



Prediction of the relationship between the rate of deformation and the rate of stress relaxation in glassy polymers



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ABSTRACT

Kim, et al. (*Polymer*, 54(15), 3949, 2013) recently reported on the unexpected relaxation behavior of an amorphous polymer in the T_g -region, where the rate of stress relaxation increased with deformation at a strain rate of $1.5 \times 10^{-4} \text{ s}^{-1}$ but decreased at a strain rate of $1.2 \times 10^{-5} \text{ s}^{-1}$. This inversion in the ordering with strain rate challenges the underlying structure of the existing nonlinear viscoelastic and viscoplastic constitutive models, where the key nonlinearity is a deformation dependent material clock. The nonlinear stress relaxation predictions of a recently developed stochastic constitutive model, SCM, (Medvedev, et al., *J. Rheology*, 57(3), 949, 2013) that acknowledge dynamic heterogeneity of the glass have been investigated. The SCM predicts the inversion in the ordering of the mobility with the loading strain rate as reported by the stress relaxation response. The change in perspective on the nonlinear viscoelastic behavior of glassy polymers engendered by the SCM is discussed.

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1. Introduction

In a previous study of the stress relaxation response following constant strain rate uniaxial extension and compression of an amorphous epoxy resin, we reported on a very unexpected observation concerning the effect of strain rate on the rate of relaxation [1]. Specifically, it was shown that there were loading strain rates where the rate of stress relaxation increased with increasing strain; however, at a slower strain rate the rate of stress relaxation unexpectedly decreased with increasing strain. This unexpected change in the ordering of the rate of nonlinear stress relaxation with the loading strain rate occurred both in uniaxial extension and compression, at several temperatures and at two sub- T_g annealing times. This data calls into serious question the basic assumption employed in the current nonlinear viscoelastic [3–5] and viscoplastic [6–10] constitutive equations developed to describe glassy polymers – the assumption that increasing deformation induces an increase in the mobility that eventually results in yield and post-yield flow. The existing constitutive models are built around a material time t^* defined by $t^* = \int_0^t d\xi/a(\xi)$, where $a(t)$ is the generalized shift factor that is a function of the temperature and deformation or deformation history. The shift factor $a(t)$ is a measure of the mobility in the material. A number of models have been

proposed for the $\log a$ mobility function including free volume [5], stress [4], strain [11], configurational entropy [12], and configurational internal energy [3]. In all of these $\log a$ models the mobility increases with increasing deformation; thus, experimental data that clearly shows that depending upon the loading strain rate the mobility can decrease with increasing deformation is extremely problematic. It remains an open question if there is some way to modify the existing material time based constitutive models to incorporate the effect of strain rate (see Ref. [1] for a discussion of the challenges of employing strain rate as a variable in the $\log a$ mobility function).

Recently Medvedev, et al. [2] have proposed a Stochastic Constitutive Model (SCM) that explicitly incorporates the nano-scale dynamic heterogeneity [13] that is a critical signature of the glassy state. The key feature of the SCM is that the model only employs a single relaxation time to describe the behavior of a meso-domain, where the experimentally observed non-exponential response to changes in temperature and/or deformation is a consequence of the distribution of nano-scale mobilities resulting from fluctuations in the state variables that control the $\log a$ mobility function of a domain. The shape of the resulting distribution of relaxation times is not constant, but undergoes significant changes during the thermal-deformation history experienced by the material, i.e. the material is thermorheologically complex. As a consequence of the stochastic nature of the SCM and the associated evolution of the relaxation spectrum, the SCM is able to naturally predict not only yield, but post-yield softening and its

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annealing time dependence, without the introduction of a new *ad hoc* relaxation mechanism that becomes active at yield.

Because of the success of the SCM in being able to naturally predict the post-yield stress softening and its annealing time dependence, in this communication we will examine if the SCM is also able to predict the unanticipated strain rate dependence of the nonlinear stress relaxation response previously reported [1]. The rest of this communication will be organized as follows: First we will briefly review the experimental stress relaxation data in order to provide a clear context of the constitutive modeling challenge, where the complete presentation of the experimental data is given in the original publication [1]. Then, we will show the predictions of the SCM and how they are able to naturally explain the observed strain rate dependence of the nonlinear stress relaxation data. Next, we will analyze what features in the SCM enable it to describe the nonlinear stress relaxation data. The main result is that for a constant strain rate deformation the strain rate emerges as a controlling parameter even though the $\log a$ describing the mobility of a meso-domain is only a function of the fluctuating local stress and entropy and of the current average temperature and volume, but not the strain rate. Finally, the implications of the results of this analysis for the understanding of the glassy state and the deformation of glassy materials will be discussed.

2. Nonlinear stress relaxation response

In a previous paper we reported on the nonlinear stress relaxation of a neopentyl glycol diglycidyl ether epoxy resin (i.e. DGENG) cured with a stoichiometric amount of 4,4'-methylenedianiline (i.e. 4,4'MDA) amine curing agent to produce amorphous glassy polymer with a T_g by DSC of 72 °C [1]. Using an Instron 5567 testing instrument, the sample was loaded in uniaxial extension at a constant strain rate to a predetermined pre-yield, yield or post-yield strain at which time the strain was held constant and the ensuing stress relaxation was monitored. Typical stress vs. time data at $T_g - 15$ °C with 0.5 h sub- T_g aging prior to the deformation is shown in Fig. 1.

