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The response of a glassy polymer in a loading/unloading deformation: The stress memory experiment

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ABSTRACT

A 'stress memory' experiment was designed to expose the nonlinear viscoelastic relaxation processes in a glassy epoxy polymer. The stress memory experiment consists of (i) constant strain rate uniaxial loading to a pre-yield, yield or post-yield condition, (ii) unloading at the same strain rate to zero stress, (iii) holding the strain constant and (iv) monitoring the subsequent stress memory response, where the stress first increases to a maximum and then relaxes to an equilibrium value for that strain. This is an analog to the classic volume memory experiment by Kovacs (Fortschr Hochpolym Forsch, 3, 394, 1964). The stress memory response showed a strong dependence on the loading/unloading strain rate which cannot be predicted by linear viscoelasticity and also provides a significant challenge to a current nonlinear constitutive models. A recently developed Stochastic Constitutive Model (J Rheol, 57(3), 949, 2013) qualitatively predicts the effect of strain rate on the stress memory response.

1. Introduction

The relaxation behavior of glassy polymers depends in a complex way upon the applied thermal and deformation history, where the relaxation response can provide valuable information on the physical processes that result in the glassy state [1,2]. In the classic specific volume 'memory experiment' of Kovacs [3] a poly(vinyl acetate) sample was brought to the nominal equilibrium value of the specific volume at a given sub-T_g temperature via (i) a down-jump in temperature from above T_g, (ii) annealing for a prescribed time, and (iii) an up-jump in temperature. Although the specific volume of the material at the end of this thermal history was at the equilibrium value at the final temperature, instead of remaining at the equilibrium the specific volume as measured by the dilatometer increased, passed through a maximum and finally returned to the equilibrium specific volume. The magnitude of the volume overshoot depended upon the details of the thermal history, including the down-jump temperature and the length of the annealing time, etc. Kovacs recognized that the specific volume overshoot in the memory experiment indicates that there must be a spectrum of relaxation times [3–5].

In the Kovacs volume relaxation experiments the deformation was isotropic and driven by changes in temperature. An alternative way of perturbing the state of a glassy material is by isothermally imposing a deformation, where deformation induces changes in the mobility of the glass. Deformation induced mobility changes are the key feature of the current class of nonlinear viscoelastic [6–9] and viscoplastic [10–15] constitutive models that have been developed to describe nonlinear relaxation behavior of glassy polymers. Consider the situation where a glassy material is first loaded and then unloaded, and then the stress is monitored. In an approximate sense, the application of a strain large enough to take the material through yield induces a mobility change similar to that of an up-jump in temperature, whereas the unloading effects a mobility change corresponding to a temperature down-jump. In this communication we will study the time dependent stress response of an epoxy glass in the T_g-region at constant strain after constant strain rate loading and then unloading at the same strain rate to zero stress, where the resulting stress response will first increase and then relax to equilibrium. The loading history and material response is the deformation analog to the temperature history and specific volume response in the Kovacs memory experiment [3,16]; thus, we designate the particular deformation history employed in this communication the 'stress memory' experiment. A similar deformation history was employed in compression by Quinson et al. [17], where the experiments were conducted so far below T_g that only increasing portion of the stress response was observed. Since the overshoot behavior and final decrease in stress to the equilibrium value was never observed, the authors [17] called the phenomenon "antistress relaxation",

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because the stress was increasing, i.e. 'anti', rather than relaxing toward zero. In our opinion, 'antistress relaxation' is an inappropriate designation for the relaxation phenomena following unloading to zero stress, because the stress increases and then decreases if observed for sufficient time. We will use the term 'stress memory' which we believe is a fuller description of the phenomenon.

The overshoot behavior observed in the memory experiment is not necessarily a non-linear effect. The basic *linear* viscoelastic model as defined by the Boltzman superposition integral [2] exhibits a stress overshoot when subjected to a strain history consisting of a constant strain rate loading to a given strain, a constant strain rate unloading to a strain at which the stress becomes zero and then holding this strain constant. The stress overshoot is a straightforward consequence of the existence of the spectrum of the relaxation times. As will be shown in this communication, when the maximum strain during loading is such that the material is in the flow regime (i.e. the linear viscoelastic equivalent of post-yield) the linear viscoelastic model exhibits two important features: (i) the magnitude of the overshoot is proportional to the strain rate of the loading/unloading deformation and (ii) the position of the overshoot peak on the time axis is independent of the strain rate. However, neither of these predictions is supported by the experimental data, clearly demonstrating that the non-linear effects are at play. Thus, a systematic investigation of stress overshoot as function of various experimental parameters for the stress memory deformation history described above, i.e. loading/unloading strain rate, temperature and aging time prior to deformation, can provide a discriminating test of the various nonlinear constitutive models of glassy polymers.

