Thermomechanical behavior of shape memory elastomeric composites

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\textbf{A B S T R A C T}

Shape memory polymers (SMPs) can fix a temporary shape and recover their permanent shape in response to environmental stimuli such as heat, electricity, or irradiation. Most thermally activated SMPs use the macromolecular chain mobility change around the glass transition temperature ($T_g$) to achieve the shape memory (SM) effects. During this process, the stiffness of the material typically changes by three orders of magnitude. Recently, a composite materials approach was developed to achieve thermally activated shape memory effect where the material exhibits elastomeric response in both the temporary and the recovered configurations. These \textit{shape memory elastomeric composites} (SMECs) consist of an elastomeric matrix reinforced by a semicrystalline polymer fiber network. The matrix provides background rubber elasticity while the fiber network can transform between solid crystals and melt phases over the operative temperature range. As such it serves as a reversible “switching phase” that enables shape fixing and recovery. Shape memory elastomeric composites provide a new paradigm for the development of a wide array of active polymer composites that utilize the melt–crystal transition to achieve the shape memory effect. This potentially allows for material systems with much simpler chemistries than most shape memory polymers and thus can facilitate more rapid material development and insertion. It is therefore important to understand the thermomechanical behavior and to develop corresponding material models. In this paper, a 3D finite-deformation constitutive modeling framework was developed to describe the thermomechanical behavior of SMEC. The model is phenomenological, although inspired by micromechanical considerations of load transfer between the matrix and fiber phases of a composite system. It treats the matrix as an elastomer and the fibers as a complex solid that itself is an aggregate of melt and crystal phases that evolve from one to the other during a temperature change. As such, the composite consists of an elastomer reinforced by a soft liquid at high temperature and a stiff solid at low temperature. The model includes a kinetic description of the non-isothermal crystallization and melting of the fibers during a temperature change. As the fibers transform from melt to crystal during cooling it is assumed that new crystals are formed in an undeformed state, which requires careful tracking of the kinematics of the evolving phases which comes at a significant computational cost. In order to improve the computational efficiency, an effective phase model (EPM) is adopted to treat the evolving crystal phases as an effective medium. A suite of careful thermomechanical experiments with a SMEC was carried out to calibrate various model parameters, and then to demonstrate the ability of the
1. Introduction

Shape memory polymers (SMPs) are an emerging class of smart materials that can fix a temporary shape and recover the permanent shape in response to environmental stimuli such as heat, electricity, or irradiation (Lendlein and Kelch, 2002, 2005). Compared to shape memory alloys, the advantages of SMPs are low density, the ability to endure large shape changes in excess of 400%, and relatively inexpensive fabrication processes (Lendlein and Kelch, 2002, 2005). A large number of SMPs have been developed for microsystem actuation components, biomedical devices, aerospace deployable structure, and morphing structures.

In SMPs triggered by a temperature change, an undeformed sample in its permanent shape is heated to \( T_H > T_{trans} \) where it exhibits elastomeric behavior, deformed to a desired shape, and then cooled to \( T_L < T_{trans} \). After unloading at \( T_L \), the sample is fixed in a temporary shape. Heating back to \( T_H \) recovers the permanent shape. The most common mechanism in thermally triggered SMP is the second-order transition from the rubbery state to the glassy state (Nguyen et al., 2008; Qi et al., 2008), which is accompanied by a large change in material modulus from a few MPa to a few GPa. This large change in modulus offers the advantage of easy programming as the temporary shape is formed by deforming the material at a high temperature where the material modulus is low. However, in some applications, especially in biomedical applications such as biomimetic sensing and actuation, soft materials are desirable. Recently, several attempts have been made to create new soft and elastomeric SMPs. Rousseau and Mather (2003) developed a smectic-C liquid crystalline elastomer (LCE) exhibiting the shape memory effects based on the smectic-C-to-isotropic transition of the LCE Weiss et al. (2008) introduced a new type of SMP consisting of an elastomeric ionomer and low mass fatty acids or their salts, where the ionomer provided a strong intermolecular bond between the fatty acid crystal and the polymer to form a secondary network of the fatty acid with a transition temperature related to the melting temperature of the fatty acid. However, these materials involve complex, custom chemical synthesis, which presents an inherent challenge for large-scale production (Luo and Mather, 2009).

