad (5.8)$$

Having these associated equations and the relaxation time function, the specific

volume of each layer during the filling and packing steps can be calculated from Eqn. (5.6).

The non-equilibrium volumes created from the prior histories are remembered and brought into the cooling step. During the cooling step these equations, except the $\varphi(t)$ and $d\varphi(t)/dt$, continue to be used. The pressure $\varphi(t)$ of the cooling step (and thus $d\varphi(t)/dt$) is obtained numerically by a trial-and-error solution such that the boundary condition (Eqn. (5.2)) is satisfied. A fourth-order Runge-Kutta method is used for solving the differential volume equation. The iteration procedure continues for 16 *sec* during the cooling step. The computer program for the time-dependent PVT case is presented in Appendix C. The various pressure decreases predicted during the cooling step will now be compared with the literature data.

5.2 Fitting the Literature Data

Experimental pressure data for comparison were taken from the Cornell work [191]. The dimensions of the cavity and the processing conditions in that work (see Figure 5.1) were employed in the simulation. Theoretical predictions from both cases will now be compared with the pressure decreases at point 3.

5.2.1 Theoretical Fitting of the Equilibrium PVT Case

The material constants, except $\bar{\kappa}$, and the initial specific volume V_0 of polystyrene in Eqns. (5.3), (5.4) and (5.5) were taken directly from the experi-

mental measurements of Greiner and Schwarzl [54]. The value of the average $\bar{\kappa}$ was used as an adjustable parameter in order to fit the data at point 3. The material constants and the adjustable parameter used in the equilibrium ϕ VT case are summarized in Table 5.1. As shown in Figure 5.3, good fits were obtained by using a value of $1.72 \times 10^{-10} \text{ cm}^2/\text{dyne}$ for $\bar{\kappa}$. Typical values of κ_g and κ_r of polystyrene, as found in the Ferry's book [37], are $9.10 \times 10^{-11} \text{ cm}^2/\text{dyne}$ and $3.03 \times 10^{-11} \text{ cm}^2/\text{dyne}$ for the glassy and rubbery state, respectively. Compared with these typical values the $\bar{\kappa}$ value chosen for fitting the data is too high. A larger value of $\bar{\kappa}$ may be due partly to the neglect of the time effects on volume changes in the simulation. The predicted specific volume distribution in the gapwise direction after the cooling step becomes uniform finally, as one expects if the time effects are neglected.

5.2.2 Theoretical Fitting of the Time-dependent PVT Case

Eqns. (5.3) and (5.6), combined with the associated functions, were simultaneously solved by guessing the pressure decreases $\phi(t)$ so as to satisfy the boundary condition of Eqn. (5.2). The material constants, except $\bar{\kappa}$, again follow the values of Greiner and Schwarzl [54]. The time constant ($\tau_{\lambda 0}$) and shift factors (β_T and β_v) were obtained from fitting the dilatometric volume data of Greiner and Schwarzl, as described in Chapter 4. One notes that the cooling rates in injection molding can be as high as hundreds of degrees per second near the mold wall. A large extrapolation cannot be avoided, because of the lack of volume data at such high cooling rates. The pressure shift factor parameter β_p

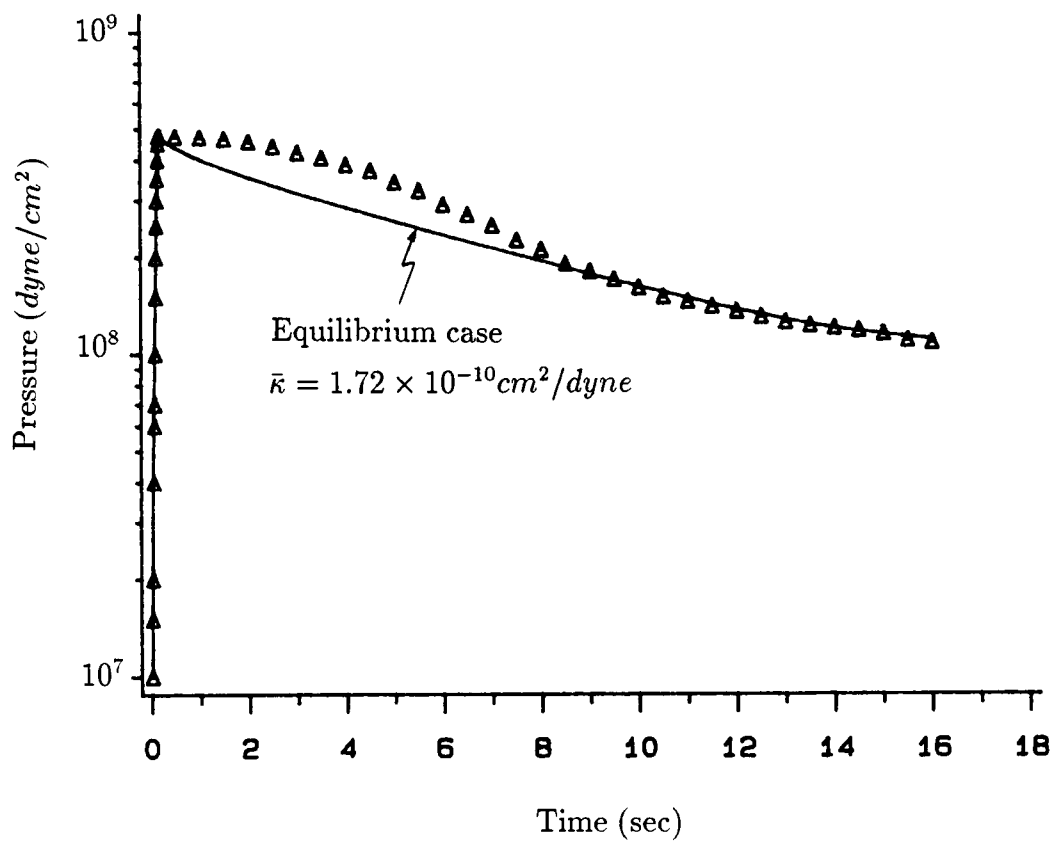


Figure 5.3: Comparison of literature data with simulated pressures for the cooling step, for the equilibrium PVT case. (Symbols are experimental data of the Cornell group [191], solid line is theoretical prediction of the equilibrium case.)

was obtained from the equivalence effects of temperature and pressure on T_g . The measurements of dT_g/dP by Oels and Rehage [126], Zehavi and Filisko [209], and Greener [53] all give the values of β_p in good agreement with each other (about $1.40 \times 10^{-8} \text{ cm}^2/\text{dyne}$). An average value of $\bar{\kappa}$ is needed in the associated function V_e , because a “pressure-induced glass transition point” is not clearly defined as a “temperature-induced glass transition point.” This has been discussed in more detail in the paper (see Appendix A). The adjustable parameter $\bar{\kappa}$ and the other material constants are summarized in Table 5.2 for the time-dependent ρVT case.

As shown in Figure 5.4, good fits to the pressure data at point 3 were obtained by using a value of $9.00 \times 10^{-11} \text{ cm}^2/\text{dyne}$ for $\bar{\kappa}$. This value is within the range of κ_r and κ_g and is somewhat more reasonable. The corresponding specific volume profile in the gapwise direction is shown in Figure 5.5. One finds that a predicted specific volume profile persists in the molded part even after the temperature distribution becomes uniform. That is shown here for possible feature only, because no data for comparison are available.

Comparisons of pressure prediction between these two cases are also made in Figure 5.4. For the curve marked “time-dependent case” a $\bar{\kappa}$ value of $9.00 \times 10^{-11} \text{ cm}^2/\text{dyne}$ and time effects were both introduced; for the curve marked “equilibrium case”, the same value of $\bar{\kappa}$ ($9.00 \times 10^{-11} \text{ cm}^2/\text{dyne}$) was used alone. One sees clearly that the equilibrium case in Figure 5.4 cannot predict the right trend; although in the previous section one can fit the data by choosing a much larger value of $\bar{\kappa}$ ($1.72 \times 10^{-10} \text{ cm}^2/\text{dyne}$). Finally, from these comparisons we

can conclude that, while fits to the data can be obtained in both cases, the time-dependent case can be fit using a more reasonable choice of $\bar{\kappa}$.

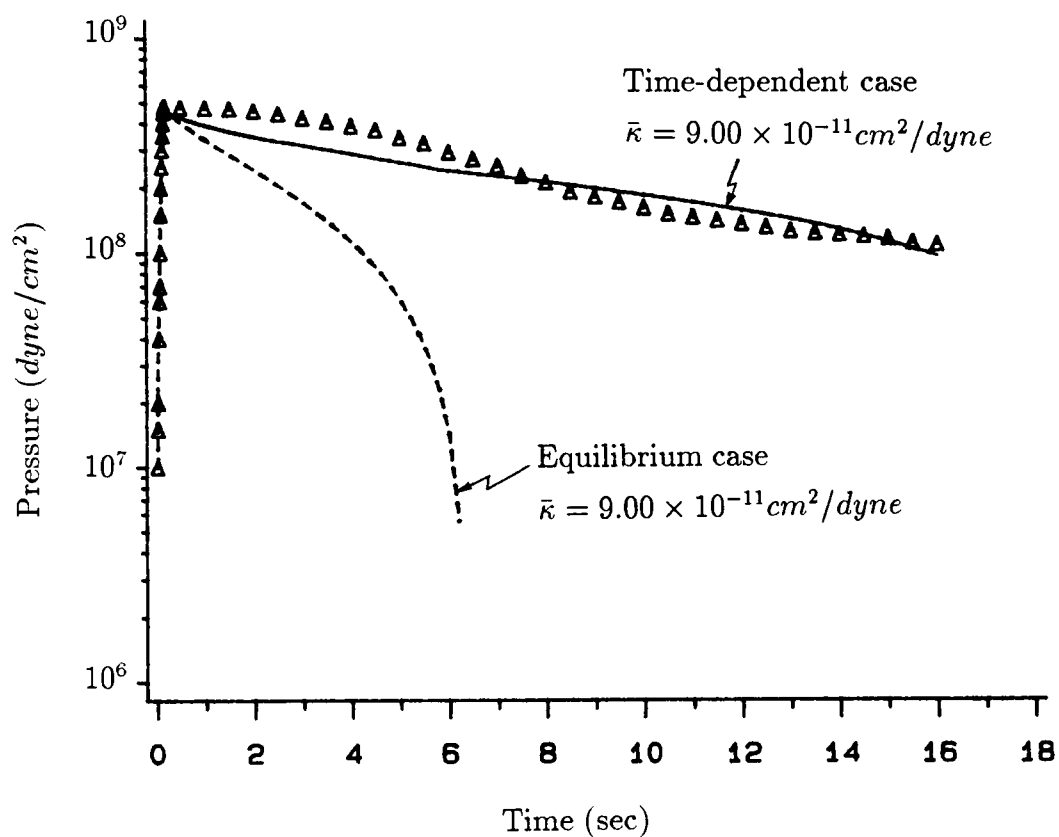


Figure 5.4: Comparison of literature data with simulated pressures for the cooling step, for the time-dependent PVT case. (Symbols are experimental data of the Cornell group [191], solid line is theoretical prediction of the time-dependent case.)

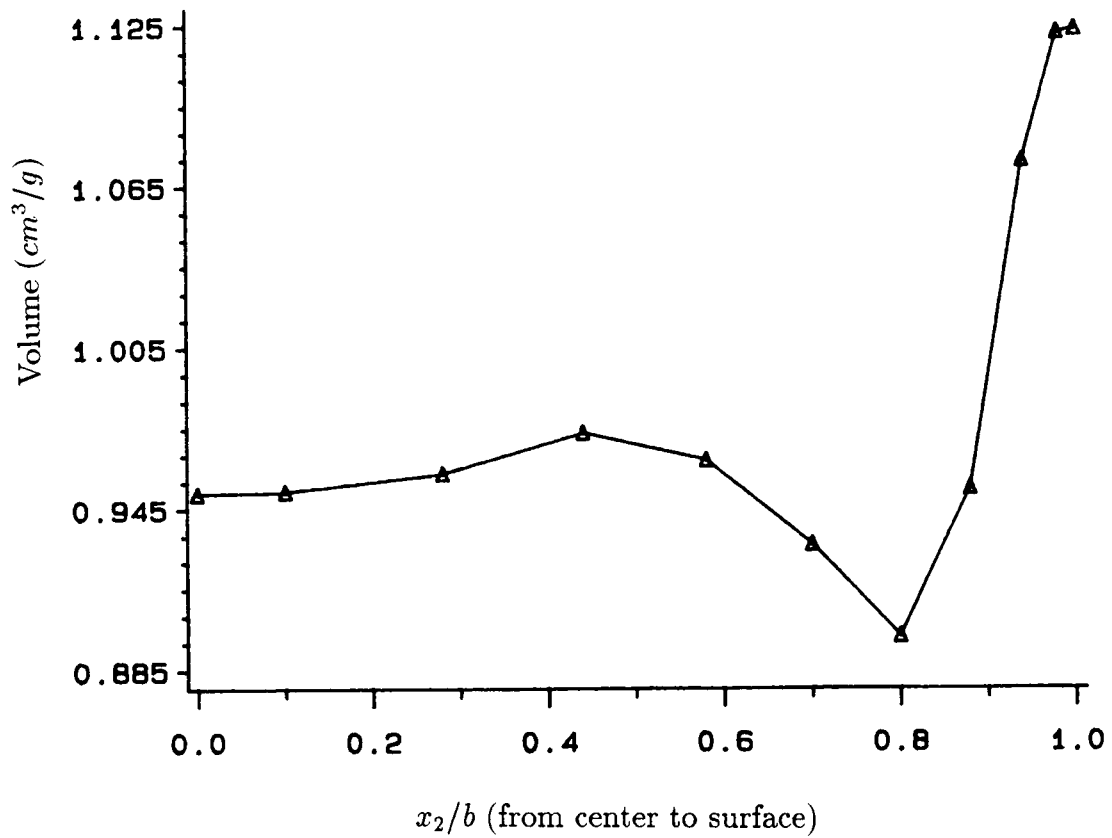


Figure 5.5: Gapwise specific volume profile predicted at the end of the cooling step, for the time-dependent PVT case.

Table 5.1: Summary of material constants and parameters used in the simulation of the cooling step in injection molding, for the equilibrium PVT case.

Material constants (values in reasonable agreement with prior literature):	
V_0	$= 1.0536 \text{ cm}^3/g \quad (\text{at } 200 \text{ }^\circ\text{C})$
α_r	$= 5.68 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$
α_g	$= 2.48 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$
α	$= 6.33 \times 10^{-4} \text{ cm}^2/sec \quad (\text{thermal diffusivity})$
Adjustable parameters (values adjusted empirically in the present work):	
$\bar{\kappa}$	$= 1.72 \times 10^{-10} \text{ cm}^2/dyne$

Table 5.2: Summary of material constants and parameters used in the simulation of the cooling step in injection molding, for the time-dependent PVT case.

Material constants (values in reasonable agreement with prior literature):	
V_0	$= 1.0536 \text{ cm}^3/\text{g}$ (at 200 °C)
$\tau_{\lambda 0}$	$= 2.54 \times 10^{-8} \text{ sec}$ (at 200 °C)
α_r	$= 5.68 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$
α_g	$= 2.48 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$
α	$= 6.33 \times 10^{-4} \text{ cm}^2/\text{sec}$ (thermal diffusivity)
β_T	$= 0.47 \text{ }^\circ\text{C}^{-1}$
β_p	$= 1.4 \times 10^{-8} \text{ cm}^2/\text{dyne}$
β_v	$= 4.0 \times 10^2$
T_{ge}	$= 85 \text{ }^\circ\text{C}$
Adjustable parameters (values adjusted empirically in the present work):	
$\bar{\kappa}$	$= 9.00 \times 10^{-11} \text{ cm}^2/\text{dyne}$

CHAPTER 6

ANALYSIS OF RESIDUAL STRESSES IN RAPIDLY COOLED SAMPLES

Volume-induced residual stresses are caused by the non-uniform cooling of the various layers of a thick sample, the sample in this case being a free (non-stressed) slab of initially uniform temperature which is suddenly quenched. The classical theory centers on the theory of Lee, Rogers and Woo [99], and various special cases of it [1], as reviewed in Chapter 3. Instead of that formulation a direct interpretation of what is happening in each layer is easier to imagine and to derive from the Ko-Bogue equations [87]. In this chapter the necessary theoretical development for the analysis of residual stresses is presented first, followed by theoretical fits to the experimental data taken from the literature [75,77]. The study will again be focused on amorphous polymers.

6.1 Theoretical Development

One imagines a slab similar to that shown in Figure 6.1, which is square and comparatively long in the x_1 and x_3 directions compared with the x_2 direction. The initially non-stressed, homogeneous slab is quenched from a temperature well above its T_g to well below T_g . One also imagines equally divided layers (in

the x_1x_3 plane) having the same initial specific volume and thus the same mass. The specific volume may change during cooling but the mass of each layer will always be constant. Due to the rapid cooling both ends of the overall sample (in the long directions) solidify as a "moving cage". Therefore both of the long dimensions (x_1 or x_3) contract uniformly over all of the layers according to $L(t)$, a function of time only. This function is obtained numerically by trial-and-error such that the integral of the stresses in x_2 direction is, on the average, zero at any time:

$$\int_{-b}^b \sigma(x_2, t) dx_2 = 0 \quad (6.1)$$

where b is half of the slab thickness and $\sigma = \sigma_{11} = \sigma_{33}$.

Although the length $L(t)$ of the slab is uniform for all of the layers, strains are not uniform and are dependent on the thermal history of each layer. This thermal history can be traced by the transient heat transfer theory, as shown in Chapter 5. Free lateral expansion in the x_2 direction is also permitted to satisfy the compatibility requirement among layers. This is done at each time step by calculating the thickness change of each layer, according to the following equation:

$$s(x_2, t) = \frac{m V(x_2, t)}{L^2(t)} \quad (6.2)$$

where $s(x_2, t)$ and $V(x_2, t)$ are the thickness and specific volume of each layer at time t , respectively; m is the constant mass of each layer; and $L(t) = L_{11}(t) = L_{33}(t)$ is the length of both of the long dimensions of the slab at time t . From these $s(x_2, t)$ the new half thickness (b) of the slab and the new dimensionless

distance (x_2/b) of each layer are obtained. These new values of b and x_2/b are also brought to the heat transfer equation for calculating the temperature distributions in the next time step.

Instantaneous stress responses from the temperature drop and volume changes are assumed. To simplify the analysis, a "step change" of material properties is applied to the modulus G , thermal coefficient of expansion α , and pressure coefficient of expansion κ . That is, the modulus G is zero for the rubbery state and changes suddenly to some constant value for the glassy state; while typical values of α and κ are used for both states. Therefore the stresses vanish in the molten layers (with temperature above T_{ge}) and are functions of volume changes in the solid layers (with temperature below T_{ge} .) When the molten layers cool down to room temperature, the volume changes are traced by equations of state. Two cases of PVT equations are included in this study: an equilibrium case and a time-dependent case. Both are derived from Equation (2) in Appendix A.

The volume changes in each layer are coupled with the instantaneous stresses, which are calculated from linear elasticity theory. If the summation of the stresses for each layer fits the boundary condition (Eqn. (6.1)), then the iteration procedure is repeated for the next time step until all the layers cool down to room temperature. This cooling results finally in a slab of uniform temperature for the equilibrium case and continues to include 24 hour aging for the time-dependent case. Following are the details of the theoretical developments for each case.

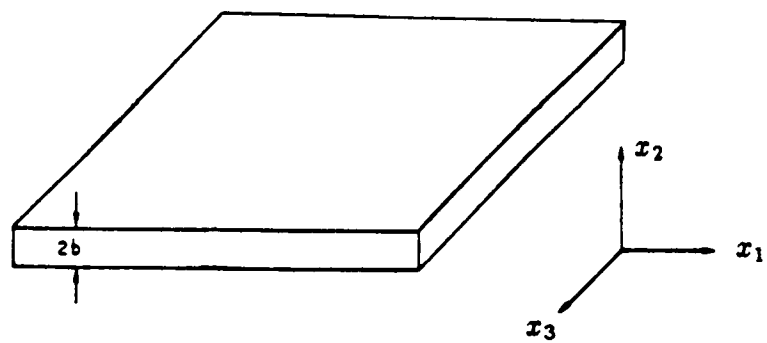


Figure 6.1: Schematic diagram of the square slab for residual stress analyses

6.1.1 Equilibrium PVT Case for Residual Stresses

Noting the volume changes will be small, one can write down the relation between the linear normal strains and the volume change for every layer (with temperature above or below T_{ge}) as follows:

$$\tilde{\epsilon}_{22} = \frac{\Delta V}{V_0} - 2\tilde{\epsilon}_{11} \quad (6.3)$$

where $\tilde{\epsilon}_{22}$ is the lateral strain and the other terms are specified by

$$\begin{aligned} \frac{\Delta V}{V_0} &= \frac{V(x_2, t) - V_0}{V_0} \\ \tilde{\epsilon}_{11}(x_2, t) &= \frac{L(t) - L_0(x_2)}{L_0(x_2)} = \tilde{\epsilon}_{33}(x_2, t) \end{aligned}$$

The longitudinal strains $\tilde{\epsilon}_{11}(x_2, t)$ are not uniform for the layers because the reference length $L_0(x_2)$ depends on the thermal history of each layer. Here $L_0(x_2)$ is defined by the length of each layer as it passes through the glass transition temperature. This definition comes from a certain assumption about the modulus to account for linear elastic strains in each layer. The assumption is that the modulus G is zero above T_{ge} and some constant value below T_{ge} .

The stress components for solid layers (that is, below T_{ge}) can be obtained from the linear elasticity theory as follows:

$$\sigma_{22} = 0 = -\wp + G \left(2\tilde{\epsilon}_{22} - \frac{2}{3} \frac{\Delta V}{V_0} \right) \quad (6.4)$$

$$\sigma_{11} = \sigma_{33} = -\wp + G \left(2\tilde{\epsilon}_{11} - \frac{2}{3} \frac{\Delta V}{V_0} \right) \quad (6.5)$$

where $G = G_g$ is a characteristic modulus which is treated as an adjustable parameter in the analysis. Substituting Eqn. (6.3) into Eqn. (6.4) and solving

for $\wp$, one has

$$\wp(x_2, t) = 4G_g \left(\frac{1}{3} \frac{\Delta V}{V_0} - \tilde{\epsilon}_{11} \right) \quad (6.6)$$

Replacing the $\wp$ in Eqn. (6.5), the stresses are then expressed as

$$\sigma_{11}(x_2, t) = 2G_g \left(3\tilde{\epsilon}_{11} - \frac{\Delta V}{V_0} \right) \quad (6.7)$$

One notes that $\sigma_{kk} = -3\wp$ satisfies the requirement of linear elasticity theory. The above equations are valid for instantaneous stress responses no matter whether the volume changes are assumed to be equilibrium changes or time-dependent changes.

For the equilibrium case, the volume changes can be defined by Eqn. (4) in Appendix A; letting $\Delta\theta = 0$, one obtains finally

$$\frac{\Delta V}{V_0} = -\alpha_r(T_0 - T_{ge}) - \alpha_g(T_{ge} - T) - \bar{\kappa}\wp \quad (6.8)$$

where P_0 , the atmospheric pressure, has been taken as zero by thinking of $\wp$ as “gauge pressure”. Other symbols have been defined in the paper [87]. The temperature distribution $T(x_2, t)$ of the slab is calculated by transient heat transfer theory with an infinite heat transfer coefficient, similar to the injection molding analysis in Chapter 5 (using Eqn. (5.3) with different boundary conditions for the residual stress analysis).

Instead of simultaneously solving Eqns. (6.6) and (6.8), one may substitute $\wp$ into Eqn. (6.8) and rewrite the volume changes for the solid layers as

$$\frac{\Delta V}{V_0} = [-\alpha_r(T_0 - T_{ge}) - \alpha_g(T_{ge} - T) + 4\bar{\kappa}G_g\tilde{\epsilon}_{11}] \left(\frac{3}{3 + 4\bar{\kappa}G_g} \right) \quad (6.9)$$

By neglecting the modulus in Eqn. (6.9), it reduces to the volume changes for layers with temperature above T_{ge} :

$$\frac{\Delta V}{V_0} = -\alpha_r(T_0 - T) \quad (6.10)$$

Although stresses are absent in these layers at temperatures above T_{ge} , specific volumes from this equation must still be used in Eqn. (6.2) in order to calculate lateral expansions for satisfying the compatibility requirement.

Volume changes and thus residual stresses are obtained numerically from Eqn. (6.9) by guessing the length $L(t)$ and calculating the strains of each layer such that the boundary condition (Eqn. (6.1)) is satisfied. The free lateral expansions (or the new thickness of each layer) are then calculated by Eqn. (6.2); the thickness summation of each layer gives the new slab thickness. Therefore, the compatibility condition among layers can be satisfied. The iteration procedure then continues until every layer approaches room temperature. The computer program for the equilibrium PVT case is presented in Appendix D.

