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Characterization and calibration of a viscoelastic simplified potential energy clock model for inorganic glasses

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ABSTRACT

To analyze the stresses and strains generated during the solidification of glass-forming materials, stress and volume relaxation must be predicted accurately. Although the modeling attributes required to depict physical aging in organic glassy thermosets strongly resemble the structural relaxation in inorganic glasses, the historical modeling approaches have been distinctly different. To determine whether a common constitutive framework can be applied to both classes of materials, the nonlinear viscoelastic simplified potential energy clock (SPEC) model, developed originally for glassy thermosets, was calibrated for the Schott 8061 inorganic glass and used to analyze a number of tests. A practical methodology for material characterization and model calibration is discussed, and the structural relaxation mechanism is interpreted in the context of SPEC model constitutive equations. SPEC predictions compared to inorganic glass data collected from thermal strain measurements and creep tests demonstrate the ability to achieve engineering accuracy and make the SPEC model feasible for engineering applications involving a much broader class of glassy materials.

1. Introduction

The extensive use of glass in optics, flat panel displays and glass-to-metal seals requires a knowledgeable way to manage the dimensional changes and tensile residual stresses induced by thermal processing. Thermal gradients, compaction and mismatches in thermal strains generated during cooling through the glass transition can produce unacceptable optical distortions or fractures. Although engineering analyses can provide useful information for designing robust manufacturing processes, these predictions must come from physically based material models that have been accurately calibrated and validated for the specific glasses of interest.

There are two important relaxation mechanisms that contribute to the solidification behavior in a cooling glass. The first arises from the intrinsic viscoelasticity creating a fading memory of past deformation history that eventually locks stresses in place as the viscosity increases. The second is associated with an on-going structural rearrangement of atoms as the material compacts towards the meta-stable equilibrium state of the supercooled liquid. Accurate predictions of the temporal and spatial inhomogeneities in stresses and deformations generated under general thermal processing environments must account for both mechanisms. This has been discussed by Narayanaswamy [1] in considering an analysis of the tempering process. The instant freezing approach (elastic model), stress relaxation only (viscoelastic model) and combined stress and volume relaxation (structural model) were compared, and the importance of capturing both stress and volume relaxation was demonstrated clearly.

These relaxation phenomena are not unique to inorganic glasses. Organic glassy thermosets physically age in a similar manner exhibiting both stress and volume relaxation over time. Furthermore, the basic modeling attributes required to analyze the stresses and strains generated in a polymer transitioning from the rubbery state to the glassy state are common to those needed to analyze the solidification of an inorganic glass. From a modeling perspective, it would be quite attractive to be able to implement a single constitutive framework in a finite element analysis code to predict the behavior of both material families, requiring only different sets of input parameters.

In the present work, the nonlinear viscoelastic simplified potential energy clock (SPEC) model [2] developed and validated for stress analyses of glassy thermosets is applied to an inorganic glass. In Section 2, the SPEC constitutive equations are summarized and compared to the structural relaxation model developed by Narayanaswamy [3]. Key features of the formalisms governing relaxation rates and thermal strains are discussed including a description of the competing mechanisms for predicting structural relaxation. Section 3 presents a coupled experimental and modeling approach for calibrating the SPEC constitutive equations and demonstrates its applicability to an inorganic sealing

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glass. The characterization data and model fitting results are presented along with comparisons between SPEC predictions and validation data collected from creep and volume relaxation tests conducted under complex temperature histories. The experiments, data and model predictions are discussed in Section 4 and conclusions are drawn in Section 5.

2. Theory and calculation

2.1. Linear viscoelasticity with changing time scales

Typically, stress relaxation is defined by a stress relaxation modulus computed from the time-varying stress that results following the imposition of a step strain at a fixed temperature, Tref. In the case of simple shear, the shear stress relaxation modulus, G, is written as

$$G(t, T_{ref}) = \left.\frac{\sigma_{xy}(t)}{\Delta\gamma}\right|_{Tref} \tag{1}$$

where σ_{xy} is the shear stress and $\Delta\gamma$ is the step change in shear strain. For a linear viscoelastic material, the Boltzmann superposition principle can be used to compute the contributions to the total stress from successive, multiple step strains applied at times t_1, t_2, and so on. In the limit, this leads to the classic hereditary stress integral:

$$\begin{aligned}\sigma_{xy}(t) &= H(t-t_1)G(t-t_1)\Delta\gamma_1 + H(t-t_2)G(t-t_2)\Delta\gamma_2 + \dots \\ &\rightarrow \int_0^t ds\, G(t-s)\frac{d\gamma}{ds} \text{ in the limit}\end{aligned} \tag{2}$$

where H is the Heaviside step function.

