An Effective Temperature Theory for the Nonequilibrium Behavior of Amorphous Polymers

Rui Xiao and Thao D. Nguyen^a

^a*Department of Mechanical Engineering, The Johns Hopkins University
Baltimore, MD 21218, USA, Email: vicky.nguyen@jhu.edu(T. D. Nguyen)*

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.

Key words: Aging and rejuvenation, thermodynamics, effective temperature, glass transition

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 (C. G'Sell and G. B. McKenna 1992). The 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, Dupaix 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 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 (1998b,a, 2001), Ottinger (1975), 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 extended the shear transformation zone theory to describe the linear rate-dependent behavior and the Kovacs memory effect (Bouchbinder and Langer 2010, 2011) 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 for the configurational subsystems that describes mechanical rejuvenation and configurational temperature diffusion. The energy sub-balances are applied to develop a reduced entropy inequality that constrains the constitutive relations for heat conduction and internal state variables.

We applied the theory to describe the thermomechanical behavior of an acrylate thermoset by postulating constitutive relations for the temperature-dependent and structure-dependent relaxation time and rate of inelastic deformation. The parameters of the model were determined from standard dynamic mechanical experiments and isothermal uniaxial tensile experiments (Nguyen et al. 2008, 2010, Xiao et al. 2013). We applied the thermomechanical model to simulate the effect of physical aging and plastic deformation on the stress response and enthalpy change of the acrylate thermoset and found good agreement with experiments. The results show that the effective temperature theory can potentially provide a unifying framework for predictive modeling of a wide range of non-equilibrium behavior of polymers.

2 Methods

2.1 *Experimental methods*

2.1.1 *Materials and specimen preparation*

The material used for this study was a tert-butyl acrylate (tBA), poly(ethylene glycol) dimethacrylate (PEGDMA) and di(ethylene glycol) dimethacrylate (DEGDMA) random copolymer crosslinked network, with 10 wt% PEGDMA-DEGDMA (XLS) crosslink density. The tBA-co-XLS polymer has been studied in previous works as a shape memory polymer (Qi et al. 2008, Nguyen et al. 2008, 2010, Yakacki et al. 2012, Xiao et al. 2013). The compounds were ordered from Sigma Aldrich and used in their as-received conditions. A crosslinker solution was synthesized by mixing 30 wt% DEGDMA with 70 wt% PEGDMA, with typical molecular weight $M_n = 550$. The comonomer solution was prepared by adding the PEGDMA-DEGDMA solution at 10%wt of the total comonomer solution and a photoinitiator, 2,2-dimethoxy-2-phenylacetophenone, at 0.1 wt% to the tBA monomer solution. The comonomer solution was mixed manually until fully dissolved. The solution was injected between 2 glass slides separated by a 1 mm spacer to create film specimens for dynamic mechanical testing. The solution was also injected into polyethylene tubing to create cylindrical specimens for uniaxial compression testing. Polymerization was achieved by exposure to UV light (Black Ray B100 A/R) for 15 min. The specimens were thermally cured in an oven at 70°C for 1 hour to ensure complete polymerization. A laser cutter was used to cut 1.0mm × 5.0mm × 25.0mm film specimens. The cylindrical specimens were cut to 6 mm in length and machined to 6mm in diameter. The cut surfaces were sanded to provide a smooth, flat surface for compression tests.

2.1.2 *Dynamic frequency sweep tests*

The temperature-dependent and time-dependent properties of tBA-co-XLS has been characterized extensively in previous works (Qi et al. 2008, Nguyen et al. 2008, 2010, Xiao et al. 2013). We previously determined the viscoelastic relaxation spectrum, i.e., distribution of stress relaxation

times, from the master curve of the frequency-dependent storage modulus (Xiao et al. 2013). Dynamic frequency sweep tests were performed on the film specimens using the TA Q800 Dynamic Mechanical Analyzer (DMA) in multifrequency mode. The film specimens were positioned in the tension grips to give a 15 mm gage section. The temperature was increased from 0°C to 120°C in 5°C increments and annealed at each temperature step for 5 minutes to achieve thermal equilibrium. The strips were subjected to a 0.2% dynamic strain at 0.32 Hz, 1.0 Hz, 3.2 Hz, 10.0 Hz, and 31.6 Hz to measure the storage modulus at each temperature $G(\omega, T)$. The storage modulus as a function of frequency at each temperature was shifted along the $\log \omega$ axis to the reference temperature $T_0 = 75^\circ\text{C}$ using the method described by Ferry (1980) to obtain the time-dependent shift factor $a_T(T)$ and the master curve $G(a_T \omega)$. The Williams-Landel-Ferry (WLF) equation was fit to the temperature-dependent shift factor,

$$\log a_T(T) = \frac{-C_1^0(T - T_0)}{C_2^0 + T - T_0}, \quad (1)$$

where C_1^0 and C_2^0 are the WLF constants for the reference temperature T_0 . Finally, the WLF constants at T_0 were shifted to the glass transition temperature $T_g = 36^\circ\text{C}$, measured from the thermal contraction caused by a 1°C/min cooling rate (Xiao et al. 2013), using the relations, $C_2^g = C_2^0 + T_g$ and $C_1^g C_2^g = C_1^0 C_2^0$ (Ferry 1980).

2.1.3 Temperature-induced isothermal recovery

We previously characterized the structural relaxation behavior of tBA-co-XLS by measuring the time-dependent thermal strain recovery from a sudden temperature change at zero stress (Xiao et al. 2013). The film specimen was placed in the tension grips of the TA Q800 DMA and equilibrated at 70°C for 30 minutes. The specimen was cooled to the first test temperature, $T_g + 8^\circ\text{C}$, at 1°/min and held for 60 minutes. The time-dependent evolution of the thermal contraction was measured by the DMA under zero-force mode. The specimen was then subjected a series of 4°C temperature drops at 6°C/min until $T_g - 8^\circ\text{C}$. The specimen was annealed and the time-evolution of the thermal contraction response was measured at each test temperature. The nonequilibrium thermal contraction was defined for the n th temperature step as,

$$\delta(t, T_n) = \varepsilon_T(t, T_n) - \sum_{j=1}^N \alpha_r \Delta T_j, \quad t_{n-1}^+ < t \leq t_n^-, \quad (2)$$

where $\varepsilon_T(t, T_n)$ is the total thermal contraction measured from the beginning of the experiment, α_r is the rubbery coefficient of thermal expansion, t_{n-1}^+ and t_n^- indicate the times at the beginning and end of the 60 minute temperature step. The response function for each temperature step is defined as (Xiao et al. 2013),

$$\rho(t - t_{n-1}, T_n) = \frac{1}{\Delta \alpha \Delta T_n} (\delta(t, T_n) - \delta(t_{n-1}, T_{n-1})), \quad (3)$$

where $\delta(t_{n-1}, T_{n-1})$ is the nonequilibrium thermal contraction at the end of the previous temperature step, $\Delta T_n = -4^\circ\text{C}$, $\Delta \alpha = \alpha_r - \alpha_g$, and α_g is the glassy coefficient of thermal expansion. The

response function measured at different temperatures can be superposed to form a master curve $\rho(u(T, t))$ by plotting as a function of the reduced time defined as (Kovacs et al. 1979),

$$u(T, t) = \int_{t-t_{n-1}}^t \frac{d\xi}{a(T, \delta(\xi, T_n))}, \quad (4)$$

where t_{n-1} is the time at the end of the previous temperature step, and $a(T, \delta)$ is the temperature-dependent and structure-dependent shift factor. We developed the following model (Nguyen et al. 2008) based on the nonlinear Adam-Gibbs model (Adam and Gibbs 1965, Scherer 1984, Hodge 1987) for $a(T, \delta)$,

$$\log a(T, \delta) = -C_1^g \left(\frac{C_2^g (\delta/\Delta\alpha) + T (T - T_g + \delta/\Delta\alpha)}{T (C_2^g + T - T_g + \delta/\Delta\alpha)} \right), \quad (5)$$

where C_1^g and C_2^g are the WLF constants for $T_g = 36^\circ\text{C}$ determined from the dynamic frequency sweep tests in Sec. 2.1.2. The model assumes that stress relaxation and structural relaxation share the same dependence on temperature and nonequilibrium structure, described by δ . Xiao et al. (2013) showed that the WLF parameters C_1^g and C_2^g determined from dynamic mechanical tests can be applied to construct the master curve of the response function $\rho(u)$ for stress-free isothermal recovery, which validated the assumption for the tBA-co-XLS material.