6.1.2 Time-dependent PVT Case for Residual Stresses

Due to the rapid cooling of the slab, the non-equilibrium volume and its relaxation are not negligible. Volume effects and thus volume-stress-time coupling behavior should be considered for a rigorous analysis of residual stresses. As shown in Chapter 3, we have a time-dependent PVT equation which can, in principle at least, accommodate such complicated behavior. It is rewritten here for calculating the specific volume at a certain position x_2 of the slab (or at the

midpoint of each layer.)

$$\frac{dV}{dt} = - \left(\frac{V - V_e}{\tau_\lambda} \right) + V_0 \alpha_g \frac{dT}{dt} - V_0 \kappa_g \frac{d\wp}{dt} \quad (6.11)$$

where the relaxation time $\tau_\lambda(x_2, t)$ is a function of time in that it depends, by means of suitable shift factors, on some combination of temperature, pressure (scalar stress) and non-equilibrium free volume. A single-element relaxation function will be used for simplicity in showing the relaxation characteristics. This function and the equilibrium volume $V_e(x_2, t)$ will be explicitly written later. The time constant for cooling is obtained from fitting the literature volume data of Greiner and Schwarzl [54] and treated as a "semi-adjustable" parameter. A single-element relaxation function is used for simplicity in showing the relaxation characteristics. The temperature and temperature gradient are again obtained from the transient heat transfer theory with an infinite heat transfer coefficient. That is, one uses Eqns. (5.3) and (5.7) in Chapter 5 with different initial temperature and surface temperature imposed in the present analysis.

Retaining the assumption of instantaneous stress responses in the solid layers, as in equilibrium case, Eqns. (6.6) and (6.7) continue to be used for the solid layers in the time-dependent case also. Taking the derivative on $\wp$ with respect to time at a certain position x_2 , the pressure gradient is obtained:

$$\frac{d\wp}{dt} = \frac{4}{3} \frac{G_g}{V_0} \frac{dV}{dt} - 4G_g \frac{d\tilde{\epsilon}_{11}}{dt} \quad (6.12)$$

where

$$\frac{d\tilde{\epsilon}_{11}}{dt} = \frac{1}{L_0(x_2)} \frac{dL(t)}{dt}$$

The definitions (but not the magnitudes) of $L(t)$ and $L_0(x_2)$ are the same as that in the equilibrium case. Replacing the pressure gradient in Eqn. (6.11), one has the following volume rate equation for the solid layers with temperature below T_{ge} .

$$\frac{dV}{dt} = \left[- \left(\frac{V - V_e}{\tau_\lambda} \right) + V_0 \alpha_g \frac{dT}{dt} + 4V_0 \kappa_g G_g \frac{d\tilde{\epsilon}_{11}}{dt} \right] \left(\frac{3}{3 + 4\kappa_g G_g} \right) \quad (6.13)$$

where the associated functions are specified by

$$\begin{aligned} V_e(x_2, t) &= V_0 - \alpha_r(T_0 - T_{ge})V_0 - \alpha_g(T_{ge} - T)V_0 - \bar{\kappa}\wp V_0 \\ \Delta\theta(x_2, t) &= \bar{\kappa}\wp + \frac{V - V_0}{V_0} - \bar{\alpha}(T - T_0) = \frac{V - V_e}{V_0} \\ \tau_\lambda(x_2, t) &= \tau_{\lambda 0} \exp[-\beta_T(T - T_0)] \exp[\beta_p \wp] \exp[-\beta_v \Delta\theta] \end{aligned}$$

For layers with temperature above T_{ge} , the equation can be reduced from Eqn. (6.13) by taking G_g and $\wp$ to be zero.

$$\frac{dV}{dt} = - \left(\frac{V - V_e}{\tau_\lambda} \right) + V_0 \alpha_g \frac{dT}{dt} \quad (6.14)$$

where

$$\begin{aligned} V_e(x_2, t) &= V_0 - \alpha_r(T_0 - T)V_0 \\ \Delta\theta(x_2, t) &= \frac{V - V_0}{V_0} - \alpha_r(T - T_0) = \frac{V - V_e}{V_0} \\ \tau_\lambda(x_2, t) &= \tau_{\lambda 0} \exp[-\beta_T(T - T_0)] \exp[-\beta_v \Delta\theta] \end{aligned}$$

Although no stresses are present in the layers at temperatures above T_{ge} , the thermal history and thus the volume effects of each layer are remembered as they cool down to room temperature. Therefore, the volume change and its relaxation should be traced from the beginning. Lateral expansions are calculated by Eqn. (6.2), as discussed in the equilibrium case.

Specific volumes and thus residual stresses can be obtained from Eqns. (6.13) and (6.14) by guessing the length $L(t)$ and calculating the strains of each layer such that the boundary condition (Eqn. (6.1)) is satisfied. The numerical algorithm for solving the differential equations is more complicated here, compared with the equilibrium case, which involves only algebraic equations. The new thickness of each layer and thus the slab thickness are then calculated by Eqn. (6.2), same as the equilibrium case, in order to satisfy the compatibility condition inside the slab. After every layer cools down to room temperature, the iteration continues to account for aging of 24 hours. The volume rate equation for aging can be obtained from Eqn. (6.13) by neglecting the temperature gradient and holding a constant room temperature, as follows:

$$\frac{dV}{dt} = \left[- \left(\frac{V - V_e}{\tau_\lambda} \right) + 4V_0\kappa_g G_g \frac{d\tilde{\epsilon}_{11}}{dt} \right] \left(\frac{3}{3 + 4\kappa_g G_g} \right) \quad (6.15)$$

where

$$V_e(x_2, t) = V_0 - \alpha_r(T_0 - T_{ge})V_0 - \alpha_g(T_{ge} - T_{room})V_0 - \bar{\kappa}\wp V_0$$

$$\Delta\theta(x_2, t) = \bar{\kappa}\wp + \frac{V - V_0}{V_0} - \bar{\alpha}(T_{room} - T_0) = \frac{V - V_e}{V_0}$$

$$\tau_\lambda(x_2, t) = (\tau_{\lambda 0})_{aging} \exp[\beta_p \wp] \exp[-\beta_v \Delta\theta]$$

Even though temperature is kept constant, the relaxation time for aging is still a function of time because it depends on pressure (scalar stress) and non-equilibrium free volume. The time constant for aging at room temperature is obtained from fitting the experimental volume aging data of Snow [159]. The equation for this fitting can be obtained from Eqn. (6.15) by taking G_g and $\wp$ to be zero, as shown below:

$$\frac{dV}{dt} = - \left(\frac{V - V_e}{\tau_\lambda} \right) \quad (6.16)$$

where V_e is the equilibrium specific volume after aging and other variables are specified by

$$\Delta\theta(x_2, t) = \frac{V - V_e}{V_0}$$

$$\tau_\lambda(x_2, t) = (\tau_{\lambda 0})_{aging} \exp[-\beta_v \Delta\theta]$$

The value of $(\tau_{\lambda 0})_{aging}$ is not adjustable in the present analysis.

One notes that the volume-stress-time interactions are clearly shown in the equations presented here. They thus provide a direct mechanism to interpret what is happening in each layer and how the residual stresses are created. The computer program for the time-dependent PVT case is given in Appendix E. Theoretical fits of both cases to the literature data follow in the next section.

6.2 Fitting the Literature Data

Experimental data of volume-induced residual stresses in rapidly cooled polystyrene slabs have been given by Isayev and Crouthamel [75,77]. Their

data are replotted here for comparison with the theoretical predictions from the Ko-Bogue equations. The dimensions of the slabs and experimental conditions are summarized in Table 6.1. Figures 6.2 and 6.3 show the residual stress data with different initial temperatures, 130 °C and 150 °C , respectively. The initially non-stressed slabs were suddenly put into water and quenched to a room temperature of 23 °C . The layer removal method, as discussed in Chapter 2, was then used to measure the stress profiles. For density measurements the quenched slabs were kept at room temperature for 24 hours of aging. Small pieces were then cut from each layer and put into a density gradient column of room temperature to measure the associated density profiles, which are shown in Figure 6.4.

The removal of small pieces for density measurements necessarily causes some release of the residual stresses. Thus the densities measured in the density gradient column will be different from the densities inside the slab before cutting. Isayev and Crouthamel [75,77] argue that the shape of the density profiles in Figure 6.4 is due to the residual stresses (or the Poisson's ratio effect). That is, the compressive stresses near the surface cause higher densities there, as compared with lower densities near the center, which are caused by tension stresses. It is difficult to think of any other plausible explanation for the shapes in Figure 6.4 and we agree with Isayev and Crouthamel's discussion. However, because of the relieving of the residual stresses from cutting, one must argue that the Poisson's ratio effect will persist even in the small pieces; although it

Table 6.1: Summary of dimensions of the slabs and experimental conditions for the residual stress data in the literature (measured by Isayev and Crouthamel [75,77]).

For measured residual stress profiles* :

slab : $5.08\text{ cm} \times 5.08\text{ cm} \times 0.26\text{ cm}$

T_0 = $130\text{ }^{\circ}\text{C}$ and $150\text{ }^{\circ}\text{C}$ (initial temperatures)

T_w = $23\text{ }^{\circ}\text{C}$ (quench temperature)

* stresses were measured at about 90 minutes after quenching.

For measured density profiles* :

slab : $7.62\text{ cm} \times 7.62\text{ cm} \times 0.38\text{ cm}$ for $T_0 = 130\text{ }^{\circ}\text{C}$

slab : $5.08\text{ cm} \times 5.08\text{ cm} \times 0.26\text{ cm}$ for $T_0 = 170\text{ }^{\circ}\text{C}$

T_0 = $130\text{ }^{\circ}\text{C}$ and $170\text{ }^{\circ}\text{C}$ (initial temperatures)

T_w = $23\text{ }^{\circ}\text{C}$ (quench temperature)

* densities were measured at about 24 hours after quenching.

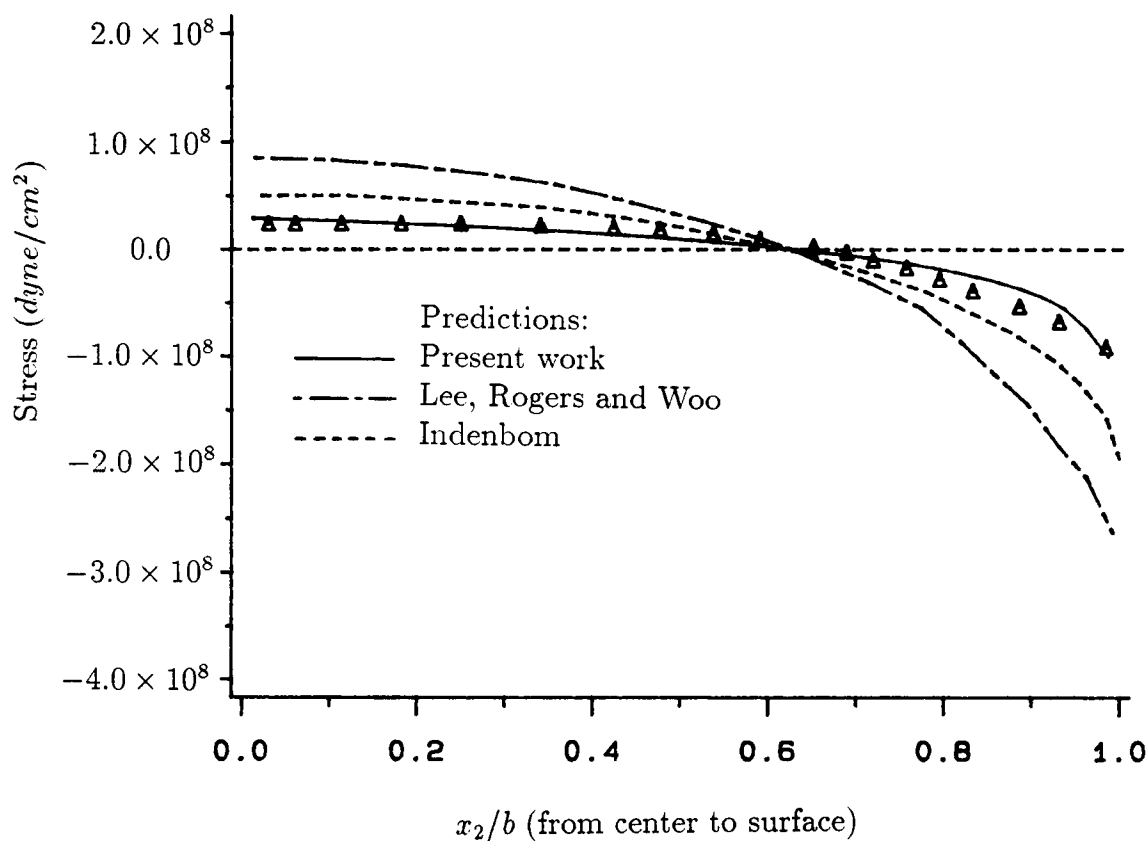


Figure 6.2: Comparison of literature residual stress profiles with predictions of the equilibrium PVT case for 130 °C initial temperature. (Symbols for Isayev and Crouthamel's data [75,77]; lines for theoretical predictions: solid line for the equilibrium case of the present work, long broken line for Lee, Rogers and Woo theory as reported by Isayev et al. , short broken line for the Indenbom equation as reported by Isayev et al. [75,77].)

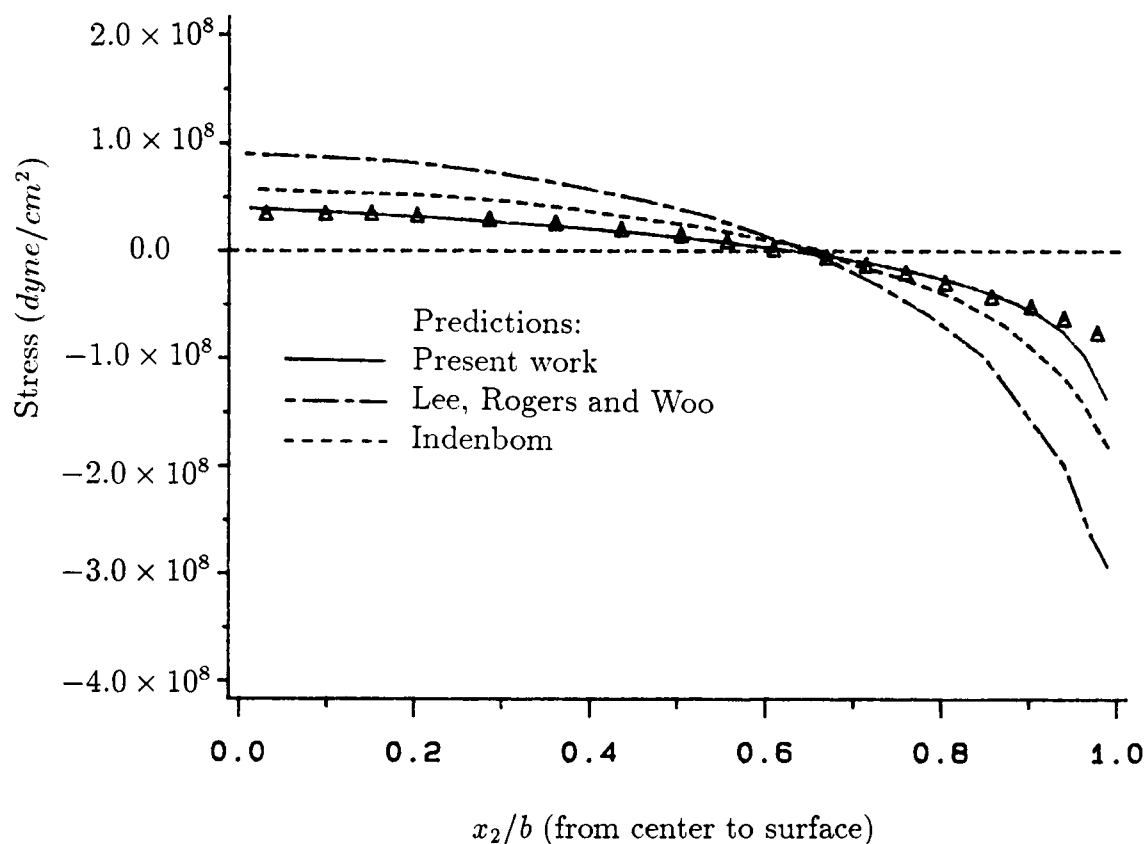


Figure 6.3: Comparison of literature residual stress profiles with predictions of the equilibrium PVT case for 150 °C initial temperature. (Symbols for Isayev and Crouthamel's data [75,77]; lines for theoretical predictions: solid line for the equilibrium case of the present work, long broken line for Lee, Rogers and Woo theory as reported by Isayev et al. , short broken line for the Indenbom equation as reported by Isayev et al. [75,77].)

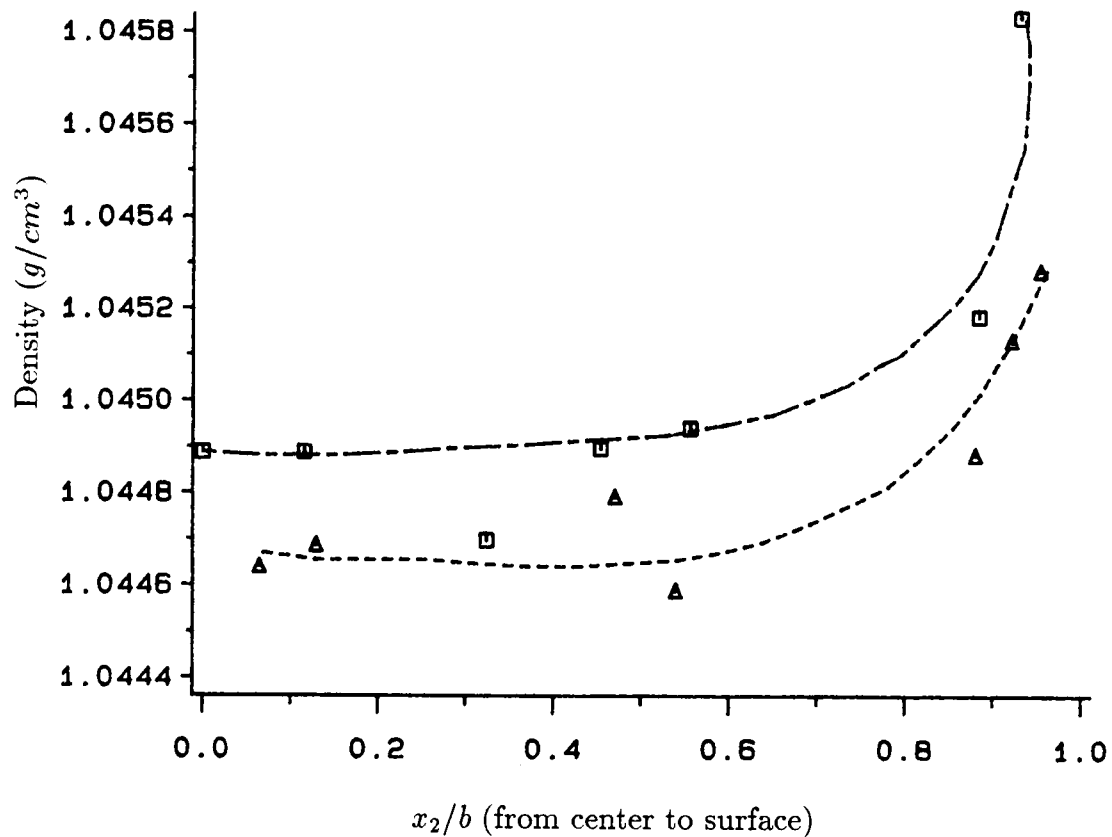


Figure 6.4: Experimental gapwise density profile in quenched polystyrene slab measured by Isayev and Crouthamel [75,77]. (Triangles and short broken line for 130 °C initial temperature, squares and long broken line for 170 °C initial temperature.)

may not be so big as in the slab. In view of the stress relieving effect it cannot be expected that the densities predicted for the uncut sample will be the same as those measured in the density gradient column.

In addition to the comparison with data, Figures 6.2 and 6.3 also include the predictions from the theories of Lee, Rogers and Woo and of Indenbom, which were also given by Isayev and Crouthamel in the same literature [75,77]. While the density profile could not readily be extracted from these existing theories, it can be obtained from the Ko-Bogue equations without any extra manipulations. Theoretical fits from analyses of the present work to the literature data will now be discussed.

6.2.1 Theoretical Fitting of the Equilibrium PVT Case

Equation (6.9) was numerically solved by guessing the slab length $L(t)$ so as to satisfy the boundary condition of Eqn. (6.1). For the layers at a temperature above T_{ge} , Eqn. (6.10) was used to calculate the specific volume. Free lateral expansions were then calculated from Eqn. (6.2) to satisfy the compatibility condition among layers. The initial specific volume V_0 and thermal coefficients of expansion (α_r , α_g) were taken directly from the experiments of Greiner and Schwarzl [54]. The value of $\bar{\kappa}$ is estimated by an arithmetic average of κ_r and κ_g , which in turn are taken from the Ferry's book [37]. The modulus G_g was treated as an adjustable parameter in order to fit the residual stress data of Isayev and Crouthamel [75,77]. Table 6.2 summarizes the material constants and the only adjustable parameter G_g for the equilibrium case.

As shown in Figures 6.2 and 6.3, the residual stress data of different initial temperatures are fit quite well. The value of the adjustable parameter G_g is $5 \times 10^8 \text{ dyne/cm}^2$, which is a reasonable value. As noted in Figure 4.3, a typical modulus in the rubbery state is about 10^6 dyne/cm^2 and about $10^{10} \text{ dyne/cm}^2$ in the glassy state. Because of the step change (directly from a melt to a solid) in the model, it is probably not plausible to presume that a completely glassy modulus would be reached immediately. The predictions for the density profile are found to have the right trends, but higher absolute magnitudes, as compared with the experimental data. Only an initial temperature of 130°C is shown in Figure 6.5. The predicted higher densities from the equilibrium PVT case may be due in part to the neglect of time effects in the rapidly cooled samples, but probably are due largely to the stress relieving mechanism in cutting the small pieces, as discussed above.

After the comparison with experimental data, one may look at other predictions for the equilibrium PVT case. Figures 6.6 and 6.7 show the predicted influences of temperature gradients (created by different initial temperatures) on the residual stresses and densities, respectively. Higher values of residual stresses and densities are predicted, as expected, for a higher temperature gradient in the slab. A slight difference in the slab thickness (for example, 0.254 cm and 0.380 cm thick slabs, both quenched from 130°C to room temperature) shows no obvious differences in the residual stresses and the associated density profiles. In the above analysis an equilibrium PVT relationship has been assumed. Now a more rigorous analysis, including time effects, will be done.

Table 6.2: Summary of material constants and parameters used in the residual stress analysis, for the equilibrium PVT case.

