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# Modeling of delayed elasticity in glass

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ABSTRACT

We have developed a numerical model based on finite element analysis (FEA) with a viscoelastic material model coupling stress relaxation and structural relaxation, using the Mauro-Allan-Potuzak (MAP) non-equilibrium viscosity equation as the shift function. A modeling study of the delayed elasticity behavior in glass under different equilibrium viscosity and non-equilibrium viscosity conditions is conducted. The delayed elastic response is found to be well described by a stretched exponential function with three parameters: the maximum delayed elasticity response, the retardation time of delayed elasticity response, and the stretching exponent of delayed elasticity response. The delayed elasticity magnitude is seen to increase with lower values of the stretching exponent $b_{stress}$. At equilibrium viscosity, the retardation time shows a linear relationship with the stress relaxation time. However, when the temperature drops sharply in the non-equilibrium viscosity cases, the delayed elastic response may be frozen resulting in a lower magnitude for the delayed elasticity and the retardation time is not linear any more with the stress relaxation time. The delayed elasticity stretching exponent is seen to vary slightly at different relaxation times and normalized delayed elasticity response can roughly be collapsed into a single master curve. The impact of liquid fragility is also studied.

## 1. Introduction

Glass is a material formed by quenching a liquid from equilibrium fast enough to avoid crystallization. In the glass transition temperature region, glass deformation exhibits viscoelastic behavior, where the material has both viscous and elastic characteristics when undergoing deformation. In this temperature range, the molecular rearrangements occur on a scale of minutes or hours, appearing as relaxation characteristics that can be well described by viscoelastic models. Two primary types of glass relaxation are structural relaxation and stress relaxation. Structural relaxation describes the time-dependent change in structural configuration due to the thermodynamic disequilibrium of the glass. Stress relaxation involves the decay of internal stress in the glass and entails a conversion from elastic strain to viscous strain. Historically, the dependence of the stress relaxation function on temperature can be accounted for by the assumption of thermo-rheological simplicity (TRS), based on the shift function concept. The shift function is closely related to the viscosity of the glass, characterizing the relaxation time dependence on the temperature and also fictive temperature [1]. One choice of shift function is the WLF (Williams-Landel-Ferry) [2] shift function, which does not consider the fictive temperature dependence. Another shift function widely used in glass simulation is the Tool-Narayanaswamy shift function [3,4], which has been used in viscoelastic simulations coupling the structural relaxation and stress relaxation to predict the fictive temperature and stress calculation in the glass annealing or tempering process [5–10]. The Tool-Narayanaswamy shift function is implemented and available in the commercial finite element analysis (FEA) software ANSYS® [11]. Users can take advantage of the capability to run simulations of structural relaxation and stress relaxation to track the fictive temperature and residual stress evolution in a glass object undergoing relaxation. Zheng and Zhang [12] implemented the structural relaxation calculation with the Tool-Narayanaswamy shift function, together with the stress relaxation in the COMSOL® software. Mauro et al. [13–16] have proposed a new non-equilibrium viscosity model, the MAP (Mauro-Allan-Potuzak) model, based on enthalpy landscape and temperature-dependent constraint theories. It is demonstrated that the proposed model gives an excellent fit to the measurement viscosity data. This new non-equilibrium viscosity model provides a better option for the choice of shift function, in terms of accurately capturing the non-equilibrium viscosity behaviors.

Under a constant load, the viscoelastic response of a material has three components: instantaneous elastic strain, delayed elastic strain, and viscous deformation [17]. The instantaneous elastic response and

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viscous response are dependent on the modulus and viscosity, respectively, so it is particularly important to understand the mechanisms and key parameters affecting the delayed elasticity. The delayed elasticity can be mistaken as an elastic response due to its recoverable nature, or it can be mistaken as a viscous response due to its time-dependent/delayed nature. Owing to the complicated nature of delayed elasticity, it has attracted widespread attention in the research community [17–22]. Every type of glass chemistry can display delayed elasticity. For example, bulk metallic glasses (BMG) also show distinctive creep and stress relaxation behaviors, as well as non-Newtonian features and mixed relaxation kinetics [23–25].

In this work, the MAP non-equilibrium viscosity model is implemented in the viscoelastic material model for both structural relaxation and stress relaxation inside the COMSOL® software. The viscoelastic material model is then coupled together with finite element analysis (FEA) to study how the glass deforms and how the stress evolves during loading/unloading near the glass transformation range.

## 2. Viscoelasticity and delayed elasticity

Viscoelastic materials show a combination of viscous and elastic responses. At constant strain or displacement, this manifests as stress relaxation, where the stress decays with time. At constant loading, it manifests as creep, where the strain increases with time. The viscoelastic material model describes the time-dependent constitutive relationship between the stress and the strain, which can be written as

$$\sigma = \int_0^t \mathrm{D}(t - t')\frac{d\epsilon}{dt'} \tag{1}$$

where σ is the stress tensor, D is the modulus matrix and $\epsilon$ is the strain tensor. We see that the stress is an integration of the previous history, meaning that the stress has a "memory effect." The viscoelastic behavior may be represented by combinations of spring and dashpot elements [17]. Each spring and dashpot element represent the elastic and viscous response, respectively. There are different ways to connect the spring and dashpot elements. Some of the simple models are shown in Fig. 1, where the single element Maxwell model, single element Voigt model, and Burger model are presented. The single element Maxwell model consists of a spring and a dashpot connected in series, the single element Voigt model consists of a spring and a dashpot connected in parallel, and the Burger model is a combination of the two. One can extend the models by including multiple pairs of spring-dashpot in series, in parallel, or both.