2.1.4 Differential Scanning Calorimetry

Differential scanning calorimetry was used to measure the temperature-dependent heat capacity. Square specimens weighing 6 mg were cut from the tBA-co-XLS films and placed in a TA Q20 differential scanning calorimeter (DSC). To remove the effects of physical aging, the specimen was heated from -10°C to 80°C at $10^\circ\text{C}/\text{min}$. The specimen was then cooled to -10°C within 20 minutes then heated again from -10°C to 80°C at $10^\circ\text{C}/\text{min}$.

2.1.5 Uniaxial compression

Isothermal uniaxial compression experiments were used to investigate the effect of physical aging and mechanical rejuvenation on the viscoplastic behavior of tBA-co-XLS. The cylindrical specimens were first heated in an oven to 70°C and held for 30 min to remove the effects of physical aging. The specimens then were either quenched in 20°C water for 5 min or cooled to 20°C at $3^\circ\text{C}/\text{min}$, and annealed for 30 min, 1 day or 14 days in an Echotherm IN30 incubator (Torrey Pines Scientific, Inc, Carlsbad, CA, USA). The specimens were transferred to an MTS Insight 5 electromechanical testing system, equipped with an environmental temperature chamber (Thermcraft, Inc. Winston Salem, NC, USA) set at 20°C , and subjected to two load-unload cycles with different annealing times between each cycle. In the first cycle, the specimen was compressed to 30% engineering strain at 0.001/s or 0.01/s strain rate and unloaded. The compressed specimen was annealed at 20°C for 1 min, 10 min, 1 day or 14 days before being compressed again by an addition 15% engineering strain at 0.001/s or 0.01/s. In addition, we performed uniaxial compression tests

at different temperatures. Specimens were cooled to 60°C or 40°C at 3°C/min, and annealed for 30 min. The specimens were compressed to 30% engineering strain at 0.001/s or 0.01/s.

2.2 Modeling Methods

2.2.1 Kinematics

We begin with the basic definition of a continuum deformation field, $\mathbf{x} = \boldsymbol{\varphi}(\mathbf{X})$, which uniquely maps points $\mathbf{X}$ in the undeformed material configuration to points $\mathbf{x}$ in the deformed spatial configuration. The deformation gradient is defined as, $\mathbf{F} = \partial \boldsymbol{\varphi} / \partial \mathbf{X}$. To describe the time-dependent deformation of polymers, we decompose the deformation gradient multiplicatively into N parallel elastic and inelastic components,

$$\mathbf{F} = \mathbf{F}_i^e \mathbf{F}_i^v, \quad i = 1..N. \quad (6)$$

For simplicity, we do not consider the effect of thermal deformation in the kinematic description, which was incorporated in previous works (Nguyen et al. 2008, 2010, Xiao et al. 2013). The Cauchy-Green deformation tensors is defined as $\mathbf{C} = \mathbf{F}^T \mathbf{F}$. In addition, we define the elastic Cauchy-Green deformation tensors as,

$$\mathbf{C}_i^e = \mathbf{F}_i^{eT} \mathbf{F}_i^e = \mathbf{F}_i^{v^{-T}} \mathbf{C} \mathbf{F}_i^{v^{-1}}. \quad (7)$$

The spatial and inelastic velocity gradients are defined as, $\mathbf{L} = \dot{\mathbf{F}} \mathbf{F}^{-1}$ and $\mathbf{L}_i^v = \dot{\mathbf{F}}_i^v \mathbf{F}_i^{v^{-1}}$.

2.2.2 General constitutive theory

The following section describes the development of a coupled thermomechanical theory for amorphous polymers near and below the glass transition. The central assumption of the theory is that the degrees of freedom of an amorphous material near or below the glass transition temperature can be separated into fast kinetic degrees of freedom and a distribution of slow configurational degrees of freedom. During cooling, the kinetic degrees of freedom equilibrate instantaneously to the temperature, T , while the configurational degrees of freedom become trapped by a vanishing molecular mobility in a distribution of nonequilibrium states characterized by higher effective temperatures. The continuous distribution of nonequilibrium states are represented here as a discrete distribution of P configurational subsystems with effective temperatures T_{e_i} . We further assume that the configurational subsystems are weakly coupled to the kinetic subsystem, such that heat flows between the kinetic and configurational subsystems to drive T_{e_i} towards T . For simplicity, we neglect the thermal coupling between the configurational subsystems, though such interactions are needed for a more complete thermodynamic description. The first law of thermodynamics can be written for the material system in the reference configuration as,

$$\dot{e} = \mathbf{S} : \frac{1}{2} \dot{\mathbf{C}} - \nabla_{\mathbf{X}} \cdot \mathbf{Q}, \quad (8)$$

where $\mathbf{S}$ is the second Piola-Kirchhoff stress tensor. The second law of thermodynamics can be expressed in the reference configuration as,

$$\dot{\eta} + \nabla_{\mathbf{X}} \cdot \mathbf{H} \geq 0. \quad (9)$$

Each subsystem is characterized by an internal energy density, entropy density, nominal heat flux, and nominal entropy flux. The total entropy, internal energy, heat flux and entropy flux of the material system can be expressed as the sum of the contributions from the subsystems as,

$$\begin{aligned} \eta &= \eta^k + \sum_i^P \eta_i^c, & e &= e^k + \sum_i^P e_i^c, \\ \mathbf{Q} &= \mathbf{Q}^k + \sum_i^P \mathbf{Q}_i^c, & \mathbf{H} &= \mathbf{H}^k + \sum_i^P \mathbf{H}_i^c, \end{aligned} \quad (10)$$

We apply the definition of the kinetic and configurational entropy flux introduced by Kamrin and Bouchbinder (2014),

$$\mathbf{H}^k = \frac{\mathbf{Q}^k}{T}, \quad \mathbf{H}_i^c = \frac{\mathbf{Q}_i^c}{T_{e_i}}. \quad (11)$$

The classical definition of the entropy flux, $\mathbf{H} = \mathbf{Q}/T$, is recovered at equilibrium, where $T_{e_i} = T$.

The second law can be expanded as follows by applying the decompositions in eqs. (10) and (11) for the entropy and entropy flux,

$$\dot{\eta}^k + \sum_i^P \dot{\eta}_i^c + \frac{\nabla_{\mathbf{X}} \cdot \mathbf{Q}^k}{T} + \sum_i^P \frac{\nabla_{\mathbf{X}} \cdot \mathbf{Q}_i^c}{T_{e_i}} - \frac{1}{T^2} \mathbf{Q}^k \cdot \nabla_{\mathbf{X}} T - \sum_i^P \frac{1}{T_{e_i}^2} \mathbf{Q}_i^c \cdot \nabla_{\mathbf{X}} T_{e_i} \geq 0. \quad (12)$$

To develop constitutive relations for the stress and entropy, we define the Helmholtz free energy density of the material as (Nieuwenhuizen 1998b),

$$\Psi = \underbrace{e^k - T\eta^k}_{\Psi^k} + \sum_i^P \underbrace{e_i^c - T_{e_i}\eta_i^c}_{\Psi_i^c}. \quad (13)$$

The free energy density describes the thermodynamic state of the material, and can depend in general on the temperature, effective temperatures, total deformation, and internal state variables as, $\Psi(T, T_{e_1} \dots T_{e_P}, \mathbf{C}, \mathbf{C}_1^c \dots \mathbf{C}_N^c)$. Here, the internal state variables are the N inelastic components of the deformation gradients $\mathbf{F}_j^v$. The free energy density depends on $\mathbf{F}_j^v$ through the elastic deformation tensor $\mathbf{C}_k^c$ defined in eq. (7). In more general cases, the free energy density can also depend on additional internal variables to describe various inelastic deformation mechanisms, such as orientation hardening. We omit these effects in the following development for simplicity. Applying eq. (13) to eq. (8), the first law can be rewritten in terms of the Helmholtz free-energy density as,

$$T\dot{\eta}^k + \nabla_{\mathbf{X}} \cdot \mathbf{Q}^k + \sum_i^P T_{e_i} \dot{\eta}_i^c + \sum_i^P \nabla_{\mathbf{X}} \cdot \mathbf{Q}_i^c = \mathbf{S} : \frac{1}{2} \dot{\mathbf{C}} - \eta^k \dot{T} - \sum_i^P \eta_i^c \dot{T}_{e_i} - \dot{\Psi} \quad (14)$$

