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Thermomechanics of printed anisotropic shape memory elastomeric composites

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ABSTRACT

Shape memory polymers (SMPs) are a class of active materials that have the capability of fixing a temporary shape and recovering to a permanent shape in response to environmental stimuli. While SMPs have been studied intensively, researchers paid comparatively fewer attentions to SMPs exhibiting anisotropic mechanical and shape memory behaviors by controlling the microscopic architectures. At the same time, the rapidly developed three-dimension (3D) printing technologies enable us to directly print complex 3D structures with multimaterials and provide possibilities to fabricate anisotropic shape memory polymer by precisely controlling the microstructure of fibers. In this paper, we present a new approach for fabricating printed anisotropic shape memory elastomeric composites (p-ASMECs) by taking advantage of 3D printing. In the fabrication process, an elastomer is first printed as matrix and the orientation of fibers is defined by the precisely printed channels. By interrupting the printing process, the printed channels are filled with the crystallizable polymeric fibers that endow the shape memory effect into the composite system. The p-ASMECs exhibit large, controllable anisotropy in both mechanical and shape memory behaviors that can be precisely controlled by geometric parameters of the microstructure such as fiber's volume fraction and position in space. To facilitate design of p-ASEMCs, we also developed a thermomechanical constitutive framework to describe the complex, anisotropic, larger deformation thermomechanical behaviors of p-ASEMCs. The developed constitutive model, used to explain the phenomenon that the lowest stiffness of p-ASEMCs occurs at the fiber orientation angle $\theta \approx 55°$, successfully predicts the anisotropic shape memory behavior of p-ASMECs, guides the design to enhance the temporary shape fixity, and simulates the shear deformation of the temporary shape after completely releasing the external constraints.

1. Introduction

Shape memory polymers (SMPs) are a class of active materials that have the capability of fixing a temporary shape and recovering to a permanent shape in response to an environmental stimulus such as: heat (Lendlein and Kelch, 2002, 2005; Liu et al., 2007; Mather et al., 2009; Xie, 2011), light (Jiang et al., 2006; Koerner et al., 2004; Lendlein et al., 2005; Li et al., 2003; Long et al., 2010b, 2011, 2009; Scott et al., 2006, 2005), moisture (Huang et al., 2005), magnetic field (Mohr et al., 2006), among others. While SMPs have been investigated intensively, researchers paid comparatively fewer attentions to SMPs exhibiting anisotropic mechanical and shape memory behaviors by controlling the microscopic architectures (Burke and Mather, 2012; Ge et al., 2013c; Ishida et al., 2012; Rodriguez et al., 2013). Recently, Luo and Mather Luo and Mather, (2009) reported a novel approach of using electrospinning to fabricate shape memory elastomeric composites (SMECs). In a SMEC system, the matrix behaves as an elastomer over the entire operating temperature range and the crystallizable polymer is taken as fibers and has a melting temperature T_m within the temperature range. At a temperature above T_m, the fibers are viscous melts with a stiffness less than that of the elastomeric matrix (often it can be taken to be zero). Below T_m, they are a semicrystalline solid with a stiffness greater than that of the elastomeric matrix. This transition allows a composite to be deformed at a high temperature T_H ($T_H > T_m$) and then when cooled to a low temperature T_L ($T_L < T_m$), the melt-crystal transition of the fibers serves as a switch to fix the deformation. Upon heating, the fibers melt and the original shape is recovered. Based on the natural paradigm for SMECs, Rodriguez et al. (Rodriguez et al., 2013)

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developed a method of constructing anisotropic shape memory composites (ASMECs) by electrospinning aligned fibers and infiltrating with an elastomeric matrix. Characterization tests show that both thermomechanical properties and shape memory behaviors of the composites are anisotropic and highly fiber orientation dependent. Thanks to the fast development of three-dimension (3D) printing technology, scientists and researchers nowadays are able to directly print complex 3D structures with active materials (Ge et al., 2014a, 2013c, 2016; Mao et al., 2015a; Raviv et al., 2014; Sydney Gladman et al., 2016; Tibbits, 2013). As the printed 3D structures change configurations over time in response to external stimuli, 3D printing with active materials is also referred to as "4D printing" (Ge et al., 2014a, 2013c). Due to high resolution of the current multi-material 3D printers, the micro architecture of the printed structures can be precisely controlled. Thus, the macro behavior of the printed structures can be well designed and engineered, as long as the environmental-mechanical behaviors of the used active materials are thoroughly understood (Ge et al., 2014a, 2013c).

Along with the rapid development of SMPs, constitutive models also have been developed for the purpose of understanding the shape memory behavior and application design. For example, thermoviscoelastic constitutive models have been developed for amorphous SMPs (Ames et al., 2009; Anand et al., 2009; Castro et al., 2010; Diani et al., 2006; Nguyen et al., 2008; Qi et al., 2008; Srivastava et al., 2010a, b; Westbrook et al., 2011; Yu et al., 2014); Thermomechanical constitutive models using the notion of multiple natural configurations have been developed for semicrystalline SMPs (Barot et al., 2008; Chen and Lagoudas, 2008a, b; Westbrook et al., 2010). Recently, Ge et al. developed a 3D thermomechanical constitutive model for SMECs, which consists of an elastomer matrix and crystallizable fiber networks (Ge et al., 2012). In that model, the SMEC is developed by treating matrix and fiber network as a homogenized system of multiple phases, and the fiber networks are taken to be an aggregate of melt and crystalline regions. It also gives an evolution rule for crystallization and melting from existing theories (Ge et al., 2012). Besides the constitutive models for the isotropic soft materials, hyperelastic constitutive models for anisotropic fiber-reinforce composites have been studied intensively (deBotton et al., 2006; Guo et al., 2006, 2007; Idiart, 2008; Kao et al., 2010; Lopez-Pamies and Idiart, 2010, 2011; Merodio and Ogden, 2003, 2005; Qiu and Pence, 1997a, b; Rudykh and deBotton, 2012; Spencer, 1972, 1984). However, the studies on modeling of anisotropic shape memory polymers were comparatively limited (Mao et al., 2015b; Nguyen et al., 2007).