Although Eq. (2) suggests a way to compute the isothermal stresses in a viscoelastic material, it does not address the response of materials subjected to changing temperatures. That insight was provided by the time–temperature equivalence hypothesis of Leadermann [4]. It was observed that for many materials the "shape" of the relaxation function does not change with temperature. Instead, the function merely shifts along the logarithmic time scale as illustrated in Fig. 1 where higher temperatures produce faster relaxations. This observation provided a convenient way to predict the stress relaxation modulus at different temperatures by using a new "material time", t^* (denoted by the asterisk superscript). The new material time is computed from the real time using a so-called shift function, $\phi(T)$, or its inverse the shift factor, $a(T) = 1/\phi(T)$. For constant temperatures, $t^* = \phi(T) \cdot t = t / a(T)$. Using the material time and the stress relaxation modulus from a known reference temperature, Tref, it is then possible to compute the relaxation function at any other temperature:

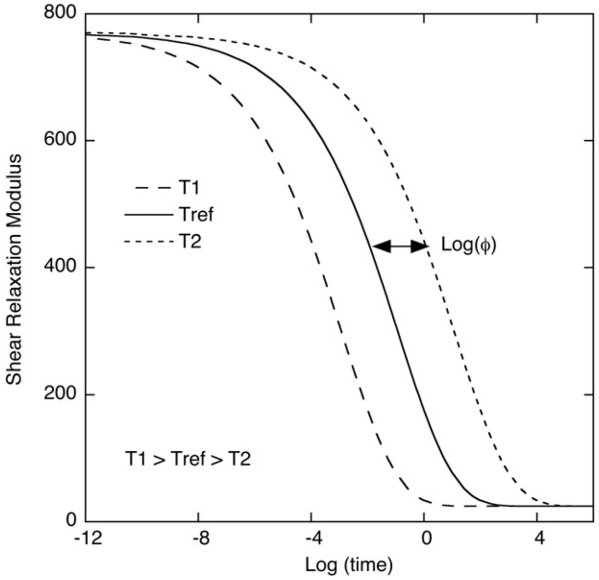

Fig. 1. Plots of shear relaxation moduli at different temperatures illustrating the uniform shape of the relaxation function and the shifting of curves on the log time axis as the temperature is changed.

$$G(t, T) = G\left(t^*, T_{ref}\right). \tag{3}$$

In the general case where temperature is changing with time, the material time must be computed by integration:

$$t^* = \int_0^t ds\quad \phi(T(s)) = \int_0^t \frac{ds}{a(T(s))}. \tag{4}$$

It is also important to note that if the time–temperature equivalence hypothesis is valid, then the overall shape of the stress relaxation function can be constructed by collecting the individual portions of the relaxation curves measured during isothermal tests at different temperatures and shifting them along the log time axis relative to a selected reference temperature curve. This process defines the shape of the underlying relaxation "master curve" at Tref as well as the temperature dependence of the shift function/factor. Specific details are provided in Section 3.2. Schwarzl and Staverman [5] used the term "thermorheological simple" to describe materials that behave in this way. The validity of the hypothesis for a given material is readily determined by how well the shifting procedure works.

2.2. Viscoelastic model with structural relaxation

In the classical development of the linear viscoelastic response of isotropic materials subjected to changing temperatures, the time–temperature equivalence hypothesis of Leaderman [4] is used to construct master curves governing the bulk (volumetric) and shear (distortional) relaxation behavior. The use of these master relaxation curves, along with a material clock defining the logarithmic time–temperature shifts, provides a natural means to capture the effect of temperature history in modulating the rates of stress relaxation. Morland and Lee [6] used this formalism to investigate the viscoelastic response of thermorheologically simple materials under nonhomogeneous temperature fields. The linear viscoelastic constitutive equations for infinitesimal deformations in an isotropic, thermorheologically simple material have the tensorial form:

$$\begin{aligned}\underline{\underline{\sigma}}(t) = {} & \left[\{K_g - K_{eq}\}\int_0^t ds\, f_1(t^* - s^*)\left\{\frac{dI_1}{ds}(s) - 3\,\frac{d\varepsilon_{th}}{ds}(s)\right\}\right]\underline{\underline{I}} \\ & + 2\{G_g - G_{eq}\}\int_0^t ds\, f_2(t^* - s^*)\frac{d\underline{\underline{\varepsilon}}_{dev}}{ds}(s) + \left[K_{eq}\{I_1(t) - 3\varepsilon_{th}(t)\}\right]\underline{\underline{I}} \\ & + 2G_{eq}\underline{\underline{\varepsilon}}_{dev}(t)\end{aligned} \tag{5}$$

where $\underline{\underline{\sigma}}$ is the stress tensor, $\underline{\underline{\varepsilon}}$ is the strain tensor, f_1 and f_2 are normalized relaxation functions varying from 1 to 0 as time increases, I_1 is the trace of the strain tensor, $\underline{\underline{I}}$ is the identity tensor, ε_{th} is the linear thermal strain, $\underline{\underline{\varepsilon}}_{dev}$ is the deviatoric strain tensor, G is the shear modulus and K is the bulk modulus. By convention, the subscripts "g" and "eq" on the moduli denote the instantaneous glassy and long time equilibrium values, respectively. The first bracketed term in Eq. (5) describes the pressure contribution to the decaying stress coming from mechanically induced volumetric strains where the thermal strain from temperature is subtracted from the total volume strain, I_1. The second integral includes the distortional relaxation arising from shear. The remaining elastic terms define the equilibrium pressure and shear stress state, i.e., the stresses when the material is fully relaxed and the integrals have vanished. When applied to the solidification of a viscous fluid (e.g., inorganic glass), the equilibrium shear modulus is set to zero. The material clock typically is specified through the use of a shift