The above expression can be applied to eliminate the kinetic contributions to the entropy and heat flux from the second law in eq. (12),

$$\sum_i^P (T - T_{e_i}) \dot{\eta}_i^c + \sum_i^P (T - T_{e_i}) \frac{\nabla_{\mathbf{x}} \cdot \mathbf{Q}_i^c}{T_{e_i}} - \frac{1}{T} \mathbf{Q}^k \cdot \nabla_{\mathbf{x}} T - \sum_i^P \frac{T}{T_{e_i}^2} \mathbf{Q}_i^c \cdot \nabla_{\mathbf{x}} T_{e_i} + \mathbf{S} : \frac{1}{2} \dot{\mathbf{C}} - \eta^k \dot{T} - \sum_i^P \eta_i^c \dot{T}_{e_i} - \dot{\Psi} \geq 0. \quad (15)$$

The rate of change of free energy density can be evaluated as,

$$\dot{\Psi} = \frac{\partial \Psi}{\partial T} \dot{T} + \sum_i^P \frac{\partial \Psi}{\partial T_{e_i}} \dot{T}_{e_i} + 2 \frac{\partial \Psi}{\partial \mathbf{C}} : \frac{1}{2} \dot{\mathbf{C}} + \sum_j^N \frac{\partial \Psi}{\partial \mathbf{F}_j^v} : \dot{\mathbf{F}}_j^v. \quad (16)$$

It can be shown that, $\frac{\partial \Psi}{\partial \mathbf{F}_j^v} : \dot{\mathbf{F}}_j^v = -\mathbf{C}_j^e \frac{\partial \Psi}{\partial \mathbf{C}_j^e} : \mathbf{L}_j^v$. Substituting eq. (16) into the second law in eq. (15) gives,

$$\sum_i^P (T - T_{e_i}) \dot{\eta}_i^c + \sum_i^P (T - T_{e_i}) \frac{\nabla_{\mathbf{x}} \cdot \mathbf{Q}_i^c}{T_{e_i}} - \frac{1}{T} \mathbf{Q}^k \cdot \nabla_{\mathbf{x}} T - \sum_i^P \frac{T}{T_{e_i}^2} \mathbf{Q}_i^c \cdot \nabla_{\mathbf{x}} T_{e_i} + \left(\mathbf{S} - 2 \frac{\partial \Psi}{\partial \mathbf{C}} \right) : \frac{1}{2} \dot{\mathbf{C}} - \left(\eta^k + \frac{\partial \Psi}{\partial T} \right) \dot{T} - \sum_i^P \left(\eta_i^c + \frac{\partial \Psi}{\partial T_{e_i}} \right) \dot{T}_{e_i} + \underbrace{\sum_k^N \mathbf{C}_k^e \frac{\partial \Psi}{\partial \mathbf{C}_k^e} : \mathbf{L}_k^v}_{\mathcal{W}^{\text{int}}} \geq 0, \quad (17)$$

where $\mathcal{W}^{\text{int}}$ is the internal power from inelastic deformation. Following the arguments of Coleman and Gurtin (1967), we arrive at the constitutive relations,

$$\mathbf{S} = 2 \frac{\partial \Psi}{\partial \mathbf{C}}, \quad \eta^k = -\frac{\partial \Psi}{\partial T}, \quad \eta_i^c = -\frac{\partial \Psi}{\partial T_{e_i}}, \quad (18)$$

to satisfy the second law for arbitrary $\dot{\mathbf{C}}$, $\dot{T}$, and $\dot{T}_{e_i}$. Applying the constitutive relations to eq. (15) yields a reduced inequality,

$$\sum_i^P (T - T_{e_i}) \dot{\eta}_i^c + \sum_i^P (T - T_{e_i}) \frac{\nabla_{\mathbf{x}} \cdot \mathbf{Q}_i^c}{T_{e_i}} - \frac{1}{T} \mathbf{Q}^k \cdot \nabla_{\mathbf{x}} T - \sum_i^P \frac{T}{T_{e_i}^2} \mathbf{Q}_i^c \cdot \nabla_{\mathbf{x}} T_{e_i} + \mathcal{W}^{\text{int}} \geq 0, \quad (19)$$

that constrains the entropy production from heat conduction and inelastic deformation.

To develop constitutive relations for the internal heat flux and inelastic deformation, eqs. (18) and (16) are substituted into the first law in eq. (14) to give.

$$T \dot{\eta}^k + \sum_i^P T_{e_i} \dot{\eta}_i^c = -\nabla_{\mathbf{x}} \cdot \mathbf{Q}^k - \sum_i^P \nabla_{\mathbf{x}} \cdot \mathbf{Q}_i^c + \mathcal{W}^{\text{int},k} + \sum_i^P \mathcal{W}_i^{\text{int},c}, \quad (20)$$

where we have partitioned $\mathcal{W}^{\text{int}}$ into kinetic and configuration contributions, $\mathcal{W}^{\text{int},k} = \sum_j^N \mathbf{C}_j^e \frac{\partial \Psi}{\partial \mathbf{C}_j^e} : \mathbf{L}_j^v$ and $\mathcal{W}_i^{\text{int},c} = \sum_j^N \mathbf{C}_j^e \frac{\partial \Psi}{\partial \mathbf{C}_j^e} : \mathbf{L}_j^v$, based on the decomposition of Ψ in eq. (13). We now make the following

assumptions. 1) Heat Q_i^{kc} flows between the kinetic and configurational subsystems and allows T_{e_i} to equilibrate with T (Kamrin and Bouchbinder 2014). 2) The configurational subsystems have negligible interactions; thus heat does not flow between the P configurational subsystems. Moreover, we assume that the entropy of a subsystem depends on the characteristic temperature of that subsystem and not on the temperatures of other subsystems. These assumptions allow the first law to be split into energy balances for each subsystem as,

$$T\dot{\eta}^k = -\nabla_{\mathbf{x}} \cdot \mathbf{Q}^k - \sum_i^P Q_i^{kc} + \mathcal{W}^{\text{int},k} \quad (21)$$

$$T_{e_i}\dot{\eta}_i^c = -\nabla_{\mathbf{x}} \cdot \mathbf{Q}_i^c + Q_i^{kc} + \mathcal{W}_i^{\text{int},c}, \quad i = 1 \dots P. \quad (22)$$

Equation (22) is used to eliminate the configurational heat flux from the second law in (19):

$$\sum_i^P - (T_{e_i} - T) \frac{Q_i^{kc}}{T_{e_i}} - \frac{1}{T} \mathbf{Q}^k \cdot \nabla_{\mathbf{x}} T - \sum_i^P \frac{T}{T_{e_i}^2} \mathbf{Q}_i^c \cdot \nabla_{\mathbf{x}} T_{e_i} + \sum_j^N \left(\sum_i^P \frac{T}{T_{e_i}} \mathbf{C}_j^e \frac{\partial \Psi_i^c}{\partial \mathbf{C}_j^e} + \mathbf{C}_j^e \frac{\partial \Psi^k}{\partial \mathbf{C}_j^e} \right) : \mathbf{L}_j^v \geq 0, \quad (23)$$

We now consider that the temperatures, temperature gradients, and $\mathbf{L}_j^v$ are independent variables and examine a specific case, where $T_{e_i} = T$ and $\mathbf{L}_j^v = 0$. The entropy inequality in eq. (23) for this case reduces to the sum of the heat conduction terms. Since the temperature gradients are independent variables, the heat conduction inequality can be satisfied only if the heat flux of each subsystem depends only on the corresponding temperature gradient, which implies that each term is non-negative, $-\mathbf{Q}^k \cdot \nabla_{\mathbf{x}} T \geq 0$ and $-\mathbf{Q}_i^c \cdot \nabla_{\mathbf{x}} T_{e_i} \geq 0$. The heat conduction inequality of each subsystem can be satisfied by a linear Fourier-type conduction law for the temperature and effective temperatures,

$$\mathbf{q}^k = -k^k \nabla_{\mathbf{x}} T, \quad \mathbf{q}_i^c = -k_i^c \nabla_{\mathbf{x}} T_{e_i}, \quad (24)$$

where $\mathbf{q}^k = 1/\det(\mathbf{F}) \mathbf{F} \mathbf{Q}$ and $\mathbf{q}_i^c = 1/\det(\mathbf{F}) \mathbf{F} \mathbf{Q}_i^c$ are the kinetic and configurational contributions to the spatial heat flux, and $k^k \geq 0$ and $k_i^c \geq 0$ are the thermal conductivity associated with kinetic and configurational heat conduction.

