Coarse-grained simulation of molecular mechanisms of recovery in thermally activated shape-memory polymers

Brendan C. Abberton [a], Wing Kam Liu [b], Sinan Keten [c],*

[a] Theoretical & Applied Mechanics, Northwestern University, Evanston, IL 60208, United States
[b] Department of Mechanical Engineering, Northwestern University, Evanston, IL 60208, United States
[c] Departments of Mechanical Engineering and Civil & Environmental Engineering, Northwestern University, Evanston, IL 60208, United States

ABSTRACT

Thermally actuated shape-memory polymers (SMPs) are capable of being programmed into a temporary shape and then recovering their permanent reference shape upon exposure to heat, which facilitates a phase transition that allows dramatic increase in molecular mobility. Experimental, analytical, and computational studies have established empirical relations of the thermomechanical behavior of SMPs that have been instrumental in device design. However, the underlying mechanisms of the recovery behavior and dependence on polymer microstructure remain to be fully understood for copolymer systems. This presents an opportunity for bottom-up studies through molecular modeling; however, the limited time-scales of atomistic simulations prohibit the study of key performance metrics pertaining to recovery. In order to elucidate the effects of phase fraction, recovery temperature, and deformation temperature on shape recovery, here we investigate the shape-memory behavior in a copolymer model with coarse-grained potentials using a two-phase molecular model that reproduces physical crosslinking. Our simulation protocol allows observation of upwards of 90% strain recovery in some cases, at time-scales that are on the order of the timescale of the relevant relaxation mechanism (stress relaxation in the unentangled soft-phase). Partial disintegration of the glassy phase during mechanical deformation is found to contribute to irrecoverable strain. Temperature dependence of the recovery indicates nearly full elastic recovery above the trigger temperature, which is near the glass-transition temperature of the rubbery switching matrix. We find that the trigger temperature is also directly correlated with the deformation temperature, indicating that deformation temperature influences the recovery temperatures required to obtain a given amount of shape recovery, until the plateau regions overlap above the transition region. Increasing the fraction of glassy phase results in higher strain recovery at low to intermediate temperatures, a widening of the transition region, and an eventual crossover at high temperatures. Our results corroborate experimental findings on shape-memory behavior and provide new insight into factors governing deformation recovery that can be leveraged in biomaterials design. The established computational methodology can be extended in straightforward ways to investigate the effects of monomer chemistry, low-molecular-weight solvents, physical and chemical crosslinking, different phase-separation morphologies, and more complicated mechanical deformation toward predictive modeling capabilities for stimuli-responsive polymers.

© 2013 Elsevier Ltd. All rights reserved.

* Corresponding author. Tel.: +1 847 491 5282.
  E-mail address: s-keten@northwestern.edu (S. Keten).

1. Introduction

Shape-memory polymers (SMPs) are a promising class of responsive polymeric materials with the capability of being programmed into a temporary shape and then recovering their permanent shape upon exposure to post-deformation external stimuli, including moisture, light, and temperature (Gall et al., 2002; Lendlein et al., 2005; Sokolowski et al., 2007; Gunes and Jana, 2008; Huang et al., 2010; Behl et al., 2010). A wide variety of applications have been conceived for these materials, including self-healing or shape-shifting structural materials, variable-stiffness substrates for cell culturing, and smart biomaterials such as stents and sutures (Wischke and Lendlein, 2010; Yakacki et al., 2007, 2008; Yoshida et al., 2006; Lendlein and Langer, 2002; Bellin et al., 2006; Vaia and Baur, 2008; Davis et al., 2011). The shape-memory behavior in polymers emerges as a result of the material's microstructure, which simplistically can be thought of as a combination of static netpoints that facilitate structural memory and dynamic switching domains, which undergo phase transformation upon triggering. In copolymer SMPs, such as polyurethane-poly ($\epsilon-$caprolactone) (PU-PCL), a miscibility gap between molecular blocks leads to a phase-separated microstructure consisting of frozen hard and active soft phases (D'hollander et al., 2010). The rapid change in molecular mobility upon phase transition in the active phase is the driving force that enables the transition from kinetic arrest in the deformed shape to shape recovery upon relaxation (Lendlein et al., 2005; Behl and Lendlein, 2007; Mather et al., 2009; Behl et al., 2010).

