Indentation of shape memory polymers: Characterization of thermomechanical and shape recovery properties

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ABSTRACT

A framework for understanding the structure (shape memory and thermomechanical)—property relationships in shape memory polymers (which could be reasonably modeled as comprising of a soft phase and a hard phase) using indentation is developed. A finite element model is developed to predict the complete stress—strain—temperature characteristics of shape memory polymers under uniaxial and indentation loading conditions. By invoking the indentation load—depth response characteristics for a range of temperatures, it is demonstrated that the indentation method predicts the variation of the mechanical properties of shape memory polymers (i.e., elastic modulus) as a function of temperature and microstructural state (i.e., 'glassy' vs. 'rubbery') for materials that exhibit a wide range of transitions (i.e., gradual and sharp). By invoking the indentation deformation characteristics of shape memory polymers for a range of indenter geometries and temperatures, it is demonstrated that the extent of shape recovery is strongly dependent on temperature, microstructural state and constraint loads. By invoking the spatial evolution of stresses during the indentation deformation process and the subsequent recovery process, it is demonstrated that the increase in the internal stresses during the deformation process and the rate of dissipation of the internal stresses during the recovery process is dependent on the indenter geometry and temperature. The predictions of the finite element model for the variations of the mechanical properties and shape recovery characteristics of shape memory polymers with temperature are in reasonable agreement with the trends observed in experiments.

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1. Introduction

Shape memory polymers (SMP), with their unique combination of properties such as their large recoverable strains, low cost, good manufacturability, biocompatibility and biodegradability, are being actively considered for applications in many fields such as in automotive and aerospace structures, biomedical devices, and microsystems [1–11]. Consequently, several experimental studies have focused on developing and characterizing new shape memory polymers with enhanced properties and several modeling studies have focused on developing constitutive models that are capable of accurately capturing the complex thermomechanical properties of shape memory polymers [12–26].

Tobushi et al. [13–15] proposed a simple constitutive model based on spring, dashpot, and frictional elements, which can be applied to some SMPs and has been demonstrated to agree with experiments qualitatively. Liu et al. [12] developed a phenomenological model for small deformations of SMPs where in two internal state variables, i.e., the frozen phase volume fraction, ϕ_f, and the stored strain, ε_s, which describes the strain that is stored in the material during freezing, were invoked to describe the microstructural features of SMPs. Chen et al. [23,24] developed a three-dimensional constitutive theory for large deformations and corresponding linearized small deformations, by extending the work of Liu et al. [1]. Their model was built on nonlinear thermoelasticity and has been shown to describe the thermomechanical properties of the active and frozen phases of the SMPs well. Recently, Srivastava et al. [11] also developed thermomechanically coupled large-deformation constitutive theory to predict the thermomechanical properties of the SMPs and validated their theory with both numerical simulations and experiments.

Alongside the developments in the area of shape memory polymers, there has been considerable interest in developing indentation- or nanoindentation-based methods for the characterization of the mechanical and electromechanical properties of a wide range of materials such as metals, alloys, composites, ceramics, polymers, and piezoelectric materials, e.g. [27–40]. However, limited work has been done to investigate the utility of indentation as a method to characterize the thermomechanical properties and the shape memory characteristics of shape memory

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polymers, e.g. [20,21,41]. Hence, the objectives of the present study are as follows:

(i) to develop a framework based on finite element modeling to capture the key features of the indentation response of shape memory polymers;

(ii) to characterize the variation of mechanical properties of shape memory polymers as a function of temperature and micro-structural state (i.e., 'glassy' vs. 'rubbery') using the indentation method;

(iii) to systematically assess the effects of experimental, environmental and material variables such as indenter geometry, temperature and mechanical properties, respectively, on the effective shape recovery characteristics of shape memory polymers; and

(iv) to validate the finite element models with experimental results.

This paper is organized as follows. Important microstructural features of shape memory polymers, their thermomechanical characteristics as captured by constitutive models, and the basics of the indentation method for characterizing the properties of materials are presented in Section 2. The finite element model developed in the present study to capture the indentation response of SMPs and their shape recovery characteristics are discussed and compared to experimental results in Section 3. Principal conclusions from the present study are highlighted in Section 4.