Removing the heat conduction inequalities from eq. (23), provides a stronger non-negative criteria for the entropy production from the inter-subsystem heat exchange and internal inelastic power. The criteria can be satisfied most generally by requiring each term to be non-negative. For isotropic materials, we can show that the stress tensor,

$$\mathbf{M}_j = \sum_i^P \frac{T}{T_{e_i}} \mathbf{C}_j^e \frac{\partial \Psi_i^c}{\partial \mathbf{C}_j^e} + \mathbf{C}_j^e \frac{\partial \Psi^k}{\partial \mathbf{C}_j^e}, \quad (25)$$

in eq. (23) is symmetric. This allows the positive dissipation criteria for inelastic deformation and internal heat conduction to be written as,

$$\left(\sum_i^P \frac{T}{T_{e_i}} \mathbf{C}_j^e \frac{\partial \Psi_i^c}{\partial \mathbf{C}_j^e} + \mathbf{C}_j^e \frac{\partial \Psi^k}{\partial \mathbf{C}_j^e} \right) : \mathbf{D}_j^v \geq 0, \quad (26)$$

$$- (T_{e_i} - T) Q_i^{kc} \geq 0,$$

where $\mathbf{D}_j^v = 1/2 (\mathbf{L}_j^v + \mathbf{L}_j^{vT})$ is the inelastic rate of deformation tensor. The above criteria can be satisfied by specifying the following constitutive relations,

$$\mathbf{D}_j^v = \frac{1}{v_j} \left(\sum_i^P \frac{T}{T_{e_i}} \mathbf{C}_j^e \frac{\partial \Psi_i^c}{\partial \mathbf{C}_j^e} + \mathbf{C}_j^e \frac{\partial \Psi^k}{\partial \mathbf{C}_j^e} \right), \quad j = 1 \dots N, \quad (27)$$

$$Q_i^{kc} = -K_i (T_{e_i} - T) \geq 0, \quad i = 1 \dots P, \quad (28)$$

where $v_j > 0$ and $K_i > 0$.

2.3 Governing equation for temperature and effective temperatures

The governing equations for the temperature and effective temperatures are derived from the energy balances in for the kinetic and configurational subsystems, Expanding $\dot{\eta}$ and $\mathcal{W}^{\text{int}}$ in eqs. (21) and (22) and applying the constitutive relations in eqs. (24) and (28) for the heat flux gives,

$$c_g \dot{T} = \kappa^k \nabla_{\mathbf{X}} \cdot (\mathbf{C}^{-1} \nabla_{\mathbf{X}} T) + \sum_i^P K_i (T_{e_i} - T) + \sum_j^N \mathbf{C}_j^e \frac{\partial \Psi^k}{\partial \mathbf{C}_j^e} : \mathbf{D}_j^v - \underbrace{T 2 \frac{\partial \eta^k}{\partial \mathbf{C}} : \frac{1}{2} \dot{\mathbf{C}}}_{\mathcal{H}^{e,k}} + \underbrace{T \sum_j^N \mathbf{C}_j^e \frac{\partial \eta^k}{\partial \mathbf{C}_j^e} : \mathbf{D}_j^v}_{\mathcal{H}^{\text{in},k}} \quad (29)$$

$$\Delta c_i \dot{T}_{e_i} = \kappa_i^c \nabla_{\mathbf{X}} \cdot (\mathbf{C}^{-1} \nabla_{\mathbf{X}} T_{e_i}) - K_i (T_{e_i} - T) + \sum_j^N \mathbf{C}_j^e \frac{\partial \Psi_i^c}{\partial \mathbf{C}_j^e} : \mathbf{D}_j^v - \underbrace{T_{e_i} 2 \frac{\partial \eta_i^c}{\partial \mathbf{C}} : \frac{1}{2} \dot{\mathbf{C}}}_{\mathcal{H}_i^{e,c}} + \underbrace{T_{e_i} \sum_j^N \mathbf{C}_j^e \frac{\partial \eta_i^c}{\partial \mathbf{C}_j^e} : \mathbf{D}_j^v}_{\mathcal{H}_i^{\text{in},c}}, \quad (30)$$

where $c_g = -T \frac{\partial^2 \Psi}{\partial T^2}$ is the heat capacity of the kinetic subsystem and $\Delta c_i = -T_{e_i} \frac{\partial^2 \Psi}{\partial T_{e_i}^2}$ are the heat capacities of the configurational subsystems. The $\mathcal{H}^{e,k}$ and $\mathcal{H}_i^{e,c}$ are the kinetic and configurational contributions to the thermoelastic coupling term, and $\mathcal{H}^{\text{in},k}$ and $\mathcal{H}_i^{\text{in},c}$ are the thermo-inelastic coupling terms. Finally, we divide eq. (30) through by Δc_i to provide a more familiar expression

for the effective temperatures,

$$\dot{T}_{e_i} = \frac{1}{\tau_{R_i}} (T_{e_i} - T) + \frac{1}{\Delta c_i} \sum_j^N \mathbf{C}_j^e \frac{\partial \Psi_i^c}{\partial \mathbf{C}_j^e} : \mathbf{D}_j^v - \underbrace{\frac{T_{e_i}}{\Delta c_i} 2 \frac{\partial \eta_i^c}{\partial \mathbf{C}} : \frac{1}{2} \dot{\mathbf{C}}}_{\mathcal{H}_i^{e,c}} + \underbrace{\frac{T_{e_i}}{\Delta c_i} \sum_j^N \mathbf{C}_j^e \frac{\partial \eta_i^c}{\partial \mathbf{C}_j^e} : \mathbf{D}_j^v}_{\mathcal{H}_i^{\text{in},c}} + \frac{k_i^c}{\Delta c_i} \nabla_{\mathbf{x}} \cdot (\mathbf{C}^{-1} \nabla_{\mathbf{x}} T_{e_i}), \quad (31)$$

where $\tau_{R_i} = A_i/\Delta c_i > 0$ is the structural relaxation time that characterize the rate at which the configurational degrees of freedom evolve to an equilibrium state.

2.4 General Remarks

We now point out important features of the governing equations that arise from the effective temperature thermodynamic framework. These features also appear in the thermomechanical theory of Kamrin and Bouchbinder (2014), though they applied different constitutive assumptions, and provide explanations for a wide variety of nonequilibrium behaviors. The first term on the right hand side of the governing equation (31) for the effective temperatures describes physical aging (structural relaxation) where the inter-subsystem heat transfer drives T_{e_i} to the equilibrium temperature T . In the absence of the remaining terms, eq. (31) simplifies to the structural relaxation model of Tool (Tool 1946). The second term describes the effects of mechanical rejuvenation, where the configurational contributions to the inelastic power drive T_{e_i} away from equilibrium. The competition between physical aging and mechanical rejuvenation allows T_{e_i} to attain a steady-state value different than the equilibrium temperature T in the presence of large plastic deformation. Previously, Buckley et al. (Buckley et al. 2004) developed a constitutive model with mechanical rejuvenation by adding a term dependent on the effective inelastic strain rate to the structural relaxation model of Tool (Tool 1946). Mechanical rejuvenation produces the dynamic softening in the post-yield stress response, which is typically modeled by evolving an internal variable for the intrinsic yield strength with the effective inelastic strain rate (Arruda and Boyce 1993). The final term describes the diffusion of the effective temperatures. Previous works have shown that the coupling between the structural diffusion and inelastic deformation can have significant implications for the development of strain localization (Buckley et al. 2004, Manning et al. 2007, 2009)

The remaining terms are thermomechanical coupling terms caused by the dependence of configurational entropy on the total and inelastic deformation. The coupling terms are also general features of the effective temperature framework that are made explicit in the present constitutive developments. Specifically for amorphous polymers, the thermoelastic coupling term $\mathcal{H}_i^{e,c}$ arise from entropy elasticity and provides a negligible contribution to structural evolution below T_g . The thermo-inelastic coupling term, $\mathcal{H}_i^{\text{in},c}$, potentially provides another source of mechanical rejuvenation in addition to the inelastic power. However, the inelastic deformation below T_g are

accommodate primarily by the stretching of intermolecular and intramolecular bonds, thus $\mathcal{H}_i^{\text{in,c}}$ is also expected to be negligible.

The kinetic and configurational energy sub-balances in eq. (29) and (30) can be summed to give,

$$c_g \dot{T} + \sum_i^P \Delta c_i \dot{T}_{e_i} = -\nabla_{\mathbf{X}} \cdot \mathbf{Q} + \mathcal{W}^{\text{int}} + \mathcal{H}^e + \mathcal{H}^{\text{in}}. \quad (32)$$

Equation (32) shows that the internal inelastic power causes an increase in both $\dot{T}$ and $\dot{T}_{e_i}$. This provides an explanation for the incomplete conversion of the inelastic power to heat as measured by $\dot{T}$. This phenomena is observed for all materials, but is particularly pronounced in polymers, where the fraction of inelastic power converted to heat can be as low as 0.4 (Buckley et al. 2004, Rittel 1999). Moreover, the combined first law also describes the increase in the heat capacity that occurs during the glass transition. Below T_g and in the absence of significant inelastic deformation, it is expected that structural evolution, $\dot{T}_{e_i}$, is small because of the vanishing molecular mobility. Then, the heat capacity in eq. (32) is c_g of the glass. Above T_g , $T_{e_i} = T$, and the heat capacity of the material at equilibrium is $c_r = c_g + \sum_i \Delta c_i$.