Recently, Luo and Mather (2009) reported a novel approach to develop a shape memory elastomeric composite (SMEC) by embedding a crystallizable thermoplastic fiber network into an elastomeric matrix. In the approach, a poly (ε-caprolactone) (PCL; \( M_w = 65000 \text{ g/mol} \), Sigma-Aldrich, St Louis, MO) is first electrospun into a fiber network (or mat). This fiber network is then immersed into a silicone rubber (Sylgard 184, Dow Corning Corp., Midland, MI) pre-polymer solution, which is 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 thermomechanical cycle, the SMEC is heated to \( T_H > T_{trans} \) (\( T_{trans} \) is \( T_m \), the melting temperature of PCL), deformed at \( T_H \), then cooled to \( T_L < T_{trans} \) while maintaining the external load. During cooling, the PCL fiber network undergoes a phase transformation from a polymer melt to a semicrystalline polymer. After unloading at \( T_L \), a temporary shape is fixed due to the crystallized PCL. Heating back to \( T_H \) where PCL melts and the stress stored in the semicrystalline PCL is released, the SMEC recovers its permanent shape. Because the operational temperatures in a shape memory cycle are much higher than the glass transition temperatures for both Sylgard and PCL, the modulus of the SMEC is a few MPa at \( T_H > T_{trans} \) and \( \sim 10 \text{ MPa} \) at \( T_L < T_{trans} \).

The approach developed by Luo and Mather (2009) 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. It is therefore important to understand the thermomechanical behaviors and to develop corresponding material models of the phenomena. In this paper, a 3D finite-deformation constitutive model is developed to describe the shape memory behavior of shape memory elastomeric composites. In Section 2, we introduce a SMEC material system and carry out experiments to characterize its thermomechanical (including shape memory) behavior. In Section 3, a general 3D, finite-deformation constitutive model that describes the melt–crystal evolution of the fiber network during thermomechanical loading and the resulting effect on the behavior of the composite is presented in detail. We also present and use an effective phase model to simulate the mechanics of the evolving phases in a more computationally efficient manner. In Section 4, results from the model are compared with those from experiments and we explore the effects of environmental and microstructural variables including the thermal rate and the composite volume fraction.

2. Materials and thermomechanical behavior measurements

2.1. Materials

A SMEC was prepared using a silicone rubber (Sylgard 184) as the elastomeric matrix and electrospun PCL as the crystallizable fiber reinforcement. Details regarding the fabrication process and the resulting morphology of the isotropic
Sylgard/PCL SMEC can be found in Luo and Mather (2009) and are briefly presented in Supplementary material. The material is then cut into 13.86 × 2.77 × 0.68 mm rectangular thin film samples for testing.

2.2. Physical and mechanical properties

Dynamic mechanical analysis (DMA) tests for the Sylgard/PCL SMEC and neat Sylgard were conducted using a dynamic mechanical analyzer (Q800 DMA, TA Instruments). From DMA (see Fig. S2a and b), it was found that the glass transition temperature of the neat Sylgard is −127 °C. The glass transition and crystallization temperatures of PCL are −49.5 °C and 27.2 °C, respectively. At 80 °C, the storage modulus for the Sylgard/PCL SMEC is 1.4 MPa, while for the neat Sylgard it is 3.16 MPa. More details about the DMA tests are reported in the Supplementary materials.

2.3. Shape memory behavior

Shape memory behavior of an SMEC results from a four-step thermomechanical loading–unloading cycle, as illustrated in Fig. 1. In Step 1 (S1), the SMEC is isothermally predeformed (stretched in this paper) at \( T_H > T_m \) (the melting temperature of PCL). Step 2 (S2) cools the material to \( T_l < T_c \) (the crystallization temperature of PCL) whilst the stretching force is maintained. After unloading (Step 3, S3), the SMEC is fixed at (or programmed to) the temporary shape at \( T_l \). The SMEC can maintain this shape as long as the temperature does not change. In the final step (Step 4, S4), the shape memory effect is realized by raising the temperature to \( T_H \) and the initial shape is recovered.