Material constants (values in reasonable agreement with prior literature):	
V_0	$= 0.9922 \text{ cm}^3/g \quad (\text{at } 130 \text{ }^\circ\text{C})$
V_0	$= 1.0035 \text{ cm}^3/g \quad (\text{at } 150 \text{ }^\circ\text{C})$
V_0	$= 1.0490 \text{ cm}^3/g \quad (\text{at } 170 \text{ }^\circ\text{C})$
α_r	$= 5.68 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$
α_g	$= 2.48 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$
$\bar{\kappa}$	$= 6.00 \times 10^{-11} \text{ cm}^2/\text{dyne}$
α	$= 6.33 \times 10^{-4} \text{ cm}^2/\text{sec} \quad (\text{thermal diffusivity})$
Adjustable parameters (values adjusted empirically in the present work):	
G_g	$= 5.0 \times 10^8 \text{ dyne/cm}^2$

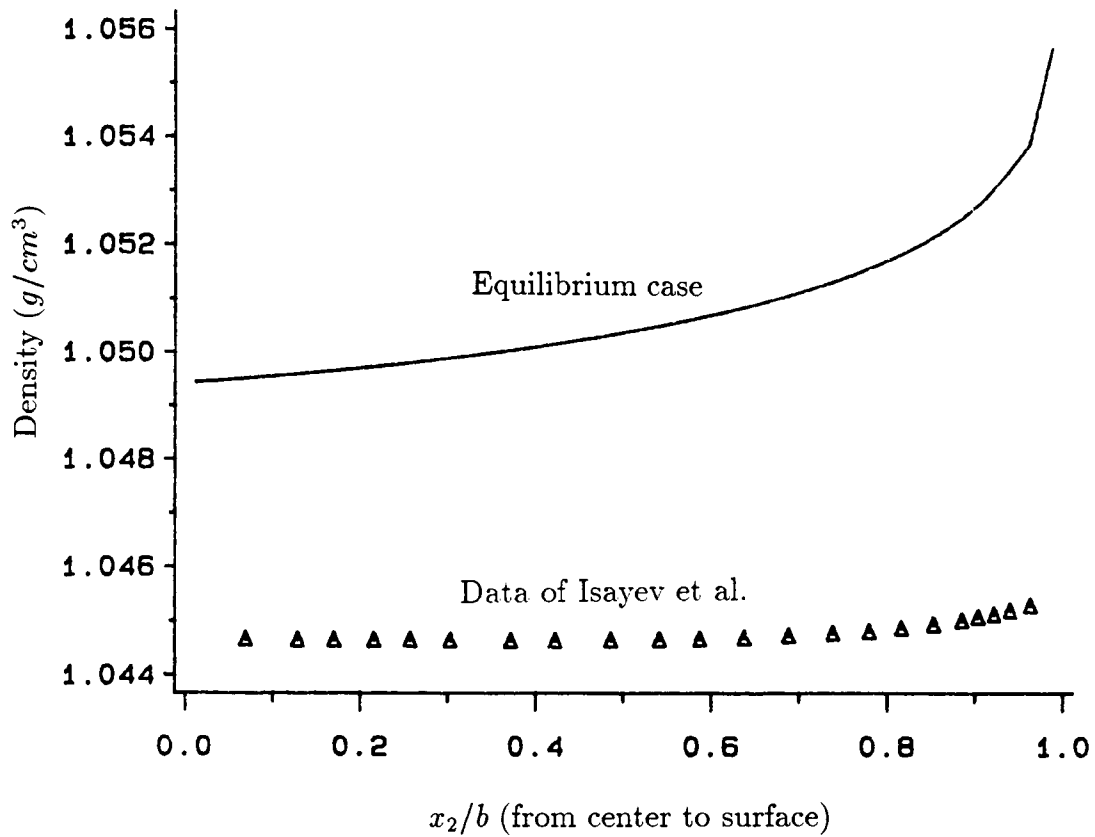


Figure 6.5: Comparison of literature density profiles with predictions of the equilibrium PVT case for 130 °C initial temperature. (Symbols for Isayev and Crouthamel's data [75,77], line for predictions of the present work.)

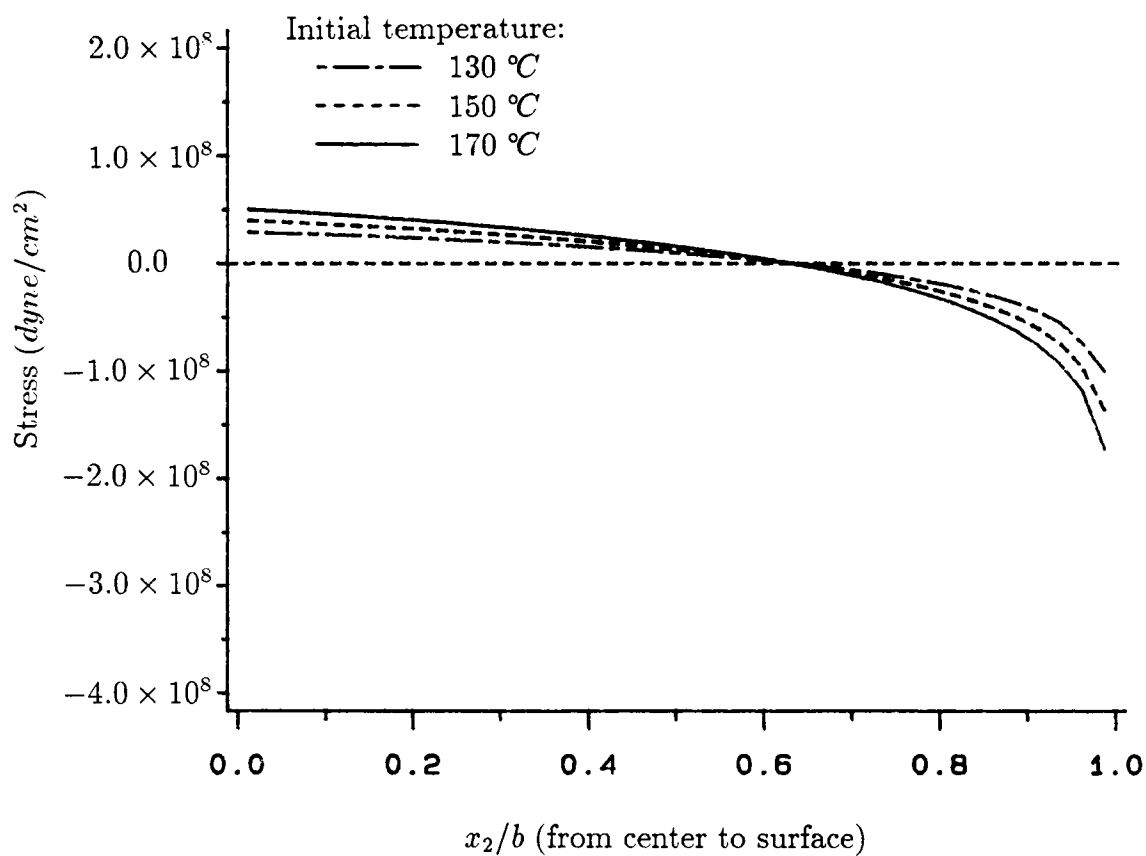


Figure 6.6: Comparison of predicted residual stress profiles of the present work for different initial temperatures, for the equilibrium PVT case.

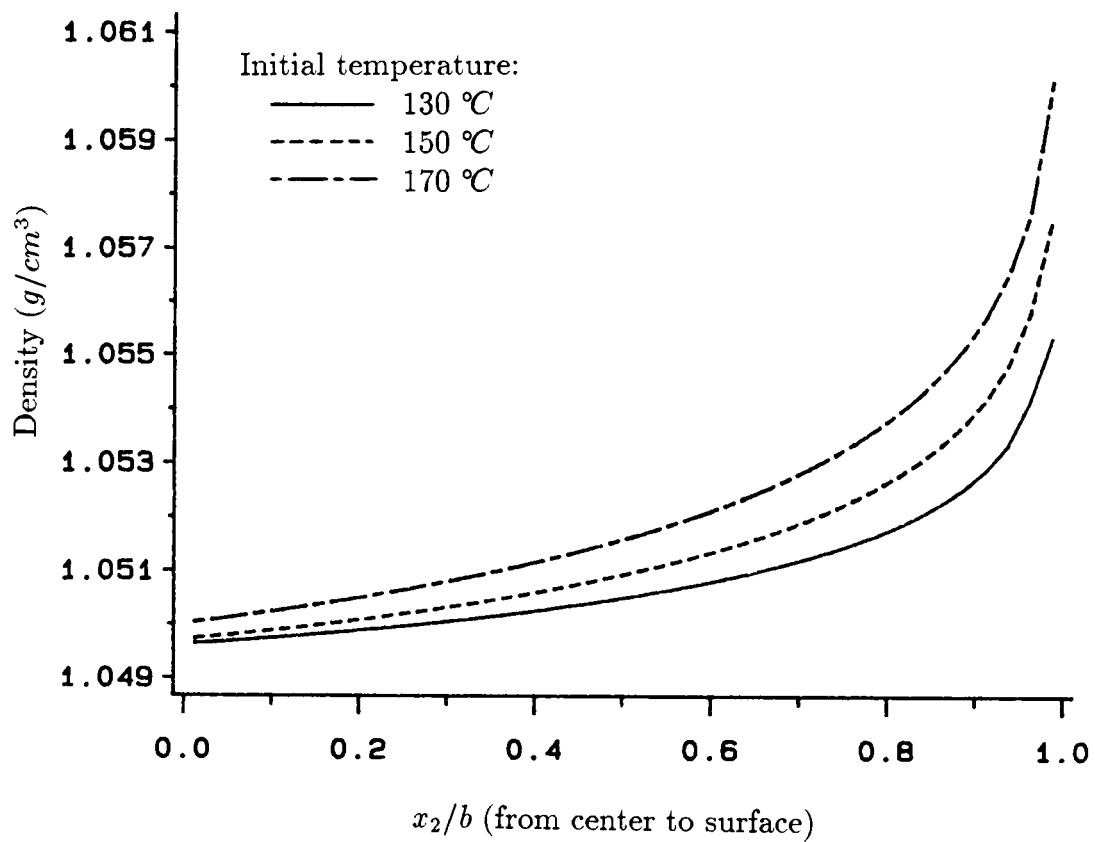


Figure 6.7: Comparison of predicted density profiles of the present work for different initial temperatures, for the equilibrium PVT case.

6.2.2 Theoretical Fitting of the Time-dependent PVT Case

During the cooling of the slab down to room temperature, Eqns. (6.13) and (6.14) were numerically solved using a modified fourth-order Runge-Kutta method to predict the residual stresses and the density profiles. The boundary condition and compatibility requirements were satisfied at each time step, as discussed in the previous section. Since the cooling rates near the slab surface can be extremely high (that is, hundreds of degrees per seconds) in the beginning of a water quench, there is a need for very small iteration steps and thus long computer runs for the time-dependent PVT case. Due to the lack of volume change data under such high cooling rates, the experiments of Greiner and Schwarzl [54] must again be used here to estimate the time constant for cooling and shift factor parameters. That is, $\tau_{\lambda 0}$, β_T and β_v are obtained from fitting their data, as discussed in Chapter 4. The initial specific volume V_0 and thermal coefficients of expansion (α_r , α_g) are taken directly from the experimental measurements of Greiner and Schwarzl [54]. The average value $\bar{\kappa}$ is estimated by an arithmetic average of typical κ_r and κ_g , which are found in the Ferry's book [37]. The pressure shift factor parameter β_p is again obtained from the equivalence effects of temperature and pressure on T_g (see Chapter 5). The modulus G_g is treated as an adjustable parameter.

Although there is no complete sets of volume change data under high cooling rates, the final specific volumes of polystyrene samples quenched in water (without aging) were found in the literature. For example, Snow [159] gave a

final specific volume of $0.9546 \text{ cm}^3/\text{g}$ at 25°C for PS, quenched from 118°C at an estimated cooling rate of $160^\circ\text{C}/\text{sec}$. Zehavi and Filisko [209] reported a value of $0.9542 \text{ cm}^3/\text{g}$ for PS quenched from 135°C to 25°C at an estimated cooling rate of $5^\circ\text{C}/\text{sec}$. If these unaged (or nearly unaged) specific volumes are plotted on Figure 4.2, one finds that these values are in the same range as the specific volumes of Greiner and Schwarzl [54]. On the other hand, if the time constant $\tau_{\lambda 0}$ from the data of Greiner and Schwarzl is used for extrapolating to these high cooling rates ($160^\circ\text{C}/\text{sec}$ and $5^\circ\text{C}/\text{sec}$), one sees predicted specific volumes at 25°C that are much higher than the values of Snow [159] and of Zehavi and Filisko [209]. To obtain specific volumes in the range of these latter workers at 25°C , one must use a smaller time constant (at least 100 times smaller).

Since a large extrapolation to very high cooling rates cannot be avoided, we present two subcases of the cooling analysis. In Subcase A: None of the material constants or the shift factor parameters is adjustable (except the modulus G_g). In Subcase B: The modulus G_g is adjustable (but using the same value as in Subcase A), while the time constant for cooling ($\tau_{\lambda 0}$) is treated as “semi-adjustable”; that is, a value of $\tau_{\lambda 0}$ which is 100 times smaller than the value from the Greiner-Schwarzl fit is used, as explained in the previous paragraph.

After every layer has cooled down to room temperature, the same numerical algorithm can continue to be used for Eqn. (6.15) in order to account for 24 hours of aging. All of the material constants and the parameters, except the time constant for aging, are the same as those in the cooling part.

The time constant for aging $(\tau_{\lambda 0})_{aging}$ was obtained by fitting the volume aging data of Snow [159], using Eqn. (6.16). In Snow's experiments, cylindrical polystyrene fibers of 0.05 cm diameter were quenched from 118 °C to 0 °C (in ice water) and then kept at a room temperature of 25 °C for about 500 hours of aging. The cooling rate in such an ice water quench was estimated by Snow at about 160 °C/sec. From these measurements, the initial specific volume (after cooling but before aging) $V_0(25\text{ °C})$ was 0.9546 cm³/g; and the equilibrium specific volume after aging $V_e(25\text{ °C})$ was 0.9519 cm³/g. Using Eqn. (6.16) with these specific volumes and the β_v value in the cooling part, a value of 1.7×10^6 sec for $(\tau_{\lambda 0})_{aging}$ at room temperature was then obtained from fitting the Snow's volume aging data [159]. Figure 6.8 shows this fitting. This time constant $(\tau_{\lambda 0})_{aging}$ is not adjustable when it is used in the analysis. Table 6.3 summarizes the time constants, shift factor parameters and other material constants used in the time-dependent case.

As shown in Figures 6.9 and 6.10, good fits to the residual stress data for the initial temperatures of 130 °C and 150 °C were obtained for the Subcase A. The value of the modulus G_g in both initial temperatures is the same (1.5×10^9 dyne/cm²), but somewhat higher than the value in the equilibrium case (5.0×10^8 dyne/cm²). Similar predicted residual stress profiles were found for the Subcase B with the initial temperatures of 130 °C and 150 °C. Comparisons of predicted densities of both subcases with the literature data is shown in Figures 6.11 for the initial temperature of 130 °C.

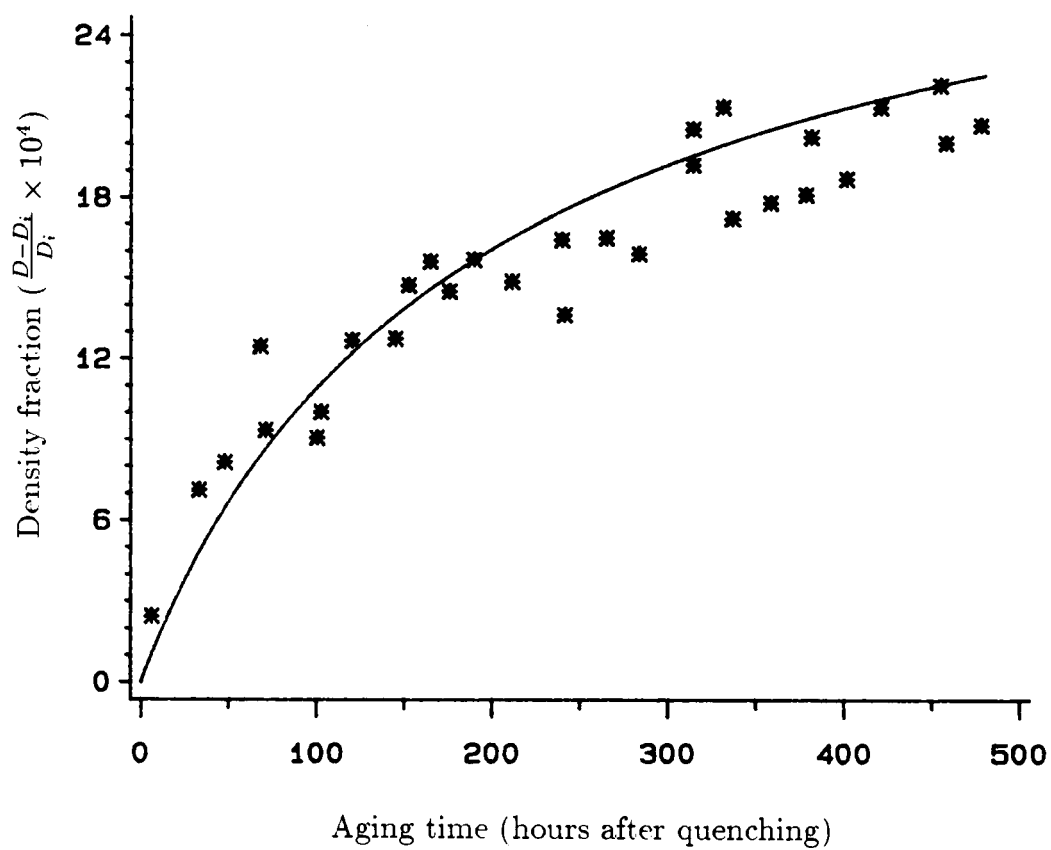


Figure 6.8: Comparison of predicted volume aging of the present work with Snow's data [159].

Table 6.3: Summary of material constants and parameters used in the residual stress analysis, for the time-dependent PVT case.

Material constants (values in reasonable agreement with prior literature):	
V_0	$= 0.9922 \text{ cm}^3/g \quad (\text{at } 130 \text{ }^\circ\text{C})$
V_0	$= 1.0035 \text{ cm}^3/g \quad (\text{at } 150 \text{ }^\circ\text{C})$
$\tau_{\lambda 0}$	$= 5.45 \times 10^{-5} \text{ sec} \quad (\text{at } 130 \text{ }^\circ\text{C})$
$\tau_{\lambda 0}$	$= 1.78 \times 10^{-6} \text{ sec} \quad (\text{at } 150 \text{ }^\circ\text{C})$
$\tau_{\lambda 0}(\text{aging})$	$= 1.7 \times 10^6 \text{ sec} \quad (\text{at } 23 \text{ }^\circ\text{C})$
α_r	$= 5.68 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$
α_g	$= 2.48 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$
$\bar{\kappa}$	$= 6.00 \times 10^{-11} \text{ cm}^2/\text{dyne}$
α	$= 6.33 \times 10^{-4} \text{ cm}^2/\text{sec} \quad (\text{thermal diffusivity})$
β_T	$= 0.47 \text{ }^\circ\text{C}^{-1}$
β_p	$= 1.4 \times 10^{-8} \text{ cm}^2/\text{dyne}$
β_v	$= 4.0 \times 10^2$
T_{ge}	$= 85 \text{ }^\circ\text{C}$
Adjustable parameters (values adjusted empirically in the present work):	
G_g	$= 1.5 \times 10^9 \text{ dyne/cm}^2$

Finally all of density results for one of the starting temperatures (130°C) are brought together in Figure 6.12. This figure shows that the predicted density profiles have the same trend as the data, and bracket the data, but clearly are not in quantitative agreement with the data. This is almost surely due to the fact that the predicted densities are those inside the uncut sample, while the experimental values have been measured from small pieces cut out of the large quenched sample. Since there is no experimental method for measuring densities *in situ*, one thus must be satisfied with comparing densities for the two different states as described.

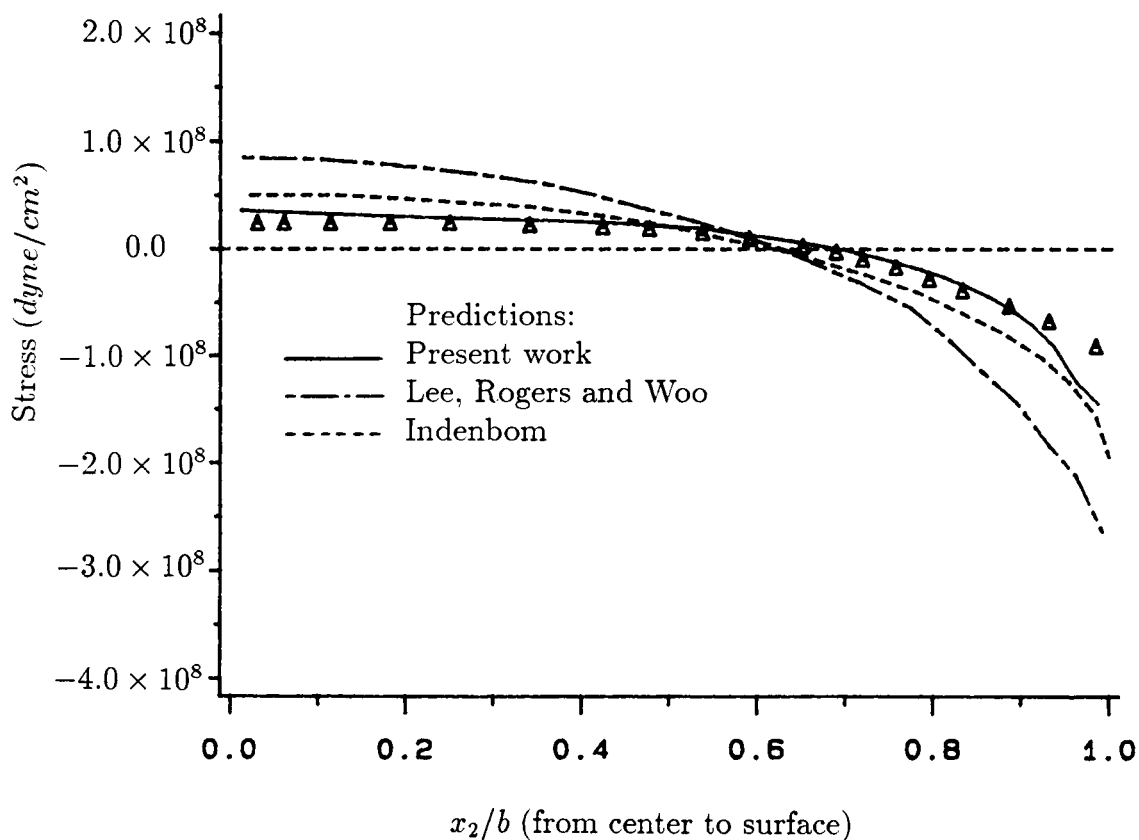


Figure 6.9: Comparison of literature residual stress profiles with predictions of the time-dependent PVT case, using time constant from Greiner-Schwarzl data, for 130 °C initial temperature. (Symbols for Isayev and Crouthamel's data [75,77]; lines for theoretical predictions: solid line for the time-dependent case of the present work, long broken line for Lee, Rogers and Woo theory as reported by Isayev et al. , short broken line for the Indenbom equation as reported by Isayev et al. [75,77].)

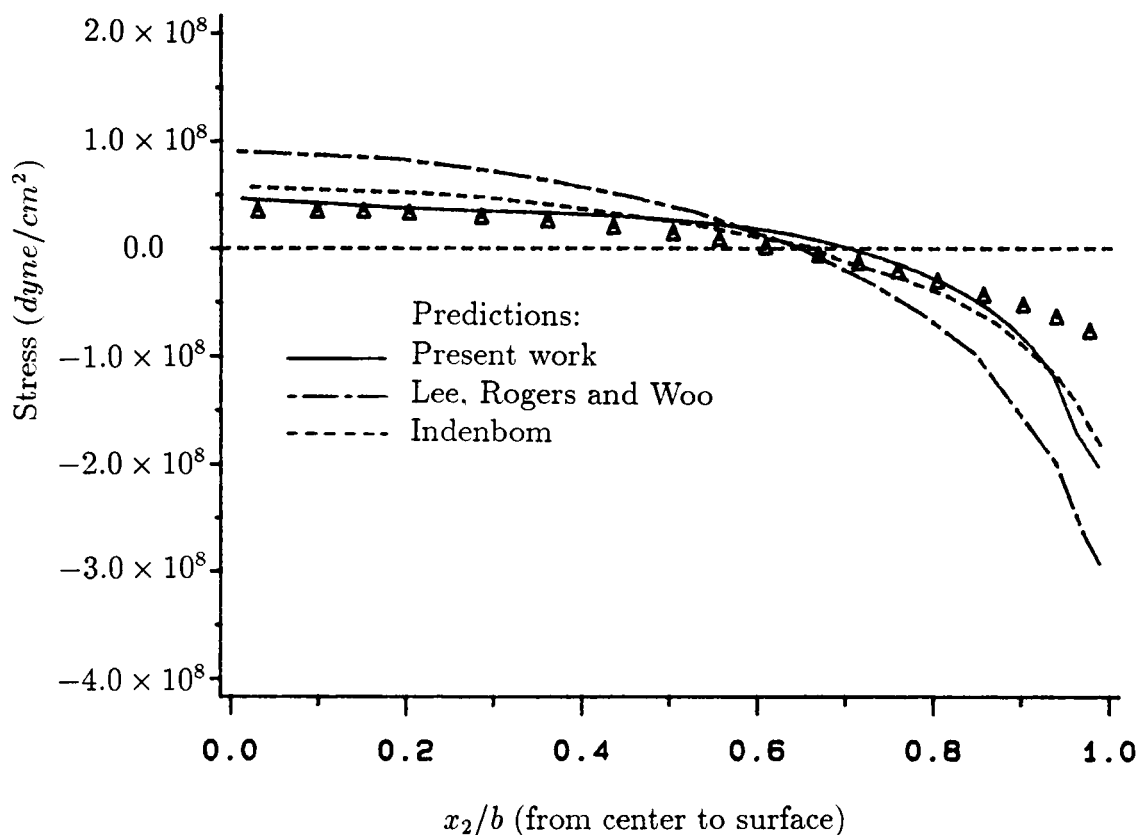


Figure 6.10: Comparison of literature residual stress profiles with predictions of the time-dependent PVT case, using time constant from Greiner-Schwarzl data, for 150 °C initial temperature. (Symbols for Isayev and Crouthamel's data [75,77]; lines for theoretical predictions: solid line for the time-dependent case of the present work, long broken line for Lee, Rogers and Woo theory as reported by Isayev et al. , short broken line for the Indenbom equation as reported by Isayev et al. [75,77].)