2.5 Constitutive model for an amorphous thermoset

In the following, we apply the thermomechanical theory to develop a constitutive model for the acrylate random copolymer network, tBA-co-XLS. For moderate deformations, we apply the decoupled Neo-Hookean functions for the internal energy and entropy densities,

$$\begin{aligned} \Psi^k &= \sum_j^N \frac{(1-a)\mu_j^{\text{neq}}}{2} \left(\text{tr}(\bar{\mathbf{C}}_j^e) - 3 \right) + \frac{\kappa}{4} (J^2 - 2 \log J - 1) + c_g (T - T_0) - c_g T \ln \frac{T}{T_0}, \\ \Psi_i^c &= \frac{T_{e_i} \mu^{\text{eq}}}{T_0} \frac{1}{2} (\text{tr}(\bar{\mathbf{C}}) - 3) + \sum_j^N \frac{a_i \mu_j^{\text{neq}}}{2} \left(\text{tr}(\bar{\mathbf{C}}_j^e) - 3 \right) + \Delta c_i (T_{e_i} - T_0) - \Delta c_i T_{e_i} \ln \frac{T_{e_i}}{T_2}, \end{aligned} \quad (33)$$

where $J = \det \mathbf{F}$ is the volumetric deformation. The $\bar{\mathbf{C}} = J^{-2/3} \mathbf{C}$ and $\bar{\mathbf{C}}_j^e = J_i^{e-2/3} \mathbf{C}_j^e$, where $J_i^e = \det \mathbf{F}_i^e$, are the isochoric parts of the total and elastic deformation tensors. The total free energy density is given by the sum of the kinetic and configurational contributions as defined in eq. (13). The parameters κ is the bulk modulus, μ_j^{neq} are the shear moduli of the N inelastic processes, and T_2 is Kauzmann temperature, where $\eta_c = 0$. We have assumed a simple partitioning of the inelastic internal energy, where $\sum_i^P a_i = a$ is the total configurational contributions to the internal inelastic energy, and $0 \leq 1-a \leq 1$ is the kinetic contribution. To reduce the number of parameters, we also assume that the configurational properties are identically distributed over the P configurational subsystems; thus $\mu_i^{\text{eq}} = \phi_i \mu^{\text{eq}}$, $\Delta c_i = \phi_i \Delta c$ and $a_i = \phi_i a$, where $0 < \phi_i < 1$, $\sum_i^P \phi_i = 1$. The μ^{eq} is the equilibrium (rubbery) shear modulus of the material and Δc is the difference between the rubbery and glassy heat capacity. When the polymer structure is at equilibrium, $T_{e_i} = T$, the total free energy density reduces to a potential that has been widely adopted in nonlinear viscoelasticity theories (Holzapfel 2000, Reese and Govindjee 1997).

The nominal stress response is evaluated according to eq. (18) as,

$$\mathbf{S} = \sum_i^P \phi_i \frac{T_{e_i}}{T_0} \mu^{\text{eq}} J^{-2/3} \left(\mathbf{I} - \frac{1}{3} \text{tr}(\mathbf{C}) \mathbf{C}^{-1} \right) + \sum_j^N \mu_j^{\text{neq}} J_j^{\text{e}-2/3} \mathbf{F}_j^{\text{v}-1} \left(\mathbf{I} - \frac{1}{3} \text{tr}(\mathbf{C}_j^{\text{e}}) \mathbf{C}_j^{\text{e}-1} \right) \mathbf{F}_j^{\text{v}-T} + \frac{\kappa}{2} (J^2 - 1) \mathbf{C}^{-1}, \quad (34)$$

and the Cauchy stress, $\boldsymbol{\sigma} = \frac{1}{J} \mathbf{F} \mathbf{S} \mathbf{F}^T$, is the push-forward of $\mathbf{S}$,

$$\boldsymbol{\sigma} = \frac{1}{J} \sum_i^P \phi_i \frac{T_{e_i}}{T_0} \mu^{\text{eq}} \left(\bar{\mathbf{C}} - \frac{1}{3} \text{tr}(\bar{\mathbf{C}}) \bar{\mathbf{C}} \right) + \frac{1}{J} \sum_j^N \mu_j^{\text{neq}} \left(\bar{\mathbf{C}}_j^{\text{e}} - \frac{1}{3} \text{tr}(\bar{\mathbf{C}}_j^{\text{e}}) \bar{\mathbf{C}}_j^{\text{e}} \right) + \frac{1}{J} \kappa (J^2 - 1). \quad (35)$$

The inelastic flow stress is evaluated from eq. (25) as,

$$\mathbf{M}_j = \sum_i^P \phi_i \left(1 + a \left(\frac{T}{T_{e_i}} - 1 \right) \right) \mu_j^{\text{neq}} \left(\bar{\mathbf{C}}_j^{\text{e}} - \frac{1}{3} \text{tr}(\bar{\mathbf{C}}_j^{\text{e}}) \bar{\mathbf{C}}_j^{\text{e}} \right), \quad (36)$$

Near the glass transition temperature, the difference between T_{e_i} and T is small. For $T/T_{e_1} \approx 1$, the flow stress $\mathbf{M}_j$ reduces to the Mandel stress tensor of nonlinear viscoelasticity theory.

From eq. (27), the inelastic rate of deformation tensor is related to the flow stress through the viscosity. We propose the following model for the dependence of the viscosity on the temperature, nonequilibrium structure, and flow stress to describe the dramatic change in the viscosity through the glass transition and stress-activation of inelastic deformation (Xiao et al. 2013, Adam and Gibbs 1965, Eyring 1936),

$$\mathbf{D}_j^{\text{v}} = \frac{1}{2\nu_j} \mathbf{M}_j, \quad \nu_j = v_j^{\text{ref}} \exp \left(\frac{B}{T \sum_i^P \eta_i^c} \right) \frac{V_S S}{RT} \left[\sinh \left(\frac{V_S S}{RT} \right) \right]^{-1}. \quad (37)$$

The parameter B is a thermal activation energy and V_S is a mechanical activation volume. We have assumed that the viscosities depend on the total flow stress, $S = (\sum_j^N \frac{2}{3} \mathbf{M}_j : \mathbf{M}_j)^{1/2}$, rather than the flow stress of each inelastic process. The latter requires introducing a spectrum of activation volumes, which would dramatically increase the number of parameters.

In the following simulations, we neglect the effect of configurational temperature diffusion, $\nabla_{\mathbf{x}} T_{e_i}$. Then for the specific free energy density potential in eq. (33), the governing equation (31) for the effective temperatures reduces to:

$$\begin{aligned} \dot{T}_{e_i} &= -\frac{T - T_{e_i}}{\tau_i} + \frac{a}{\Delta c} \sum_j^N \mathbf{M}_j : \mathbf{D}_j^{\text{v}} + \frac{J^{-2/3} T_{e_i} \mu^{\text{eq}}}{2 \Delta c T_0} \left(\mathbf{I} - \frac{1}{3} \text{tr}(\mathbf{C}) \mathbf{C}^{-1} \right) : \dot{\mathbf{C}}, \\ \tau_{R_i} &= \tau_{R_i}^{\text{ref}} \exp \left(\frac{B}{T \sum_i^P \eta_i^c} \right), \end{aligned} \quad (38)$$

where we have applied the Adam-Gibbs model (Adam and Gibbs 1965) for the structural relaxation time τ_{R_i} . In addition, we have assumed that the viscosities ν_j in eq. (37) and τ_{R_i} share the same

dependence on T and nonequilibrium structure through the total configurational entropy $\eta^c = \sum_i^P \eta_i^c$ of the material system. We confirmed this assumption experimentally for the tBA-co-XLS polymer previously in Xiao et al. (2013) as briefly described in Sec. 2.1.3. More generally, τ_{R_i} can depend on the entropy of each configurational subsystem, which would permit introduction of a spectrum of activation energies B_i , but this would dramatically increase the number of parameters.