The measured shape memory behavior of the Sylgard/PCL SMEC is shown in stress–temperature–strain (Fig. 2a) and strain–temperature plots (Fig. 2b), under three different imposed nominal stresses (0.1, 0.15, 0.2 MPa). In S1, the sample was stretched at 80 °C (\( T_H \)) by gradually ramping the tensile stress at a loading rate of 0.1 MPa/min to the predefined value (0.1, 0.15, and 0.2 MPa in the three different cases, respectively). In S2, the temperature was decreased to 5 °C (\( T_L \)) at a rate of −2 °C/min while the nominal stress was fixed. Fig. 2a and b show that, when lowering the temperature, the strain initially increased for the 0.15 and 0.2 MPa cases, but decreased for the 0.1 MPa case. At a temperature of about 30 °C, the strain dropped by ≈24% due to crystallization of PCL. In S3, the stress was quickly released at 5 °C. Here, a slight contraction of the sample can be observed. In S4, the unconstrained strain recovery was triggered by heating back to 80 °C at a rate of 2 °C/min. In order to further quantify the shape memory behavior, the fixing ratio \( R_f \) and the recovery ratio \( R_r \) are used as following (Luo and Mather, 2009; Rousseau, 2008):

\[
R_f = \frac{\varepsilon_u}{\varepsilon_m} \times 100\%, \quad R_r = \frac{\varepsilon_u - \varepsilon_p}{\varepsilon_u - \varepsilon_0} \times 100\%.
\]

Fig. 1. Schematics of the free/constrained recovery experiments. The left side shows the thermomechanical loading–unloading cycle for free recovery. The right side shows the constrained recovery cycle.
where \( \varepsilon_m \) and \( \varepsilon_n \) are the strains before and after unloading at \( T_L \), \( \varepsilon_p \) is the permanent strain after heat induced recovery and \( \varepsilon_0 \) is the initial strain at \( T_H \). The calculated \( R_f \) and \( R_r \) from our experiments are listed in Table 1 for the three different imposed nominal stress cases. The recovery ratios \( R_f \) for the three cases are \( > 98\% \), demonstrating the excellent recovery capability of the material. On the other hand, the fixing ratios \( R_r \) are \( \sim 80\% \), which are lower than those \( (> 97\%) \) reported by Luo and Mather (2009). In fact, the fixity of SMEC can be tuned by changing the Sylgard/PCL composition. This will be discussed in Section 4.3.2.

A constrained recovery experiment (schematically shown in Fig. 1) was also conducted. Note that the only difference between the free recovery and the constrained recovery is that the constrained recovery does not have the unloading step (S3). Fig. 3a and b show the results of the constrained recovery experiment with an imposed nominal stress of 0.15 MPa.

![Fig. 2. Shape memory behavior of Sylgard/PCL SMECs with different imposed stresses: (a) stress–temperature–strain plot showing the 3D shape memory cycles; (b) strain–temperature plot.](image)

![Fig. 3. The constrained recovery of the Sylgard/PCL SMEC: (a) stress–temperature–strain plot; (b) strain–temperature plot.](image)

<table>
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<th>0.1 MPa</th>
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<td>( R_f )</td>
<td>84.0%</td>
<td>88.4%</td>
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<td>( R_r )</td>
<td>98.2%</td>
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Table 1

\( R_f \) and \( R_r \) for the Sylgard/PCL SMEC at various of training stresses.
In S1, the sample was first stretched at 80 °C (T1) by gradually ramping the tensile stress to 0.15 MPa. At S2, the temperature was decreased to 5 °C (T2) at a rate of 1 °C/min while the stress was fixed as a constant. In S4, the stretched sample was heated back to 80 °C at a rate of 2 °C/min. The strain increased initially when increasing temperature. At about 60 °C, the strain decreased with increasing temperature. At 80 °C, the sample has recovered to the stretched shape in S1.

