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A thermodynamic modeling approach for dynamic softening in glassy amorphous polymers

Rui Xiao [a,*], Thao D. Nguyen [b]

[a] Institute of Soft Matter Mechanics, College of Mechanics and Materials, Hohai University, Nanjing, Jiangsu 210098, China
[b] Department of Mechanical Engineering, The Johns Hopkins University, Baltimore, MD 21218, USA

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ABSTRACT

Strain softening is highly dependent on the thermo-mechanical history. The degree of post-yield strain softening increases with the aging time, which is dependent on the aging temperature, and decreases with plastic strain. In this paper, we present two approaches to describe the strain softening. The first approach is an extension of the widely applied dynamic softening method that evolves the yield strength with the effective plastic strain rate. Though this approach can quantitatively capture the main experimental observations, it is empirical and does not capture the physical mechanism behind aging and strain softening. The second approach couples inelastic deformation with an evolution of the nonequilibrium state. The approach is based on the effective temperature nonequilibrium thermodynamic framework that introduces a thermodynamic state variable, the effective temperature to characterize the nonequilibrium state. The temperature-dependent evolution of the effective temperature describes the glass transition of amorphous polymers. We show that the physical aging and dynamic softening arise from the evolution of the effective temperature towards equilibrium and with plastic deformation towards a steady-state value away from equilibrium.

1. Introduction

The stress response of glassy polymers typically exhibits four different regions: a linear increase in stress with strain (elastic region), a drop in stress with strain (post-yield strain softening), a nearly constant stress with strain (steady state draw), and an increase in stress with strain (orientation hardening). Understanding the strain softening of glassy amorphous polymers is crucial in many applications, because softening induces strain localization that leads to failure of polymers [1,2]. The post-yield softening behavior is strongly dependent on temperature, strain rate and thermo-mechanical loading history [3–6]. When glassy polymers are annealed, the yield strength increases with annealing time, known as physical aging [3,6–8]. In contrast, the steady state flow stress is independent of previous thermal history [6]. The post-yield stress drop can be eliminated by large plastic pre-deformation such as in cold rolling and cold drawing [5]. This phenomena is opposite to physical aging, and is referred as mechanical rejuvenation by Struik [4]. The softening recovers with time indicating a renewed physical aging after cessation of plastic deformation.

To describe this complex dynamic softening behavior, numerous constitutive models have been developed that used an internal variable to describe the nonequilibrium structure and its effect on the yield strength [9–16]. Boyce et al. [9] proposed the evolution of the yield strength to a steady state value with plastic strain rate, which has been widely employed to model the strain softening. Hasan

* Corresponding author.
E-mail address: rxiao@hhu.edu.cn (R. Xiao).

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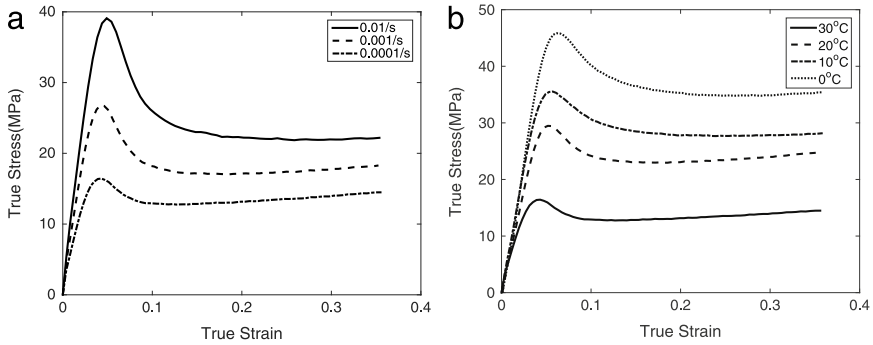

Fig. 1. Experimental results of uniaxial compression response of acrylate-based copolymer (a) at 30 °C (b) at 0.0001/s.

and Boyce [10] developed an evolution equation for the number of shear transformation sites to describe the strain softening behaviors of quenched and annealed specimens of poly(methyl methacrylate), while Klompen et al. [11] developed an evolution equation for a phenomenological state variable to describe the softening behaviors of polycarbonate. Buckley et al. [12] applied fictive temperature (T_f) concept of Tool [17] to model the strain softening. They proposed a phenomenological evolution equation for the fictive temperature that increases with the effective viscous strain rate to represent the mechanical rejuvenation.

