Mobility evolution during tri-axial deformation of a glassy polymer

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A B S T R A C T

In this study, the evolution of mobility with deformation in a glassy polymer is compared in cases of dilatationally dominated longitudinal and deviatorically dominated uniaxial deformation. The mobility is evaluated via stress relaxation experiments performed at various points along the stress–strain curve, including pre-yield, yield, and post-yield regions. At $T_g-5\ ^\circ$C the mobility decreases with deformation in uniaxial extension, but increases with deformation in tri-axial extension. The τ_{eff} relaxation time calculated for longitudinal deformation exhibits a dramatically different dependence on the excess volume than the relaxation time obtained in structural relaxation experiments. Finally, the criterion for cavitational failure is proposed based on the thermodynamic stability considerations.

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1. Introduction

It is generally accepted that the nonlinear mechanical behavior of glassy polymers is a direct consequence of deformation induced mobility evolution. Evidences of mobility enhancement during finite deformations include (i) macroscopic measurements of the instantaneous rate of stress relaxation [1] and small deformation dynamic responses [2] and (ii) measurement of molecular mobility via solid state NMR [3,4] and the re-orientation dynamics of photoactive dye molecules [5,6]. In the work by this group mobility increase during constant strain rate uniaxial extension was studied using stress relaxation as a method to probe the mobility in the material just prior to the commencement of the relaxation [1]. In a recent communication, Kim et al. [7] used stress relaxation to study deformation induced mobility evolution in an epoxy glass, where the mobility was studied as a function of temperature, aging time, and strain rate in uniaxial extension and compression. The findings of this study are summarized as follows.

1. The mobility as determined from the initial rate of stress relaxation changes as the material is deformed up to yield, but remains nearly constant from yield through the post-yield flow region.
2. At temperatures of $T_g-15\ ^\circ$C and lower the effect of deformation on mobility depends critically on the strain rate but not temperature or aging time, where the mobility *increases* through

yield at the strain rates of $1.5 \times 10^{-4}\ \text{s}^{-1}$ and higher and *decreases* through yield at the slower strain rate of $1.2 \times 10^{-5}\ \text{s}^{-1}$.
3. At $T_g-5\ ^\circ$C mobility decreases with deformation through yield irrespective of the strain rate.

These results were observed both in uniaxial extension and compression. The behavior at $T_g-5\ ^\circ$C is what would be expected of a linear viscoelastic material. However, the observation at lower temperatures that the rate of stress relaxation increases with deformation is a clear indication that the non-linearity is at play, where the relaxation times and/or the shape of the spectrum are a function of deformation. The fact that at faster strain rates the mobility as determined via the initial rate of stress relaxation increases with deformation, but at slower strain rates the mobility decreases with deformation, seriously challenges the simple deformation induced mobility ideas that are used in the current class of nonlinear viscoelastic [8–11] and viscoplastic constitutive models [12–14] for glassy polymers.

In the study described above the relationship between mobility and deformation was determined in uniaxial extension and compression [7], where the volume change is relatively small and the behavior is predominantly controlled by the deviatoric component of the stress/strain tensors. Recently, our group has reported on the first observation of yield in a longitudinal deformation, where the volumetric component of the strain is an order of magnitude, or more, larger than the dilatation in uniaxial experiments [15]. In this communication we will report on longitudinal stress relaxation immediately following a constant strain rate longitudinal deformation in order to determine how the mobility (as reported by the initial rate of stress relaxation) evolves in a dilatation dominated

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deformation. If there are qualitative differences in how mobility evolves during deformation in the deviatorically dominated uniaxial experiments vs. the dilatationally dominated longitudinal experiments, this would have significant implications for understanding the deformation of glassy polymers and the associated constitutive models.

2. Experimental

The epoxy system used in this study is the same as that used in the previous longitudinal [15] and stress relaxation studies [7]. The epoxy is a neopentyl glycol diglycidyl ether epoxy resin (DGENG, Miller−Stephenson Chemical Co.) cured with 4,4′-methylenedianiline (MDA, Sigma Aldrich), where the curing procedure and manufacturing process for the longitudinal test specimen have been reported previously [15]. The following experimental protocol for the longitudinal stress relaxation experiment was utilized, where four stress relaxation experiments were performed on the same specimen: (1) prior to the *first* experiment the test specimen is aged for 30 min inside the Instron thermal chamber at T_g-5 °C, (2) the specimen is deformed at constant strain rate of 1.2×10^{-5} s^{-1} to a specified strain at which point the deformation is stopped and the stress relaxation is recorded, (3) the specimen is released from the grips and allowed to relax for 10 min at the working temperature of T_g-5 °C, (4) the specimen is re-gripped and (5) the steps 2 through 4 are repeated for a different strain value. It would have been preferable to heat the sample to well above T_g between the various tests, but this was not possible due to (i) temperature limits on the strain gages and butyl rubber and (ii) the extreme sensitivity of the longitudinal test fixture to misalignment resulting in cracks. As will be discussed subsequently, the thermal history above was sufficient to remove the effect of previous deformations.

As reported previously [7,15], (i) the T_g of the fully cured DGENG−44′MDA epoxy system was 72 °C as determined with Q2000 DSC (TA Instruments) during heating at 10 °C/min, (ii) the PVT behavior was determined using a Gnomix pressure dilatometer and (iii) the temperature dependent dynamic shear modulus was determined with an ARES LS2 rheometer (TA Instruments) using a rectangular torsion specimen.

