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Modeling memory effects in amorphous polymers

R. Sujithra, S.M. Srinivasan *, A. Arockiarajan

Department of Applied Mechanics, Indian Institute of Technology, Chennai 600036, India

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ABSTRACT

A model that can describe the shape memory behavior of amorphous polymers based on theory of multiple natural configurations is presented and implemented for use in applications. The thermodynamic framework presented considers evolution of multiple natural configurations and models the key features, especially, the temperature and deformation dependent change in stiffness and shape memorizing characteristics. A single parameter called *the degree of glass transition* is used to describe the memory locking and releasing characteristics. Using this framework and specialization to small deformations, the developed model is implemented in ABAQUS through VUMAT subroutine feature and correlated with existing epoxy shape memory experiments. Various thermomechanical conditions on structural components such as rods under tension and compression and beams are analyzed. Simulations results confirm that the model is capable of predicting the memory characteristics including the multi-shape memory locking and release mechanisms.

1. Introduction

Shape memory polymers (SMPs) are classified as smart material due to the capability to change their shape temporarily from a permanent shape by the application of a thermo-mechanical stimulus that renders this material can be tuned to possess numerous temporary shapes. While maintaining the operating temperature, it remains in the temporary shape (under low mechanical loads); and by reheating the SMP, it reverts back to the permanent shape. Since it remembers one shape at a time, this process is referred as one way actuation process or one way shape memory effect (Lendlein & Kelch, 2002). The shape change phenomena over the transition temperature makes this material to act as a sensor and also as an actuator. Shape memory polymers are inexpensive, light weight, malleable, damage tolerant, bio-degradable, can be molded into a variety of complex shapes by conventional processing technique and also provide large recoverable strains with distributed actuation for complex shape changes (Monkman, 2000). These highlighted features make shape memory polymers a unique material with wide range of applications in various fields such as deployable components in aerospace structures, bio-medical, smart textiles, self-healing composite systems, optical reflectors, morphing skins and automobile actuators (Lendlein & Langer, 2002; Leng, Lan, Liu, & Du, 2011).

Shape memory polymers are classified based on the cross-links and the transition temperatures (Lendlein & Kelch, 2002; Liu & Mather, 2007). Some of the commonly used shape memory polymers are polyurethanes, polyolefin, epoxy and polyether esters; for an overview refer (Lendlein & Kelch, 2002). Based on the application, SMPs can be tailor-made based on the transition temperature, varying the chemical composition and the preparation method. Material design at the molecular level plays a prominent role in tuning these polymers. Though, lot of experiments are being carried out and reported in

* Corresponding author.
E-mail address: mssiva@iitm.ac.in (S.M. Srinivasan).

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the literature for the successful development of shape memory polymer-based devices, it is necessary to develop theoretical models to predict the shape memory behavior; to be specific in the memory-dependent characteristics (Leng et al., 2011; Xie, 2011).

Several models have been proposed in literature (Zhang & Qing-Sheng, 2012) to describe the behavior of shape memory polymer. The constitutive modeling can be distinguished based on the assumptions of different approaches namely: rheological (Tobushi, Okumura, Hayashi, & Ito, 2001; Bhattacharyya & Tobushi, 2000; Li & Wei, 2011), micromechanical (Liu, Gall, Dunn, Greenberg, & Diani, 2006; Chen & Lagoudas, 2008), phenomenological (Qi, Nguyen, Castrao, Yakacki, & ShandaSa, 2008; Kim, Kang, & Yu, 2010), plasticity (Pritha & Srinivasa, 2011; Baghani, Naghdabadi, Arghavani, & Sohrabpour, 2012; Ghosh & Srinivasa, 2013) and rate dependent (incorporating structural relaxation) models (Nguyen, Qi, Castrao, & Long, 2008; Nguyen, 2013; Westbrook, Kao, Castro, Ding, & Qi, 2011). A thermo-mechanical constitutive model was developed by modifying a standard linear viscoelastic model wherein a slip element is introduced to take into account of internal friction (Tobushi, Hashimoto, Hayashi, & Yamada, 1997). A micro-mechanical model was proposed using the free energy function (ClausiusDuhem inequality) wherein the thermo-mechanical behavior of SMPs can be described using the concept of entropy and internal energy (without explicitly considering the molecular interactions) (Liu et al., 2006). A simple thermo-visco-elastic model (neglect the effects of heat conduction and of pressure on the structural relaxation and inelastic behavior) was presented by incorporating the nonlinear Adam–Gibbs model of structural relaxation into a continuum finite-deformation (Nguyen et al., 2008). Recently, a simple one-dimensional model was proposed in which the hysteretic behavior during heating and cooling phenomena was captured by introducing a yield-stress function (Pritha & Srinivasa, 2011).