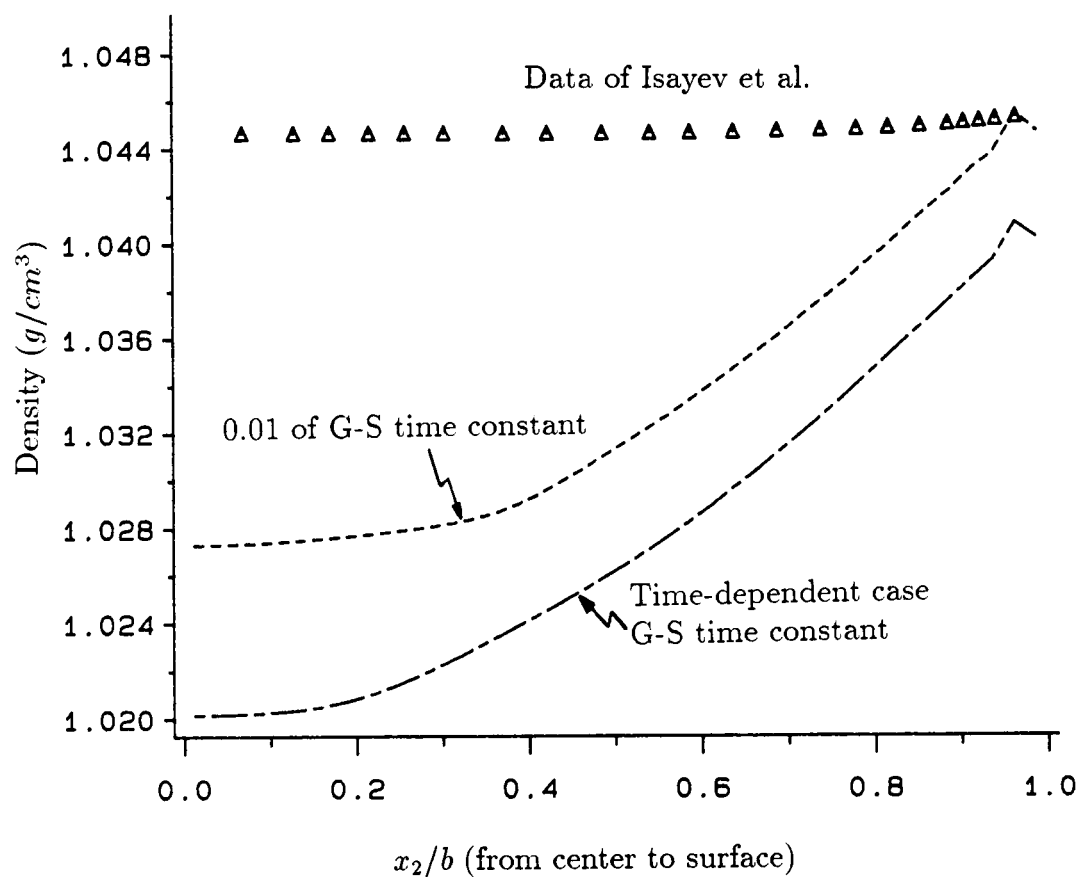


Figure 6.11: Comparison of literature density profiles with predictions of the time-dependent PVT case for 130 °C initial temperature. (Symbols for Isayev and Crouthamel's data [75,77]; lines for predictions of the present work: long broken line for Greiner-Schwarzl (G-S) time constant, short broken line for time constant 100 times smaller.

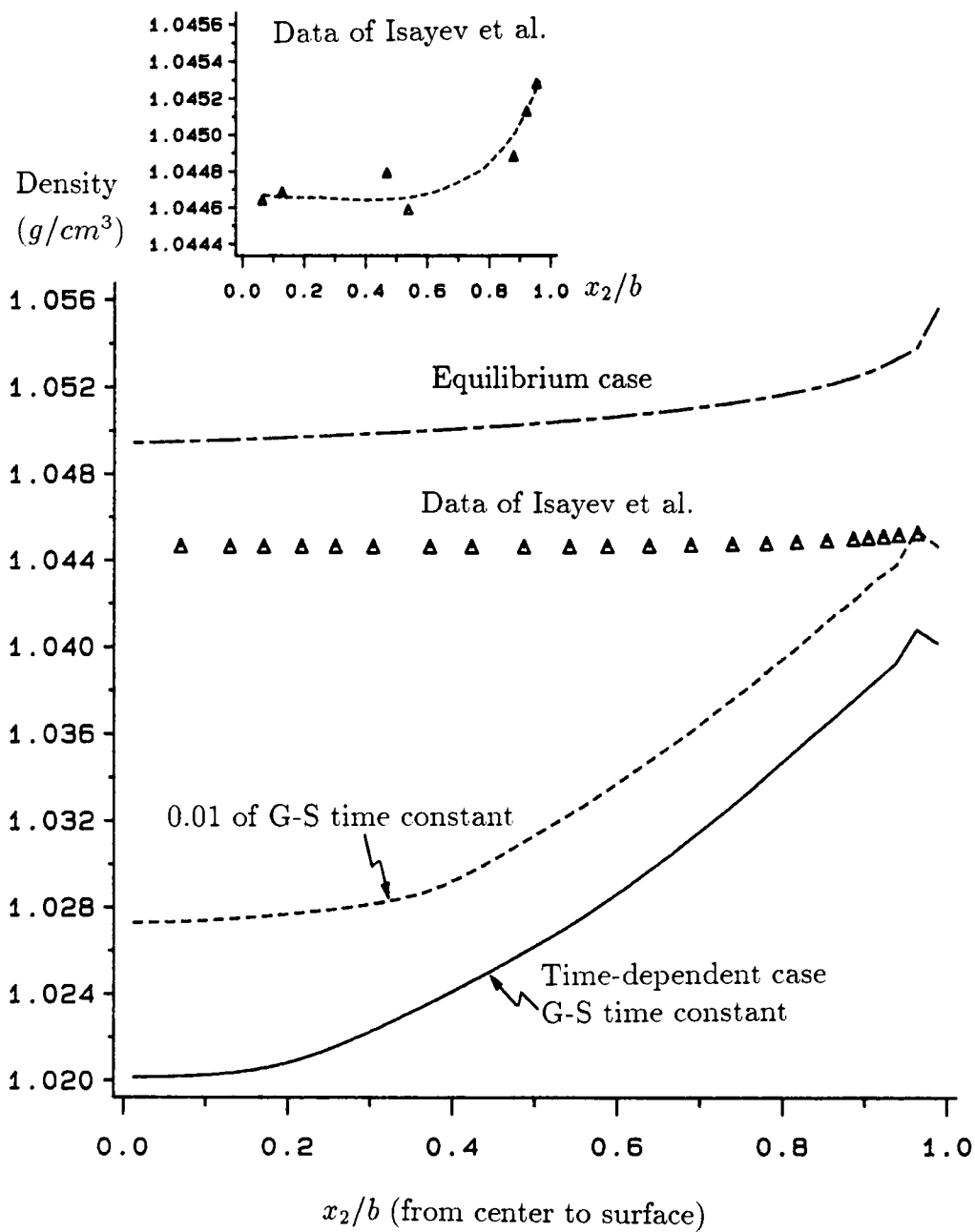


Figure 6.12: Comparison of literature density profiles [75,77] with predictions of the time-dependent PVT case and the equilibrium PVT case, for 130 °C initial temperature.

CHAPTER 7

CONCLUSIONS

In general the present work was concerned with developing and using an equation for coupling the effects of volume changes and stress changes in amorphous polymers. The work consisted of four parts: first, a theoretical development of a constitutive equation including compressibility (volume) effects; second, an analysis of the stress build-up in a fiber-like sample which was simultaneously pulled and cooled, with the results being compared with data from the present work; third, a simulation of the cooling step in injection molding, with the predictions being compared with the data of the Cornell group; and fourth, an analysis of the volume-induced residual stress problem — that is, the problem of freezing-in stresses and densities in a rapidly cooled free sample, with the analysis being compared with the data of Isayev. Conclusions from these four parts of the work will now be summarized, followed by overall remarks of a general nature.

7.1 A Constitutive Equation Including Compressibility Effects

In earlier work at the University of Tennessee Snow and Bogue set down a generalized equation which couples the effects of volume changes and stress

changes. The integral statement there is quite complicated and difficult to execute except in the simplest deformations. In the present work that equation is restated in a considerably different form which is more tractable. In the new formulation which has been published (Ko and Bogue [87]), a scalar stress $\wp$ is introduced which couples the volume effects of a generalized $\wp$ VT rate equation with the generalized viscoelastic constitutive equation. The $\wp$ VT rate equation is motivated by the volume rate equations presently in the literature. But the new form allows for pressure-volume-time experiments as well as temperature-volume-time experiments, or any experiments involving any two of these three (temperature, pressure and volume) as independent variables. The time-dependent effects can be easily built-in and executed by using either a single-element or a multiple-element relaxation function.

7.2 Analysis of Simultaneous Pulling and Cooling Experiments

The experiment consisted of pulling small fiber-like samples of polystyrene in an air-oven while they were simultaneously cooled. An analysis of such experiments involves knowledge of the modulus as a function of temperature and also the volume changes as a function of temperature and time. The modulus function was obtained from the literature. The volume change function was generated by fitting the dilatometry volume data of Greiner and Schwarzl. A single-element relaxation function was used in this fitting (and also used in the following parts of this work) for simplicity in showing the essential char-

acteristics of volume relaxation. With these functions and the appropriate analysis from the Ko-Bogue equations, predictions of the stress build-up as a function of time were made. The analysis and the data are in reasonable agreement, although the results are strongly dependent on the presumed modulus-temperature function. The fit of theory to data is generally satisfactory; it is, however, not a definitive check because the effect of volume changes is quite small in the experiments involved. Further testing of the theory is being continued in separate work [79].

7.3 Simulation of the Cooling Step in Injection Molding

The complicated processes involved in the various steps of injection molding were simplified such that the basic features of the cooling step can be simulated. The analysis is a "simulation" in the sense that it assumes there is no temperature and pressure gradients in the plane along the flow directions. Also the effect of residual stresses on the volume changes (from the constraints of the mold walls) was not included.

The cooling step was simulated by a time-dependent pVT equation, derived from the Ko-Bogue equations, using the assumptions noted above. The material function concerning the temperature-volume-time behavior was generated from the second part of the work. Since high pressures are involved in injection molding, pressure-volume-time effects must also be introduced into the relaxation function. The only adjustable parameter was the average compressibility coef-

ficient $\bar{\kappa}$. The predictions of the pressure decrease during the cooling step were then compared with the experimental data of the Cornell group. Satisfactory fits were obtained.

An equilibrium ϕ VT equation, reduced from the Ko-Bogue equations, was also used for comparison with the analysis of the Cornell group. The assumptions mentioned above continued to be used and satisfactory fits to the data were found. But an empirical adjustment of $\bar{\kappa}$ needed to be made. However, it was concluded that the choice for $\bar{\kappa}$ in the time-dependent ϕ VT case ($9.0 \times 10^{-11} \text{ cm}^2/\text{dyne}$) was more reasonable than the choice for $\bar{\kappa}$ in the equilibrium ϕ VT case ($1.72 \times 10^{-10} \text{ cm}^2/\text{dyne}$), as compared with typical literature values ($3.03 \times 10^{-11} \text{ cm}^2/\text{dyne}$ and $9.10 \times 10^{-11} \text{ cm}^2/\text{dyne}$ for the rubbery and glassy states, respectively).

7.4 Volume-induced Residual Stresses in Rapidly Cooled Samples

As a free sample is quenched rapidly, the various layers do not cool off uniformly, which introduces residual stresses in the sample. The analysis of residual stresses in an initially stress-free sample is a classical problem. The governing equations are those of Lee, Rogers and Woo, and various special cases of it (such as the Aggarwala and Saibel equation). In these theories equilibrium (time-independent) PVT behavior is always assumed. In the present work, the problem was restated in a much tractable form by considering the behavior of individual layers of the sample separately. The new form (reduced from our

generalized ρVT equation) allows one to introduce various kinds of assumptions regarding the time-dependence of either the volume changes or the stress changes, or both of them.

In this work time-dependent volume changes were introduced (the so-called time-dependent ρVT case). But the stress response was simplified in the manner of the Aggarwala and Saibel analysis — that is, the material was considered to be a fluid which changes discontinuously to a glassy solid at the glass transition temperature. Even though the framework of the new formulation is quite different, it is concluded that the results of the new formulation are similar to that of the previous work of Aggarwala and Saibel. The new formulation is more useful in that the density profile as a function of time can also be extracted without any extra manipulations. It thus provides a direct interpretation of what is happening in each layer and how the residual stresses are created.

The analysis was compared with the data of Isayev, who measured the residual stress profile and also the density profile in the thin dimension. The material function for the temperature-volume-time behavior was again generated from the second part of the work. The literature data used there must be extrapolated to cooling rates much beyond those measured. The time constant for cooling was thus treated as a “semi-adjustable” parameter in the analysis. The pressure effects were included in the relaxation function. Aging at room temperature for 24 hours was also included in the analysis, as was done in the data measurements. From fitting the volume aging data of Snow, the time constant

for aging at room temperature was obtained and not adjusted in the analysis. The modulus G_g was finally taken as an adjustable parameter.

Parallel to the analysis mentioned above, an equilibrium ϕ VT equation was also used for comparison with the time-dependent behavior. The experimental residual stress profiles (showing tension in the center and compression in the surface) could be satisfactorily fit in both analyses with reasonable values of G_g . The choice for G_g was $1.5 \times 10^9 \text{ dyne/cm}^2$ in the time-dependent ϕ VT case and was $5.0 \times 10^8 \text{ dyne/cm}^2$ in the equilibrium ϕ VT case, as compared with typical values in the rubbery and glassy states of 10^6 dyne/cm^2 and $10^{10} \text{ dyne/cm}^2$, respectively. The corresponding density profiles predicted by the two analyses have the correct trend but the magnitudes are considerably different.

The density profile problem is a complicated one, even in principle. The data show an increasing density as one moves toward the surface, a shape which Isayev attributes to the Poisson's ratio effect (to the presence of tensile stresses near the center and compressive stresses near the surface). Such a physical picture is also suggested by the density predictions from the analyses — one notes that the predictions show the same trend as the data and bracket the data (but are not in quantitative agreement with the data). A major experimental difficulty in making a quantitative comparison is that small pieces must be cut out of the large quenched sample to be used in the density gradient column. This cutting must release part of the residual stresses. In contrast, the analyses predict the densities in an uncut, as-quenched sample.

Finally, it is concluded that the essential features of the residual stress prob-

lem can be predicted by the present analysis and restated in a considerably more tractable form (as regards the numerical computations) than the prior analytical theories.

7.5 Concluding Remarks

The formulation of an integrated framework for coupling stress changes and volume changes has been presented and applied to several problems of practical interest. Since the rapid cooling in these problems forces the material to pass quickly from the rubbery state through the transition state to the glassy state, an unusually large data base must be generated to deal with them rigorously. One needs, for example, multi-element relaxation functions for volume changes and also stress changes over wide ranges of temperatures and time scales. In the absence of such extensive data bases, one must, in practice, make simplifying assumptions or introduce adjustable parameters to deal with particular problems. If one makes such simplifications, then the generalized theory of the present work can be applied to several problems of some complexity with a reasonable (if not unique) choice of parameters.

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APPENDICES

8.1 Appendix A: A Paper of Ko and Bogue

Wen-Chien Ko and Donald C. Bogue, "A Constitutive Equation Including Compressibility Effects," *J. Rheol.*, **31**(6), 425 (1987).

A Constitutive Equation Including Compressibility Effects

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Synopsis

Rheological theory including volume (compressible) effects is important in a practical sense in that many polymer processes involve rapid cooling to a final, typically nonequilibrium, glassy state. There are also compressible effects in the sense of Poisson's ratio—that is, deformation-induced volume changes occur even at constant temperature. In earlier work we (Snow and Bogue) set down a generalized constitutive equation which includes these various effects. The integral statement there is quite complicated, however, and is difficult to execute except in the simplest deformations. The present work is a restatement of the prior formulation in a more tractable and slightly modified form.

INTRODUCTION

In most of existing viscoelastic theory (the rheological constitutive equations) one assumes incompressible behavior (see, for example, Refs. 1 and 2). In the case of the usual problems worked out for cross-linked rubbers or for rubbery melts, incompressible behavior means that the volume does not change during deformation (in uniaxial pulling, Poisson's ratio, the negative of the lateral contraction to the axial elongation, is taken to be $1/2$). Such an assumption cannot be made in the glassy state, however, since the increase of volume upon pulling (or the decrease upon contraction) is an important characteristic of that state. Compressibility in a different sense—a volume change resulting from a change in temperature or hydrostatic pressure—has been considered in the context of equations of state (PVT relations), as treated in some detail at a recent symposium of the Society of Rheology.³ But considering rate effects in PVT equations, or equivalently, introducing compressible effects into rheological

theory, has not been done extensively, although there is now a growing literature on volume changes (aging) in the glassy state. A review of compressible effects in the various forms discussed above has been given by Snow and Bogue,⁴ and more recently by Landel and Peng.⁵

Compressible theory is important in a practical sense in that most polymer processes involve shaping a polymer in the melt state and cooling it, often rapidly, to a solid state. In such processes nonequilibrium specific volumes and also nonequilibrium orientations⁶ are often frozen-in, properties which can affect the mechanical behavior and may also change (age) with time. Crystallization behavior is also, of course, of considerable importance but the complex mechanisms involved there are not included in the present work, which is limited to amorphous polymers. Examples of volume-related problems of practical interest are residual stresses in rapidly quenched samples⁷ and shrinkage in injection molding.^{1,8}

In our prior work,⁴ we set down a generalized constitutive equation which includes compressible effects. In particular we developed an integral rate equation for volume changes and combined it with existing integral constitutive theory for anisotropic stresses. This generalized result was shown finally to reduce to the following special cases: (1) linear elasticity theory, (2) existing (incompressible) viscoelastic theory, (3) a differential rate equation for volume changes when the stresses are isotropic, and (4) an equilibrium PVT equation at infinite time. The general integral statement is quite complicated, however, and would be difficult to execute on a computer except in the simplest deformations. The present paper is a restatement of the prior formulation in a more tractable and slightly modified form.

THE NEW FORMULATION

An important result to come out of the prior work was a generalized differential rate equation for isotropic (PVT) deformations [Eq. (9) in Ref. 4]. The proposal here is to use that equation generally and not restrict it to isotropic deformations. We do that by introducing a negative scalar stress ($\mathcal{P}$) which is the hydrostatic pressure in isotropic deformations but has a more general meaning in anisotropic deformations (i.e., those with unequal normal stresses). In the new notation we propose the following:

$$\frac{D(\theta + \phi_f)}{Dt} = \frac{-\Delta\theta}{\tau_\lambda} \quad (1)$$

where $D(\cdot)/Dt [= \partial(\cdot)/\partial t + v_k \partial(\cdot)/\partial x_k]$ is the material derivative. For homogeneous deformations, Eq. (1) reduces to

$$\frac{d(\theta + \phi_f)}{dt} = \frac{-\Delta\theta}{\tau_\lambda} \quad (2)$$

The function ϕ_f will be discussed later. The quantity θ , a variable characterizing the PVT state, is defined by

$$\theta(t) = \mathcal{P}(t)/\lambda^*(t) + V(t)/V_0 - \alpha(t)T(t) \quad (3)$$

where $\lambda^*(t) [= \lambda(t) + (2/3)G(t)]$ is the bulk modulus, $\alpha(t)$ is the thermal coefficient of expansion, $\mathcal{P}(t)$ is the negative scalar stress (to be discussed further below), $V(t)$ is the volume, $T(t)$ is the temperature, and V_0 is the volume in an arbitrary pressure-volume-temperature initial state (P_0, V_0, T_0) , presumed to be at equilibrium. The elastic moduli λ and G shown in the redefinition of λ^* are the so-called Lamé constants. The notation (t) denotes the value of the quantity indicated at the time of consideration t . The symbol S in the prior paper was changed to θ here to avoid any confusion with entropy. Also θ is now distinguished from $\Delta\theta$, the latter being defined by

$$\Delta\theta(t) = [\mathcal{P}(t) - P_0]/\bar{\lambda}^*(t) + [V(t) - V_0]/V_0 - \bar{\alpha}(t)[(T(t) - T_0)] \quad (4)$$

where the overbars on $\bar{\lambda}^*(t)$ and $\bar{\alpha}(t)$ denote averages between the initial time and the time of consideration t . The quantity $\Delta\theta$ can be interpreted as follows: if $\Delta\theta = 0$, a steady state exists, if $\Delta\theta \neq 0$, a steady state does not exist. By "steady state" we mean that the dependent variable among $\mathcal{P}$, V , or T (two are independent and one is dependent) is satisfying an equilibrium $\mathcal{PVT}$ equation at the moment of consideration. We do not imply any thermodynamic interpretation beyond that.

The time constant $(\tau_\lambda(t))$ in Eq. (1) or (2) is a function of time in that it depends, by means of suitable shift factors, on some combination of $\mathcal{P}$, T and V , or quantities such as free volume which could be determined by these variables. We do not write here a specific form for the factor $a_{\mathcal{PVT}}$ (a composite shift factor, often the product of individual shift factors for temperature, pressure, etc.), but we can define its use by writing

$$\tau_A(t) = a_{PVT}(t)\tau_A^\circ \quad (5)$$

where τ_A° is the time constant in the reference state. There is considerable experience with temperature shift factors in the rubbery state, mostly of the Williams, Landel, and Ferry (WLF) form,⁹ and some experience with pressure shift factors.¹⁰ The specification of volume shift factors in the nonequilibrium glassy state is not an easy matter and requires, in the case of temperature factors, other kinds of state parameters (cf. Refs. 11–13).

All of the above theory is formulated in terms of a single relaxation time τ_A . For simple cooling histories this form appears to be qualitatively correct, but for cooling/reheating histories, the behavior is considerably more complicated and requires the introduction of multiple relaxation times^{14,15} or some other generalization. For the sake of simplicity, however, we will continue the development here with the simpler (one time constant) model as stated by Eqs. (1)–(5) since it does, we feel, describe the essential aspects of the compressibility problem in most applications. We will in a later section suggest a generalization to multiple time constants.

The function ϕ_f in Eqs. (1) and (2) is the driving force for change of the $\mathcal{P}VT$ state and might, for example, be modelled in terms of a free energy difference between the equilibrium rubbery and glassy states. There will be no time delay in the volume response unless this function is non-zero now or at some "not-yet-forgotten" past time. We will here model ϕ_f by thinking of it as having to do with the potential for creating free volume. In a general way it has to do with the difference between the $\mathcal{P}VT$ surface for the rubbery state and the (extrapolated) $\mathcal{P}VT$ surface for the glassy state, these two surfaces merging on a line which can be thought of as the locus of the infinitely long time (equilibrium) glass transition. Though a number of $\mathcal{P}VT$ equations exist,³ none is simple enough to use in the analyses we wish to do; also it is likely that they will not be valid under highly anisotropic stress loadings. (More will be said on this latter point in the concluding remarks.) We will therefore linearize the $\mathcal{P}VT$ response (using the coefficients α and λ^*) and direct our attention to two cases: (1) constant $\mathcal{P}$, with the temperature changing with time, $T(t)$; and (2) constant T , with the scalar stress $\mathcal{P}$ changing with time, $\mathcal{P}(t)$. In the first case, there will be an associated equilibrium glass transition temperature (T_{ge}) and in the second case, an associated equi-

librium glass transition pressure $\mathcal{P}_{ge}$. In the two cases we would define ϕ_f as follows:

$$\phi_f(t) = \Delta\alpha(t)[T(t) - T_{ge}] \quad (\mathcal{P} \text{ constant}, T > T_{ge}) \quad (6)$$

and

$$\phi_f(t) = -\Delta\kappa(t)[\mathcal{P}(t) - \mathcal{P}_{ge}] \quad (T \text{ constant}, \mathcal{P} < \mathcal{P}_{ge}) \quad (7)$$

In these expressions $\Delta\alpha = \alpha_r - \alpha_g$ and $\Delta\kappa = \kappa_r - \kappa_g$, α being the thermal coefficient of expansion, $\kappa [= 1/\lambda^*]$ being the pressure coefficient of expansion, and the subscripts r and g referring to the rubbery and glassy states, respectively. The parenthetical notation (t) is to indicate that the various α 's and κ 's are, in general, not constant, but dependent on the instantaneous state. In the glassy state ($T < T_{ge}$ or $\mathcal{P} > \mathcal{P}_{ge}$ in the two cases above), we have, by definition, $\phi_f = 0$.