2.4. Thermal deformation

We measured the thermal deformation of the SMEC and the results are shown in Fig. 4. A small stretching force (1 × 10^{-4} N) was applied to ensure the sample was straight. The temperature was decreased from 80 to −10 °C at a rate of 2 °C/min and heated back to 80 °C at the same rate. In Fig. 4, the material first contracted linearly with a coefficient of thermal expansion (CTE) of 2.66 × 10^{-4}/°C, and then nonlinearly contracted by about 1% due to crystallization over the temperature range from about 25–15 °C. Below 15 °C, the material again contracted linearly with a CTE of 1.57 × 10^{-4}/°C. The total thermal strain at 5 °C was −2.11%. When heating from −10 to 80 °C, the material expanded roughly linearly, then ascended abruptly by about 1% due to melting in the narrow temperature range from about 50–60 °C, and finally expanded almost linearly again closing the loop at 80 °C.
2.5. Effects of thermal rates

In order to investigate the effect of thermal rates on the shape memory behavior, four different thermal rates (1, 2, 5 and 10 °C/min)\(^1\) with a 0.15 MPa nominal stress were applied to free recovery experiments (Fig. 5a and b). For the 1 and 2 °C/min cases, the curves show a similar trend and about 90% of deformation can be fixed after unloading. For the 5 °C/min case and 10 °C/min cases, crystallization does not finish completely upon cooling resulting in poorer shape fixity; \(R_f\sim 60\%\), for the 5 °C/min and \(\sim 40\%\) for the 10 °C/min case (Fig. 5b).

3. Model description

3.1. Overall model

In this section, we develop a continuum thermomechanical constitutive model framework for shape memory elastomeric composites by treating the matrix and fiber network as a homogenized system of multiple phases. The matrix is taken as a conventional elastomer and the fiber network is idealized as a two-phase aggregate of melt and crystalline regions; it is a melt at high temperatures and is an elastic solid at low temperatures. The evolution of the melt and crystalline phases in the fiber is described by existing theories of crystallization. Our goal is to develop a modeling approach for this class of materials and so at this point, some levels of detailed understanding are sacrificed in favor of a reasonably simple way to describe the complex thermomechanical phenomena and therefore several assumptions are made:

(i) Since the fiber (PCL) melts behave like liquids, they can only carry hydrostatic pressure under compressive conditions. Since the fiber sits in an interconnected network, some fiber melts may leak out of the SMEC under hydraulic pressure. To simplify the model, we assume that the melt phase does not support loads. Future studies should consider the load carrying capability of the melt phase that can be assessed using micromechanics considerations.
(ii) Since the melting temperature of the fiber (PCL) is much higher than its glass transition temperature, the relaxation time of the fiber melts is fast at the temperature near its melting temperature. Therefore, it is assumed that the external loading does not affect the morphology of the fiber crystals.
(iii) During crystallization, the fiber crystals are formed in a stress-free (natural) configuration (Rajagopal and Srinivasa, 1998a,b). The fiber crystals formed at different times thus have a different deformation history.
(iv) During crystallization, the deformation transfer is simplified by an averaging scheme that assumes that both the matrix and the crystalline phase undergo a small deformation increment.
(v) Since deformation of the crystals is limited (\(\sim 1\%\) tensile at S2 and \(\sim 1\%\) compressive at S3) in a shape memory cycle, their inelastic deformation is not considered.
(vi) In order to reflect the complex load sharing among the fiber network and matrix, we use the concentration factor approach, motivated by micromechanical considerations. For simplicity, though, we assume the stress concentration factors are constant during a shape memory cycle. A more detailed analysis would consider their evolution as the fiber network evolves.

Fig. 6 shows a 1D representation of the constitutive model. We decompose the deformation of the material into a multiplicative split of a thermal and mechanical component:

\[
G = G^M G^T = FG^T, \quad F = G^M,
\]

where \(G\) is the total deformation gradient, \(G^M\) is the mechanical deformation gradient and gives rise to stress, \(G^T\) is the deformation gradient due to thermal deformation. For the convenience of model description, we set \(F = G^M\) and use \(F\) to represent the mechanical deformation gradient. The mechanical contribution from the matrix is represented by a hyperelastic spring in Fig. 6 because it is always in the rubbery state with a low tan \(\delta\) (\(= 0.06\)) during the temperature cycle. The fiber network changes its crystallinity with temperature: When \(T > T_m\), melt phases do not carry load; when \(T < T_c\), the fiber network crystallizes and can carry load. Since crystallization of fibers is a continuous and time dependent process, we further divide the fiber network into small crystalline phases formed at different times with a volume fraction of \(\Delta t_i\) and a deformation gradient of \(F_{i,m}\). More details will be described in the next section of the 3D generalized theory.