Earlier experimental, analytical, and computational studies have focused on developing a description of the thermomechanical behavior of thermally actuated SMPs. Thus far, constitutive formulations have focused primarily on thermosets with irreversible covalent cross-links. Nonlinear thermoviscoelastic models with elastic coefficients that depend exponentially on temperature have been proposed to reproduce the large change in material properties above and below T_g (Tobushi et al., 2001; Diani et al., 2006). This was combined with a phenomenological viscosity–temperature relationship. Follow-up studies have incorporated a different approach where the distribution of the glassy or rubbery phases has been defined by simple evolution laws of frozen (glassy) and active (rubbery) microdomains (Liu et al., 2006; Qi et al., 2008). A homogenization approach was used to predict the behavior of the SMP from the stress formulation of the individual phases. In an attempt to escape from phenomenological descriptions and circumvent the need to assume volume fractions and their evolution, Nguyen et al. (2008) incorporated the underlying molecular mechanisms responsible for the shape effect to the constitutive model by using a nonlinear Adam-Gibbs model for structural relaxation. More recently, Srivastava et al. proposed a generally applicable theory for SMPs that also takes into account the viscoplastic behavior (Srivastava et al., 2010a, 2010b; Chester and Anand, 2010).

Advancements in phenomenological models have facilitated improved description of the thermomechanical behavior of SMPs, which has been instrumental in device design. However, the underlying physical principles of the mechanical behavior of these materials are very complex, involving intricate relations between temperature, moisture, polymer chemical structure, as well as morphological dynamics of the hierarchical polymer network. For example, it is currently not possible to accurately predict the shape transition temperature and shape-recovery kinetics in SMPs simply from the molecular design of the polymer. As such, there is a need for molecular modeling and a bottom-up approach to the study of SMPs and the effects of molecular design parameters on shape recovery. In pursuit of this fundamental understanding, Diani and Gall (2007) have performed the pioneering work using fully atomistic molecular dynamics (MD) to study the shape-memory properties of *cis*-polyisoprene (*cis*-PI), a homopolymer that can be used to form the switching domains in an SMP. However, the need to take into account the microstructural organization and longer term relaxation behavior in SMP copolymers requires length and time scales that exceed all-atom molecular dynamics simulations. Coarse-grained molecular dynamics (CGMD) offers a mesoscopic modeling paradigm that can potentially bridge the gap between continuum models and all-atom simulations systematically, thereby closing the loop of a bottom-up strategy. A CGMD methodology allows one to reach greater length and time scales, making it possible to impose greater programmed deformations and to observe a larger fraction of the recovery process (perhaps, for some systems, its entirety). Additionally, it allows the study of systems composed of both switching domains *and* netpoints through straightforward assignment of soft- and hard-phase properties within designated geometric/block regions through generic effective potentials. However, there are also significant challenges in using CGMD. For instance, in order to study the effect of polymer chemical structure, a coarse-grained potential must be created for each structure of interest using mathematically rigorous methodologies such as the Inverse Boltzmann Method (IBM) (Müller-Plathe, 2002; Faller, 2004; Sun and Faller, 2006).

In a first attempt to assess the potential of CGMD approach for studying shape-memory behavior in copolymer systems, here we present an analysis of the shape recovery behavior of a two-phase CG polymer model with generic potential terms for hard and soft phases. We reproduce the shape-memory cycle of a thermally activated, binary, shape-memory copolymer through coarse-grained simulation, and we investigate and explain the effects of phase fraction, deformation temperature, and recovery temperature on shape recovery. We discuss how molecular design parameters as well as shape programming conditions can be tailored to alter recovery characteristics, such as the recovery temperature and its breadth. Finally, we conclude with an outlook of the modeling approach on elucidating the effects of moisture, polymer chemistry as well as phase morphology on SMP performance.

2. Materials and methods

2.1. Generic coarse-grained potentials

The key components of a thermally activated copolymer SMP are a glassy phase that remains glassy, and a rubbery phase that undergoes a glass transition, over the range of operating temperatures. It is this combination of glassy and rubbery