While designing SMP based devices, it is important to understand the response of SMP under complex force and different temperature protocols which will help to get an optimal device design. To be specific, it is important to have a minimalistic model with the flexibility of being able to add the additional features such as rate effects, large deformations, cyclic damage and ageing. An attempt has been made by Barot, Rao, and Rajagopal (2008) and Rajagopal and Srinivasa (2004) to model the memory effects for the crystallizable polymers using a thermodynamic framework based on the theory of multiple natural configurations. The evolution equation for the natural configuration during phase change is obtained by maximizing the rate of entropy production. This natural configuration approach (Rajagopal & Srinivasa, 2004) is capable of describing a variety of responses ranging from traditional plasticity to smart materials under a single framework. However, it would be appropriate to choose parameters in the model that directly link to the physical basis of the function characterizing the response. From the designers perspective, for complex geometries, it may be necessary to introduce the simplistic model within finite element framework.

Thus, objective of this work is to model the fundamental behavior of shape memory polymers and conduct numerical test for the memory locking and releasing characteristics by using glass transition temperature as the primary locking mechanism. Multiple natural configuration theory is used as the basic framework for the proposed model and simulation. Two unique features of shape memory polymer, namely the change in stiffness and shape memory characteristics rendered by controlling temperature and deformation (stress) are characterized using a single parameter that is chosen directly link to evolution of multiple natural configurations and therefore, the memory response. The proposed model is limited to small deformations and is implemented using a material subroutine in an existing commercial finite element software (ABAQUS) to analyze device related structural elements. Simulated results based on the developed model is compared with available experimental observations. In addition to that, thermo-mechanical history based memory characteristics, thermal expansion characteristics and multiple shape memory effect are simulated to show the performance of the model.

The paper is organized as follows: Section 2 briefly reviews the structure–property relationship for the shape memory effect exhibited by amorphous polymers in order to highlight the importance of introducing the glass transition degree parameter in this model. The proposed modeling framework is elaborated in Section 3. Section 4 focusing on explaining the framework is specialized to small deformations by assuming that the strains of order 10% or less with linear elastic response in the rubbery as well glassy phases. Simulation results at the material point level as well as for a simple prismatic bar and beam of the material are presented in Section 5. The capabilities of simulating various features of a typical SMP are shown also discussed. Finally, various numerical simulations are carried to show that the model is capable of capturing typical memory characteristics of the SMPs.

2. Structure property relationship in SMPs

The shape memory effect observed in shape memory polymer is represented by the shape memory cycle as shown in Fig. 1 and the corresponding thermo-mechanical loading cycle is shown in Fig. 2, in which the stress (or strain) and the temperature are controlled at different time steps. Depending on temperature, amorphous polymers exist in two different states, the rubbery state and the glassy state. Here, T_g act as a transition switch between these two states. There are three representative temperatures that is generally used to describe the shape memory behavior through glass transition. A high temperature, T_{high} that sees beyond the completion of the effect of glass transition and similarly, a low temperature, T_{low} that sees near completion of the freezing effect of glass transition. The shape memory polymer network consists of chain segments which are interconnected by net points. At temperature above T_g, it exists in rubbery phase. This is characterized by the long chain molecules, oriented in a random fashion and molecules vibrating vigorously with high kinetic energy. The effect of interactions between molecules are generally negligible that it exhibits a state akin to an ideal gas. At T_{high} (step-1), the