A more general definition of ϕ_f would require a theoretical formulation, which we do not attempt here, allowing one to postulate the onset of the glass transition in terms of a separate variable (or a separate criterion), which might be, for example, a free volume in a very general equation of state. However, we feel for a large number of mechanical problems (excluding, however, those at very large hydrostatic pressures) that the imposed scalar stresses will be small enough not to have a large effect on the glass transition. In such cases we would propose

$$\begin{aligned} \phi_f(t) = & \Delta\alpha(t)[T(t) - T_{ge}] \\ & - \Delta\kappa(t)[\mathcal{P}(t) - P_0] \quad (\text{moderate } \mathcal{P}, T > T_{ge}) \end{aligned} \quad (8)$$

It is understood here that P_0 is small (typically atmospheric pressure) and that the second term is relatively small (but of either sign) compared with the first. In many anisotropic deformations, the applied stresses are positive ($\mathcal{P} - P_0 = \text{negative}$) and both terms will be creating free volume. In contrast, in the compressive case ($\mathcal{P} - P_0 = \text{positive}$), the second term will make a correction in the direction of decreasing the free volume. As before, for $T < T_{ge}$, we have $\phi_f = 0$.

Having stated an equation for the isotropic (volume) deformation, one must also have an equation involving the anisotropic deformation. For that purpose we could write a convected Maxwell model (cf. Refs. 16 or 2), which would be differential model to stand in parallel with Eq. (1). However, such models are not eas-

ily generalized to incorporate a spectrum of relaxation times nor easily made nonlinear to account for non-Newtonian viscosities. Therefore, we shall retain an integral statement, which in the simplest (one element) case takes the form:⁶

$$\sigma_{ij} = -\mathcal{P}\delta_{ij} + \int_{-\infty}^t \frac{G(t')}{\tau_G(t')} \exp\left[-\int_{t'}^t \frac{dt''}{\tau_G(t'')}\right] c_{ij}^{-1*} dt' \quad (9)$$

where $\sigma_{ij}(t)$ is the total stress, δ_{ij} is the Kronecker delta, $c_{ij}^{-1*}(t, t')$ $[= c_{ij}^{-1} - \delta_{ij} - (2/3)(\Delta V/V(t'))\delta_{ij}]$ is a normalized relative Finger strain tensor, $c_{ij}^{-1}(t, t')$ is the conventional (unnormalized) form of that tensor, $\Delta V [= V(t) - V(t')]$ is a relative volume difference, where t denotes the time of consideration, and t' and t'' denote an arbitrary past time. The normalized strain tensor was introduced by Snow and Bogue⁴ in order to express volume changes entirely with the first term in cases where the deformation is isotropic. A similar separation of the isotropic (volume) and nonisotropic effects has been made by Penn¹⁷ and Peng,¹⁸ who defined new, volume-normalized strain invariants. The material parameters $G(t')$ and $\tau_G(t')$ are, respectively, the modulus and time constant for anisotropic deformations; both are functions of time in that they depend on temperature, pressure, and possibly other parameters (such as free volume) which depend on time. The time constant τ_G would be made dependent on one or more of these variables by means of a shift factor (or factors), analogous to Eq. (5). The negative scalar stress $\mathcal{P}$ is the same as that which appears in Eq. (2) [with Eqs. (3) and (4)] and Eq. (9) and is determined by a simultaneous solution of the equations in which it appears. More about $\mathcal{P}$ will be said in the next section.

Finally, a restriction on the kinematics is imposed by the relationship

$$\sqrt{\det c_{ij}^{-1}} = V(t)/V(t') \quad (10)$$

where $\det c_{ij}^{-1}(t, t')$ means the determinant of the components of the unnormalized relative Finger strain tensor. (Cartesian tensors are understood in the present paper; if not, mixed components would be required in forming the determinant.) In many problems the left side of Eq. (10) can be linearized to yield a simple relationship between an unknown component of strain and the volume change.

The new formulation consists, then, of the set of simultaneous equations given by Eq. (1) [or Eq. (2)], Eq. (9) and Eq. (10), plus

the associated equations which define symbols in the basic relationships. Since most problems of practical interest involve temperature changes, with stress or strain constraints, the solution of the governing equations will have to be done numerically. However, a few special cases, to be discussed below, illustrate the way in which the general formulation incorporates classical theory.

SPECIAL CASES

Equilibrium and Rate-Dependent *PVT* Equations

It is presumed that the initial state (P_0, V_0, T_0) is an equilibrium state, either a glass or a rubber. Thus $\Delta\theta$ will be zero initially. If one remains in the glassy state, then $\phi_f = 0$ and $\Delta\theta$ will remain at zero. That is, we are imagining that the short range motions characteristic of the glassy state are (essentially) instantaneous. In the other extreme (well into the rubbery state) ϕ_f will not be zero but the time constant (τ_λ) will be very small, which rapidly drives the system to equilibrium. Thus one has almost instantaneous *PVT* response in the two limits, but for different reasons.

For rate-dependent *PVT* (isotropic) problems one must use Eq. (2), which requires one to deal with $\mathcal{P}$. Since the volume changes will be small, one can reasonably linearize them, as was done in creating the normalized Finger strain tensor.⁴ Letting $\epsilon_I(t, t')$ be a typical linear normal strain, we can approximate a typical Finger normal component $c_I^{-1}(t, t')$ and the volume change as follows:¹⁹

$$c_I^{-1} \approx 1 + 2\tilde{\epsilon}_I \quad (11)$$

and

$$\Delta V/V(t') = (c_I^{-1})^{3/2} - 1 \approx 3\tilde{\epsilon}_I \quad (12)$$

Thus in isotropic deformations the normalized tensors c_{11}^{-1*} , c_{22}^{-1*} , and c_{33}^{-1*} will be zero, as they are intended to be. Noting that $\sigma_{11} = \sigma_{22} = \sigma_{33} = -P$ (the hydrostatic pressure) in isotropic deformations, Eq. (9) leads us to the conclusion that $\mathcal{P} = P$. Satisfaction of Eq. (10) may also be demonstrated by using the linearized relations shown in Eqs. (11) and (12). Finally, then, the general isotropic (*PVT*) equation can be dealt with by solving Eq. (2) [with $\mathcal{P} = P$ in Eqs. (3) and (4)]. In such problems any two of the three variables P , V , and T are independent and one is dependent.

The most common problem of this kind is one in which the pressure is held constant and the temperature is changed. Following Snow and Bogue⁴ but with a change from an average $\bar{\alpha}$ to a point α in the derivative term, Eq. (2) reduces to

$$\frac{dV}{dt} = \frac{-(V - V_e)}{\tau_\lambda} + V_0 \frac{d\{\alpha(t) - \Delta\alpha(t)\}T}{dt} \quad (13)$$

where $V_e [= V_0 + V_0\bar{\alpha}(T - T_0)]$ is the volume which would exist at the instantaneous temperature if equilibrium were allowed to occur. We restrict now to constants α 's. Above T_{K^*} , we have $\alpha = \alpha_r$ and $\Delta\alpha = \alpha_r - \alpha_g$, and below T_{K^*} , we have $\alpha = \alpha_g$ and $\Delta\alpha = 0$; in either case the bracketed factor reduces to α_g . Thus Eq. (13) becomes

$$\frac{dV}{dt} = \frac{-(V - V_e)}{\tau_\lambda} - V_0 R \alpha_g \quad (14)$$

where $R [= -dT/dt]$ is the cooling rate. This is essentially Kovacs' one parameter rate equation,²⁰ except that we have linearized around V_0 and not V_∞ (see the discussion in our prior work⁴).

As noted previously, the one parameter model is not adequate for complicated thermal histories, especially those involving reheating. We suggest here a possible generalization similar to those that have been proposed in the literature (cf. Refs. 14 and 15 for recent reviews). The rate expression is generalized to incorporate a number of relaxation times ($\tau_{\lambda,i}$), each associated with some portion of the volume change. In that spirit we would propose to generalize Eq. (2) to the following:

$$\frac{d(\theta_i + \phi_f)}{dt} = \frac{-\Delta\theta_i}{\tau_{\lambda,i}} \quad (15)$$

where

$$\theta_i(t) = \mathcal{P}(t)/\lambda^*(t) + v_i(t)/v_{oi} - \alpha(t)T(t) \quad (16)$$

where $\sum_i v_i = V$ and $\sum_i v_{oi} = V_0$. Similarly $\Delta\theta$ may be generalized to $\Delta\theta_i$ by replacing V and V_0 with v_i and v_{oi} , respectively. As in the prior literature we do not give a specific physical picture of what we are imagining by these small volume elements; in the final equation one has a series of *free* volume elements and one might reasonably associate this spectrum with a distribution of hole (void) sizes, each with a different time-dependent behavior. Pro-

ceeding in a manner analogous to Eqs. (13) and (14), we obtain

$$\frac{dV}{dt} = -\sum_i \frac{[v_i - v_{ei}]}{\tau_{\lambda,i}} - V_0 \alpha_g R \quad (17)$$

where $v_{ei} = v_{oi} + v_{oi} \bar{\alpha}(t) [T(t) - T_0]$. This is similar to, but not identical to, multiparameter form of Kovacs and co-workers,¹² the main difference being that we are linearizing about an arbitrary initial state V_0 as noted above.

Linear Elasticity Theory and the Scalar $\mathcal{P}$

The form of θ and the equation for σ_{ij} have been strongly influenced by the need to reduce to linear elasticity theory, which would be appropriate, for example, in the equilibrium glassy state and also in the rubbery state if the deformations were small and the experimental time scale short. We will here and in the further discussion take $P_0 = 0$, which is equivalent to thinking of all stresses and pressures as being defined relative to some arbitrary base (typically atmospheric pressure, in which case one can think of the pressures as "gauge pressures"). At steady state $\Delta\theta = 0$, which leads to

$$0 = \mathcal{P}/\lambda^* + [(V - V_0)/V_0] - \alpha[T - T_0] \quad (18)$$

where $\lambda^* = \lambda + (2/3)G$. Subscripts have been omitted from the moduli and the thermal coefficient with the understanding that we are considering the point value for the particular state being discussed.

Elasticity theory results when the time constant τ_G is made large, which has the effect that the material does not "forget" its past history. Thus the undeformed state (taken to be that at $t = -\infty$) serves as a reference state for the definition of strain and relative strain tensors are not needed. For the present discussion, involving small strains, c_{ij}^{-1} may be linearized to:¹⁹

$$c_{ij}^{-1} - \delta_{ij} = 2\tilde{\epsilon}_{ij} \quad (19)$$

where $\tilde{\epsilon}_{ij}$ is the linear strain tensor. Noting also that $(V - V_0)/V_0 = \tilde{\epsilon}_{kk}$, Eq. (9) reduces to

$$\sigma_{ij} = -\mathcal{P} \delta_{ij} + G[2\tilde{\epsilon}_{ij} - (2/3)\tilde{\epsilon}_{kk} \delta_{ij}] \quad (20)$$

Now if one writes out Eq. (20) for the three normal stress compo-

nents one obtains equations such as

$$\sigma_{11} = -\mathcal{P} + G[2\tilde{\epsilon}_{11} - (2/3)(\tilde{\epsilon}_{11} + \tilde{\epsilon}_{22} + \tilde{\epsilon}_{33})] \quad (21)$$

Similarly for σ_{22} and σ_{33} . Adding the three normal stress components one finds that all of the strain terms on the right cancel out, leading to

$$\mathcal{P} = -(1/3)\sigma_{kk} \quad (22)$$

This result, which is familiar in linear theory, comes about naturally and does not have to be introduced as an assumption. The desire to obtain Eq. (22) was part of the motivation for introducing the normalized strain tensor c_{ij}^{-1*} , as opposed to c_{ij}^{-1} itself. Another motivation has to do with making $\mathcal{P} = P$ for the case where only a hydrostatic pressure P is applied as the stress state; without this limiting case, $\mathcal{P}$ would be without physical meaning in a classical sense. It is important to note, however, that Eq. (22) is not generally true and will not be valid in nonlinear deformations, as will be illustrated below. In the prior work⁴ we avoided (with one exception) introducing a scalar stress $\mathcal{P}$ and thus did not have to face the problem of defining it. The exception was in the definition of ϕ_f [Eqs. (7) and (8) here], where we used a pressure defined in the manner of Eq. (22); that arbitrary linearization is avoided in the present work.

Finally, linear elasticity theory can be retrieved by eliminating $\mathcal{P}$ between Eqs. (18) and (20), resulting in a form which is used in the analysis of thermal stresses [see Eq. (2) in Ref. 4 and p. 456 in Ref. 21]. For the more familiar isothermal case ($T = T_0$), the result is

$$\sigma_{ij} = \lambda \tilde{\epsilon}_{kk} \delta_{ij} + 2G \tilde{\epsilon}_{ij} \quad (23)$$

which is classical linear elasticity theory.²¹

To complete the analysis of linear behavior one must show that Eq. (10) is satisfied. Using Eq. (19), presuming elastic (not relative) strain tensors, and noting that $(V - V_0)/V_0 = \tilde{\epsilon}_{kk}$, the square root of the determinant linearizes to

$$\sqrt{\det c_{ij}^{-1}} \approx \sqrt{1 + 2\tilde{\epsilon}_{kk}} \approx 1 + \tilde{\epsilon}_{kk} \approx V/V_0 \quad (24)$$

which satisfies Eq. (10).

Large Deformation Viscoelastic Theory and the Scalar $\mathcal{P}$

We have not been able to imagine problems in large deformation viscoelasticity which can be worked out analytically. One

must solve Eqs. (2), (9), and (10) simultaneously and in general this will require computer solutions. However, the limiting case of incompressible deformations (incompressible in the sense of Poisson's ratio) is instructive in understanding the nature of $\mathcal{P}$ and the behavior of the equations more generally.

A classical problem of this kind is the uniaxial extension of an incompressible, isothermal material at a constant extension rate E' in the 1-direction. The kinematics are $c_{11}^{-1} = \exp(2E's)$ and $c_{22}^{-1} = c_{33}^{-1} = \exp(-E's)$, where $s = t - t'$. These kinematics directly satisfy Eq. (10), if one notes that $V(t)/V(t') = 1$ for incompressible materials. The stresses on the side faces of the sample are zero ($\sigma_{22} = \sigma_{33} = 0$) which, using Eq. (9), leads to

$$\mathcal{P} = \int_{-\infty}^t (G/\tau_G) \exp(-s/\tau_G) [\exp(-E's) - 1] dt' \quad (25)$$

Integrating gives the result

$$\mathcal{P} = -(G\tau_G E')/(1 + E'\tau_G) \quad (26)$$

Now the stress in the pulling direction (σ_{11}) is obtained by inserting the kinematics for c_{11}^{-1} into Eq. (9) [analogously to Eq. (25)] and using Eq. (26) to eliminate $\mathcal{P}$. The result is

$$\sigma_{11} = \frac{3G\tau_G E'}{(1 + E'\tau_G)(1 - 2E'\tau_G)} \quad (27)$$

One can see from Eqs. (26) and (27) that there is not a simple relationship between $\mathcal{P}$ and the applied stresses. However, at small extension rates ($E'\tau_G \ll 1$), one obtains the results $\mathcal{P} = -G\tau_G E'$ and $\sigma_{11} = 3G\tau_G E'$, leading to

$$\mathcal{P} = -(1/3)\sigma_{11} \quad (\text{for small } E') \quad (28)$$

This is the expected result: $-\mathcal{P}$ is one third the trace of the stresses in the Hookean elastic limit (small strains) and also in the Newtonian viscous limit (small strain rates). But in the general case $\mathcal{P}$ will be determined by consideration of the constraints and the set of simultaneous relations Eqs. (2), (9), and (10). Note also that $\mathcal{P}$ is negative in this case ($-\mathcal{P}$ and σ_{11} are positive) and does not have the physical meaning of "pressure" as we normally think of it. The $\mathcal{P}$ in the PVT equation (more accurately the $\mathcal{P}VT$ equation) can be of either sign: in uniaxial extension the applied stress increases the volume (the Poisson's ratio effect).

Consideration of the equation for $\Delta\theta$ also leads to some interesting insights. As discussed in Snow and Bogue⁴ the criterion for incompressibility in the Poisson's ratio sense is that $\lambda/G \gg 1$. In the present case one can insert the result for $\mathcal{P}$ [Eq. (26)] into Eq. (2) and consider the limit of $\lambda/G \gg 1$. This eliminates the $\mathcal{P}$ term from consideration, which means that $\mathcal{P}$ is indeterminate in a $\mathcal{PVT}$ sense. Note, however, that the volume could be changing because of a change of temperature (and not necessarily instantaneously), that process, however, having no effect on the calculation of $\mathcal{P}$, which would be determined from constraints imposed by Eq. (9) and not by Eq. (2).

The compressible isothermal analog of the incompressible isothermal case discussed above would involve specifying E'_1 in the 1-direction, $\sigma_{22} = \sigma_{33} = 0$ in the 2- and 3-directions, and solving simultaneously the following four equations: Eq. (2) (for a prescribed thermal history); two equations from Eq. (9); and Eq. (10). There would be four unknowns in these equations: $\sigma_{11}(t)$, $\mathcal{P}(t)$, $E'_2(t')$ [$= E'_3(t')$], and $V(t')$. ($E'_2(t)$ and $V(t)$ are the special cases at $t' = t$.) Note that the volume equation and the anisotropic stress/strain equation are necessarily coupled: both depend on $\mathcal{P}$ and the volume change. In addition, the equations for the shift factors would be coupled, depending, for example, on the instantaneous (usually nonequilibrium) free volume.

One can see from this and other examples that there must be an imposed normal component of stress for a volume change to occur. Simple shear will produce a difference in normal stresses but no change in volume, unless one applies a tensile or compressive stress on the boundaries beyond that produced by the shear, or changes the temperature.

CONCLUDING REMARKS

To solve polymer processing problems involving rapid cooling, one must deal with compressible effects, both those imposed directly by the temperature change and those imposed indirectly through the build-up of stresses. The proposed framework here—a restatement of our prior integral theory in a more tractable form—provides a set of simultaneous equations which couple the change of volume and the change of anisotropic stress/strain. One requires a *scalar* $\mathcal{P}$ in an equation of state and

the question finally becomes one of defining it in a plausible way; if we had simple polynomial theories, it might be possible to define $\mathcal{P}$ in terms of the second and/or third invariants of stress. But with the complicated viscoelastic theories presently in use, no simple relationship like this is evident. We thus propose the idea of leaving it undefined in the sense of invariants, but defined in the sense of satisfying a certain set of simultaneous equations. Ours is not, of course, a unique way to proceed but appears to be a reasonable one since it reduces to certain special cases: in particular, in isotropic (*PVT*) deformations, $\mathcal{P}$ is the hydrostatic pressure P , and in linear deformations, $\mathcal{P} = -(\frac{1}{3})\sigma_{kk}$. This latter expression and also our scheme more generally allows $\mathcal{P}$ to be of either sign, as must be the case physically: compressive loading decreases the volume and tensile loading increases it.

In order to obtain the result $\mathcal{P} = P$ in isotropic deformations, a special kind of (normalized) Finger strain tensor, similar in principle to ones used earlier by Penn¹⁷ and Peng¹⁸, is introduced. While forcing the result $\mathcal{P} = P$ in the isotropic case is essential if $\mathcal{P}$ is to have an identifiable physical meaning, the consequence of this normalization in our framework requires more discussion. Note that it is sometimes so that volume changes in an anisotropic stress field (for example, uniaxial pulling) will be different than volume changes in an isotropic field (i.e., one must allow for a Poisson's ratio other than 1/2). We satisfy this requirement by constructing equations which reduce to linear elasticity theory. But what happens outside the linear range is unexplored territory: existing *PVT* equations are not intended for nonlinear, anisotropic loadings. As one creates—and remembers—a highly anisotropic stress/strain history, the resulting anisotropic solid will have direction-dependent moduli (a fourth-order tensor)²² and the volume response will surely be complicated also. These complications will require another level of generalization. What we present here is the simplest assumption, via the normalized strain tensor, which allows one to introduce nonlinear strains [Eq. (9)] and still be consistent with existing theory for rate-dependent *PVT* deformations and for linear compressible solids (i.e., linear elasticity theory).

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8.2 Appendix B: Classical Residual Stress Theory

A brief summary of the theory of Lee, Rogers and Woo (LRW) [99] for the calculation of residual stresses in quenched slabs will be presented first, followed by an outline of the theory of Aggarwala and Saibel (AS) [1] and the Indenbom theory [71,72]. (A detailed description has been given by Wust [206].) In these theories instantaneous (time-independent) PVT response has been assumed. In the LRW theory the only time-dependence is associated with the modulus; but in the AS theory the modulus is assumed to be either zero or a large constant value in the rubbery and glassy states, respectively.

Following the LRW theory, one starts with linear viscoelasticity and writes the deviatoric stress in the form

$$\sigma_{ij}(x, t) = \int_0^t 2G(t - t') \frac{\partial \epsilon_{ij}(x, t')}{\partial t'} dt' \quad (8.1)$$

where t is time at consideration, $G(t, t')$ is the relaxation shear modulus, and $\epsilon_{ij}(x, t')$ is the linear strain. Note that $2G$ appears because the shear strain component here is one half of the classical shear component. Nonisothermal effects are included by introducing a reduced time ξ , which is defined as

$$\xi(x, t) = \int_0^t \frac{dt'}{\tau_G(T)} \quad (8.2)$$

where $\tau_G(T)$ is a temperature-dependent relaxation time. Thus

$$\sigma_{ij}(x, \xi) = \int_0^\xi 2G(\xi - \xi') \frac{\partial \epsilon_{ij}(x, \xi')}{\partial \xi'} d\xi' \quad (8.3)$$

One imagines a slab similar to that shown in Figure 8.1 but of infinite extent in the 1- and 3-directions. One must also imagine a solidification mechanism at

both ends for averaging out the stresses there (and in fact elsewhere along the 1- and 3-directions). That is a boundary condition for an initially stress-free sample, as expressed by

$$\int_0^b \sigma(x_2, t) dx_2 = 0 \quad (8.4)$$

where $\sigma = \sigma_{11} = \sigma_{33}$. By assuming no shear stresses and permitting free lateral expansion in 2-direction (i.e., $\sigma_{22} = 0$), the "squeezing stress" (σ) can be obtained from Eqn. (8.3), as follows

$$\sigma(x_2, \xi) = \int_0^\xi 2G(\xi, \xi') \frac{\partial [\epsilon_1(\xi') - \epsilon_2(x_2, \xi')]}{\partial \xi'} d\xi' \quad (8.5)$$

where $\epsilon_1 = \epsilon_{11}(\xi') = \epsilon_{33}(\xi')$ and $\epsilon_2 = \epsilon_{22}(x_2, \xi')$ are linear strains.

Since an equilibrium PVT relation is assumed, the trace of stress σ_{kk} is presumed to be instantaneously related to the volume change (ϵ_{kk}) and the temperature change. That is,

$$2\sigma(x_2, t) = 3\kappa \{ \epsilon_2(x_2, t) + 2\epsilon_1(t) - 3\alpha [T(x_2, t) - T(x_2, 0)] \} \quad (8.6)$$

where κ is the bulk modulus (taken to be equal to the Young's modulus of initial deformation), and α is the thermal coefficient of expansion.

Solving Equation (8.6) for $\epsilon_2(x_2, t)$ and then substituting into Equation (8.5), one obtains

$$\begin{aligned} \sigma(x_2, \xi) = \int_0^\xi 2G(\xi - \xi') \frac{\partial}{\partial \xi'} \left\{ \epsilon_1(\xi') - \frac{2\sigma(x_2, \xi')}{3\kappa} \right. \\ \left. + 2\epsilon_1(\xi') - 3\alpha [T(x_2, \xi') - T(x_2, 0)] \right\} d\xi' \end{aligned} \quad (8.7)$$

By rearranging and taking the Laplace transform (for the partial differential

and for the integral) leads to the result of

$$\sigma(x_2, \xi) = 3 \int_0^\xi R(\xi - \xi') \frac{\partial [\epsilon_1(\xi') - \alpha T(x_2, \xi')]}{\partial \xi'} d\xi' \quad (8.8)$$

Rewriting Eqn. (8.8) in terms of real time gives the final form

$$\sigma(x_2, t) = 3 \int_0^t R[\xi(x_2, t) - \xi(x_2, t')] \frac{\partial [\epsilon_1(t') - \alpha T(x_2, t')]}{\partial t'} dt' \quad (8.9)$$

where $R(\xi - \xi')$ is an auxiliary modulus function satisfying

$$\frac{4}{3\kappa} \int_0^\xi G(\xi - \xi') \frac{\partial R(\xi')}{\partial \xi'} d\xi' + R(\xi) = 2G(\xi) \quad (8.10)$$

This is the theory of Lee, Rogers and Woo [99], in which Eqn. (8.9) and Eqn. (8.4) are simultaneously solved for residual stresses in rapidly cooled samples. One notes that in this theory the time-dependent modulus provides the only mechanism for stress relaxation.

