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Counter-Intuitive Stress Relaxation Behavior of Glass Forming Materials and the Ability of Sandia's "Material Clock" Nonlinear Viscoelastic Model to Represent it

Jamie M. Kropka and Kevin N. Long

Sandia National Laboratories, Albuquerque, NM

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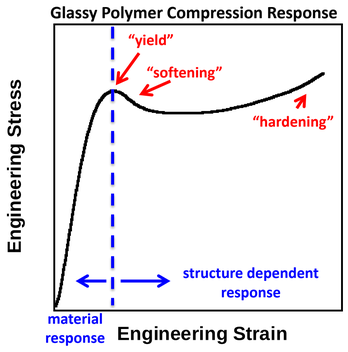
Sandia National Laboratories

Deformation Induced Mobility

Glassy polymers exhibit a change in slope, or potentially even a local maximum, for stress-strain response during a constant strain rate deformation experiment. This behavior is often referred to as "yield". While the terminology is convenient, it is important to distinguish the physics that occurs in amorphous glassy polymers to affect yield from the physics that occurs in crystalline materials. For glassy polymers, the decrease in slope of the stress-strain response is associated with an increase in the rate of relaxation in the glass. The faster relaxation can eventually prevent the material from supporting any further increase in stress and result in a local maximum, or even a "post-yield softening region" where the stress decreases with further increases in strain. The increase in rate of relaxation is often called "flow" or maybe "runaway non-linear viscoelasticity"[1] for those that do not feel comfortable saying that materials like highly crosslinked polymer thermosets can flow, since covalent chemical linkages prevent flow in a macroscopic fluid-like sense.

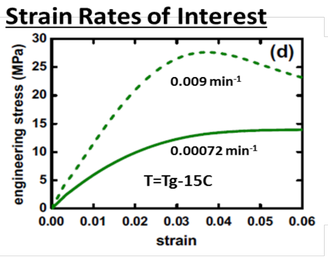
The increase in glassy polymer relaxation rates under a mechanical deformation is often referred to as deformation induced mobility. Direct evidence for deformation induced changes in mobility is found in solid state NMR data[2] and reorientation dynamics of photoactive dye molecules dispersed in a polymer matrix.[3,4] It has also been argued that stress relaxation experiments can provide indirect evidence of this phenomenon.[5,6]



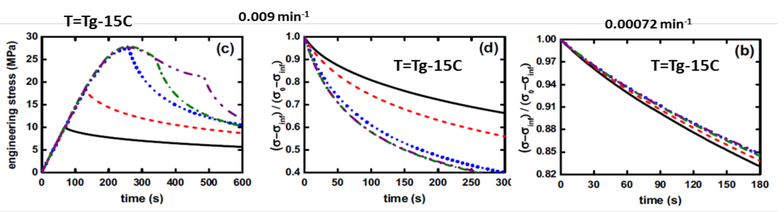
1 Adolf et al., *J Adhes* 86 **2010** 1111-1131
2 Loo et al., *Science* 288 **2000** 116-119
3 Lee et al., *Science* 323 **2009** 231-234
4 Lee et al., *J Pol Sci Pol Phys* 47 **2009** 1713-1727
5 Lee et al., *J Pol Sci Pol Phys* 48 **2010** 2399-2401
6 Kim et al., *Polymer* 54 **2013** 3949-3960

Recent Observations from Stress Relaxation Tests

Strain Rates of Interest



Stress Relaxation and Normalization Results



"Mobility increases with deformation"

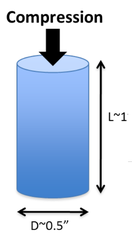
"Mobility decreases with deformation"

Kim et al., *Polymer* 54 **2013** 3949-3960

"These observations challenge the simple picture of deformation induced mobility"

Sandia's non-linear viscoelastic (NLVE) models are based upon thermorheological simplicity AND deformation induced mobility — what implications do the recent findings have on Sandia's predictive capability?

Boundary Value Problem and Material Constitutive Representation

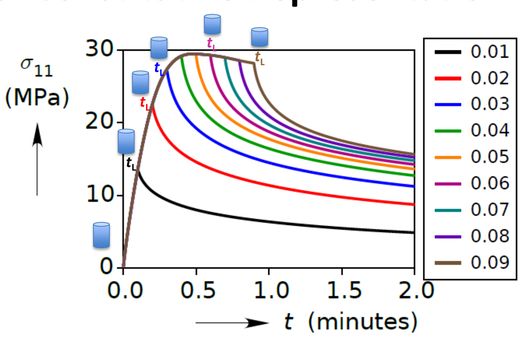


$$\dot{\varepsilon} = constant\ for\ 0 \le t \le t_L$$

$$\dot{\varepsilon} = 0\ for\ t > t_L$$

$$Normalized\ Stress\ During\ Relaxation = \frac{\sigma(t - t_L) - \sigma_\infty(\epsilon_L)}{\sigma(t_L) - \sigma_\infty(\epsilon_L)}$$

t_L = time stress relaxation begins
ε_L = strain at t_L
$\sigma_\infty(\varepsilon_L)$ = (equilibrium "stiffness")ε_L = equilibrium stress