3 Model parameters

The time-dependent behavior of the polymer network is described by a structural relaxation spectrum, that characterizes the evolution of T_{e_i} , and a viscoelastic stress relaxation spectrum, that characterizes the evolution of $\mathbf{F}_j^v$ to equilibrium. For the convenience of parameter determination, we rewrite the structural relaxation times in eq. (38) for T_g as the reference temperature, and express the viscosities in eq. (37) as stress relaxation times at T_g . The configurational entropy can be determined from the free energy density in eq. (33) according to eq. (18),

$$\eta^c(T_{e_i}, \mathbf{C}) = \sum_i^P \left(\Delta c_i \ln \frac{T_{e_i}}{T_2} - \frac{\Delta c_i}{\Delta c T_0} \frac{\mu^{eq}}{2} (\text{tr}(\bar{\mathbf{C}}) - 3) \right). \quad (39)$$

The stress relaxation time is defined as $\tau_{S_j} = \nu_j / \mu_j^{neq}$. The stress and structural relaxation times at T_g are determined by evaluating the stress and structural relaxation times for $\mathbf{F} = \mathbf{1}$ and $T = T_{e_i} = T_g$

$$\begin{aligned} \tau_{S_j}^g &= \nu_j^{ref} \exp \left(\frac{B}{T_g \eta^c(T_g, \mathbf{1})} \right), j = 1 : N, \\ \tau_{R_i}^g &= \tau_i^{ref} \exp \left(\frac{B}{T_g \eta^c(T_g, \mathbf{1})} \right), i = 1 : P. \end{aligned} \quad (40)$$

Combing the above equation with eq. (37) and (38) yields the viscosity and structural relaxation time at any arbitrary temperature T , effective temperature T_{e_i} and deformation as,

$$\begin{aligned} \tau_{S_j} &= \tau_{S_j}^g \exp \left(\frac{B}{T \eta^c(T_{e_i}, \mathbf{C})} - \frac{B}{T \eta^c(T_g, \mathbf{1})} \right) \frac{V_S S}{RT} \left[\sinh \left(\frac{V_S S}{RT} \right) \right]^{-1}, \\ \tau_{R_i} &= \tau_{R_i}^g \exp \left(\frac{B}{T \eta^c(T_{e_i}, \mathbf{C})} - \frac{B}{T \eta^c(T_g, \mathbf{1})} \right). \end{aligned} \quad (41)$$

The following parameters need to be determined for the constitutive model: equilibrium modulus μ^{eq} , bulk modulus κ , thermal activation energy B , Kauzmann temperature T_2 , activation energy for viscous flow V_S , configurational contribution to the internal inelastic energy a , heat capacity of kinetic system c_g , heat capacity of configurational subsystems Δc , stress relaxation spectrum $(\tau_{S_j}^g, \mu_j^{neq})$ and structural relaxation spectrum $(\tau_{R_i}^g, \phi_i)$. Table 1 lists the parameters, their physical significance, and values determined for the 10 wt% tBA-co-XLS material.

Table 1

Parameters of the constitutive model for the polymer-solvent system.

Parameter	Values	Physical significance
μ^{eq} (MPa)	0.53	equilibrium shear modulus
κ (MPa)	1333.3	bulk modulus
$V_S(\text{cm}^3/\text{mol})$	897.5	activation volumen for viscous flow
$B(\text{J/g})$	258.1	thermal activation energy
$T_2(\text{K})$	276.5	Kauzmann temperature
$T_g(\text{K})$	309	glass transition temperature
$T_0(\text{K})$	348	reference temperature
c_g (J/(gK))	1.2	heat capacity of kinetic subsystem
Δc (J/(gK))	0.25	excess heat capacity of configurational subsystems
a	0.5	configurational contribution to the internal inelastic energy
$(\tau_{S_j}^g, \mu_j^{\text{neq}})$	–	discrete stress relaxation spectrum
$(\tau_{R_i}^g, \phi_i)$	–	discrete structural relaxation spectrum

3.1 Determining the stress relaxation spectrum

The onset glass transition temperature $T_g = 36^\circ\text{C}$ was measured from the thermal contraction caused by a $1^\circ\text{C}/\text{min}$ cooling rate (Xiao et al. 2013). The discrete stress relaxation spectrum $(\tau_{S_j}^g, \mu_j^{\text{neq}})$, equilibrium modulus μ^{eq} and bulk modulus κ were determined from the master curve of the storage modulus at reference temperature $T_0 = 75^\circ\text{C}$, obtained from dynamic frequency tests described in Sec. 2.1.2. The method for determining the stress relaxation spectrum was described in detail in Xiao et al. (2013) and was based on a semi-analytical method of Haupt et al. (2000) by using a fractional-derivative model. Here the general procedures were briefly described. For the small-strain uniaxial deformation, the frequency-dependent storage and loss moduli for discrete model and fractional model can be written as,

$$\begin{aligned}
 E'_{\text{disc}}(\omega) &= E^{\text{eq}} + \sum_j^N \frac{E_j^{\text{neq}} \omega^2 \tau_{S_j}^2}{1 + \omega^2 \tau_{S_j}^2}, & E'_{\text{frac}}(\omega) &= E^{\text{eq}} + \frac{E^{\text{neq}}((\omega\xi)^{2\alpha} + (\omega\xi)^\alpha \cos(\alpha\pi/2))}{1 + (\omega\xi)^{2\alpha} + (\omega\xi)^\alpha \cos(\alpha\pi/2)}, \\
 E''_{\text{disc}}(\omega) &= \sum_j^N \frac{E_j^{\text{neq}} \omega \tau_{S_j}}{1 + \omega^2 \tau_{S_j}^2}, & E''_{\text{frac}}(\omega) &= \frac{E^{\text{neq}}((\omega\xi)^\alpha \sin(\alpha\pi/2))}{1 + (\omega\xi)^{2\alpha} + (\omega\xi)^\alpha \cos(\alpha\pi/2)},
 \end{aligned} \tag{42}$$

where E^{eq} is the equilibrium Young's modulus, E_j^{neq} are the nonequilibrium Young's moduli,

$E^{\text{neq}} = \sum_j^N \mu_j^{\text{neq}}$, ξ is the characteristic stress relaxation time and $0 \leq \alpha \leq 1$ represents the breadth of the stress relaxation spectrum. ξ and α were fitted to the master curve of storage modulus.

The viscoelastic relaxation spectra $h_{\text{disc}}(\nu)$ and $h_{\text{frac}}(\nu)$ were calculated from the complex moduli $E^*(i\omega) = E'(\omega) + iE''(\omega)$ using the inverse Stieltjes transform (Haupt et al. 2000). The cumulative spectra $H(\nu) = \int_0^\nu h(u)du$ for the discrete and fractional model can be expressed as,

$$\begin{aligned} H_{\text{disc}}(\nu) &= \sum_j^N E_j^{\text{neq}} \langle \nu - \nu_j \rangle, \\ H_{\text{frac}}(\nu) &= \frac{E^{\text{neq}}}{\alpha\pi} \left[\arctan \left(\frac{(\lambda\xi)^\alpha + \cos(\alpha\pi)}{\sin(\alpha\pi)} \right) - \pi \left(\frac{1}{2} - \alpha \right) \right], \end{aligned} \quad (43)$$

where $\langle \nu - \nu_j \rangle = 1$ for $\nu \geq \nu_j$.

We then assumed a power law distribution for the relaxation frequencies,

$$\nu_j^0 = \nu_{\min}^0 \left(\frac{\nu_{\max}^0}{\nu_{\min}^0} \right)^{\frac{j-1}{N-1}}. \quad (44)$$

where $\nu_{\max}^0$ and $\nu_{\min}^0$ are the maximum and minimum of relaxation frequencies which are chosen based on the frequency region of the master curve.

The nonequilibrium moduli E_j^{neq} were calculated such that $H_{\text{disc}}(\nu)$ forms a step-wise approximation for $H_{\text{frac}}(\nu)$ as shown in Fig. 1.a,

$$\begin{aligned} E_1^{\text{neq}} &= \frac{1}{2}(H(\nu_1^0) + H(\nu_2^0)), \\ E_j^{\text{neq}} &= \frac{1}{2}(H(\nu_{j+1}^0) - H(\nu_{j-1}^0)), 1 < j < N-1, \\ E_N^{\text{neq}} &= E^{\text{neq}} - \sum_j^{N-1} E_j^{\text{neq}}. \end{aligned} \quad (45)$$

The shear moduli are related with Young's moduli through $\mu^{\text{eq}} = E_r/(2(1 + \nu_r))$ and $\mu_j^{\text{neq}} = E_j^{\text{neq}}/(2(1 + \nu_g))$ assuming the rubbery Poisson's ratio $\nu_r = 0.5$ and glassy Poisson's ratio $\nu_g = 0.35$. The bulk modulus can be calculated as $\kappa = E^{\text{neq}}/(3(1 - 2\nu_g))$. The stress relaxation time $\tau_{S_j}^g$ can be evaluated from ν_j^0 ,

$$\tau_{S_j}^g = \frac{1}{\nu_j^0} \exp \left(\frac{B}{T\eta^c(T_g, \mathbf{I})} - \frac{B}{T\eta^c(T_0, \mathbf{I})} \right). \quad (46)$$

The discrete stress relaxation spectrum is plotted in Fig. 1b for $N = 20$ relaxation processes. Figure 2 compares the experimental data and model simulation for the master curve of storage modulus for different number N . Decreasing the number of discrete processes from $N = 20$ to $N = 12$ slightly

Fig. 1. Relaxation spectrum of tBA-co-XLS networks with 10 wt% crosslinker (a) cumulative spectrum, (b) discrete viscoelastic spectrum.

