



An effective temperature theory for the nonequilibrium behavior of amorphous polymers



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ABSTRACT

Amorphous polymers lack an organized microstructure, yet they exhibit structural evolution, where physical properties change with time, temperature, and inelastic deformation. To describe the influence of structural evolution on the mechanical behavior of amorphous polymers, we developed a thermomechanical theory that introduces the effective temperature as a thermodynamic state variable representing the nonequilibrium configurational structure. The theory couples the evolution of the effective temperature and internal state variables to describe the temperature-dependent and rate-dependent inelastic response through the glass transition. We applied the theory to model the effect of temperature, strain rate, aging time, and plastic pre-deformation on the uniaxial compression response and enthalpy change with temperature of an acrylate network. The results showed excellent agreement with experiments and demonstrate the ability of the effective temperature theory to explain the complex thermomechanical behavior of amorphous polymers.

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1. Introduction

Amorphous polymers exhibit a wide range of complex time-dependent and temperature-dependent behavior, from elastic and rubbery to viscoplastic and glassy. The physical properties of amorphous polymers are determined by the mobility of structural components spanning multiple length-scales and these can be observed macroscopically as temperature-dependent relaxation processes occupying multiple time-scales. At high temperatures, the polymer structures are mobile and can rearrange quickly in response to a mechanical load or temperature change. The mobility decreases with the temperature, and cooling drives an initially rubbery material out of equilibrium and induces the glass transition, which brings about dramatic changes in physical properties. The glass transition is an inherently time-dependent process, and the glass transition temperature T_g changes with the cooling rate. Slower cooling rates produce lower glass transition temperatures, because more time is available for the polymer structure to rearrange towards an equilibrium configuration (Kovacs, 1958). Whether the glass transition temperature has an equilibrium limit is an open question. However, structural relaxation (Scherer, 1984) can be observed readily near the glass transition as the time-dependent evolution of thermodynamic properties, such as volume and enthalpy, to equilibrium (Struik, 1976; Tool, 1945; Hutchinson, 1993; Hodge, 1995; Meijer and Govaert, 2005). The effect of structural relaxation can also be observed in the mechanical behavior of glassy polymers as physical aging, where the flow-resistance and yield strength increase with time (G'Sell and McKenna, 1992). The

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structure of amorphous glasses can be rejuvenated to a more mobile state by plastic deformation (Meijer and Govaert, 2005; Struik, 1997), and mechanical rejuvenation is responsible for the strain-softening behavior following yield in polymer glasses. Large plastic deformation also decreases the yield strength and erases the yield peak developed from structural relaxation (Meijer and Govaert, 2005; Hasan and Boyce, 1995). In differential scanning calorimetry measurements (DSC), structural relaxation produces an endothermic overshoot at T_g that increases with annealing time corresponding to the yield strength. Large plastic deformation erases the endothermic overshoot at T_g and induces a pre- T_g exothermic undershoot that increases with plastic strain and corresponds to the post-yield strain-softening (Hasan and Boyce, 1993).

Modeling the nonequilibrium behavior of amorphous polymers is important for fundamental studies of the glass transition and for practical applications, such as improving manufacturing processes (e.g., hot embossing) and controlling material performance (e.g., shape memory behavior) that operate through the glass transition. Though viscoelasticity and structural relaxation both arise from time-dependent structural rearrangements, they are described by different theoretical approaches. The internal state variable thermodynamics theory, introduced by Coleman and Gurtin (1967), has been applied successfully to model the viscoelastic behavior of elastomers above the T_g (Lion, 1997; Reese and Govindjee, 1998; Bergstrom and Boyce, 1998) and the viscoplastic behavior of glassy polymers below T_g (Boyce et al., 1988; Arruda and Boyce, 1993; Tervoort et al., 1996; Anand and Ames, 2006). The stress response is derived from a free energy density that depends on the total deformation and internal state variables describing the effects of inelastic deformation. The theory provides a definition for the internal dissipation and temperature-dependent evolution equations are prescribed for the internal variables to guarantee positive dissipation. Additional structural variables, such as the yield strength, are introduced and evolved with the plastic strain rate to model strain-softening (Hasan and Boyce, 1995; Klompen et al., 2005). Recent efforts have applied the internal state variable theory to describe the glass transition (Anand and Ames, 2006; Dupaux and Boyce, 2007; Srivastava et al., 2010), where temperature-dependent moduli are prescribed to describe the dramatic change in the mechanical properties during the glass transition.