A special case of the LRW theory is due to Aggarwala and Saibel [1]. The simplification can be made by assuming the modulus to be either zero (completely "fluid") or a large constant (completely "solid"), depending on the temperature relative to the glass transition. That is, the material has either no memory at all or complete memory, as expressed by

$$R[\xi(x_2, t) - \xi(x_2, t')] = 0 \quad \text{at } 0 < x_2 < \bar{x}_2 \quad 0 < t < \bar{t} \quad (8.11)$$

$$R[\xi(x_2, t) - \xi(x_2, t')] = R_c \quad \text{at } \bar{x}_2 < x_2 < b \quad \bar{t} \leq t < \infty \quad (8.12)$$

where $\bar{t}(x_2)$ is the time at which a particular position x_2 passes through T_g , $\bar{x}_2(t)$ is the position of the solidification line at time t , and R_c is the characteristic modulus in the glassy state.

Using the notation of Aggarwala and Saibel, the LRW and AS theories can be connected by

$$R_c = 2\beta = \frac{2E}{6(1-\nu)} \quad (8.13)$$

where ν is Poisson's ratio and E is Young's modulus. Considering the modulus in Eqns. (8.11) and (8.12), the LRW theory (Eqn. (8.10)) reduces to

$$\sigma(x_2, t) = \int_{\bar{i}(x_2)}^t 6\beta \frac{\partial [\epsilon_1(t') - \alpha T(x_2, t')]}{\partial t'} dt' \quad (8.14)$$

After combining with the boundary condition (Eqn. (8.4), Eqn. (8.14) can finally be reduced to the AS theory:

$$\sigma(x_2, t) = \int_{\bar{i}(x_2)}^t 6\beta \left\{ \left(\frac{1}{b - \bar{x}_2(t)} \int_{\bar{x}_2(t)}^b \frac{\partial [\alpha T(x'_2, t')]}{\partial t'} dx'_2 \right) - \frac{\partial [\alpha T(x_2, t')]}{\partial t'} \right\} dt' \quad (8.15)$$

where 6β is an elastic modulus related to Young's modulus. The residual stresses are then obtained by integrating the strain over the solid portion. One notes that in the right-hand side of Eqn. (8.15) the term inside the parentheses is actually an average strain over the solid region, while the second term is the strain at a particular position x_2 . If one considers at the time when the slab temperature has uniformly reached its asymptotic value and also a constant thermal coefficient of expansion, then such a special case of the AS equation is equivalent to the Indenbom theory, which will be described below.

According to Indenbom [71,72], the total strain ϵ is uniform across the slab thickness and is composed of three components:

$$\epsilon(t) = \epsilon_e(x_2, t) + \epsilon_p(x_2, t) + \alpha[T(x_2, t) - T_0] \quad (8.16)$$

where ϵ_e is the elastic strain which is zero above T_g , ϵ_p is the "plastic" strain which occurs above T_g and is frozen-in as a time-independent strain below T_g , and T_0 is the initial temperature. When the slab temperature becomes uniform ($T = T_\infty$ at the time $t = \infty$), Indenbom sets $\bar{\epsilon} = \epsilon$ with $\bar{\epsilon}_e = 0$, where the overbar denotes the average values across the slab thickness. That gives

$$\bar{\epsilon}_p = \epsilon_p(x_2) + \epsilon_e(x_2) \quad (8.17)$$

The final stress is thus expressed, based on the linear elasticity, as

$$\sigma(x_2) = \frac{E\epsilon_e(x_2)}{1-\nu} = \frac{E}{1-\nu}(\bar{\epsilon}_p(x_2) - \epsilon_p(x_2)) \quad (8.18)$$

where $\bar{\epsilon}_p(x_2)$ is the average plastic strain across the slab thickness.

The plastic strain $\epsilon_p(x_2)$ in the above equation can be calculated by considering the strain when point x_2 freezes. That is, at $x_2 = \bar{x}_2$ the temperature $T(\bar{x}_2, t) = T_g$ and $\epsilon_e(\bar{x}_2, t) = 0$, which results in

$$\epsilon(\bar{x}_2, t) = \epsilon_p(\bar{x}_2, t) + \alpha(T_g - T_0) \quad (8.19)$$

For the solid region where $T < T_g$, the average elastic strain $\bar{\epsilon}_e$ is zero and the corresponding average total strain $\bar{\epsilon}(t)$ is

$$\bar{\epsilon}(t) = \bar{\epsilon}_p(x_2) + \alpha[\bar{T}(x_2, t) - T_0] \quad (8.20)$$

Since the total strain is assumed to be independent of x_2 , the preceding two expressions can be equated by $\epsilon(\bar{x}_2, t) = \bar{\epsilon}(t)$. After algebraic rearrangements it gives

$$\epsilon_p(\bar{x}_2, t) + \alpha(T_g - T_0) = \frac{1}{b - \bar{x}_2} \int_{\bar{x}_2}^b \{\epsilon_p(x_2, t) + \alpha[T(x_2, t) - T_0]\} dx_2 \quad (8.21)$$

From this equation the plastic strain $\epsilon_p(x_2, t)$ can be obtained with the given temperature $T(x_2, t)$ and the assumption of time-independent ϵ_p at $T < T_g$.

To obtain the strain from the freezing time $\bar{t}(x_2)$ to the final time $t = \infty$, one takes the time derivative for the above equation and then integrates over the elapsed time. Substituting ϵ_p and its average value $\bar{\epsilon}_p$ into Eqn. (8.18) leads to the final result:

$$\sigma(x_2) = \int_{\bar{t}(x_2)}^t 6\beta \left\{ \left(\frac{1}{b - \bar{x}_2} \int_{\bar{x}_2(t)}^b \frac{\partial \epsilon_p(x'_2, t')}{\partial t'} dx'_2 \right) - \frac{\partial \epsilon_p(x_2, t')}{\partial t'} \right\} dt' \quad (8.22)$$

where $6\beta = E/(1 - \nu)$, as defined in Eqn. (8.13). Because the plastic strain is time-independent at $T < T_g$, the strain actually depends on the thermal history of $\alpha[T(x_2, t) - T_0]$. The final form of Indenbom theory is thus equivalent to the special case of the AS theory, as compared with Eqn. (8.15).

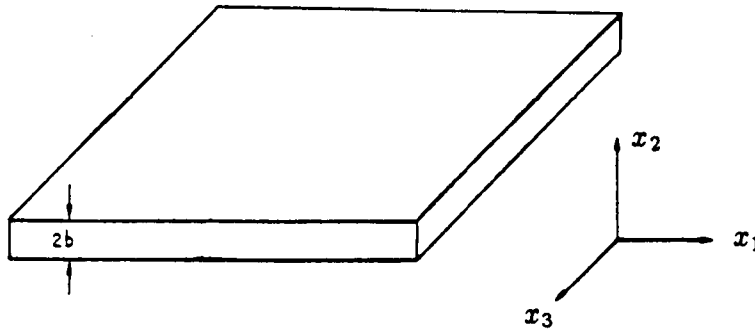


Figure 8.1: Schematic diagram of the slab used in analysis of residual stresses.

8.3 Appendix C: Modulus $G(T)$ and Computer Program for the Analysis of Simultaneous Pulling and Cooling Experiments

Modulus $G(T)$ as a function of temperature (as shown in Figure 4.3: the upper and lower limits and the values used in the analysis):

temperature ($^{\circ}\text{C}$)	modulus (dyne/cm ²)		
	upper limit	values used	lower limit
125.0	3.50E6	2.30E6	1.60E6
124.0	3.70E6	2.40E6	1.70E6
122.0	4.30E6	2.70E6	1.90E6
120.0	5.00E6	3.10E6	2.20E6
118.0	6.40E6	3.90E6	2.50E6
116.0	8.20E6	4.90E6	3.00E6
114.0	1.15E7	6.60E6	3.70E6
112.0	1.70E7	9.00E6	5.00E6
110.0	2.60E7	1.30E7	8.00E6
108.0	4.80E7	2.30E7	1.60E7
106.0	1.50E8	8.00E7	4.50E7
104.0	5.00E8	3.10E8	1.80E8
102.0	1.80E9	8.00E8	4.00E8
100.0	3.50E9	1.60E9	7.50E8
98.0	5.60E9	2.70E9	1.40E9
96.0	7.60E9	4.00E9	2.10E9
94.0	9.20E9	5.40E9	3.00E9
93.0	1.00E10	6.00E9	3.40E9
92.0	1.07E10	6.60E9	4.00E9
90.0	1.20E10	7.80E9	4.80E9
88.0	1.32E10	8.40E9	5.60E9
86.0	1.45E10	9.00E9	6.20E9
84.0	1.50E10	9.00E9	6.70E9
82.0	1.50E10	9.00E9	7.10E9
80.0	1.50E10	9.00E9	7.40E9
78.0	1.50E10	9.00E9	7.50E9
76.0	1.50E10	9.00E9	7.50E9
75.0	1.50E10	9.00E9	7.50E9

```

*****
* ANALYSIS OF SIMULTANEOUS PULLING AND COOLING EXPERIMENTS *
*****
* COOLING RATE R=2.50 (C/SEC), PULLING SK=5.0 (CM/MIN).      *
* THE CSMP PROGRAM IS EMPLOYED IN THE ANALYSIS.              *
*****
MACRO Y=FLOW(XA)
  PROCEDURAL
  IF(XA)1,2,3
1    IF(XA .GE. -150.) GO TO 10
      XA=-150.
10   Y=EXP(XA)
      GO TO 100
2    Y=1.
      GO TO 100
3    IF(XA .LE. 150.) GO TO 30
      XA=150.
30   Y=EXP(XA)
100  CONTINUE
ENDMAC
INITIAL
PARAMETER R=2.50,TIMEF=0.40,VTF=0.98874,VTFDOT=-1.40E-3
CONSTANT SLO=16.93,C2=0.22,TAU20=324.0,TEMPI=125.0,...
          EDOT=4.92E-3,SK=5.0,BETA=0.47,...
          TAU10=1.77E-4,ALFG=2.48E-4,ALFR=5.68E-4,...
          DALF=3.20E-4,TGE=75.0,TEMPI=125.0,VO=0.98930,...
          CR=9.10E-11,CG=3.33E-11,CAVG=6.20E-11,GAMA=4.00E2
NOSORT
  WRITE(6,150)
150  FORMAT(/, 5X,'VTF',9X,'VTFDOT',5X,'BEFORE EACH STEP')
      WRITE(6,120)VTF,VTFDOT
120  FORMAT(F12.5,E15.5,/)
SORT
* MODULUS, G(T), FOR THE STRESS TERM.
FUNCTION MOD=(0.0,3.0E+6),(0.400,3.20E+6),...
  (0.800,3.50E+6),(1.200,3.80E+6),...
  (1.600,4.00E+6),(2.000,4.50E+6),...
  (2.400,5.00E+6),(2.800,5.60E+6),(3.200,6.00E+6),...
  (3.600,7.00E+6),(4.000,8.00E+6),...
  (4.400,9.60E+6),(4.800,1.10E+7),...
  (5.200,1.30E+7),(5.600,1.60E+7),...
  (6.000,2.00E+7),(6.400,2.60E+7),...
  (6.800,3.80E+7),(7.200,6.00E+7),...
  (7.600,1.00E+8),(8.000,2.20E+8),...
  (8.400,4.50E+8),(8.800,7.00E+8),...
  (9.200,9.80E+8),(9.600,1.20E+9),...
  (10.00,1.60E+9),(10.40,1.90E+9),...
  (10.80,2.20E+9),(11.20,2.50E+9),...
  (11.60,2.90E+9),(12.00,3.20E+9),...
  (12.40,3.50E+9),(12.80,3.80E+9),...
  (13.20,4.00E+9),(13.60,4.30E+9),...
  (14.00,4.60E+9),(14.40,4.90E+9),...
  (14.80,5.20E+9),(15.20,5.40E+9),...
  (15.60,5.60E+9),(16.00,5.80E+9),...
  (16.40,6.10E+9),(16.80,6.40E+9),...
  (17.20,6.60E+9),...

```

```

(17.60,6.90E+9),(18.00,7.10E+9),...
(18.40,7.30E+9),...
(18.80,7.30E+9),(19.20,7.50E+9),...
(19.60,7.50E+9),...
(20.00,7.50E+9),(20.40,7.50E+9),...
(20.80,7.50E+9),...
(21.20,7.50E+9),(21.60,7.50E+9),...
(22.00,7.50E+9),...
(22.40,7.50E+9),(22.80,7.50E+9),...
(23.20,7.50E+9),...
(23.60,7.50E+9),(24.00,7.50E+9)
B10=VO * ALFG * R
B11=VO * CG
DYNAMIC
40    TEMP=TEMPI-(R*TIME)
      TEMPF=TEMPI-(R*TIMEF)
PROCEDURE VET=GOD(VO,ALFR,ALFG,TEMPI,TGE,TEMP,CR,CAVG,SP)
      IF(TEMP .GE. TGE) GO TO 50
      VET=VO-ALFR*(TEMPI-TGE)*VO-ALFG*(TGE-TEMP)*VO
        -CAVG*SP*VO
      GO TO 60
50    CONTINUE
      VET=VO-ALFR*(TEMPI-TEMP)*VO-CR*SP*VO
60    CONTINUE
ENDPROCEDURE
      B1=VT-VET
      DELTA=B1/VO
      B2=BETA*(TEMPI-TEMP)
      B3=FLOW(B2)
      B4=GAMA*DELTA
      B5=FLOW(B4)
      TAU=TAU10*B3*B5
      VTDOT=-(B1/TAU)-B10-(B11*SPDOT)
      VT=INTGRL(0.98930,VTDOT)
* EQUATIONS IN THE STRESS TERM.
      A1=1.0/EXP(C2*R*TIMEF)
      A2=1.0/EXP(C2*R*TIME)
      A3=TAU20*C2*R
      A41=ABS(A1-A2)
      A42=A41/A3
      A51=FLOW(A42)
      A5=1.0/A51
      A6=EDOT*(TIMEF-TIME)
      A7=FLOW(A6)
      A8=2.0*A6
      A9=FLOW(A8)
      MODULS=FUNGEN(MOD,2,TIME)
      A10=VT*VT
      A15=((EDOT*VT)-VTDOT)/(A10*A7)
      A16=2.0*EDOT*A9
      A17=MODULS*A5
      A18=A17*((VTF*A15)+A16)
      STRESS=INTGRL(0.0,A18)
      A20=(2.0*VTDOT)/(3.0*A10)
      A21=A17*VTF*(A15+A20)
      SCP=INTGRL(0.0,A21)

```

```

      SP=- SCP
      A30=EDOT*VTF*A17*A15
      A32=INTGRL(0.0,A30)
      GTF=FUNGEN(MOD,2,TIMEF)
      A33=VTFDOT/VTF
      A34=(A33-(A1/TAU20))*SP
      A35=GTF*((A33/3.0)-EDOT)
      SPDOT=A35+A34+A32
NOSORT
      IF(TIME .LT. TIMEF) GO TO 90
      V=VT
      VDOT=VTDOT
      IF((ABS(V-VTF).LE. 5.E-5).AND.(ABS(VDOT-VTFDOT)
        .LE. 1.E-6))GO TO 80
      VTF=V
      VTFDOT=VDOT
      GO TO 40
80     CONTINUE
90     CONTINUE
TERMINAL
METHOD STIFF
RELERR VT=0.00005,STRESS=0.00005,SCP=0.00005
ABSERR VT=0.00005
TIMER FINTIM=.400,PRDEL=.400,OUTDEL=.400,DELMIN=1.0E-70
FINISH TEMP=68.0
PRINT TEMP,VT,STRESS,SP,VTF
END
PARAMETER TIMEF=0.800
TIMER FINTIM=0.800,PRDEL=0.800,OUTDEL=0.800
END
PARAMETER TIMEF=1.200
TIMER FINTIM=1.200,PRDEL=1.200,OUTDEL=1.200
END
PARAMETER TIMEF=1.600
TIMER FINTIM=1.600,PRDEL=1.600,OUTDEL=1.600
END
PARAMETER TIMEF=2.000
TIMER FINTIM=2.000,PRDEL=2.000,OUTDEL=2.000
END
PARAMETER TIMEF=2.400
TIMER FINTIM=2.400,PRDEL=2.400,OUTDEL=2.400
END
PARAMETER TIMEF=2.800
TIMER FINTIM=2.800,PRDEL=2.800,OUTDEL=2.800
END
PARAMETER TIMEF=3.200
TIMER FINTIM=3.200,PRDEL=3.200,OUTDEL=3.200
END
PARAMETER TIMEF=3.600
TIMER FINTIM=3.600,PRDEL=3.600,OUTDEL=3.600
END
PARAMETER TIMEF=4.000
TIMER FINTIM=4.000,PRDEL=4.000,OUTDEL=4.000
END
PARAMETER TIMEF=4.400
TIMER FINTIM=4.400,PRDEL=4.400,OUTDEL=4.400

```

END
PARAMETER TIMEF=4.800
TIMER FINTIM=4.800,PRDEL=4.800,OUTDEL=4.800
END
PARAMETER TIMEF=5.200
TIMER FINTIM=5.200,PRDEL=5.200,OUTDEL=5.200
END
PARAMETER TIMEF=5.600
TIMER FINTIM=5.600,PRDEL=5.600,OUTDEL=5.600
END
PARAMETER TIMEF=6.000
TIMER FINTIM=6.000,PRDEL=6.000,OUTDEL=6.000
END
PARAMETER TIMEF=6.400
TIMER FINTIM=6.400,PRDEL=6.400,OUTDEL=6.400
END
PARAMETER TIMEF=6.800
TIMER FINTIM=6.800,PRDEL=6.800,OUTDEL=6.800
END
PARAMETER TIMEF=7.200
TIMER FINTIM=7.200,PRDEL=7.200,OUTDEL=7.200
END
PARAMETER TIMEF=7.600
TIMER FINTIM=7.600,PRDEL=7.600,OUTDEL=7.600
END
PARAMETER TIMEF=8.000
TIMER FINTIM=8.000,PRDEL=8.000,OUTDEL=8.000
END
PARAMETER TIMEF=8.400
TIMER FINTIM=8.400,PRDEL=8.400,OUTDEL=8.400
END
PARAMETER TIMEF=8.800
TIMER FINTIM=8.800,PRDEL=8.800,OUTDEL=8.800
END
PARAMETER TIMEF=9.200
TIMER FINTIM=9.200,PRDEL=9.200,OUTDEL=9.200
END
PARAMETER TIMEF=9.600
TIMER FINTIM=9.600,PRDEL=9.600,OUTDEL=9.600
END
PARAMETER TIMEF=10.000
TIMER FINTIM=10.000,PRDEL=10.000,OUTDEL=10.000
END
PARAMETER TIMEF=10.400
TIMER FINTIM=10.400,PRDEL=10.400,OUTDEL=10.400
END
PARAMETER TIMEF=10.800
TIMER FINTIM=10.800,PRDEL=10.800,OUTDEL=10.800
END
PARAMETER TIMEF=11.200
TIMER FINTIM=11.200,PRDEL=11.200,OUTDEL=11.200
END
PARAMETER TIMEF=11.600
TIMER FINTIM=11.600,PRDEL=11.600,OUTDEL=11.600
END
PARAMETER TIMEF=12.000

TIMER FINTIM=12.000,PRDEL=12.000,OUTDEL=12.000
END
PARAMETER TIMEF=12.400
TIMER FINTIM=12.400,PRDEL=12.400,OUTDEL=12.400
END
PARAMETER TIMEF=12.800
TIMER FINTIM=12.800,PRDEL=12.800,OUTDEL=12.800
END
PARAMETER TIMEF=13.200
TIMER FINTIM=13.200,PRDEL=13.200,OUTDEL=13.200
END
PARAMETER TIMEF=13.600
TIMER FINTIM=13.600,PRDEL=13.600,OUTDEL=13.600
END
PARAMETER TIMEF=14.000
TIMER FINTIM=14.000,PRDEL=14.000,OUTDEL=14.000
END
PARAMETER TIMEF=14.400
TIMER FINTIM=14.400,PRDEL=14.400,OUTDEL=14.400
END
PARAMETER TIMEF=14.800
TIMER FINTIM=14.800,PRDEL=14.800,OUTDEL=14.800
END
PARAMETER TIMEF=15.200
TIMER FINTIM=15.200,PRDEL=15.200,OUTDEL=15.200
END
PARAMETER TIMEF=15.600
TIMER FINTIM=15.600,PRDEL=15.600,OUTDEL=15.600
END
PARAMETER TIMEF=16.000
TIMER FINTIM=16.000,PRDEL=16.000,OUTDEL=16.000
END
PARAMETER TIMEF=16.400
TIMER FINTIM=16.400,PRDEL=16.400,OUTDEL=16.400
END
PARAMETER TIMEF=16.800
TIMER FINTIM=16.800,PRDEL=16.800,OUTDEL=16.800
END
PARAMETER TIMEF=17.200
TIMER FINTIM=17.200,PRDEL=17.200,OUTDEL=17.200
END
PARAMETER TIMEF=17.600
TIMER FINTIM=17.600,PRDEL=17.600,OUTDEL=17.600
END
PARAMETER TIMEF=18.000
TIMER FINTIM=18.000,PRDEL=18.000,OUTDEL=18.000
END
PARAMETER TIMEF=18.400
TIMER FINTIM=18.400,PRDEL=18.400,OUTDEL=18.400
END
PARAMETER TIMEF=18.800
TIMER FINTIM=18.800,PRDEL=18.800,OUTDEL=18.800
END
PARAMETER TIMEF=19.200
TIMER FINTIM=19.200,PRDEL=19.200,OUTDEL=19.200
END

```
PARAMETER TIMEF=19.600
TIMER FINTIM=19.600,PRDEL=19.600,OUTDEL=19.600
END
PARAMETER TIMEF=20.000
TIMER FINTIM=20.000,PRDEL=20.000,OUTDEL=20.000
END
PARAMETER TIMEF=20.400
TIMER FINTIM=20.400,PRDEL=20.400,OUTDEL=20.400
END
PARAMETER TIMEF=20.800
TIMER FINTIM=20.800,PRDEL=20.800,OUTDEL=20.800
END
PARAMETER TIMEF=21.200
TIMER FINTIM=21.200,PRDEL=21.200,OUTDEL=21.200
END
PARAMETER TIMEF=21.600
TIMER FINTIM=21.600,PRDEL=21.600,OUTDEL=21.600
END
PARAMETER TIMEF=22.000
TIMER FINTIM=22.000,PRDEL=22.000,OUTDEL=22.000
END
PARAMETER TIMEF=22.400
TIMER FINTIM=22.400,PRDEL=22.400,OUTDEL=22.400
END
PARAMETER TIMEF=22.800
TIMER FINTIM=22.800,PRDEL=22.800,OUTDEL=22.800
END
STOP
ENDJOB
END
```

8.4 Appendix D: Computer Program for the Simulation of the Cooling Step in Injection Molding

```

C*****
C COOLING STEP IN INJECTION MOLDING (EQUILIBRIUM PVT CASE) *
C*****
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION TXT(11),VX(11),XSTAR(11)
      COMMON TXT,VX,WF,W1,W2,W3,W4,W5,W6,W7,W8,W9,W10
      DATA XSTAR/0.,.10,.28,.44,.58,.70,.80,.88,.94,.98,1.0/
C**** BEFORE COOLING STEP.
      TIME=1.0D-2
      H=1.0D-2
10      CALL TEMP(TIME)
      SP=7.7D7*DEXP(12.3*TIME)-7.7D7
      CALL VOL(SP)
      IF(TIME-1.5990D-1)20,30,30
20      TIME=TIME+H
      GO TO 10
30      CONTINUE
      WRITE(8,170)WF
170     FORMAT(/ 3X,'** FOR COOLING STEP **',1X,
1 'WTSUM=',D18.10,2X,'AS THE BOUNDARY CONDITION.')
C**** GUESS PRESSURE TO SATISFY THE BOUNDARY CONDITION.
C**** BI-SECTIONAL METHOD FOR TRY AND ERROR PROCEDURE.
      WTSUM=WF
      EPS=1.0D-8
      PA=SP
      PDEL=1.0D5
      TIMEA=TIME
      H=2.0D-2
900     TIMEB=TIMEA + H
      CALL TEMP(TIMEB)
      PB=PA-PDEL
      PWI=PA
1000    PWF=PB
      CALL VOL(PB)
      IF(DABS(WF-WTSUM) .LE. EPS) GO TO 5000
      IF(WF .GT. WTSUM) GO TO 2000
1200    PB=(PWI+PWF)/2.
      PW=PB
      CALL VOL(PB)
      IF(DABS(WF-WTSUM) .LE. EPS) GO TO 5000
      IF(WF .GT. WTSUM) GO TO 1500
      PWF=PW
      GO TO 1200
1500    PWI=PW
      GO TO 1200
2000    CONTINUE
      PWI=PWF
      PB=PWF-PDEL
      GO TO 1000
5000    CONTINUE