As shown in Fig. 6, the model arranges stresses on the matrix and fiber network in parallel and the total Cauchy stress \(\sigma_{total}\) is given by:

\[
\sigma_{total} = v_{Mx} \sigma_{Mx} + v_{Fx} \sigma_{Fx},
\]

\(^1\) In a previous study (Westbrook et al., 2010, Improved testing system for thermomechanical experiments on polymers using uniaxial compression equipment. Polymer Testing 29(4), 503–512.), it was found that the main factors affecting the temperature distribution within a sample were the size of the sample and the contact between the sample and the fixture. For a cylindrical sample (10 mm in diameter and height) with improved fixture design, the maximum temperature difference within the sample was \(5.3 \degree C\) for a thermal rate of \(10 \degree C/min\). Since the sample used in this paper was a thin film under a tensile testing setup, we expect that the temperature difference within the sample is even smaller.
where $\sigma^{Mx}$ and $\sigma^{Fb}$ are the stresses in the matrix and the PCL fiber network, respectively. $v_{Mx}$ and $v_{Fb}$ are the corresponding volume fractions which satisfy $v_{Mx} + v_{Fb} = 1$.

In reality, the stress distribution in the phases depends on the details of the microstructure, including the geometry, and architecture of the spatial arrangement of the phases, and the evolution of their properties. We attempt to account for the departure of stress distribution among the phases by borrowing the concept of a stress concentration factor from the micromechanics of heterogeneous solids in linear and nonlinear elasticity (Benveniste, 1987; Castaneda, 1991; Dunn, 1998). Introducing stress concentration factors for the fiber and matrix, the total Cauchy stress $\sigma^{total}$ is written as

$$\sigma^{total} = \gamma_{Mx} v_{Mx} \sigma^{Mx} + \gamma_{Fb} v_{Fb} \sigma^{Fb},$$

(4)

where $\gamma_{Mx}$ and $\gamma_{Fb}$ are stress concentration factors of the matrix and the fibers and $\gamma_{Mx} v_{Mx} + \gamma_{Fb} v_{Fb} = 1$. For the sake of convenience, $\gamma_{Mx} v_{Mx}$ and $\gamma_{Fb} v_{Fb}$ are denoted by $\gamma_{Mx}$ and $\gamma_{Fb}$.

### 3.2. Crystallization and melting of the fiber network

Since the crystal–melt transition is the trigger that imparts the shape memory effect to the SMEC, it is essential to capture the kinetics of crystallization and melting of the fibers. The classic theory to describe crystallization kinetics is Avrami’s phase transition theory (Avrami, 1939, 1940, 1941). The original derivations by Avrami were simplified by Evans (1945) with the “raindrop” theory, in which one idealizes the crystallization kinetics as a drop falling into a pool (representing nucleation of a crystal) that creates a wave-front that subsequently propagates (representing the growth front of a crystal). A drop falls at time $t$ and its front propagates from $t$ to $t$. The probability that $i$-th wave passes over a point $P$ in space is given by Poisson’s equation (Ozawa, 1971):

$$p_i = e^{-\frac{E}{i!}},$$

(5)

where $E$ is the expectancy and is equal to the average number of such wave fronts. In the crystallization process, a point in melt state is a point that has not been passed over by any growing front. Therefore, $i=0$ gives the probability of a point being in the melt (Ozawa, 1971):

$$p_0 = e^{-E}.$$

(6)

In the case of crystallization, the expectancy $E$ is equal to $V(t)$, the volume fraction of crystals without impingement (intersection of growth fronts) (Sperling, 2006). Therefore, the relative volume fraction of the amorphous phase is (Sperling, 2006):

$$1 - \chi(t) = e^{-V(t)},$$

(7)

where $\chi(t)$ is the relative degree of crystallinity.