In this paper, in order to enrich material selections and add new mechanisms to trigger the structure motion as well as to study the shape memory effect of anisotropic SMPs, we introduce an approach of fabricating printed anisotropic shape memory elastomeric composites (p-ASMECs) *via* control of the composite architecture by taking advantage of three-dimension (3D) printing. In the fabrication process, an elastomer is first printed as matrix and the orientation of fibers is defined by the precisely printed channels. By interrupting the printing process, the printed channels are filled with the crystallizable polymeric fibers that endow the shape memory effect into the composite system. Through thermomechanical experiments, we observe the p-ASMECs exhibit large, controllable anisotropy in both mechanical and shape memory behaviors. As 3D printing allows us to construct composites with complex microscopic architectures by varying fiber's volume fraction and position in space, we envision that this approach can be used to realize composites with much more complex, but highly-tailorable, shape memory behavior. To better understand the complex anisotropic thermomechanical phenomenon of p-ASMECs and to facilitate the material and structure design with p-ASMECs, we also developed a thermomechanical constitutive framework that incorporates the phase evolution theory for soft active materials (SAMs) (Ge et al., 2012; Long et al., 2010a; Rajagopal and Srinivasa, 1998a, b) into the existing theories for fiber reinforced hyperelastic composites (Agoras et al., 2009; deBotton et al., 2006; Guo et al., 2006, 2007; Lopez-Pamies and Idiart, 2010, 2011). The developed framework successfully predicts the complex anisotropic thermomechanical behaviors, analyzes the anisotropy by investigating the deformation on fibers, the shear stress/deformation on composites, and simulates the shear deformation of temporary shape after completely releasing the external constraints. This paper is arranged in the following manner: In Section 2, the fabrication process of p-ASMECs is introduced; the thermomechanical experiments for p-ASMECs are presented, including DMA tests, uniaxial tensions, shape memory behavior tests and thermal strain measurements. Section 3 introduces the development of the anisotropic thermomechanical constitutive framework. In Section 4, we introduce the parameter identification, compare the model predictions of shape memory behaviors to experimental results, perform the parametric studies, and simulate the shear deformation of temporary shape after completely releasing the external constraints.

2. Materials and experiments

2.1. Fabrication and composite lamina

The concept of p-ASMECs is realized *via* a processing approach shown in Fig. 1a-d along with the snapshots (Fig. 1e-h) during the fabrication. We first design the composite lamina consisting of a thin layer with a single row of fibers oriented with an angle θ from the loading (x-) direction (Fig. 1i and j) in a CAD file. In the composite lamina, the matrix is printed with the elastomeric material and the fibers are defined as void channels to be filled with a sacrificial material (a hydrophilic gel) that can be easily removed. We designed samples with variable fiber orientations (θ =0°, 15°, 30°, 45°, 60°, 75° and 90°) and fiber volume fraction (v_f=0.167). Fibers are square with a side length of 1 mm and the lamina is 3 mm thick (Fig. 1i). During the fabrication, the 3D printer deposits droplets of polymer ink (64 μm in standard mode; 32 μm in high-resolution mode) at ~70 °C, and then wipes them into a smooth film and photopolymerizes the film with ultraviolet (UV) (Ge et al., 2014a, 2013c). Once the channels form completely, we implant crystallizable polymer, poly (ε-caprolactone) (PCL; M_w =70000g/mol, Sigma-Aldrich, St Louis, MO), fibers into the printed elastomeric matrix by interrupting the printing (Fig. 1a and e), removing sacrificial fibers (Fig. 1b and f), and impregnating the cavities with PCL melts at ~80 °C, a temperature at which the viscosity of PCL is adequate to permit impregnation and wiping to yield embedded fibers with a smooth surface (Fig. 1c and g). We then complete printing of the matrix which completely encapsulates the PCL fibers (Fig. 1d and h). In order to precisely control the point where the printing process needs to stop for removing the sacrificial fibers, we also design an indicator mark that can easily be monitored visually and alert us to pause the printing process (Fig. 1a-d). While we impregnate the vacated cavities with PCL to create crystallizable thermoplastic fibers, one can also embed more rigid fibers or other components (Stiltner et al., 2011) to realize different functionalities.

2.2. DMA tests

DMA tests were conducted using a dynamic mechanical analyzer (Q800 DMA, TA Instruments) for p-ASMECs with different fiber orientations and the neat elastomeric matrix material. The dimension of all samples is ~15 mm × 7 mm × 3 mm. Before tests, samples were equilibrated at 30 °C for 60 min to make fibers (PCL)

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