```

```

C**** WHEN THE BOUNDARY CONDITION IS SATISFIED, WRITE
C**** THE RESULT.
      WRITE(9,135)TIMEB,PB,WF,WTSUM
      IF(TIMEB - 17.0D0)5500,6000,6000
5500   PA=PB
      TIMEA=TIMEB
      IF(TIMEB .LE. 0.999D0) GO TO 900
          H=2.0D-1
          GO TO 900
6000   WRITE(9,180)
135    FORMAT(1X,4D19.10)
180    FORMAT(2X,'END OF JOB')
      STOP
      END

C
C*****
C
      FUNCTION FLOW(XA)
      IMPLICIT REAL*8 (A-H,O-Z)
C**** TO AVOID UNDER- AND OVER-FLOW.
      IF(XA)1,2,3
1      IF(XA .GE. -120.) GOTO 10
          XA=-120.
10     FLOW=DEXP(XA)
          RETURN
2      FLOW=1.0
          RETURN
3      IF(XA .LE. 120.) GOTO 30
          XA=120.
30     FLOW=DEXP(XA)
          RETURN
      END

C
C*****
C
      SUBROUTINE TEMP(TIME)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION XSTAR(11),TXT(11),SUMN(11),A3(11),A4(11),
1      ADD(11),TEMPLS(11)
      COMMON TXT
      DATA XSTAR/0.,.10,.28,.44,.58,.70,.80,.88,.94,.98,1.0/
C**** INFINITE BIOT NUMBER IS USED IN HEAT TRANSFER.
      PI=3.141592654D0
      TI=200.0D0
      TWALL=32.0D0
      B=0.1270D0
      DIFFU=6.33D-4
      TIMELS=DIFFU*TIME/(B*B)
C**** LOOP FOR EACH LAYER.
      DO 300 I=1,11
          ONE=-1.0
          IM=0
          DO 10 J=1,11
10         SUMN(J)=0.0
200        CONTINUE
          N=FLOAT(IM)

```

```

HALF=N+0.50
PH=PI*HALF
PHSQ=-(PH*PH*TIMELS)
EBAR=FLOW(PHSQ)
A3(I)=PH*XSTAR(I)
A4(I)=DCOS(A3(I))
ONE=- ONE
ADD(I)=ONE*EBAR*A4(I)/PH
A5=-((PH*PH*DIFFU)/(B*B))
SUMN(I)=SUMN(I)+ADD(I)
IM=IM+1
IF(EBAR .GT. 1.0D-4) GO TO 200
    TEMPLS(I)=2.0*SUMN(I)
    TXT(I)=TEMPLS(I)*(TI-TWALL)+TWALL
300 CONTINUE
RETURN
END

C
C*****
C
SUBROUTINE VOL(SP)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION TXT(11),VX(11)
COMMON TXT,VX,WF,W1,W2,W3,W4,W5,W6,W7,W8,W9,W10
C**** EQUILIBRIUM PVT EQUATION.
TI=200.0D0
TGE=85.0D0
ALFR=5.68D-4
ALFG=2.48D-4
AALF=4.08D-4
CAVG=1.72D-10
VO=1.05360D0
C**** LOOP FOR EACH LAYER.
DO 200 I=1,11
    IF(TXT(I) .GE. TGE) GO TO 100
    VX(I)=VO-VO*CAVG*SP-VO*ALFR*(TI-TGE)-VO*ALFG*(TGE-TXT(I))
    GO TO 200
100 VX(I)=VO-VO*CAVG*SP-VO*ALFR*(TI-TXT(I))
200 CONTINUE
W1=2.540D-2 /(VX(1)+VX(2))
W2=4.572D-2 /(VX(2)+VX(3))
W3=4.064D-2 /(VX(3)+VX(4))
W4=3.556D-2 /(VX(4)+VX(5))
W5=3.048D-2 /(VX(5)+VX(6))
W6=2.540D-2 /(VX(6)+VX(7))
W7=2.032D-2 /(VX(7)+VX(8))
W8=1.524D-2 /(VX(8)+VX(9))
W9=1.016D-2 /(VX(9)+VX(10))
W10=5.080D-3 /(VX(10)+VX(11))
WF=W1+W2+W3+W4+W5+W6+W7+W8+W9+W10
RETURN
END

```

```

C*****
C COOLING STEP IN INJECTION MOLDING (TIME-DEPENDENT CASE) *
C*****
C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION VTA(11),VX(11)
      COMMON VTA,VX,WF,W1,W2,W3,W4,W5,W6,W7,W8,W9,W10,W11,
1         P4,DOT4
C**** INITIAL VOLUME VTA(I)=1.05360 CM3/G AT 200 (C),
      DO 10 I=1,11
      VTA(I)=1.05360D0
10      CONTINUE
      EPS=1.0D-7
      TIMEA=1.0D-10
      H=1.0D-7
C**** BEFORE THE COOLING STEP.
30      TIMEB=TIMEA+H
      CALL VRK1(TIMEA,TIMEB)
      TIMEA=TIMEB
      IF(TIMEA-0.160D0)30,40,40
40      CONTINUE
      WRITE(8,120)TIMEB,P4,WF
      WRITE(8,140)VX(1),VX(2),VX(3),VX(4),VX(5)
      WRITE(8,150)VX(6),VX(7),VX(8),VX(9),VX(10),VX(11)
C**** FOR THE COOLING STEP.
C**** GUESS PRESSURE (OR ITS DECREASING RATE) TO SATISFY
C**** THE BOUNDARY CONDITION.
C**** THE FIRST GUESS IS ESTIMATED FROM THE DATA OF THE
C**** CORNELL GROUP.
      PA=P4
      DOTH=-1.0D6
      H=1.0D-7
      TIMEB=TIMEA + H
      CALL VRK2(TIMEA,TIMEB,PA,DOTH)
      WRITE(8,120)TIMEB,P4,WF
      WRITE(8,140)VX(1),VX(2),VX(3),VX(4),VX(5)
      WRITE(8,150)VX(6),VX(7),VX(8),VX(9),VX(10),VX(11)
C**** BI-SECTIONAL METHOD FOR TRY AND ERROR PROCEDURE.
      WTSUM=WF
      PA=P4
      PDEL=1.0D3
      H=1.0D-3
900      TIMEA=TIMEB
      TIMEB=TIMEA + H
      PB=PA-PDEL
      PWI=PA
1000     PWF=PB
      DOTH=(PB-PA)/H
      CALL VRK2(TIMEA,TIMEB,PA,DOTH)
      IF(DABS(WF-WTSUM) .LE. EPS) GO TO 5000
      IF(WF .GT. WTSUM) GO TO 2000
1200     PB=(PWI+PWF)/2.0
      PW=PB
      DOTH=(PB-PA)/H
      CALL VRK2(TIMEA,TIMEB,PA,DOTH)

```

```

        IF(DABS(WF-WTSUM) .LE. EPS) GO TO 5000
        IF(WF .GT. WTSUM) GO TO 1500
            PWF=PW
            GO TO 1200
1500     PWI=PW
            GO TO 1200
2000     CONTINUE
        PWI=PWF
        PB=PWF-PDEL
        GO TO 1000
5000     CONTINUE
C****  WHEN THE BOUNDARY CONDITION IS SATISFIED, WRITE
C****  THE RESULT.
        WRITE(8,130)TIMEB,P4,WF,WTSUM
        WRITE(8,140)VX(1),VX(2),VX(3),VX(4),VX(5)
        WRITE(8,150)VX(6),VX(7),VX(8),VX(9),VX(10),VX(11)
        IF(TIMEB - 17.0)5500,6000,6000
5500     PA=PB
            GO TO 900
6000     WRITE(8,180)
120     FORMAT(1X,3D18.9)
130     FORMAT(1X,4D18.9)
140     FORMAT(1X,5D18.9)
150     FORMAT(1X,6D18.9)
180     FORMAT(2X,'END OF JOB')
        STOP
        END
C
C*****
C
        SUBROUTINE VRK1(XI,XSTOP)
        IMPLICIT REAL*8 (A-H,O-Z)
        DIMENSION XSTAR(11),ITER(11),VX(11),VTA(11)
        COMMON VTA,VX,WF,W1,W2,W3,W4,W5,W6,W7,W8,W9,W10,W11,
1         P4,DOT4
        DATA XSTAR/0.,.10,.28,.44,.58,.70,.80,.88,.94,.98,.999/,
1         ITER/10*2,10/
C
C****  4TH ORDER RUNGE-KUTTA METHOD IS EMPLOYED.
C****  BEFORE THE COOLING STEP.
C****  LOOP FOR EACH LAYER.
C
        DO 200 I=1,11
            IB=ITER(I)
            XJ=XSTAR(I)
            YI=VTA(I)
            HITER=FLOAT(IB)
            DX=(XSTOP-XI)/HITER
            X=XI
            Y=YI
            DO 100 J=1,IB
                CALL FCT1(X,P,DOT)
                CALL VOL1(X,Y,P,DOT,XJ,G1)
                X2=X+DX/2.
                Y2=Y+DX*G1/2.

```

```

      CALL FCT1(X2,P2,DOT2)
      CALL VOL1(X2,Y2,P2,DOT2,XJ,G2)
      Y3=Y+DX*G2/2.
      CALL VOL1(X2,Y3,P2,DOT2,XJ,G3)
      X4=X+DX
      Y4=Y+DX*G3
      CALL FCT1(X4,P4,DOT4)
      CALL VOL1(X4,Y4,P4,DOT4,XJ,G4)
      Y=Y+(G1+2.*G2+2.*G3+G4)*DX/6.
100   X=X+DX
      VX(I)=Y
200   CONTINUE
      W1=2.540D-2 /(VX(1)+VX(2))
      W2=4.572D-2 /(VX(2)+VX(3))
      W3=4.064D-2 /(VX(3)+VX(4))
      W4=3.556D-2 /(VX(4)+VX(5))
      W5=3.048D-2 /(VX(5)+VX(6))
      W6=2.540D-2 /(VX(6)+VX(7))
      W7=2.032D-2 /(VX(7)+VX(8))
      W8=1.524D-2 /(VX(8)+VX(9))
      W9=1.016D-2 /(VX(9)+VX(10))
      W10=4.826D-3 /(VX(10)+VX(11))
      W11=1.27D-4 /VX(11)
      WF=W1+W2+W3+W4+W5+W6+W7+W8+W9+W10+W11
      DO 300 K=1,11
      VTA(K)=VX(K)
300   CONTINUE
      RETURN
      END

C
C*****
C
      SUBROUTINE FCT1(TIME,SP,SPDOT)
      IMPLICIT REAL*8 (A-H,O-Z)
C**** FUNCTIONS OF PRESSURE AND ITS DECREASING RATE
C**** BEFORE THE COOLING STEP.
      SP=7.7D7*DEXP(12.3*TIME)-7.7D7
      SPDOT=9.47D8*DEXP(12.3*TIME)
      RETURN
      END

C
C*****
C
      SUBROUTINE VRK2(XI,XSTOP,PA,DOTH)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION XSTAR(11),ITER(11),VX(11),VTA(11)
      COMMON VTA,VX,WF,W1,W2,W3,W4,W5,W6,W7,W8,W9,W10,W11,
1      P4,DOT4
      DATA XSTAR/0.,.10,.28,.44,.58,.70,.80,.88,.94,.98,0.999/,
1      ITER/10*10,20/

C
C**** 4TH ORDER RUNGE-KUTTA METHOD FOR TIME-DEPENDENT PVT
C**** EQUATION DURING THE COOLING STEP.
C**** LOOP FOR EACH LAYER.
C

```

```

DO 200 I=1,11
  IB=ITER(I)
  XJ=XSTAR(I)
  YI=VTA(I)
  HITER=FLOAT(IB)
  DX=(XSTOP-XI)/HITER
  X=XI
  Y=YI
DO 100 J=1,IB
  P=PA+DOTH*(X-XI)
  CALL VOL1(X,Y,P,DOTH,XJ,G1)
  X2=X+DX/2.
  Y2=Y+DX*G1/2.
  P2=PA+DOTH*(X2-XI)
  CALL VOL1(X2,Y2,P2,DOTH,XJ,G2)
  Y3=Y+DX*G2/2.
  CALL VOL1(X2,Y3,P2,DOTH,XJ,G3)
  X4=X+DX
  Y4=Y+DX*G3
  P4=PA+DOTH*(X4-XI)
  CALL VOL1(X4,Y4,P4,DOTH,XJ,G4)
  Y=Y+(G1+2.*G2+2.*G3+G4)*DX/6.
100  X=X+DX
  VX(I)=Y
200  CONTINUE
  W1=2.540D-2 /(VX(1)+VX(2))
  W2=4.572D-2 /(VX(2)+VX(3))
  W3=4.064D-2 /(VX(3)+VX(4))
  W4=3.556D-2 /(VX(4)+VX(5))
  W5=3.048D-2 /(VX(5)+VX(6))
  W6=2.540D-2 /(VX(6)+VX(7))
  W7=2.032D-2 /(VX(7)+VX(8))
  W8=1.524D-2 /(VX(8)+VX(9))
  W9=1.016D-2 /(VX(9)+VX(10))
  W10=4.826D-3 /(VX(10)+VX(11))
  W11=1.27D-4 /VX(11)
  WF=W1+W2+W3+W4+W5+W6+W7+W8+W9+W10+W11
DO 300 K=1,11
  VTA(K)=VX(K)
300  CONTINUE
  RETURN
  END

C
C*****
C
  FUNCTION FLOW(XA)
  IMPLICIT REAL*8 (A-H,O-Z)
C**** TO AVOID UNDER- AND OVER-FLOW.
  IF(XA)1,2,3
1    IF(XA .GE. -120.) GOTO 10
      XA=-120.
10   FLOW=DEXP(XA)
      RETURN
2    FLOW=1.0
      RETURN

```

```

3      IF(XA .LE. 120.) GOTO 30
        XA=120.
30      FLOW=DEXP(XA)
        RETURN
      END
C
C*****
C
      SUBROUTINE VOL1(TIME,VT,SP,SPDOT,XJ,GT)
      IMPLICIT REAL*8 (A-H,O-Z)
C**** INFINITE BIOT NUMBER FOR HEAT TRANSFER,
      PI=3.141592654D0
      TI=200.0D0
      TWALL=32.0D0
      B=0.1270D0
      DIFFU=6.33D-4
      ALFR=5.68D-4
      ALFG=2.48D-4
      AALF=4.08D-4
      CR=9.10D-11
      CG=3.03D-11
      CAVG=9.00D-11
      BETA=0.47D0
      BETAP=1.40D-8
      GAMA=4.0D2
      VO=1.05360D0
      TGE=85.0D0
      TAU10=2.54D-8
C**** TAU10=2.54D-8 =EXP(-17.4885) SEC. AT 200 (C).
C**** THE ARGUMENT (-17.4885) IS USED IN THE RELAXATION
C**** TIME FUNCTION.
      TIMELS=DIFFU*TIME/(B*B)
      ONE=-1.0
      I=0
      SUMN=0.0
      SUMT=0.0
250    CONTINUE
      N=FLOAT(I)
      HALF=N+0.50
      PH=PI*HALF
      PHSQ=-(PH*PH*TIMELS)
      EBAR=FLOW(PHSQ)
      A3=PH*XJ
      A4=DCOS(A3)
      ONE=- ONE
      ADD=ONE*EBAR*A4/PH
      A5=-((PH*PH*DIFFU)/(B*B))
      ADDT=ADD*A5
      SUMN=SUMN+ADD
      SUMT=SUMT+ADDT
      I=I+1
      IF((EBAR .GT. 1.0D-3) .OR. (ADDT .GT. 1.0D-3)) GO TO 250
      TEMPLS=2.0*SUMN
      TXT=TEMPLS*(TI-TWALL)+TWALL
      TXTDOT=2.0*(TI-TWALL)*SUMT

```

```

C**** VOLUME RATE EQN. IS FOLLOWING.
      IF(TXT .GE. TGE) GO TO 40
      VET=VO-ALFR*(TI-TGE)*VO-ALFG*(TGE-TXT)*VO-CAVG*SP*VO
      GO TO 60
40     CONTINUE
      VET=VO-ALFR*(TI-TXT)*VO-CAVG*SP*VO
60     CONTINUE
      DELTA=CAVG*SP+(VT-VO)/VO-AALF*(TXT-TI)
      BB=BETA*(TI-TXT)+BETAP*SP-GAMA*DELTA-1.74885D1
      TAU=FLOW(BB)
      GT=-(VT-VET)/TAU+VO*ALFG*TXTDOT-VO*CG*SPDOT
      RETURN
      END

```

8.5 Appendix E: Computer Program for the Analysis of Residual Stresses in Rapidly Cooled Samples

```

C*****
C* RESIDUAL STRESSES (EQUILIBRIUM PVT CASE) *
C*****
C* FOR STRESSES: 5.08 CM X 5.08 CM X 0.26 CM (B=0.13 CM) *
C* INITIAL TEMPERATURE: 130 (C) *
C*****
C*
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION XSTAR(40),TXT(40),VX(40),STRESS(40),
1          SPT(40),VDEL(40),XLI(40),El1(40),
2          TXTA(40),DEN(40),BH(40)
      COMMON TXT,XSTAR,COUNT,TI,TGE,TW,DIFFU,B,PI,
1          VX,STRESS,SPT,SUMS,El1,VI,ALFR,ALFG,
2          CAVG,GG,AA1,AA2,AA3,AA4,BH
      TIMEA=0.0D0
      TIMEF=1.22D2
      VI=0.9922D0
      TI=1.30D2
      TW=2.30D1
      TGE=8.50D1
      ALI=5.080D0
      B=0.13D0
      XDEL=0.01250D0
C**** INITIAL VALUES OF THE FORTY LAYERS.
      DO 10 I=1,40
          TXTA(I)=TI
          XSTAR(I)=XDEL
          XDEL=XDEL+0.0250D0
          BH(I)=B/4.0D1
10      CONTINUE
      DO 20 I=1,40
          WRITE(8,110)XSTAR(I),TXTA(I)
20      CONTINUE
110     FORMAT(1X,F6.4,1X,F7.2,2X,'XSTAR TXTA')
C**** MASS IN EACH LAYER IS CONSTANT AT ANY TIME.
      BMASS=(ALI*ALI*B*2.50D-2)/VI
      ALFR=5.68D-4
      ALFG=2.48D-4
      CAVG=6.00D-11
      GG=5.00D8
      DIFFU=6.33D-4
      AA1=- ALFR*(TI-TGE)
      AA2=4.0*CAVG*GG
      AA3=3.0/(3.0+4.0*CAVG*GG)
      AA4=4.0*GG
      PI=3.141592654D0
C**** TIME INTERVAL TO PRINT OUT THE RESULT.
      PRT=1.0D0
      PRTDEL=1.0D0
      EPS=1.0D10
      FORGET=0.0

```

```

      DEL=0.0D0
      H=1.0D-2
C**** GUESS LENGTH TO SATISFY THE BOUNDARY CONDITION.
C**** BI-SECTIONAL METHOD FOR TRIAL AND ERROR PROCEDURE.
      AL=ALI
900    TIMEB=TIMEA + H
      CALL TEMP(TIMEB)
C**** DEFINE THE REFERENCE LENGTH XLI(I) FOR EACH LAYER.
      DO 40 I=1,40
        IF((TXTA(I) .LT. TGE) .AND. (TXT(I) .LT. TGE))GO TO 40
        IF((TXTA(I) .GE. TGE) .AND. (TXT(I) .LT. TGE))GO TO 30
          XLI(I)=FORGET
          GO TO 40
30     CONTINUE
      XLI(I)=AL
40     CONTINUE
C**** TRY AND ERROR PROCEDURE AFTER HAVING TWO SOLID LAYERS.
      IF(COUNT .GE. 2.0) GO TO 45
      IF(COUNT .EQ. 1.0) GO TO 42
        GO TO 50
42     CONTINUE
C***  GUESS THE DECREASE OF LENGTH.
      DEL=2.0D-2
      GO TO 50
45     CONTINUE
      EPS=1.0D2
      DEL=1.0D-4
50     CONTINUE
      BL=AL-DEL
      WIL=AL
1000   WFL=BL
C**** CALCULATE STRAIN Ell(I) FOR EACH LAYER.
      DO 60 I=1,40
        IF(XLI(I) .NE. FORGET) GO TO 55
          Ell(I)=0.0
          GO TO 60
55     Ell(I)=(BL - XLI(I)) / XLI(I)
60     CONTINUE
      CALL VOL
      IF(DABS(SUMS) .LE. EPS) GO TO 5000
      IF(SUMS .GT. 0.0) GO TO 2000
1200   BL=(WIL+WFL)/2.0
      WML=BL
C**** CALCULATE STRAIN Ell(I) FOR EACH LAYER.
      DO 70 I=1,40
        IF(XLI(I) .NE. FORGET) GO TO 65
          Ell(I)=0.0
          GO TO 70
65     Ell(I)=(BL - XLI(I)) / XLI(I)
70     CONTINUE
      CALL VOL
      IF(DABS(SUMS) .LE. EPS) GO TO 5000
      IF(SUMS .GT. 0.0) GO TO 1500
        WFL=WML
        GO TO 1200

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```

1500      WIL=WML
          GO TO 1200
2000  CONTINUE
      WIL=WFL
      BL=WFL-DEL
      GO TO 1000
5000  CONTINUE
C****  WHEN THE BOUNDARY CONDITION IS SATISFIED,
C****  CALCULATE DENSITY AND WRITE THE RESULT.
      DO 5110 I=1,40
          DEN(I)=1.0 / VX(I)
5110  CONTINUE
C****
      IF(TIMEB .LT. PRT) GO TO 5200
      DO 5150 I=1,40
          WRITE(7,130)TIMEB,XSTAR(I),VX(I),DEN(I),STRESS(I),
1      TXT(I)
5150  CONTINUE
130    FORMAT(1X,D11.4,1X,F6.4,1X,2F9.6,1X,D12.5,1X,F7.2)
      PRT=PRT+PRTDEL
5200  CONTINUE
C****  CALCULATE NEW THICKNESS OF THE SLAB.
      IF(COUNT .GE. 1.0) GO TO 451
          GO TO 551
451    CONTINUE
      DO 452 I=1,40
          BH(I)=(BMASS*VX(I))/(BL*BL)
452    CONTINUE
C****
      B=0.0D0
      DO 455 I=1,40
          B=B+BH(I)
455    CONTINUE
551    CONTINUE
C****  CALCULATE NEW XSTAR(I) FOR EACH LAYER.
      BDEL=0.0D0
      DO 5215 I=1,40
          BHALF=BH(I) / 2.0D0
          BDEL=BDEL+BHALF
          XSTAR(I)=BDEL / B
          BDEL=BDEL+BHALF
5215  CONTINUE
      IF(TIMEB .GE. TIMEF) GO TO 6000
      DO 210 I=1,40
          TXTA(I)=TXT(I)
210    CONTINUE
          AL=BL
          TIMEA=TIMEB
C****  ADJUST THE STEP SIZE OF TIME.
      IF(TIMEB .LT. 4.0) GO TO 5650
      IF((TIMEB .LT. 16.0) .AND. (TIMEB .GE. 4.0)) GO TO 5660
          H=1.0D-1
          GO TO 5650
5660  CONTINUE
          H=1.0D-2

```

```

5650  CONTINUE
      GO TO 900
6000  CONTINUE
      WRITE(7,180)
180   FORMAT(2X,'END OF JOB')
      STOP
      END

C
C*****
C
      FUNCTION FLOW(XA)
      IMPLICIT REAL*8 (A-H,O-Z)
C**** TO AVOID UNDER- AND OVER-FLOW.
      IF(XA)1,2,3
1      IF(XA .GE. -120.0) GOTO 10
         XA=-120.0
10     FLOW=DEXP(XA)
         RETURN
2      FLOW=1.0
         RETURN
3      IF(XA .LE. 120.0) GOTO 30
         XA=120.0
30     FLOW=DEXP(XA)
         RETURN
      END

C
C*****
C
      SUBROUTINE TEMP(TIME)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION XSTAR(40),TXT(40)
      COMMON TXT,XSTAR,COUNT,TI,TGE,TW,DIFFU,B,PI
C**** INFINITE BIOT NUMBER FOR HEAT TRANSFER.
      COUNT=0.0
      TIMELS=DIFFU*TIME/(B*B)
C**** LOOP FOR EACH LAYER.
      DO 300 I=1,40
         ONE=-1.0
         IM=0
         SUMN=0.0
200    CONTINUE
         N=FLOAT(IM)
         HALF=N+0.50
         PH=PI*HALF
         PHSQ=-(PH*PH*TIMELS)
         EBAR=FLOW(PHSQ)
         A3=PH*XSTAR(I)
         A4=DCOS(A3)
         ONE=- ONE
         ADD=ONE*EBAR*A4/PH
         A5=-((PH*PH*DIFFU)/(B*B))
         SUMN=SUMN+ADD
         IM=IM+1
         IF(EBAR .GT. 1.0D-4) GO TO 200
         TEMPLS=2.0*SUMN
      END DO

