THERMO-MECHANICAL BEHAVIORS OF SHAPE MEMORY ELASTOMER COMPOSITES

Qi Ge, Martin Dunn & H. Jerry Qi
Department of Mechanical Engineering, University of Colorado, Boulder, CO, 80309, USA

Summary Shape memory polymers (SMPs) are polymers that can fix a temporary shape and recover their permanent shape in response to environmental stimuli. Recently, a novel shape memory elastomeric composite (SMEC), composed of Sylgard and PCL, was reported. In SMEC, Sylgard as an elastomeric matrix provides rubbery elasticity, while PCL, through crystal-melt transition, serves as a reversible "switch phase" for shape fixing and recovery. This paper presents a constitutive model that includes a kinetic description of non-isothermal crystallization and melting, which imparts SM capability of the SMEC system. The model assumes that the newly formed crystal phases are in the undeformed state, which tracks the kinematics of evolving phases. The model accurately captures SM behaviors of the SMEC system exhibited in experiments.

INTRODUCTION

Shape memory polymers (SMPs) are an emerging class of smart materials that can fix the temporary shape and recover their permanent shape in response to environmental stimuli[1, 2]. Compared to shape memory alloys, the advantages of SMPs are low density, large shape changes in excess of 400% and the relatively inexpensive fabrication process [1, 2]. Recently, Luo and Mather[3] reported a novel approach to develop a shape memory elastomeric composite (SMEC) by embedding a crystallizable thermoplastic fiber network into an elastomeric matrix. In their approach, a poly (ε-caprolactone) (PCL) was first electrospun into a fiber network (or mat). This fiber network was then immersed into a silicone rubber (Sylgard 184) pre-polymer solution, which was then chemically crosslinked to produce a SMEC system: Sylgard serves as an elastomeric matrix and provides rubber elasticity, while the PCL fiber serves as a reversible "switching phase" for shape fixing and recovery through the crystal-melt transition. In a thermo-mechanical cycle, the SMEC is heated to $T_H > T_m$ (T_m, the melting temperature of PCL), deformed at T_H, then cooled to $T_L < T_m$ while maintaining the external load. During cooling, PCL undergoes a phase change from a polymer melt to a semicrystalline polymer. After unloading at T_L, the temporary shape is fixed due to the crystallized PCL. Heating back to T_H, where PCL melts and the SMEC recovers its permanent shape. Because the operational temperatures for a SM cycle are much higher than the glass transition temperatures for Sylgard and PCL, the modulus of SMEC is a few MPa at $T_H > T_m$ and ~10 MPa at $T_L < T_m$. The approach by Luo and Mather for Sylgard/PCL SMEC provides a paradigm for developing a wide array of smart polymer composites with different chemistries that utilize melt-crystal transition in polymers to achieve the shape memory effect. In this paper, a three-dimension (3D) constitutive model is developed to describe the shape memory behavior of the novel SMECs.

THERMOMECHANICAL BEHAVIORS

The SMEC as received was cut into 13.86×2.77×0.68*mm* rectangular thin film samples for thermal mechanical testing to demonstrate the shape memory behaviors. The testing procedure follows the described shape memory cycle with $T_m = 27°C$, $T_H = 80°C$, and $T_L = 5°C$. The stress-temperature-strain behaviors under three different imposed nominal stresses (0.1MPa, 0.15MPa, 0.2MPa) are shown in Fig. 1.

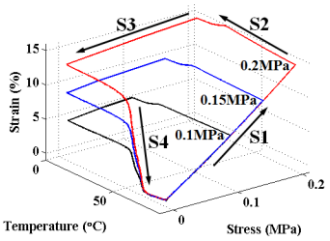

Figure 1. Shape memory behaviors of Sylgard/PCL SMEC with different imposed stresses.

BRIEF MODEL DESCRIPTION

A continuum thermo-mechanical constitutive model frame for the Sylgard/PCL SMEC is developed by treating matrix and fiber network as a homogenized system of multiple phases. The matrix is taken as a conventional elastomer and the fiber network is taken to be an aggregate of melt and crystalline regions. The evolution of the fiber aggregate is described by existing theories of crystallization. Major assumptions used in the model are: (i) the external loading does not affect the morphology of PCL crystals; (ii) During crystallization, PCL crystals are formed in a stress-free (natural) configuration [4, 5]; (iii) Inelastic deformation of PCL crystals is not considered.