2. Background on shape memory polymers and indentation

2.1. Molecular structure of shape memory polymers

The important microstructural features of shape memory polymers are highlighted below. At the atomistic scale, a carbon atom in a polymer chain may be located at any point on the revolution cone such that it subtends a 109° angle with the C−C bond. At the molecular scale, a single polymeric chain exhibits a combination of bends, twists and kinks, while at the macroscopic scale a typical polymer contains an entangled mixture of many such molecular chains. In SMPs, amidst the mass of entangled polymeric chains, characteristic netpoints and network chains can be identified. In principle, these netpoints could be created by chemical cross-linking or physical cross-linking. While more than 20 types of SMPs have been identified in the recent past [42], the epoxy-based thermosetting shape memory polymers studied in this paper are chemically cross-linked network polymers. The netpoints are connected by chain segments and determine the permanent shape of SMPs.

Fig. 1 illustrates a simple molecular mechanism for the thermally induced shape memory effect [2,6,42]. At temperatures higher than the glass transition temperature (T_g), the polymer chain segments are relaxed, flexible, and randomly coiled. When an external stress (e.g., a tensile stress) is applied, the polymer chain segments are elongated and the netpoints may also be displaced. As the temperature is reduced below the transition temperature (while the pre-deformed shape is maintained with the help of an external stress), it is envisioned that secondary cross-links are formed between the polymer chain segments that had been stretched. These secondary cross-links help fix the temporary shape (after the external stress is removed) by reducing the mobility and/or the flexibility of the polymer chain segments. Upon re-heating above the transition temperature, these secondary cross-links are released and the original shape is recovered.

The stress−strain−temperature characteristics of the shape memory polymers are quantitatively captured through constitutive models as described in the following Section 2.2.
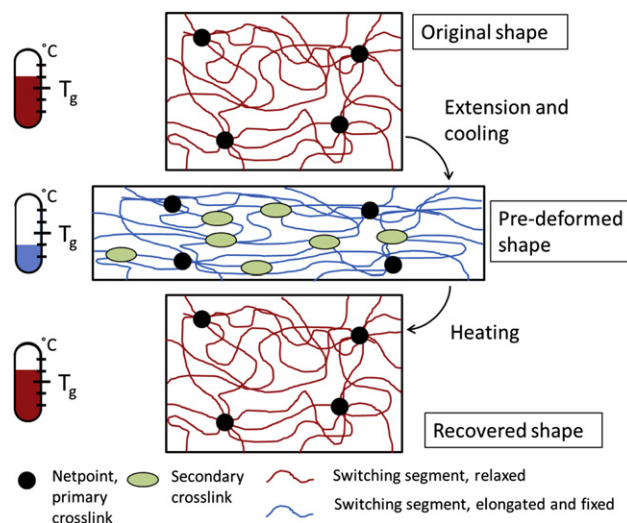

Fig. 1. (a) Schematic illustrating a simple molecular mechanism of the thermally induced shape memory effect [42].

2.2. Constitutive model for shape memory polymers

Two types of constitutive models (i.e., based on viscoelasticity or phase transition) are typically invoked to describe the thermomechanical response of SMPs. In the present study, a simplified two-phase model is invoked where in the shape memory polymer is modeled as a mixture of two phases: the "frozen phase" and the "active phase" (Fig. 2).

The frozen phase (hard phase), which consists of the frozen bonds, is the major phase of a polymer in the glassy state, where the conformational motions corresponding to the high temperature entropic deformation are locked (stored). In contrast, the active phase (soft phase) consists of active bonds so that the free conformational motions can potentially occur and the polymer can exist in the full rubbery state.

In a macroscopic continuum model proposed by Liu et al. [12], two internal state variables: the frozen fraction ϕ_f, and stored strain ε_s, are invoked to describe the evolution of the microstructures in SMPs, where the frozen fraction is the ratio of the volume of frozen phase and the total volume. The phenomenological constitutive model for small deformation of SMPs is given as follows:

$$\sigma = \left[\phi_f S_i + \left(1 - \phi_f \right) S_e \right]^{-1} : (\varepsilon - \varepsilon_s - \varepsilon_T) \tag{1}$$
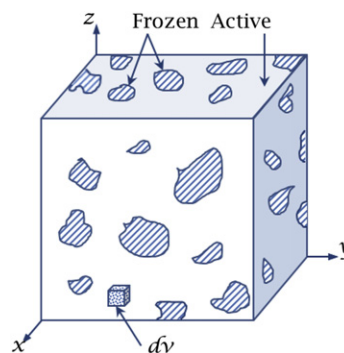

Fig. 2. Schematic illustrating the microstructural features of the shape memory polymer invoked for developing the constitutive model.