3. Results and discussion

The longitudinal stress relaxation behavior at various points along the stress−strain curve is shown in Fig. 1 for the DGENG−44′MDA epoxy at T_g-5 °C as well as the previously reported [7] stress relaxation response in uniaxial extension for the same material at two different strain rates. The underlying time dependent longitudinal stress curve shown in Fig. 1a exhibits a change in slope at 130 s that has previously been identified with longitudinal yield, where this yield stress has been shown to be consistent with the tension and compression yield using a pressure modified von Mises criterion with a linear pressure coefficient [15]. The fact that the time dependent pre-relaxation stress response is the same for the four experiments shown in Fig. 1a clearly shows that annealing for 10 min at T_g-5°C between these experiments is sufficient to remove effects of the previous deformation. It should be emphasized that the reproducibility of the loading curves shown in Fig. 1 for both longitudinal and uniaxial experiments is achieved when a single specimen is being used, where there is increased scatter for multiple specimens although the stress relaxation response is qualitatively the same.

The uniaxial extension time dependent stress relaxation responses are shown in Fig. 1b and c for the same material at T_g-5 °C for loading strain rate of 1.2×10^{-5} s^{-1} and 1.5×10^{-4} s^{-1}. The

longitudinal yield strain is 0.2%, while the uniaxial yield strain is 0.4% and 0.7%, respectively, at the specified strain rates as explained in detail in Ref. [15]. The longitudinal yield stress is roughly an order of magnitude higher than the uniaxial yield stress when deformed at the same strain rate, i.e. 9.0 MPa vs. 0.74 MPa. The longitudinal yield strain is 0.2% vs. 0.4% in uniaxial extension, although the significant curvature in the uniaxial stress−strain curve does not allow an unambiguous determination of the yield strain.

In order to examine how the rate of stress relaxation changes during deformation, the normalized stress response, $\bar{\sigma}$, was obtained [7] as

$$\bar{\sigma}(t-t_0) = \frac{\sigma(t-t_0) - \sigma_\infty(\varepsilon_0)}{\sigma(t_0) - \sigma_\infty(\varepsilon_0)} \tag{1}$$

where t_0 and $\sigma(t_0)$ are the time and the corresponding stress value at the beginning of the stress relaxation and $\sigma_\infty(\varepsilon_0)$ is the equilibrium stress at a given strain ε_0. For the uniaxial deformation of an incompressible material $\sigma_\infty(\varepsilon_0) = 3G_\infty \varepsilon_0$ where G_∞ is the equilibrium shear modulus; thus, near T_g the contribution of $\sigma_\infty(\varepsilon_0)$ to $\bar{\sigma}$ can be neglected for uniaxial extension. In contrast, for the longitudinal deformation $\sigma_\infty(\varepsilon_0) = [K_\infty + 4G_\infty/3]\varepsilon_0$ where the K_∞ term has a significant contribution. This is understandable as the longitudinal deformation is dominated by the volume dilation and the equilibrium/rubbery bulk modulus has a value of 3.08 GPa which is 70% of the glassy bulk modulus of 4.38 ± 0.08 GPa [15]. The value of K_∞ at T_g-5°C is extrapolated from the experimentally measured rubbery region of PVT from 90 °C (i.e. T_g+18 °C) to 130 °C (i.e. T_g+58 °C) using the Tait equation parameters reported previously [15]. The normalized stress relaxation responses are shown in Fig. 1d−f, where the key feature is the ordering of the curves as the strain increases. For the longitudinal deformation the normalized post-yield stress relaxation is faster than the pre-yield normalized stress relaxation in agreement with the concept of deformation induced increase in mobility. In contrast, for the uniaxial extension the ordering is reversed such that the pre-yield stress relaxation is the fastest and the post-yield stress relaxation is the slowest. The uniaxial extension results are consistent with what would be expected for a linear viscoelastic material (see Appendix in Ref. [7]), where the result is qualitatively the same for the two loading strain rates even though the stress is significantly higher in case of the faster rate.

The acceleration of the stress relaxation with deformation observed in the longitudinal deformation clearly indicates a nonlinear dependence of mobility on the deformation as compared to the uniaxial response at similar conditions, where the normalized stress relaxation is slower as the deformation proceeds. Even at the relatively slow strain rate of 1.2×10^{-5} s^{-1} and T_g-5°C where the uniaxial response is what would be expected for a linear viscoelastic material, the inverted ordering of the normalized stress relaxation curves indicates the relaxation response is highly nonlinear.

Comparing the stress relaxation responses at different axial strains (see Fig. 2), and hence different volumes, provides information on how the relaxation times depend on volume. It is instructive to compare this dependence to the one obtained in the volume relaxation experiments following the method of Kovacs [16]. The latter consists in calculating the so-called 'effective relaxation time' according to

$$\frac{1}{\tau_{\text{eff}}} = -\frac{1}{\delta}\frac{\mathrm{d}\delta}{\mathrm{d}t} \tag{2}$$

where $\delta = (V - V_\infty)/V_\infty$ is the relative volume departure from the equilibrium value $V_\infty = V_\infty(T)$. A series of volume relaxation