Fig. 2 shows the 1D analogy of the constitutive model. The model decomposes the deformation of the material into thermal deformation and mechanical deformation (Fig. 2):

$$\mathbf{G} = \mathbf{G}^M \mathbf{G}^T = \mathbf{F}\mathbf{G}^T, \mathbf{F} = \mathbf{G}^M , \tag{2}$$

where $\mathbf{G}$ is the total deformation gradient, $\mathbf{G}^M$ is the mechanical deformation gradient, $\mathbf{G}^T$ is the thermal deformation

gradient. For the convenience of model description, we set $\mathbf{F}=\mathbf{G}^{M}$ and use $\mathbf{F}$ to represent mechanical deformation gradient. The mechanical contribution from Sylgard matrix is represented by a hyperelastic spring in Fig. 2. The PCL network changes its crystallinity with temperature: When $T>T_m$, PCL melts do not carry load; when $T<T_c$, PCL crystallizes and can carry load. Since crystallization of PCL is a continuous and time dependent process, we further divide PCL crystals into small phases formed at different times with volume fraction Δv_i^c with a deformation gradient of $\mathbf{F}_{i\to m}$. The total Cauchy stress $\boldsymbol{\sigma}^{total}$ is given by:

$$\boldsymbol{\sigma}^{total}=v_{Syl}\boldsymbol{\sigma}^{Syl}+v_{Syl}\boldsymbol{\sigma}^{PCL}, \qquad (3)$$

where $\boldsymbol{\sigma}^{Syl}$ and $\boldsymbol{\sigma}^{PCL}$ are the stresses in the Sylgard matrix and the PCL network, v_{Syl} and v_{PCL} are volume fractions of the Sylgard matrix and the PCL fibers, which are determined by fabrication and $v_{Syl}+v_{PCL}=1$. More details regarding the model will be presented during the conference.

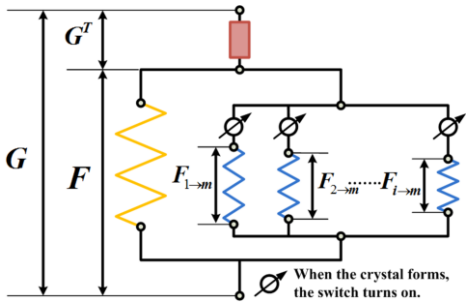

Figure 2. 1D analogy of the constitutive model for the Sylgard/PCL SMEC: The block on the top represents the thermal stretch due to thermal expansion and contraction.

RESULTS

The experimental result from the thermo-mechanical cycle with 0.15MPa imposed stress was used to fit the model parameters and the result is shown in Fig. 3a. There are totally 18 parameters, 12 parameters were obtained from fabrication, experiments, handbooks and literatures, and 6 parameters were determined by parameter fitting. These parameters were then used to predict the thermo-mechanical behaviors with 0.10MPa and 0.2MPa imposed stresses. Fig. 3b shows the comparison between model predictions and experimental results, which show an excellent agreement, validating the model capability of capturing the physics underlying the thermomechanical behaviors.

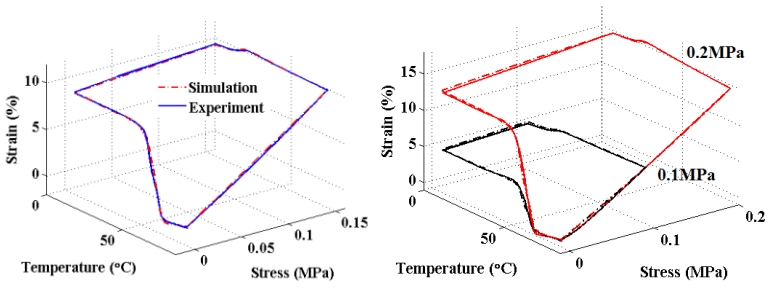

Fig. 3. A) Model fitting to the experimental result for the case of imposed stress 0.15MPa. (a) Stress-Temperature-Strain plot. (b) Strain-Temperature plot. B) Comparisons between model predictions (solid-dot line) and experimental results (solid line) for the cases of 0.1MPa (red) and 0.2MPa.

CONCLUSIONS

This paper investigates the thermomechanical behaviors of SMEC and presents a first 3D constitutive modeling frame to describe the shape memory effects of SMECs. This modeling frame includes kinetics of non-isothermal crystal-melt transition of PCL, mechanical and thermal behaviors. The kinetics for the crystal-melt transition utilizes the Evans theory and Hoffman-Lauritze expression for crystallization then expands Hoffman-Lauritze expression to consider melting. The kinematics of evolving phases is tracked by using the assumption that newly formed the crystalline phase is undeformed and stress-free. The model accurately captures thermomechanical and shape memory behaviors.

References

[1] Lendlein, A. and S. Kelch, *Shape-memory polymers as stimuli-sensitive implant materials.* Clinical Hemorheology and Microcirculation, 2005. **32**(2): p. 105-116.
[2] Lendlein, A. and S. Kelch, *Shape-memory polymers.* Angewandte Chemie International Edition in English, 2002. **41**(12): p. 2035-57.
[3] Luo, X.F. and P.T. Mather, *Preparation and Characterization of Shape Memory Elastomeric Composites.* Macromolecules, 2009. **42**(19): p. 7251-7253.
[4] Rajagopal, K.R. and A.R. Srinivasa, *Mechanics of the inelastic behavior of materials. Part II: Inelastic response.* International Journal of Plasticity, 1998. **14**(10-11): p. 969-995.
[5] Rajagopal, K.R. and A.R. Srinivasa, *Mechanics of the inelastic behavior of materials - Part 1, theoretical underpinnings.* International Journal of Plasticity, 1998. **14**(10-11): p. 945-967.