Though these models have achieved considerable success in modeling the post-yield strain softening, they cannot capture certain important features observed in experiments. For example, the internal variable approach of Boyce and coworkers cannot capture the recovery of the yield strength after cessation of plastic deformation. In this letter, we present a new thermodynamic approach to model the effect of physical aging and plastic deformation on the post-yield strain softening behavior and compare it to the widely used internal variable softening model of Boyce et al. [9], which we extend to include static recovery of the yield strength [18]. The approach is based on the effective temperature theory, which introduces the effective temperature as a thermodynamic state variable for the nonequilibrium configurational structure [19–22]. The central assumption of the effective temperature theory is that the total degrees of freedom of amorphous polymers are composed of vibrational degrees of freedom characterized by the current temperature, and configurational degrees of freedom characterized by the effective temperature. The effective temperature theory has been applied successfully to describe amorphous metals and granular matter [20–24]. The ability of the effective temperature model to describe softening has been demonstrated by STZ theory and discussed in [22,25].

Here, we show that the effective temperature approach can be used to describe the yield and dynamic softening response of polymers. For amorphous polymers, we develop models for the viscoelastic internal energy and entropy density of the vibrational and configurational subsystems, based on the entropy elasticity model of Chadwick [26]. We introduce a distribution of viscous deformation and effective temperatures, along with discrete spectrums of structural and stress relaxation times, to accurately represent the time-dependent stress response and physical aging. Finally, we develop a model for the stress and structural relaxation times that depends on temperature and the nonequilibrium structure through the configurational entropy. In the model, the increase in the yield stress with physical aging occurs because the nonequilibrium structure evolves towards a more ordered state, decreasing the molecular mobility and retarding plastic flow. When deformed, part of the plastic work is stored in configurational rearrangements to a more disordered state, which increases the molecular mobility, promoting plastic flow and producing strain softening [27]. This is one of fundamental differences between the effective temperature thermomechanical theory and classic thermomechanical theory. In the classic thermomechanical theory, all the plastic power is transferred into regular heat and entropy, which is not consistent with the following experimental observations [12,28]. The steady-state flow stress is obtained when the rejuvenation effect balances the aging effect. In the following sections, we show that the effective temperature approach can capture more accurately the time-dependent and temperature-dependent effect of physical aging and mechanical rejuvenation on dynamic softening, and more generally on the stress response, than the internal variable approach.

2. Experimental observation

We performed a series of uniaxial compression experiments on an acrylate-based random copolymer [29] to characterize the rate-dependence and time-dependence of the post-yield softening response. The polymer has a 10% cross-linker density and exhibits a T_g at 36 °C. We used cylindrical specimens 6.0 cm in diameter and height. The specimens were first thermally rejuvenated at 70 °C for 30 min, cooled to 30 °C, 20 °C, 10 °C or 0 °C at 3 °C/min, and annealed for 30 min. The specimens were compressed to 30% engineering strain at an engineering strain rate 0.0001/s, 0.001/s or 0.01/s using an MTS Insight 5 electromechanical testing system. As shown in Fig. 1, the stress response showed the typical features of yield, a post-yield stress drop to a steady-state draw stress. The yield strength, post-yield stress drop, and flow stress increased with increased strain rate and decreased temperature.

We next investigated the effect of physical aging and plastic pre-deformation on the stress response by performing a series of load–unload–reload tests in compression. After heating and equilibrating at 70 °C for 30 min,

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