Fig. 2. Experimental data and model fit of master curve of storage modulus.

increased the error of the discrete model representation of the master curve. A further reduction to $N = 8$ produced a noticeably wavy representation of the master curve.

3.2 Determining the structural relaxation spectrum

Numerous works have shown that structural relaxation of different properties are described by different relaxation functions (DeBolt et al. 1976, Scherer 1984). Thus, the enthalpy relaxation spectrum is different than the relaxation spectrum for thermal strains. However, measuring the master curve for enthalpy relaxation is challenging. For this work, we assumed that the thermal strains and enthalpy share the same relaxation spectrum. To determine the structural relaxation spectrum, the temperature-dependent isothermal volumetric relaxation tests were performed as described in Sec. 2.1.3. The master curve can be represented using the discrete structural relaxation

spectrum as (Xiao et al. 2013),

$$\rho_{\text{disc}}(u) = \sum_i^P \phi_i \exp\left(-\frac{u}{\tau_{R_i}^g}\right). \quad (47)$$

Instead of directly fitting $2P$ parameters of the discrete model to the master curve, the following Kohlrausch-Williams-Watts (KWW) stretched exponential model was adopted,

$$\rho_{\text{KWW}}(u) = \exp\left(-\left(\frac{u}{\chi}\right)^\beta\right), \quad (48)$$

where χ is the characteristic structural relaxation time, and $0 \leq \beta \leq 1$ represents the breadth of the structural relaxation spectrum.

The continuous relaxation spectrum for KWW model can be generally represented as (Lindsey and Patterson 1980),

$$h_{\text{KWW}}(\tau) = -\frac{\chi}{\pi\tau^2} \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} \sin(\pi\beta k) \Gamma(\beta k + 1) \left(\frac{\tau}{\chi}\right)^{\beta k + 1}, \quad (49)$$

where $\Gamma(\cdot)$ is the gamma function.

Similar to the procedure of determining the discrete stress relaxation spectrum, we also defined a power law distribution for structural relaxation time,

$$\tau_{R_i}^g = \tau_{\min} \left(\frac{\tau_{\max}}{\tau_{\min}}\right)^{\frac{i-1}{P-1}}. \quad (50)$$

As shown in Fig. 3.a, the discrete structural relaxation spectrum can be determined by a step-wise approximation of the cumulative relaxation spectrum $H(\tau) = \int_0^\tau h(t) dt$ as,

$$\begin{aligned} \phi_1 &= \frac{1}{2} \left(H_{\text{KWW}}(\tau_{R_1}^g) + H_{\text{KWW}}(\tau_{R_2}^g) \right), \\ \phi_i &= \frac{1}{2} \left(H_{\text{KWW}}(\tau_{R_{i+1}}^g) - H_{\text{KWW}}(\tau_{R_{i-1}}^g) \right), \quad 1 < i < P-1, \\ \phi_P &= 1 - \sum_i^{P-1} \phi_i. \end{aligned} \quad (51)$$

The discrete structural relaxation spectrum $(\tau_{R_i}^g, \phi_i)$ is plotted in Fig. 3b for $P = 20$ structural relaxation processes. Figure 4 shows the experimental data and model fit of the master curve of the structural relaxation function for different P processes. Decreasing the number of discrete processes from $P = 20$ to $P = 8$ slightly increased the discrepancy between the experimental measurements and the discrete representation of the master curve of the structural relaxation function.

The choice of N and P is a tradeoff between accuracy and computational efficiency. We chose $N =$

Fig. 3. Structural relaxation spectrum of of tBA-co-XLS networks with 10 wt% crosslinker (a)cumulative spectrum, (b) discrete structural relaxation spectrum

Fig. 4. Experimental data and model fit of master curve of storage modulus.

20 and $P = 20$ for the simulations to accurately describe both the stress and structural relaxation spectrums, which are typically very broad for amorphous polymers. In general, the number of relaxation processes for stress and structural relaxation do not need to be equal.

3.3 Determining the temperature-dependent and stress-dependent parameters

Additional model parameters are needed to describe the dependence of the relaxation times on the temperature, configurational structure, and activation stress. The parameters B and T_2 were determined from the temperature-dependent shift factor $a(T)$ obtained for the master curve of the storage modulus. The activation volume V_S was fit to the difference in the difference in the yield strength of the uniaxial compression stress response measured at two strain rate 0.01/s and 0.001/s at $T = 20^\circ\text{C}$ and with 30 minute prior annealing time as described in Sec. 2.1.5. The DSC experiments were used to determine the excess heat capacity $\Delta c = \sum \Delta c_i$ of the configurational subsystems and heat capacity of the kinetic subsystem c_g . The results of the DSC measurement plotted in Fig. 5 show a slight temperature dependence. However, we assumed a constant value for

c_g for simplicity. The remaining parameter $0 < a < 1$ controls the rate of strain softening. We fit a to the stress response of specimens deformed at 20°C and strain rate 0.01/s with annealing 30 minutes prior deformation described in Sec. 2.1.5.

Fig. 5. DSC scan of the undeformed specimens

4 Results

Equations (35)-(38) describes the constitutive model for the thermomechanical behavior of tBA-co-XLS, assuming negligible effective temperature gradients. The model parameters and methods for determining the parameters from thermomechanical tests are described in Sec. 3. The model was implemented numerically for material point calculations of the uniaxial stress response under different temperatures, annealing times, and deformation conditions corresponding to the experiments described in Sec. 2.1.5. We neglected the effect of temperature change, $\dot{T}$, from heat transfer and inelastic deformation in the simulations. In the following comparisons between modeling and experimental results, only the uniaxial compression tests at $T = 20^\circ\text{C}$, shown in Fig. 6, were used to determine 2 of the model parameters as described in Sec 3. The remainder of the uniaxial compression experiments were outside the range of model calibration.

Figure 6 plots the uniaxial compression stress response at different temperatures spanning the glass transition for strain rates 0.01/s and 0.001/s comparing the experimental results and model predictions. The model was able to capture the transition from a rubbery viscoelastic response to a glassy viscoplastic response, characterized by a yield peak and dynamic softening, with decreasing temperature. Moreover, the model accurately described the effect of strain rate on the temperature-dependence of the stress response through the glass transition, and in particular the decrease in the elastic modulus and the yield strength with strain rate.

Figure 4 compares experimental and model predictions for the uniaxial compression response at $T = 20^\circ\text{C}$ for two consecutive load-unload cycles for different annealing times before the first loading and 1 min annealing time before the second loading as described in Sec. 2.1.5. In the first cycle, the stress response increased until the yield peak at 5% strain then softened to a minimum draw stress before increasing again. The yield peak increased dramatically with the annealing time,

Fig. 6. Uniaxial compression response of tBA-co-XLS networks with 10 wt% crosslinker at different temperatures spanning the glass transition region for applied engineering strain rates (a) 0.01/s and (b) 0.001/s.

attaining a value of 50.5 MPa after annealing for 14 days compared to 33 MPa for the quenched specimen deformed at 0.001/s. The stress response for the different annealing times collapsed onto a single curve during the post yield softening response and remained nearly identical during the second compression cycle. The modeling was able to reproduce all the features of the experiments except the strain hardening response after softening.

Figure 4 plots the experimental and simulation results of specimens with the same thermomechanical history before the first cycle but annealed at different time before the second compression cycle. The specimens exhibited significant recovery during the annealing step before the second compression cycle, because the annealing temperature was only 16°C below the onset glass transition temperature. The yield strength again increased with annealing time, indicating renewed physical aging after cessation of deformation. The model results accurately predicted the magnitude of strain recovery during annealing as well as the increase in the yield strength. Figure 9 compares the yield strength of the first and second uniaxial compression response for different prior annealing times. The results demonstrated good agreement between experiments and simulation. The simulation predicted a smaller yield strength for quenched specimens which indicates the structural relaxation spectra did not fully capture the relaxation processes with short relaxation time. The largest discrepancy occurred for the second compression cycle with a prior 1 min annealing time, where the yield strength predicted by the model was 6 MPa smaller than measured by experiments. We believed that the discrepancy occurred because the model did not take into account orientation hardening, which was evident in the experiments after 20% strain.