Simplified Potential Energy Clock (SPEC) Model

$$\underline{\underline{\sigma}} = \left\{K_g(T(t)) - K_\infty(T(t))\right\}\int_0^t ds\, f_v(t^* - s^*)\frac{dI_1}{ds}(s)\,\underline{\underline{I}} - \left\{K_g(T(t))\alpha_g(T(t)) - K_\infty(T(t))\alpha_\infty(T(t))\right\}\int_0^t ds\, f_v(t^* - s^*)\frac{dT}{ds}(s)\,\underline{\underline{I}}$$

$$+ 2\left\{G_g(T(t)) - G_\infty(T(t))\right\}\int_0^t ds\, f_s(t^* - s^*)\frac{d\underline{\underline{\varepsilon}}_{dev}}{ds}(s) + \left\{K_\infty(T(t))I_1 - K_\infty(T(t))\alpha_\infty(T(t))\left[T(t) - T_{sf}\right]\right\}\underline{\underline{I}}$$

Material Clock

Material time is computed by using a shift factor, a

$$t^* - s^* = \int_s^t \frac{dw}{a(w)} \qquad and \qquad \log a = -\hat{C}_1\left(\frac{N}{\hat{C}_2 + N}\right)$$

The shift factor is a function of temperature, volume, and deformation histories

$$N = \left\{\left[T(t) - T_{ref}\right] - \int_0^t ds\, f_v(t^* - s^*)\frac{dT}{ds}(s)\right\} + C_3\left\{I_1(t)_{ref} - \int_0^t ds\, f_v(t^* - s^*)\frac{dI_1}{ds}(s)\right\}$$

$$+ C_4\left\{\int_0^t\int_0^t ds\,du\, f_s(t^* - s^*, t^* - u^*)\frac{d\underline{\underline{\varepsilon}}_{dev}(s)}{ds} : \frac{d\underline{\underline{\varepsilon}}_{dev}(u)}{du}\right\}$$

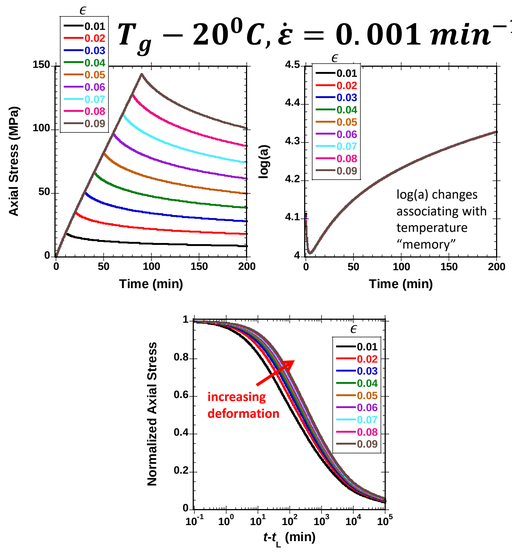
Caruthers, J.M. *et al*. *Polymer* **2004**, 45, 4577
Adolf, D.B. *et al*. *Polymer* **2004**, 45, 4599
Adolf, D.B. *et al*. *Polymer* **2009**, 50, 4257