Tool (1946) introduced the fictive temperature approach for modeling structural relaxation in glasses. In a cooling experiment, the fictive temperature T_f is defined as the equilibrium temperature from which the material is quenched to obtain a property at the current temperature. Tool (1946) developed a nonlinear first order evolution equation for T_f towards the equilibrium temperature T , where the relaxation time depends on T and T_f to account for the changing structure of the glass. These features allowed the model to describe the dependence of T_g on the cooling rate, asymmetry in the structural relaxation response to cooling and heating, and hysteresis in the temperature dependence during a cooling-heating cycle. Subsequent developments for polymers have produced more physical models for the temperature dependence and structure dependence of the relaxation time (Adam and Gibbs, 1965; Hodge, 1987; Scherer, 1986), and introduced a distribution of relaxation times (Macedo and Napolitano, 1967; Aklonis, 1981; Kovacs et al., 1979; Narayanaswamy, 1971) to describe the memory effects observed after multiple temperature treatments. Recent glass-rubber models have applied a fictive temperature dependence in the viscosities and plastic strain rate to describe physical aging and mechanical rejuvenation of the yield and post-yield behavior of glassy polymers (Buckley et al., 2004; Nguyen et al., 2008, 2010; Li and Buckley, 2010; Choi et al., 2012; Xiao et al., 2013).

The ability of the fictive temperature concept to describe the nonequilibrium behavior of glasses has motivated the development of theories that postulate the existence of an effective temperature as a thermodynamic state variable describing the nonequilibrium state. The central idea of effective temperature theories is the degrees of freedom of a glass that can be decomposed into a fast vibrational mode that equilibrates instantaneously and slow configurational modes that exist in a quasi-equilibrium state, characterized by an effective temperature (see for example Nieuwenhuizen, 1998a,b, 2001; Ottinger, 2006; Leuzzi, 2009; Cugliandolo, 2011). The fast and slow modes have different entropies and internal energies, and can be considered weakly interacting material subsystems (Bouchbinder and Langer, 2009). The existence of an effective temperature as a thermodynamic state variable that is connected to the configurational entropy is supported by molecular dynamics simulations of an aging glass system (Cugliandolo et al., 1997; Berthier and Barrat, 2002), simulations of athermal systems (Durian, 1995; Ono et al., 2002), and granular systems (Makse and Kurchan, 2002). The issue of whether the effective temperature is a true thermodynamic state variable is far from settled, and Leuzzi (2009) provides an in-depth discussion of the distinction between the fictive and effective temperature concepts. Recent models of inelastic deformation in amorphous materials have integrated the effective temperature and internal state variable frameworks (Langer, 2004; Bouchbinder and Langer, 2009; Falk and Langer, 2011). Bouchbinder and Langer (2010, 2011) extended the shear transformation zone theory to describe the linear rate-dependent behavior and the Kovacs memory effect of polymer glasses. Kamrin and Bouchbinder (2014) developed a two-temperature thermomechanical theory, that explicitly considers the interaction of two thermodynamic subsystems, and showed that the theoretical framework can produce a wide range of nonequilibrium deformation behavior of amorphous materials.

In this paper, we develop a thermomechanical theory for the nonequilibrium behavior of amorphous polymers based on the effective temperature concepts. We adopt the basic idea that the behavior of the glass can be decomposed into a fast kinetic process at the equilibrium temperature and multiple slowly evolving configurational processes at different effective temperatures. We introduce the concept of multiple configurational processes to accurately represent the broad relaxation spectrum of polymers. The kinetic and configurational processes are characterized by different internal energies, entropies, heat flux, and entropy flux, the sum of which give the properties of the system. We begin by decomposing the balance of energy into sub-balances for the kinetic and configurational subsystems, which requires introducing heat conduction between the subsystems. This approach was first applied by Kamrin and Bouchbinder (2014) and results in an energy balance

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