```

```

      TXT(I)=TEMPLS*(TI-TW)+TW
      IF(TXT(I) .GE. TGE) GO TO 300
      COUNT=COUNT + 1.0
300   CONTINUE
      RETURN
      END

C
C*****
C
      SUBROUTINE VOL
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION XSTAR(40),TXT(40),VX(40),STRESS(40),
1     SPT(40),VDEL(40),E11(40),BH(40)
      COMMON TXT,XSTAR,COUNT,TI,TGE,TW,DIFFU,B,PI,
1     VX,STRESS,SPT,SUMS,E11,VI,ALFR,ALFG,
2     CAVG,GG,AA1,AA2,AA3,AA4,BH
C**** EQUILIBRIUM PVT EQUATION.
C**** LOOP FOR EACH LAYER.
      DO 500 I=1,40
      IF(TXT(I) .GE. TGE) GO TO 100
      VDEL(I)=(AA1 - ALFG*(TGE-TXT(I)) + AA2*E11(I))*AA3
      VX(I)=VI*(1.0 +VDEL(I))
      SPT(I)=AA4*((VDEL(I)/3.0) - E11(I))
      STRESS(I)=-(1.50*SPT(I))
      GO TO 200
100   CONTINUE
      VDEL(I)=- ALFR*(TI-TXT(I))
      VX(I)=VI*(1.0 +VDEL(I))
      SPT(I)=0.0
      STRESS(I)=0.0
200   CONTINUE
500   CONTINUE
C**** SUMMATION OF STRESSES IN SOLID LAYERS.
      SUMS=0.0
      DO 600 I=1,40
      SUMS=SUMS+(STRESS(I)*BH(I)/B)
600   CONTINUE
      RETURN
      END

```

```

C*****
C*  RESIDUAL STRESSES (TIME-DEPENDENT PVT CASE) *
C*****
C*  FOR STRESSES: 5.08 CM X 5.08 CM X 0.26 CM *
C*  INITIAL TEMPERATURE: 130 (C) *
C*****
C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION VTA(40),VX(40),TX(40,3),TXDOT(40,3),
1      XSTAR(40),STRESS(40),SPT(40),TXTA(40,3),
2      STRAIN(40),EDOT(40),XLI(40),DEN(40),
3      BEA(40),BEW(40),BEF(40),TAUB(40)
      COMMON VI3,GG4,AA1,AA2,AA3,AA4,AA5,AA6,
1      ALFR,ALFG,AALF,CR,CG,CAVG,BETA,BETAP,GAMA,GG,
2      VI,TI,TGE,TAUI,TAUA,GAMAA,AGE1,AGE2,
3      TX,TXDOT,COUNT,XSTAR,VTA,VX,SUMS,STRESS,SPT,
4      EDOT,BEA,BEW,BEF,TAUB
C**** INITIAL VALUES OF THE FORTY LAYERS.
      TIMEA=1.0D-6
      VI=0.9922D0
      TI=1.30D2
      ALI=5.080D0
      XDEL=0.0125D0
      DO 10 I=1,40
          VTA(I)=VI
          TXTA(I,3)=TI
          STRAIN(I)=0.0D0
          XSTAR(I)=XDEL
          XDEL=XDEL+0.0250D0
10      CONTINUE
      ALFR=5.68D-4
      ALFG=2.48D-4
      AALF=4.08D-4
      CR=9.10D-11
      CG=3.03D-11
      CAVG=6.00D-11
      BETA=4.70D-1
      BETAP=1.40D-8
      GAMA=4.00D2
      GG=1.50D9
      TGE=8.50D1
      TAUI=DLOG(5.450D-5)
C**** TAUI=5.450D-5 SEC. AT 130 (C).
      VI3=3.0*VI
      GG4=GG*4.0
      AA1=ALFR*VI
      AA2=ALFG*VI
      AA3=CAVG*VI
      AA4=VI-(ALFR*(TI-TGE)*VI)
      AA5=4.0*VI*CG*GG
      AA6=3.0/(3.0+4.0*CG*GG)
C**** FOR AGING AT 23 (C).
      TIMEM=5.0D1
      TIMEF=(24.1*3.60D3)+5.0
      AGE1=AA4 -(AA2*(TGE-2.30D1))

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AGE2=AALF*(TI-2.30D1)
TAUA=DLOG(1.70D6)
GAMAA=4.00D2
C***** TAU=1.70D6=EXP(14.3461) SEC. FROM FITTING
C***** SNOW'S AGING DATA.
C***** GUESS LENGTH TO SATISFY THE BOUNDARY CONDITION.
C***** BI-SECTIONAL METHOD FOR TRIAL AND ERROR PROCEDURE.
PRTDEL=2.0D-2
PRT=TIMEA
AL=ALI
H=1.0D-5
EPS=1.0D10
FORGET=0.0
DEL=1.0D-8
DTIME=H/2.0
C** SET UP TIME INTERVALS FOR ITERATION STEPS.
SHIFTA=TIMEA+(H*1.0D2)
SHIFTB=4.0D0
SHIFTC=9.0D0
SHIFTD=1.6D1
C*****
900 TIMEB=TIMEA + H
CALL TEMP(TIMEA,TIMEB,DTIME)
C***** DEFINE THE REFERENCE LENGTH XLI(I) FOR EACH LAYER.
DO 40 I=1,40
IF((TXTA(I,3) .LT. TGE) .AND. (TX(I,3) .LT. TGE))GO TO 40
IF((TXTA(I,3) .GT. TGE) .AND. (TX(I,3) .LT. TGE))GO TO 30
XLI(I)=FORGET
GO TO 40
30 CONTINUE
XLI(I)=AL
40 CONTINUE
C***** NO TRY AND ERROR BEFORE HAVING TWO SOLID LAYERS.
IF(COUNT .GE. 2.0)GO TO 45
GO TO 50
45 CONTINUE
EPS=1.0D3
DEL=1.0D-4
50 CONTINUE
C***** GUESS THE DECREASE OF LENGTH.
BL=AL-DEL
WIL=AL
1000 WFL=BL
C***** CALCULATE STRAIN AND STRAIN RATE FOR EACH LAYER.
DELAB=BL-AL
DELL=AL + (DELAB/2.0)
DO 60 I=1,40
IF(XLI(I) .NE. FORGET)GO TO 55
EDOT(I)=0.0
BEA(I)=0.0
BEW(I)=0.0
BEF(I)=0.0
GO TO 60
55 CONTINUE
EDOT(I)=DELAB/(H * XLI(I))

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        BEA(I)=STRAIN(I)
        BEW(I)=(DELL - XLI(I))/XLI(I)
        BEF(I)=(BL-XLI(I))/XLI(I)
60      CONTINUE
        CALL VRK2(DTIME)
        IF(DABS(SUMS) .LE. EPS) GO TO 5000
        IF(SUMS .GT. 0.0) GO TO 2000
1200     BL=(WIL+WFL)/2.0
        WML=BL
C****  CALCULATE STRAIN AND STRAIN RATE FOR EACH LAYER.
        DELAB=BL-AL
        DELL=AL + (DELAB/2.0)
        DO 70 I=1,40
            IF(XLI(I) .NE. FORGET)GO TO 65
            GO TO 70
65      CONTINUE
        EDOT(I)=DELAB/(H * XLI(I))
        BEA(I)=STRAIN(I)
        BEW(I)=(DELL - XLI(I))/XLI(I)
        BEF(I)=(BL-XLI(I))/XLI(I)
70      CONTINUE
        CALL VRK2(DTIME)
        IF(DABS(SUMS) .LE. EPS) GO TO 5000
        IF(SUMS .GT. 0.0) GO TO 1500
        WFL=WML
        GO TO 1200
1500     WIL=WML
        GO TO 1200
2000     CONTINUE
        WIL=WFL
        BL=WFL-DELL
        GO TO 1000
5000     CONTINUE
C****  WHEN THE BOUNDARY CONDITION IS SATISFIED,
C****  CALCULATE DENSITY AND WRITE THE RESULT.
        IF(TIMEB .LT. PRT) GO TO 5200
        DO 5100 I=1,40
            DEN(I)= 1.0 / VX(I)
5100     CONTINUE
        DO 5115 I=1,40
            WRITE(8,511)TIMEB,XSTAR(I),VX(I),DEN(I),STRESS(I),
1          TX(I,3)
5115     CONTINUE
511     FORMAT(1X,D11.4,1X,F6.4,1X,2F10.6,1X,D14.5,1X,F7.2)
        PRT=PRT+PRTDEL
5200     CONTINUE
        IF(TIMEB .GE. TIMEM) GO TO 6000
        AL=BL
        TIMEA=TIMEB
        DO 5600 I=1,40
            STRAIN(I)=BEF(I)
            TXTA(I,3)=TX(I,3)
            VTA(I)=VX(I)
5600     CONTINUE
        IF(TIMEB .LT. SHIFTA) GO TO 5650

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IF((TIMEB .LT. SHIFTB) .AND. (TIMEB .GE. SHIFTA)) GO TO 5660
IF((TIMEB .LT. SHIFTC) .AND. (TIMEB .GE. SHIFTB)) GO TO 5670
IF((TIMEB .LT. SHIFTD) .AND. (TIMEB .GE. SHIFTC)) GO TO 5680
  PRTDEL=1.0D0
  H=2.0D-2
  GO TO 5650
5680 CONTINUE
  PRTDEL=2.0D-1
  H=4.0D-4
  GO TO 5650
5670 CONTINUE
  PRTDEL=2.0D-2
  H=4.0D-5
  GO TO 5650
5660 CONTINUE
  PRTDEL=2.0D-2
  H=1.0D-5
5650 CONTINUE
  GO TO 900
6000 CONTINUE
C****
  DO 5700 I=1,40
    DEN(I)= 1.0/VX(I)
5700 CONTINUE
  DO 5800 I=1,40
    WRITE(8,511)TIMEB,XSTAR(I),VX(I),DEN(I),STRESS(I),
1      TX(I,3)
5800 CONTINUE
C**** AGING AT ROOM TEMPERATURE FROM TIME=50.0 SEC.
  DO 6100 I=1,40
    STRAIN(I)=BEF(I)
    TXTA(I,3)=2.30D1
    VTA(I)=VX(I)
6100 CONTINUE
    EPS=1.0D5
    DEL=1.0D-7
    PRTDEL=1.80D3
    PRT=1.80D3
    H=2.0D-9
    DTIME=H/2.0
C****
    PRTAGE=TIMEB +(H*1.0D1)
    PRTA1=PRTAGE + 1.0D-6
    PRTA2=PRTAGE + 1.0D-4
    PRTA3=PRTAGE + 1.0D-2
    PRTA4=PRTAGE + 1.0D0
C****
7000 CONTINUE
    AL=BL
    TIMEA=TIMEB
    TIMEB=TIMEA+H
C**** GUESS THE LENGTH.
    BL=AL-DEL
    WIL=AL
7100 WFL=BL

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C**** CALCULATE STRAIN AND STRAIN RATE FOR EACH LAYER.
      DELAB=BL-AL
      DELL=AL + (DELAB/2.0)
      DO 6150 I=1,40
        EDOT(I)=DELAB/(H * XLI(I))
        BEA(I)=STRAIN(I)
        BEW(I)=(DELL - XLI(I))/XLI(I)
        BEF(I)=(BL-XLI(I))/XLI(I)
6150    CONTINUE
      CALL VAGE(DTIME)
      IF(DABS(SUMS) .LE. EPS) GO TO 6500
      IF(SUMS .GT. 0.0) GO TO 6400
6200    BL=(WIL+WFL)/2.0
        WML=BL
C**** CALCULATE STRAIN AND STRAIN RATE FOR EACH LAYER.
      DELAB=BL-AL
      DELL=AL + (DELAB/2.0)
      DO 6210 I=1,40
        EDOT(I)=DELAB/(H * XLI(I))
        BEA(I)=STRAIN(I)
        BEW(I)=(DELL - XLI(I))/XLI(I)
        BEF(I)=(BL-XLI(I))/XLI(I)
6210    CONTINUE
      CALL VAGE(DTIME)
      IF(DABS(SUMS) .LE. EPS) GO TO 6500
      IF(SUMS .GT. 0.0) GO TO 6250
        WFL=WML
        GO TO 6200
6250    WIL=WML
        GO TO 6200
6400    CONTINUE
      WIL=WFL
      BL=WFL-DEL
      GO TO 7100
6500    CONTINUE
C**** WHEN THE BOUNDARY CONDITION IS SATISFIED,
C**** CALCULATE DENSITY AND WRITE THE RESULT.
      IF(TIMEB .LT. PRT) GO TO 7200
      DO 6510 I=1,40
        DEN(I)= 1.0 / VX(I)
6510    CONTINUE
      DO 6520 I=1,40
        WRITE(8,511)TIMEB,XSTAR(I),VX(I),DEN(I),STRESS(I),
1          TXTA(I,3)
6520    CONTINUE
C**** TIME INTERVAL TO PRINT OUT THE RESULT.
      PRT=PRT+PRTDEL
7200    CONTINUE
      IF(TIMEB .GT. TIMEF) GO TO 8000
      DO 6550 I=1,40
        STRAIN(I)=BEF(I)
        VTA(I)=VX(I)
6550    CONTINUE
C****

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```

        IF(TIMEB .LT. PRTAGE) GO TO 6800
        IF((TIMEB .LT. PRTA1) .AND. (TIMEB .GE. PRTAGE))GO TO 6780
        IF((TIMEB .LT. PRTA2) .AND. (TIMEB .GE. PRTA1))GO TO 6770
        IF((TIMEB .LT. PRTA3) .AND. (TIMEB .GE. PRTA2))GO TO 6760
        IF((TIMEB .LT. PRTA4) .AND. (TIMEB .GE. PRTA3))GO TO 6750
            H=4.0D0
            GO TO 6800
6750    CONTINUE
        H=2.0D-1
        GO TO 6800
6760    CONTINUE
        H=2.0D-3
        GO TO 6800
6770    CONTINUE
        H=2.0D-5
        GO TO 6800
6780    CONTINUE
        H=2.0D-7
6800    CONTINUE
            GO TO 7000
8000    CONTINUE
        WRITE(8,180)
180     FORMAT(2X,'END OF JOB')
        STOP
        END

```

```

C
C*****
C

```

```

        FUNCTION FLOW(XA)
        IMPLICIT REAL*8 (A-H,O-Z)
C****  TO AVOID UNDER- AND OVER-FLOW.
        IF(XA)1,2,3
1       IF(XA .GE. -120.) GOTO 10
            XA=-120.
10      FLOW=DEXP(XA)
            RETURN
2       FLOW=1.0
            RETURN
3       IF(XA .LE. 120.) GOTO 30
            XA=120.
30      FLOW=DEXP(XA)
            RETURN
        END

```

```

C
C*****
C

```

```

        SUBROUTINE VRK2(DTIME)
        IMPLICIT REAL*8 (A-H,O-Z)
        DIMENSION VX(40),VTA(40),TX(40,3),TXDOT(40,3),
1          STRESS(40),SPT(40),EDOT(40),XSTAR(40),
2          BEA(40),BEW(40),BEF(40),TAUB(40)
        COMMON VI3,GG4,AA1,AA2,AA3,AA4,AA5,AA6,
1          ALFR,ALFG,AALF,CR,CG,CAVG,BETA,BETAP,GAMA,GG,
2          VI,TI,TGE,TAUI,TAUA,GAMAA,AGE1,AGE2,

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```

3          TX, TXDOT, COUNT, XSTAR, VTA, VX, SUMS, STRESS, SPT,
4          EDOT, BEA, BEW, BEF, TAUB
C***** 4TH ORDER RUNGE-KUTTA METHOD AND BACKWARD EULER METHOD.
C***** LOOP FOR EACH LAYER TO CALCULATE VOLUME VX(I).
DO 200 I=1,40
    EA=BEA(I)
    EDOTB=EDOT(I)
    Y1=VTA(I)
    TXT=TX(I,1)
    TXTDOT=TXDOT(I,1)
    CALL VOL2(Y1, TXT, TXTDOT, EA, EDOTB, G1, TAUBB)
    EW=BEW(I)
    Y2=Y1+DTIME*G1
    TXT=TX(I,2)
    TXTDOT=TXDOT(I,2)
    CALL VOL2(Y2, TXT, TXTDOT, EW, EDOTB, G2, TAUBB)
    Y3=Y1+DTIME*G2
    CALL VOL2(Y3, TXT, TXTDOT, EW, EDOTB, G3, TAUBB)
    EF=BEF(I)
    Y4=Y1+2.0*DTIME*G3
    TXT=TX(I,3)
    TXTDOT=TXDOT(I,3)
    CALL VOL2(Y4, TXT, TXTDOT, EF, EDOTB, G4, TAUBB)
    YF=Y1+(G1+2.0*G2+2.0*G3+G4)*DTIME/3.0
C***** CORRECTOR BY EULER BACKWARD METHOD.
    CALL VOL2(YF, TXT, TXTDOT, EF, EDOTB, GEND, TAUBB)
    YEND=Y1+(GEND*DTIME*2.0D0)
    TAUB(I)=TAUBB
    VX(I)=(YF+YEND)/2.0D0
    IF(TX(I,3) .LT. TGE)GO TO 100
        SPT(I)=0.0
        STRESS(I)=0.0
        GO TO 200
100    CONTINUE
    SPT(I)=GG4*((VX(I)-VI)/VI3 - BEF(I))
    STRESS(I)=-1.50*SPT(I)
200    CONTINUE
C***** STRESS SUMMATION OF SOLID LAYERS.
    SUMS=0.0
    DO 400 I=1,40
        SUMS=SUMS+( STRESS(I) * 2.5D-2)
400    CONTINUE
    RETURN
    END

C
C*****
C
    SUBROUTINE TEMP(TIMEA, TIMEB, DTIME)
    IMPLICIT REAL*8 (A-H, O-Z)
    DIMENSION XSTAR(40), TX(40,3), TXDOT(40,3)
    COMMON VI3, GG4, AA1, AA2, AA3, AA4, AA5, AA6,
1        ALFR, ALFG, AALF, CR, CG, CAVG, BETA, BETAP, GAMA, GG,
2        VI, TI, TGE, TAUI, TAUA, GAMAA, AGE1, AGE2,
3        TX, TXDOT, COUNT, XSTAR

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C**** INFINITE BIOT NUMBER FOR HEAT TRANSFER.
      PI=3.141592654D0
      TW=23.0D0
      B=0.13D0
      DIFFU=6.33D-4
      COUNT=0.0
C**** LOOP FOR EACH LAYER.
      DO 2000 I=1,40
        TIME=TIMEA
C**** LOOP FOR EACH TIME STEP.
        DO 1000 J=1,3
          TIMELS=DIFFU*TIME/(B*B)
          ONE=-1.0
          IM=0
          SUMN=0.0
          SUMT=0.0
250      CONTINUE
          N=FLOAT(IM)
          HALF=N+0.50
          PH=PI*HALF
          PHSQ=-(PH*PH*TIMELS)
          EBAR=FLOW(PHSQ)
          A3=PH*XSTAR(I)
          A4=DCOS(A3)
          ONE=- ONE
          ADD=ONE*EBAR*A4/PH
          A5=- (PH*PH*DIFFU)/(B*B)
          ADDT=ADD*A5
          SUMN=SUMN+ADD
          SUMT=SUMT+ADDT
          IM=IM+1
          IF((EBAR .GT. 1.0D-3) .OR. (ADDT .GT. 1.0D-2)) GO TO 250
          TEMPLS=2.0*SUMN
          TX(I,J)=TEMPLS*(TI-TW)+TW
          TXDOT(I,J)=2.0*(TI-TW)*SUMT
          TIME=TIME+DTIME
1000    CONTINUE
2000    CONTINUE
          DO 2500 I=1,40
            IF(TX(I,3) .GE. TGE) GO TO 2500
            COUNT=COUNT+1.0
2500    CONTINUE
          RETURN
        END
C
C*****
C
      SUBROUTINE VOL2(VT,TXT,TXTDOT,E11,E11DOT,GT,TAU)
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON VI3,GG4,AA1,AA2,AA3,AA4,AA5,AA6,
1         ALFR,ALFG,AALF,CR,CG,CAVG,BETA,BETAP,GAMA,GG,
2         VI,TI,TGE,TAUI,TAUA,GAMAA,AGE1,AGE2
C**** VOLUME RATE EQN. IS FOLLOWING.
      IF(TXT .GE. TGE) GO TO 40
      SP=GG4*((VT-VI)/VI3 - E11)

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VET=AA4-AA2*(TGE-TXT)-AA3*SP
DELTA=(VT-VET)/VI
BB=TAUI+BETA*(TI-TXT)+BETAP*SP-GAMA*DELTA
TAU=FLOW(BB)
GT=((VET-VT)/TAU+AA2*TXTDOT+AA5*Elldot)*AA6
RETURN
40 CONTINUE
VET=VI-AA1*(TI-TXT)
DELTA=(VT-VET)/VI
BB=TAUI+BETA*(TI-TXT)-GAMA*DELTA
TAU=FLOW(BB)
GT=(VET-VT)/TAU+AA2*TXTDOT
RETURN
END

C
C*****
C
SUBROUTINE VAGE(DTIME)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION VX(40),VTA(40),TX(40,3),TXDOT(40,3),
1 STRESS(40),SPT(40),EDOT(40),XSTAR(40),
2 BEA(40),BEW(40),BEF(40),TAUB(40)
COMMON VI3,GG4,AA1,AA2,AA3,AA4,AA5,AA6,
1 ALFR,ALFG,AALF,CR,CG,CAVG,BETA,BETAP,GAMA,GG,
2 VI,TI,TGE,TAUI,TAUA,GAMAA,AGE1,AGE2,
3 TX,TXDOT,COUNT,XSTAR,VTA,VX,SUMS,STRESS,SPT,
4 EDOT,BEA,BEW,BEF,TAUB
C****
C**** 4TH ORDER RUNGE-KUTTA METHOD AND BACKWARD EULER METHOD.
C**** LOOP FOR EACH LAYER TO CALCULATE VOLUME VX(I).
DO 200 I=1,40
EA=BEA(I)
EDOTB=EDOT(I)
Y1=VTA(I)
CALL VOL3(Y1,EA,EDOTB,G1,TAUBB)
EW=BEW(I)
Y2=Y1+DTIME*G1
CALL VOL3(Y2,EW,EDOTB,G2,TAUBB)
Y3=Y1+DTIME*G2
CALL VOL3(Y3,EW,EDOTB,G3,TAUBB)
EF=BEF(I)
Y4=Y1+2.0*DTIME*G3
CALL VOL3(Y4,EF,EDOTB,G4,TAUBB)
YF=Y1+(G1+2.0*G2+2.0*G3+G4)*DTIME/3.0
C**** CORRECTOR BY EULER BACKWARD METHOD.
CALL VOL3(YF,EF,EDOTB,GEND,TAUBB)
YEND=Y1+(GEND*DTIME*2.0D0)
TAUB(I)=TAUBB
VX(I)=(YF+YEND)/2.0D0
SPT(I)=GG4*((VX(I)-VI)/VI3 - BEF(I))
STRESS(I)=-1.50*SPT(I)
200 CONTINUE
C**** STRESS SUMMATION OF SOLID LAYERS.
SUMS=0.0
DO 400 I=1,40

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      SUMS=SUMS+(STRESS(I) * 2.5D-2)
400  CONTINUE
      RETURN
      END

C
C*****
C
      SUBROUTINE VOL3(VT,E11,E11DOT,GT,TAU)
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON VI3,GG4,AA1,AA2,AA3,AA4,AA5,AA6,
1       ALFR,ALFG,AALF,CR,CG,CAVG,BETA,BETAP,GAMA,GG,
2       VI,TI,TGE,TAUI,TAUA,GAMAA,AGE1,AGE2
C**** AGING AT A ROOM TEMPERATURE OF 23.0 (C).
      SP=GG4*((VT-VI)/VI3 - E11)
      VET=AGE1 - (AA3*SP)
      DELTA=(VT-VET)/VI
      BB=TAUA+(BETAP*SP)-(GAMAA*DELTA)
      TAU=FLOW(BB)
      GT=((VET-VT)/TAU + AA5*E11DOT) * AA6
      RETURN
      END

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VITA

Wen-Chien Ko (柯文謙) was born in Kaohsiung, Taiwan on June 17, 1953. After graduating from Municipal Kaohsiung High School, he entered Feng Chia University in Taiwan in 1972, which led to a Bachelor of Science degree in June 1976 and a Master of Science degree in June 1978 both with a major in Textile Engineering. He worked at the same University as an instructor for five years before entering The University of Tennessee in September 1983. He received the Master and Doctoral degrees both with a major in Polymer Engineering in June 1987 and in August 1989, respectively. He then worked as a post doctoral research associate at the University of Tennessee. He is a member of the Society of Plastics Engineers and the International Society of Polymer Processing.