To explain the effect of time and plastic deformation on the stress response, the total configurational entropy is plotted for the uniaxial compression simulations in Figs. 4 and 4. Figure 10a shows evolution of the configurational entropy with strain for the case comparing the effects of annealing time before the first loading cycle. Specimens annealed for a longer time started with a lower configurational entropy, which lead to a larger initial resistance to plastic deformation, v_j , and larger yield stress. The configurational entropy increased dramatically to a steady-state value after yielding near 5% strain, caused by plastic deformation. This lowered the viscosity and led to

Fig. 7. Uniaxial compression response of tBA-co-XLS networks with 10 wt% crosslinker for two load-unload cycles and different annealing times prior to the first cycle and 1 min annealing time prior to the second cycle, comparing (a) 0.001/s experiments, (b) 0.001/s simulations, (c) 0.01/s experiments and (d) 0.01/s simulations.

the post-yield softening stress response. The plastic deformation drove the configurational entropy for all cases to attain the same steady-state value. Figure 10b shows the evolution of the configurational entropy during annealing before the second compression cycle. Annealing caused the configurational entropy to evolve towards equilibrium and a lower value, resulting in an increased resistance to plastic deformation and a larger yield stress. Inelastic deformation again drove the configurational entropy towards a common steady state value.

Finally, we simulated the DSC response of quenched and annealed (30 min) specimens before and after 30% compression at 20°C. In the simulation, the specimen was first cooled to -10°C at 3°C/min, and then heated to 70°C at 10°C/min. Results for the enthalpy change with temperature for all cases shown in Fig. 11 captured the features of physical aging and mechanical rejuvenation reported by experiments for amorphous polymers (Hasan and Boyce 1993). Prior to plastic deformation, annealing caused the appearance of an endothermic overshoot. This feature was absent from the quenched condition. Plastic deformation by 30% compression erased the effects created

Fig. 8. Uniaxial compression response of tBA-co-XLS networks with 10 wt% crosslinker for two load-unload cycles at 0.001/s strain rate and 30 min annealing times prior to the first cycle and different annealing time prior to the second cycle, comparing (a) experiments and (b) simulations.

Fig. 9. Yield strength of the uniaxial compression response for different prior annealing time by the prior thermal history, resulting in identical DSC curves for the quenched and annealed conditions. Moreover plastic deformation removed the endothermic overshoot after T_g and created an exothermic undershoot before T_g , which are consistent with experimental observations.

5 Discussion

We have developed a thermomechanical theory for the nonequilibrium behavior of amorphous materials, that strongly couples structural evolution and inelastic deformation. The material structure is described conceptually as configurational degrees of freedom trapped in a distribution of nonequilibrium states with higher effective temperatures. The effective temperatures are driven towards the equilibrium temperature by heat transfer with the instantaneously equilibrating ki-

Fig. 10. The evolution of the configurational entropy with strain during 2 consecutive uniaxial compression cycles comparing: (a) different annealing time prior to the first compression cycle, and (b) different annealing time prior to the second compression cycle.

Fig. 11. Simulation results of DSC for annealed and quenched specimens before and after deformation

netic subsystem and away from the equilibrium temperature by the internal inelastic power and thermomechanical coupling effects. The evolving structure affects the inelastic behavior through the dependence of the viscosity on the temperature and total configurational entropy. These features allows the theory to capture accurately a wide variety of nonequilibrium behaviors, including the glass transition, physical aging, and mechanical rejuvenation. A decrease in the temperature increases the viscosity and brings about the tremendous increase in the stiffness of the glass transition, the appearance of yielding, and plastic deformation. The evolution of the configurational subsystem towards a less mobile (lower entropy) state during physical aging at a constant temperature causes the yield stress to increase with the annealing time. For mechanical rejuvenation, plastic deformation drives the configurational subsystems towards a more mobile state, decreasing the viscosity. This leads to the post-yield strain-softening typical of glassy polymers and the disappearance of the yield peak upon reloading. In previous constitutive models, the post-yield softening behavior was described as an evolution of the yield strength with the plastic strain rate to a steady-state (Boyce et al. 1989, Xiao et al. 2013). This resulted in a steady-state flow stress that

depends on the thermal history, which is contrary to experimental observations.

The ability of the effective temperature thermodynamic framework to describe physical aging and mechanical rejuvenation was demonstrated previously by Kamrin and Bouchbinder (2014). These stem from assumptions of weakly interacting kinetic and configurational subsystems and inter-subsystem heat transfer. The assumptions allowed the first law to be decomposed into energy balances for each subsystem. The present theoretical developments differ from those of Kamrin and Bouchbinder (2014) mainly in the constitutive formulations. We assumed that the Helmholtz free energy density can be additively decomposed into kinetic and configurational contributions, as described by Nieuwenhuizen (1998b), then derived constitutive formulations for the stress, the entropies, and kinetic and configurational contributions to the inelastic power using the arguments of Coleman and Gurtin (1967).

The present theoretical developments also incorporated the effect of a distribution of configurational temperatures to describe the broad spectrum of structural relaxation times observed for glassy polymers. In preliminary studies, we found that using a single effective temperature greatly overestimated the effects of physical aging on the yielding strength. Moreover, a single process model was unable to describe the broad temperature range of the glass transition. Finally, we introduced specific models for the temperature dependence and structure dependence of the structural and stress relaxation times for an amorphous network, based on the Adam-Gibbs and Eyring models, and demonstrated the ability of the thermomechanical theory to accurately describe experimental measurements of mechanical rejuvenation, aging, strain recovery, and the glass transition.

We have made a number of strong assumptions in applying the thermomechanical theory to the tBA-co-XLS random copolymer network. The theory neglects thermal interactions between the configurational subsystems. The implications of these interactions on the structural relaxation are unclear. We assumed that the relaxation time and the viscosity of each structural and stress relaxation process shared same dependence on the temperature and nonequilibrium structure. While we have demonstrated this assumption experimentally for the stress relaxation and thermal strain recovery of tBA-co-XLS, further study is needed for a wider range of amorphous thermosets and thermoplastics. We also assumed that the configurational properties are identically distributed over the P configurational subsystems, thus can be described by the same structural relaxation spectrum. This allowed us to measure the structural relaxation spectrum for the coefficient of thermal expansion and applied it to describe the spectrum of heat capacity Δc_i and fraction of configurational inelastic work a_i . However, previous studies have shown that different properties exhibit different relaxation functions (DeBolt et al. 1976, Scherer 1984). The good quantitative agreement between the simulation and experimental results for the uniaxial compression tests suggest that the assumptions were appropriate for tBA-co-XLS networks near the glass transition temperature. However, more work is needed to develop methods to measure the relaxation functions for the enthalpy and other physical properties far below T_g . Finally, we neglected the effects of temperature changes, $\dot{T}$, and assumed a constant temperature in the material point simulations. This assumption may be valid for the low strain rate and moderate strains in the simulations, but should be included in a more rigorous study.

6 Conclusions

In conclusion, we have developed a thermodynamically consistent theory for coupling structural evolution and inelastic deformation for amorphous polymers. We have shown that with the appropriate constitutive relations for the temperature-dependence and structure-dependence of the viscosities governing inelastic flow and structural relaxation times, the effective temperature theory can capture a wide variety of nonequilibrium behaviors. The theory has the practical benefit of dramatically reducing the number of model parameters. We were able to use the same stress and structural relaxation spectrum and activation energies to reproduce the rate-dependence and time-dependence of the high temperature viscoelastic behavior, low temperature viscoplastic behavior, physical aging, and mechanical rejuvenation for the acrylate network. This provides an efficient predictive modeling tool for applications spanning a large temperature range, such as for material processing and shape memory behavior, long times, and dynamic events. We are currently investigating the ability of the model and model parameters determined from thermomechanical experiments to predict the effect of deformation and temperature history on the enthalpy (e.g, Fig. 11) and other physical properties. The results will provide further insight on the thermodynamic nature of the effective temperatures and limitations of the current modeling framework. We also plan to investigate the ability of the model to capture the effect of structural evolution on the heat generation at different strain rates and the effect of effective temperature diffusion on the development of heterogeneous strain fields and strain localization.

Acknowledgments

We thank Professor Michael Falk for insightful discussion on STZ theory and effective temperature theories. The authors also acknowledge the funding support from the National Science Foundation (CMMI-1130358) and the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-ACO4-94AL85000.

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