Results

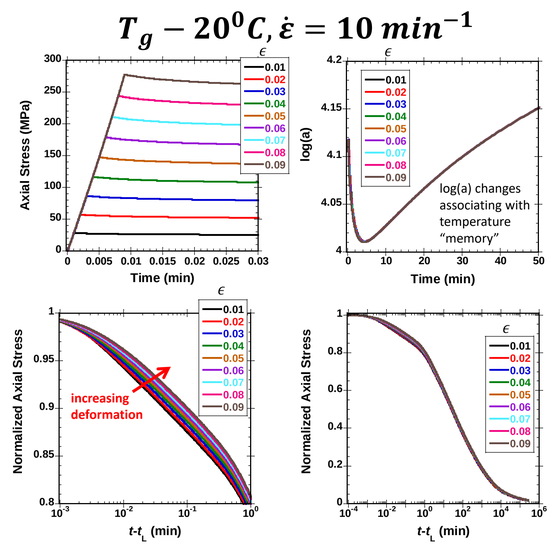
Material Validated SPEC Model

Linear Viscoelasticity

$T_g - 20^0C, \dot{\varepsilon} = 0.001\ min^{-1}$



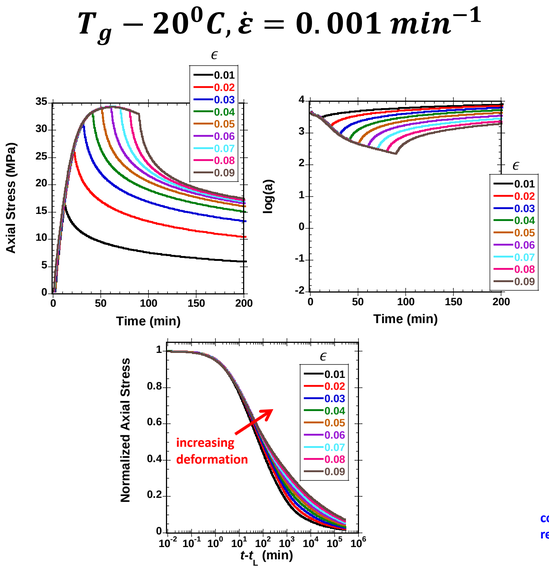
$T_g - 20^0C, \dot{\varepsilon} = 10\ min^{-1}$



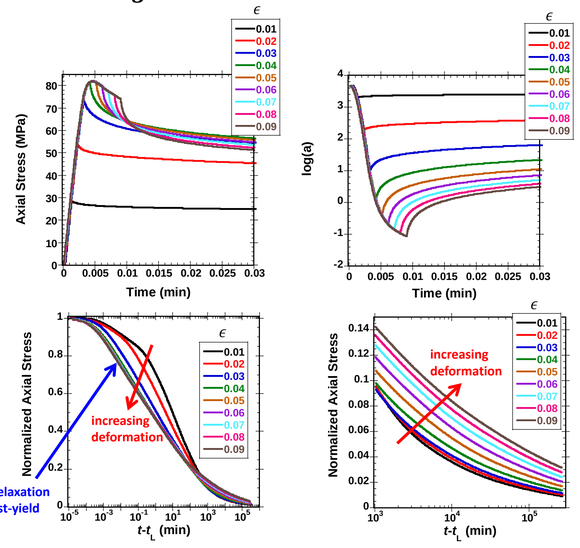
As more of the relaxation occurs during the loading process, the iso-strain relaxation is "slowed"

Non-Linear Viscoelasticity

$T_g - 20^0C, \dot{\varepsilon} = 0.001\ min^{-1}$



$T_g - 20^0C, \dot{\varepsilon} = 10\ min^{-1}$

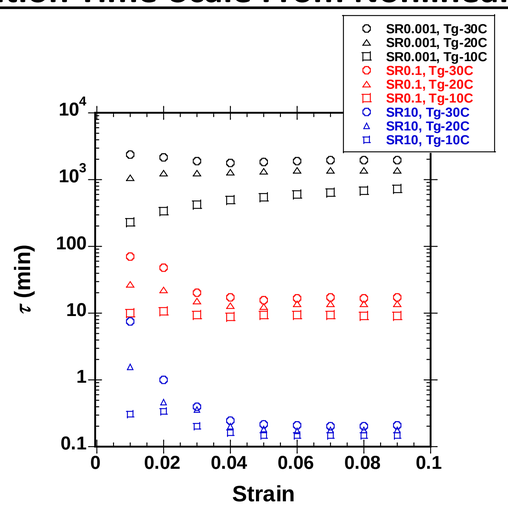


The deformation-induced mobility acceleration of the shift factor "competes" with loss of the fast relaxation modes during loading to define the early-time relaxation rate during the iso-strain hold

Faster deformation induces more acceleration of the shift factor and leads to faster relaxation for increasing deformation during the early portion of the iso-strain hold. As observed in experiments, acceleration of the relaxation rate only occurs up to "yield" strains. At strains beyond yield, the normalized relaxation response is equivalent at short times. The linear viscoelastic ordering of the normalized stress relaxation response is recovered at longer times.

Initial Relaxation Time-Scale From Nonlinear Predictions

$$\frac{1}{\tau} = -\frac{1}{\sigma}\frac{d\sigma}{dt}\bigg|_{t_L}$$



Mission Relevancy and Findings

- Current Sandia NLVE models are built on the assumption that deformation enhances the mobility of the material. If this assumption is not true at small strain rates (e.g., thermal fluctuation in stockpile storage), then models will not be able to accurately predict the stress evolution and potential failure of (e.g., polymer encapsulated) components during stockpile storage
- In order for non-linear effects associated with deformation to reverse the strain-dependent ordering of the normalized stress relaxation response (from that of LVE) in a deformation induced mobility manner, the material "clock" must be "significantly" perturbed by the deformation…**this does not occur when loading rates are not sufficiently fast relative to material relaxation rates**

The experimentally observed "decrease in mobility with increasing deformation" based on analysis of normalized stress relaxation response does not preclude the ability of thermorheologically simple material clock constitutive models to predict this behavior. Rather, Sandia's SPEC model has been shown to predict this exact behavior by examining conditions under which the clock was perturbed to varying levels by the deformation. Further, the model predicts the post-yield relaxation behavior observed in the experiments. This speaks to the physical basis of the model.

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