A widely used general form of the viscoelastic model is the generalized Maxwell model shown in Fig. 2, where $N$ Maxwell elements (spring-dashpot pair connected in series) are connected in parallel.

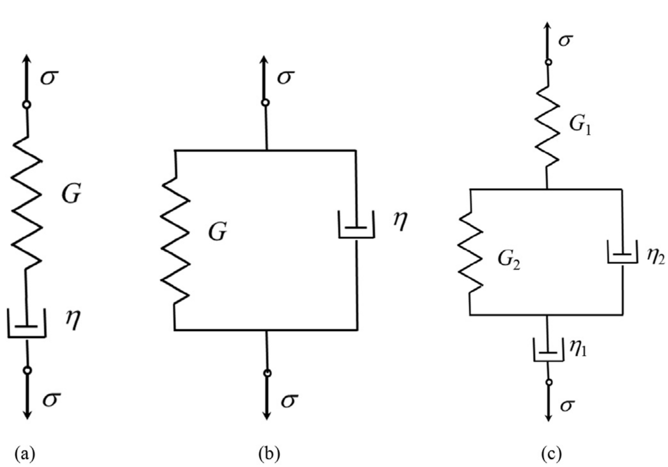


**Fig. 1.** Simple viscoelastic models. (a) single element Maxwell model (b) single element Voigt model (c) Burger model.

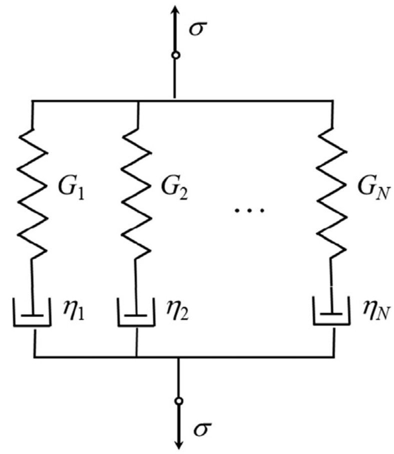


**Fig. 2.** Generalized Maxwell model.

Considering a shear stress component $\sigma_{xy}$ in Eq. (1), we will have

$$\sigma_{xy}(t) = \int_0^t 2G(t - t')\frac{d\epsilon_{xy}}{dt'}dt' \tag{2}$$

where $G(t)$ is the shear modulus relaxation function and $\epsilon_{xy}$ is the corresponding shear strain component. The shear modulus relaxation function $G(t)$ can be approximated by a Prony series, which represents the generalized Maxwell model, in the form [11].

$$G(t) = G(\infty) + (G(0) - G(\infty))\sum_{i=1}^{N} w_i e^{-\frac{t}{\tau_{si}}}, \tag{3}$$

where $N$ is the number of terms, $\tau_{si} = \frac{\eta_i}{G_i}$ are the stress relaxation times, and $w_i$ are the weight coefficients, satisfying $\sum_{i=1}^{N} w_i = 1$. Glass relaxation is found to exhibit stretched exponential relaxation behavior [17], i.e., the relaxation function for the stress $\sigma(t)$ can be written as

$$\frac{\sigma(t) - \sigma(\infty)}{\sigma(0) - \sigma(\infty)} = \varphi(t) = \exp\left[-\left(\frac{t}{\tau_s}\right)^b\right], \tag{4}$$

where $b$ is the stretching exponent and $\tau_s$ is the average stress relaxation time. Eq. (4) is a stretched exponential function, also called the $b$-function or the Kohlrausch-Williams-Watts (KWW) function [17]. The Prony series coefficients $w_i$ and $\tau_{si}$, can be chosen such that Eq. (3) approximates the stretched exponential function [30] as

$$\sum_{i=1}^{N} w_i e^{-\frac{t}{\tau_{si}}} \approx \exp\left[-\left(\frac{t}{\tau_s}\right)^b\right] \tag{5}$$

Hence, the coefficients $w_i$ and $\tau_{si}$, $i = 1, \ldots, N$ are determined from the parameters $b$ and $\tau_s$ for a given $N$. In the FEA simulations of this work, $N = 6$, meaning 6 terms of the Prony series, are used and provide satisfactory accuracy.

With the constitutive relationship between the stress and strain established, i.e., Eqs. (2) and (3), one can solve for $\sigma_{xy}(t)$ given $\epsilon_{xy}(t)$, or solve for $\epsilon_{xy}(t)$ given $\sigma_{xy}(t)$. In the case of the creep test, where we apply a constant stress and observe the strain response, it is essentially solving for $\epsilon_{xy}(t)$ given $\sigma_{xy}(t > 0) = \sigma_0$. In the special cases of the simple models shown in Fig. 1, analytical solutions can be easily obtained [17] as

$$\epsilon_{xy} = \frac{\sigma_0}{2G}\left(1 + \frac{Gt}{\eta}\right) \tag{6}$$

for a single element Maxwell model,

$$\epsilon_{xy} = \frac{\sigma_0}{2G}\left(1 - e^{-\frac{Gt}{\eta}}\right) \tag{7}$$

for a single element Voigt model, and