The relaxation data in Fig. 1 is normalized in Fig. 2a, where the relaxation time axis is defined relative to the time at which the stress relaxation begins and a normalized stress, $\bar{\sigma}$, is defined as

$$\bar{\sigma}(t - t_1) = \frac{\sigma(t - t_1) - \sigma_{\infty}(\epsilon_1)}{\sigma(t_1) - \sigma_{\infty}(\epsilon_1)} \quad (1)$$

where t_1 denotes the time at the beginning of the stress relaxation, $\sigma(t_1)$ is the value of stress at that instant and σ_{∞} is the equilibrium stress. The normalized nonlinear stress relaxation data for the same material are shown in Fig. 2b, but for a loading strain rate that is approximately one order-of-magnitude slower. The data in Figs. 1 and 2 are reproduced from Kim, et al. [1]

Examining the data in Fig. 2a (which is at the faster strain rate of $1.5 \times 10^{-4} \text{ s}^{-1}$), the relative rate of stress relaxation *increases* as the strain increases from pre-yield to yield to post-yield, where there is minimal change in the rate of relaxation as the deformation is increased past the yield point. In contrast, the data in Fig. 2b (which is at the slower loading strain rate of $1.2 \times 10^{-5} \text{ s}^{-1}$) shows that the rate of stress relaxation *decreases* as the deformation increases from pre-yield to yield to post-yield conditions. These two data sets were for the same material in uniaxial extension at $T_g - 15$ °C with 0.5 h of sub- T_g physical aging – the only difference was the loading strain rate. The data in Fig. 2a where the rate of relaxation increases with the deformation is consistent with the perspective of deformation induced increase in mobility – the perspective of the current viscoelastic and viscoplastic constitutive models for glassy polymers. In contrast, the data in Fig. 2b is counter to this

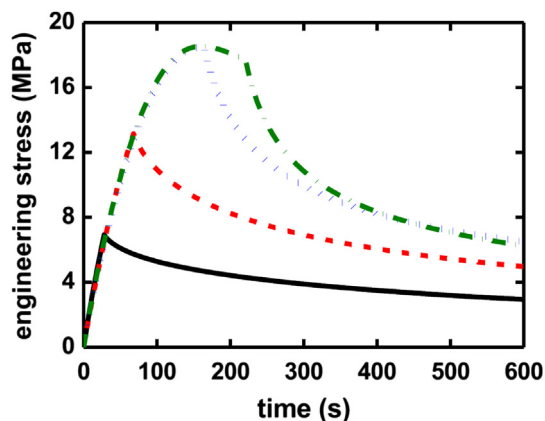


Fig. 1. Stress response of DGENG-44'MDA in uniaxial extension to a constant strain rate loading to various strains followed by stress relaxation. Test temperature is $T_g - 15$ °C and the loading strain rate is $1.5 \times 10^{-4} \text{ s}^{-1}$ (Fig. 3a from Ref. [1]). The stresses at the beginning of stress relaxation: are 6.9 MPa—solid (black); 13.2 MPa—dash (red); 18.5 MPa—dot (blue); 17.7 MPa—dash-dot (green). From: Ref. [1]—used with permission from Elsevier. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

perspective, where the mobility decreases significantly with deformation. In the previous paper, it was shown that this reversal in ordering of the mobility with strain rate was robust, occurring in (i) uniaxial extension and compression, (ii) for tests temperatures from $T_g - 15$ °C to $T_g - 30$ °C and (iii) for sub- T_g annealing times from 0.5 h– to 3 h.

The key issue in the data of Kim, et al. [1] is the *change* in the ordering of the rate of stress relaxation with strain rate, where it is important to remember that the nonlinear stress relaxation response is a combination of both the deformation dependence of the $\log a$ function that controls the material clock and the underlying viscoelastic response. A linear viscoelastic material will exhibit a flow stress (which may be identified with yield), where we have previously shown that the rate of stress relaxation decreases with increasing deformation [1]. Two difficulties with a linear viscoelastic model are: (i) the predicted yield stress is too high if the viscoelastic spectrum is determined via time–temperature superposition of the infinitesimal viscoelastic response and (ii) the yield stress scales with the strain rate vs. the experimentally observed scaling with the $\log(\text{strain rate})$. Because of these difficulties, the current set of models describing the deformation of glassy polymers employ a deformation dependent material clock, where the linear viscoelastic relaxation spectrum is shifted to shorter times with increasing deformation. In these nonlinear models the rate of nonlinear stress relaxation increases with deformation (at least when the parameters describing the material clock nonlinearity are sufficient to describe the yield behavior). Thus, the critical issue is not that the rate of nonlinear stress relaxation either increases or decreases with deformation, since both trends can be predicted; but rather, that the ordering *changes* with the loading strain rate.

3. Results

3.1. Predictions of stochastic constitutive model

A Stochastic Constitutive Model (SCM) has recently been developed [2], where the relaxation spectrum emerges naturally from taking into account the existence of the nano-scale dynamic heterogeneity of glassy materials. The goal in this publication is not to quantitatively fit the experimental curves shown in Fig. 2. This is not to dismiss the importance of the quantitative fitting of

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