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Thermoviscoplastic behaviors of anisotropic shape memory elastomeric composites for cold programmed non-affine shape change

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ABSTRACT

Shape memory polymers (SMPs) can fix a temporary shape and recover their permanent shape upon activation by an external stimulus. Most SMPs require programming at above their transition temperatures, normally well above the room temperature. In addition, most SMPs are programmed into shapes that are affine to the high temperature deformation. Recently, a cold-programmed anisotropic shape memory elastomeric composite was developed and showed interesting low temperature stretching induced shape memory behavior. There, simple, uniaxial stretching at low temperature transformed the composites into curled temporary shapes upon unloading. The exact geometry of the curled state depended on the microstructure of the composite, and the curled shape showed no affinity to the deformed shape. Heating the sample recovered the sample back to its original shape. This new composite consisted of an elastomeric matrix reinforced by aligned amorphous polymer fibers. By utilizing the plastic-like behavior of the amorphous polymer phase at low temperatures, a temporary shape could be fixed upon unloading since the induced plastic-like strain resists the recovery of the elastomer matrix. After heating to a high temperature, the permanent shape was recovered when the amorphous polymer softened and the elastomer matrix contracted. To set a theoretical foundation for capturing the cold-programmed shape memory effects and the dramatic non-affine shape change of this composite, a 3D anisotropic thermoviscoelastic constitutive model is developed in this paper. In this model, the matrix is modeled as a hyperelastic solid, and the amorphous phase of the fibrous mat is considered as a nonlinear thermoviscoplastic solid, whose viscous flow resistance is sensitive to both temperature and stress. The plastic-deformation like behavior demonstrated in the fiber is treated as nonlinear viscoplasticity with extremely high viscosity or long relaxation time at zero-stress state at low temperature. The anisotropic viscoplastic property of the fibrous mat is captured by an isotropic fibrous network superimposed with an oriented fibrous network. The material parameters in the model are identified from the experiments on the fibrous mat and on the composites, respectively. The cold-programmed shape memory behaviors of the composite are predicted by simulations and compared with experiments without further adjusting the material parameters. Good agreement is observed, indicating the ability of the present model to capture the anisotropic viscoplastic and shape memory behaviors. By using the developed constitutive model, effects of loading rate and fiber volume fraction

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on cold programmed shape memory behavior are discussed. Furthermore, the constitutive relation is applied to a mechanical model to study the cold-programmed curling of the laminates.

1. Introduction

Shape memory polymers (SMPs) have the ability to “memorize” a permanent shape. After being fixed to a temporary shape, an SMP can recover its original permanent shape upon activation by an external stimulus (Hu and Zhuo, 2010; Hu et al., 2012; Lendlein and Kelch, 2002; Leng et al., 2011; Liu et al., 2007; Lu et al., 2013; Meng and Li, 2013; Yang et al., 2014). In a typical thermally triggered SMP, which is the most common and intensively researched, the SMP is first heated to a high temperature above a transition temperature and deformed into a new shape; it is then cooled to below the transition temperature; upon removal of the external load and constraints, the SMP maintains the programmed shape. Upon heating to a temperature above the transition temperature, it recovers its original shape. The typical transition temperatures used for achieving shape memory (SM) effects include those for glass transition or crystal-melt transition (Ge et al., 2013b; Nguyen, 2013). Most applications require that the materials have the programmed shape and the permanent shape at room temperature, which means that the transition temperature should be well above the room temperature; thus, the programming temperature is typically in the range of 50–120 °C, depending on the material systems. This leads to two potential issues. First, shape programming at high temperatures is not easy, as heating is typically done in a thermal chamber, in which manipulating the sample is not a convenient task if one would like to achieve a complicated shape. Second, heating requires more energy, which in general is undesirable. It is also worth mentioning that despite the extensive number of studies on the SM phenomena, the past studies focused mainly on isotropic behaviors, and comparatively, very little attention has been given to the construction of SMP systems that exhibit anisotropic behavior while such anisotropy is very common in natural materials (Rodriguez et al., 2013). Moreover, most SM effects in SMPs so far are limited to affine programming, i.e., the temporary shape is an affine transformation of the deformed shape at high temperature. Cold programming SM effects have been explored in Li and Xu (2011), Li and Shojaei (2012), Ping et al. (2005) and Shojaei et al. (2013). For example, Li and Xu (2011) have developed an isotropic viscoelastic model which was demonstrated well in capturing isotropic cold compression shape memory effect. Li and Shojaei (2012) and Shojaei et al. (2013) studied the evolution of microstructures in fibers and the feasibility of applying them to self-healing materials. An anisotropic shape memory effect has been discussed under high temperature programming in Ge et al. (2013a). Very few non-affine transformations have been seen in the past, and systematic studies of combined cold, non-affine programming and anisotropic effects are lacking.

Recently, Rodriguez et al. (2013) reported an anisotropic shape-memory elastomeric composite (ASMEC), which was constructed by infiltrating Sylgard-184 silicone resin into the the oriented electrospun fiber mat of poly(vinyl acetate) (PVAc). The silicone was subsequently cured, forming a rubbery matrix. There, PVAc served for shape memory fixing through its glass transition, and Sylgard-184 served as the soft matrix assisting in the SM recovery. Because the fibers had a dominant orientation, the shape fixing ability depended on the fiber orientation, and thus, the composite exhibited anisotropic SM effects, as was shown in a recent study (Ge et al., 2013a). In addition, it was demonstrated that the composites could be deformed at low temperature when the fibers were still in a glassy state. The excessive deformation of the fiber mat led to plastic-like deformation, which prevented the matrix material from recovering upon removal of the external load, allowing cold programming of SMPs. Moreover, when ASMECs were laminated into a multilayer structure, the cold programming could introduce non-affine shape change. For example, a simple stretching at low temperature could change a strip of laminate into a helix due to the non-uniform shape fixing resulting from fiber anisotropy. When heating to a higher temperature above the glass transition temperature of PVAc, the PVAc fibers became a viscous melt, thus permitting the recovery of the matrix material through its rubber elasticity. Three apparent advantages of this new class of SM composites are important for potential future applications. First, a continuously varying fixity is possible as the loading direction changes, which can be taken as a new design variable. Second, the cold programming can be done at the room temperature, which is very convenient and energy saving. Third, the ability to achieve non-affine shape programming further increases the design flexibility, as deforming a sample into a complicated shape can be non-trivial whilst non-affine shape change can provide an easy solution. These advantages of ASMECs widen the application prospects in medical devices and actuators/sensors. For example, ASMECs can find application in mimicking the skin membrane of a bat wing, a distinctive soft anisotropic fibrous network. In addition, a similar mechanical anisotropy could be useful for micro-air vehicle systems featuring flapping wings, with the ASMEC helping to improve the adaptability, agility, and speed in unmanned aerodynamic vehicles (Rodriguez et al., 2013).

To establish a theoretical foundation providing a comprehensive understanding of thermomechanical behaviors for design with ASMEC materials, a constitutive model is needed. Since the cold-programmed ASMEC utilizes the plastic-like deformation behavior of the fibrous mat to obtain anisotropic shape fixity at low temperatures and the programmed shape can recover upon heating, the theoretical model should be able to capture the plastic-like and anisotropic behaviors of the