To understand the description of $V(t)$, it is instructive to first consider the case where crystal nuclei all develop simultaneously upon cooling the polymer to the crystallization temperature and then extend this development to the case of sporadic nucleation where nucleation is a function of time (Sperling, 2006). In the first case, the nucleation density is a constant and the rate of growth of $V(t)$ is

$$\frac{dV(t)}{dt} = AN \left(\frac{Gt}{t}\right)^m.$$

(8)
where $N$ is the nucleation density, $G$ is the crystal growth rate (for isothermal crystallization, $G$ is a constant at a certain temperature), and $A$ and $n$ are constants related to the dimension of the crystal. For 1D rods, $A=\pi d^2/4$, $n=1$, $d$ is the diameter of the rod; for 2D discs, $A=2\pi d$, $n=2$, $d$ is the thickness of the disc; for 3D spheres, $A=4\pi$, $n=3$. Integrating Eq. (8) over $t$ from 0 to $t_c$ (a specific time during crystallization) yields
\[ V(t_c) = B N(G(t_c))^n, \tag{9} \]
with $B=(A/n)$. For the sporadic nucleation case, the nucleation density is a function of time $N(t)$. As time increases from $t$ to $t+dt$, the number of newly formed nucleus per volume is $(dN(t)/dt)dt$ and the volume fraction of these crystalline phases at $t(t+\tau)$ is $N(t+\tau)dt/[G(t+\tau)]d\tau$. Integrating over time from 0 to $t_c$, yields the volume fraction without impingement:
\[ V(t_c) = B \int_0^{t_c} \frac{dN(t)}{dt} \left( \frac{G(t_c-t)^n}{n!} \right) dt. \tag{10} \]

Eq. (10) describes the isothermal crystallization process. In the SMEC system crystallization (and melting) is actually a non-isothermal process that occurs as the temperature is lowered continuously from a temperature above to a temperature below the crystallization temperature. As the nucleation density and the crystal growth rate are functions of temperature during non-isothermal crystallization, the nucleation density and the growth rate are functions of temperature and time, expressed as $N(T(t))$ and $G(T(t))$, respectively. Accordingly, Eq. (9) can be modified as
\[ V(t_c) = B \int_0^{t_c} \frac{dN(T(t))}{dT} \left( \frac{G(T(s))ds}{n!} \right) ds dt, \tag{11} \]
where the Hoffmann–Lauritzen expression is widely adopted to describe the growth rate $G(T(t))$ (Lauritzen and Hoffman, 1973):
\[ G(T(t)) = G_0 \exp \left\{ - \frac{U}{R(T(t)-T_m)} \right\} \exp \left\{ - \frac{K_g}{T(t)\Delta T} \right\}. \tag{12} \]

In Eq. (12), the pre-exponential factor $G_0$ is almost independent of temperature (Angelloz et al., 2000; Isayev and Catignani, 1997). The first exponential term of Eq. (12) reflects the chain mobility in the melt, where $U$ is the diffusional activation energy for the transport of crystallizable segments at the liquid–solid interface (Liu et al., 2010), $R$ is the universal gas constant, $T_m$ is the temperature $T_g-30$ K (Angelloz et al., 2000; Isayev and Catignani, 1997). The second exponential term contains the secondary nucleation effect on the crystal growth front (Angelloz et al., 2000) where $K_g$ is a nucleation constant (Liu et al., 2010), $\Delta T = T_m^0 - T(t)$ is the undercooling, where $T_m^0$ is the equilibrium melting temperature; $f = (2T(t)/[T_m^0+T(t)])$ is a correction factor used to account for the variation of the heat of fusion with temperature (Angelloz et al., 2000).

The evolution of the number of nuclei can be empirically described by (Angelloz et al., 2000; Isayev and Catignani, 1997):
\[ N(T(t)) = N_0 \exp[\beta(T_m^0 - T(t))]. \tag{13} \]

where $N_0$ is a pre-exponential factor of nucleation density and $\beta$ an empirical parameter.

Based on the understanding of kinetics of crystallization, the melting kinetics can be developed in an analogous manner. During the melting processing, the volume of the existing crystals decreases until it becomes zero. Assume melting starts at time $t=t_m$, the volume fraction of crystals at time $t=t_{ms}+t_m$ during melting can be described by
\[ V(t_m) = B \int_0^{t_{ms}} \frac{dN(T(t))}{dT} \left( \frac{G(T(t))dt}{n!} \right) \int_0^{t_m} C(t)C(t_m)dt_m \tag{14} \]
where $t_{ce}$ is the time at which crystallization ends; in general, $t_{ce}=t_m$. $C(t)$ is the rate of decrease of crystal size; in this paper, it is treated as a constant due to our low heating rate ($2$ °C/min) and narrow melting temperature range ($\sim 35$ to $\sim 65$ °C).