In this paper we will show that the time of the maximum in the stress memory response significantly changes depending upon the loading/unloading strain rate. The initial stress value in the stress memory experiment is independent of the loading/unloading strain rate, i.e. the initial stress is zero, and the strain after unloading only has a weak dependence on the loading/unloading strain rate. Consequently, the set of nonlinear constitutive models that assume that the mobility is a nonlinear function of the *current* stress and/or strain [6,8,18] will not be able to describe the strong strain rate dependence of the stress memory data. As discussed in a recent paper [19], the deterministic constitutive models for glassy polymers proposed to-date are also unable to predict the experimentally observed post-yield stress softening for constant strain rate deformations without introduction of a separate post-yield softening relaxation mechanism. Our group has recently proposed a stochastic constitutive model (SCM) [19,20] which is a new type of a constitutive model where the dynamic heterogeneity [21,22] of glassy materials is explicitly acknowledged. The SCM naturally predicts the post-yield stress softening and its dependence on the time of sub-T_g aging prior to deformation. One result of the SCM is that the shape of the instantaneous distribution of the relaxation times during a constant strain rate deformation evolves, i.e. the material is thermorheologically complex, where the relaxation time distribution depends on the strain rate. In the present communication we will apply the SCM to the stress memory deformation history used to effect the stress overshoot and demonstrate that the SCM can qualitatively predict the experimentally observed dependence of the overshoot on the strain rate.

2. Experimental

The epoxy system used in this study was synthesized with neopentyl glycol diglycidyl ether epoxy resin, DGENG, (Miller-Stephenson Chemical Co.) and 4,4′-methylenedianiline, MDA, (Sigma Aldrich). All the chemicals were used as received without any further purification. The cross-linked epoxy material was the same as produced previously, using the same (i) curing history, (ii) preparation of tensile specimens and (iii) thermal history prior to deformation [23,24]. The T_g was determined to be 72 °C by DSC using a heating rate of 10 °C/min [24].

A strip specimen (1.5 mm × 7.5 mm × 40 mm) was placed inside an Instron 3110 thermal chamber, where the temperature was precisely determined by thermocouples in close proximity to the specimen. The strain was monitored using an Instron 2663-821 video extensometer as the crosshead displacement was controlled via an Instron 5567 universal testing machine. The experimental protocol was as follows: the specimen is (i) placed in an oven at $T_g + 30$ °C for 30 min to remove the effects of the previous thermal-deformation history, (ii) quenched to room temperature by taking the specimen out of the oven, (iii) loaded in the Instron testing machine where the Instron oven temperature drops by about 8 °C during the specimen loading, which recovers to the set point within 5 min and (iv) annealed in the Instron thermal chamber at the testing temperature for a predetermined time prior to deformation. The stress memory experiments were performed on the same specimen for a given temperature, strain rate, and annealing time, leading to highly reproducible stress–stain curves prior to stress relaxation. Experiments at different conditions were performed on different specimens from the same batch of cured resin.

The multi-step uniaxial deformation experiments consisted of (i) constant strain rate loading to a predetermined stress/strain, (ii) unloading at the same strain rate to zero stress and (iii) then holding the strain constant. These experiments were performed at various temperatures, strain rates and annealing times. The stress relaxation response was measured when the loading stopped at different points along the stress–strain curve.

3. Results

In this study the stress–strain response during constant strain rate uniaxial extension and the time-dependent stress relaxation response at constant strain are investigated via two-step and three-step deformation experiments for the DGENG-44′MDA epoxy. In a two-step experiment the first step is the constant strain rate loading to a particular strain value and the second step is the stress relaxation as the strain is held constant. In a three-step experiment

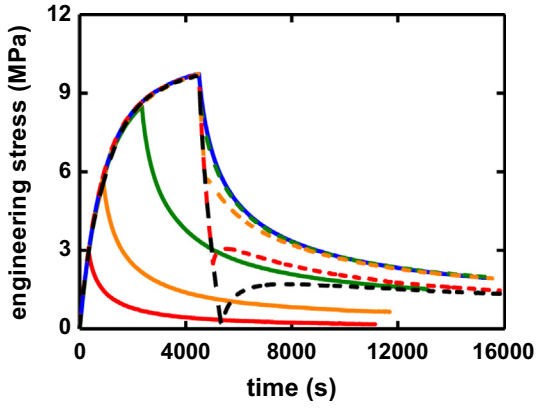

Fig. 1. Time dependent stress response for DGENG-44′MDA in uniaxial extension at T_g-15 °C with sub-T_g aging for 0.5 h. The loading/unloading strain rate is 1.2×10^{-5} s^{-1}. The stresses at the beginning of stress relaxation during loading are: 2.8 MPa ($\sigma_Y/3$, red solid); 5.7 MPa ($2\sigma_Y/3$, orange solid); 8.5 MPa (σ_Y, green solid); and 9.7 MPa (blue solid). The stresses at the beginning of stress relaxation during unloading are: 8.5 MPa (green dash); 5.7 MPa (orange dash); 2.5 MPa (red dash); and, 0 MPa (black dash). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)