By using Eq. (7) with Eqs. (11)–(14), the relative degree of crystallinity $\chi(t)$ can be calculated. However, in reality, polymer crystallinity does not reach 100% but becomes saturated at some degree of crystallinity, $H_c$. Thus, the crystallinity is expressed as
\[ \chi(t) = H_c \chi(t). \tag{15} \]

According to Kweon et al. (2003), for the PCL fiber, under conditions similar to those of this paper, $H_c=25\%$.

Using this model, we simulated the kinetics of crystallization and melting of PCL and results are shown in Fig. 7. Observable crystallization starts at $\sim 30$ °C and finishes at $\sim 20$ °C. During melting, observable melting starts at $\sim 35$ °C and finishes at $\sim 65$ °C.

3.3. Mechanical behavior

As described and shown in Fig. 1, a SMEC shape memory cycle involves four distinct thermomechanical steps. During the cooling and heating steps, mechanical deformation can be coupled with crystallization/melting processes. It therefore becomes a natural approach to describe material behavior under two thermomechanical scenarios: mechanical
deformation during crystallization and mechanical deformation during melting. In these two cases, we consider the one-way coupling where crystallization/melting can affect the mechanical deformation. The coupling in the reverse direction where mechanical deformation affects crystallization/melting kinetics is not considered. This assumption is valid for two reasons: first, during crystallization, the material deformation rate is much slower than the relaxation time of the polymer melt so that any nonequilibrium deformation can be relaxed and thus mechanical deformation will not influence crystallization. Second, during melting, mechanical deformation in the semicrystalline PCL is relatively small so that the melting kinetics will not be appreciably influenced. Nevertheless, if it were appreciable, a description of crystallization that includes a dependence on deformation could be included in our overall theory.

3.3.1. Mechanical behavior of the constituents

For convenience we take both the matrix and the fiber network to be hyperelastic solids. In our case the matrix, Sylgard, is in its rubbery state during a shape memory cycle, while the PCL crystals, although linear elastic, can be idealized as hyperelastic. As such there exist free energy functions so that the Cauchy stresses can be obtained as

\[
\sigma_{Mx}(F_{Mx}) = J_1^{-1}(F_{Mx}) \frac{\partial W_{Mx}(F_{Mx})}{\partial F_{Mx}} (F_{Mx})^T,
\]

\[
\sigma_{FbC}(F_{FbC}) = J_1^{-1}(F_{FbC}) \frac{\partial W_{FbC}(F_{FbC})}{\partial F_{FbC}} (F_{FbC})^T,
\]

where the superscripts \( Mx \) and \( FbC \) indicate the quantities associated with the matrix and crystalline component of the fiber network, respectively; \( W \) is the free energy density function; \( \sigma \) is the Cauchy stress tensor; \( F \) is the mechanical deformation gradient, and the Jacobian \( J = \det F \) characterizes the volume change. It is noted that \( \sigma_{Mx} \) and \( \sigma_{FbC} \) are the stresses carried by the matrix and the fiber crystalline phases, respectively.

3.3.2. Mechanics during crystallization

As shown in Fig. 7, crystallization and melting are continuous processes and functions of temperature and time. Our basic assumption is that when a small fraction of polymer crystals is formed from a melt, it is in a stress-free state. In order to satisfy the boundary conditions, either overall or locally, this small fraction will deform immediately. This stress-free state for new born crystalline phases was referred as a natural configuration by Rajagopol (Rajagopal and Srinivasa, 1998a, b), and was used by many researchers to study crystallizing polymers (Ma and Negahban, 1995a, b; Negahban, 1993; Negahban and Wineman, 1992), rubbers with thermally induced scissoring and reformation (Tobolsky, 1960; Wineman, 1999, 2000, 2003; Wineman and Shaw, 2008), shape memory polymers (Barot and Rao, 2006; Barot et al., 2008; Qi et al., 2008), and light activated shape memory polymers (Long et al., 2009). In this section, we deal with mechanics during crystallization. During a shape memory cycle, crystallization can occur during cooling (S2) and unloading at low temperatures (S3). As indicated below, the method in this section is also applied to the case where there is no crystallization, such as the high temperature loading step (S1).

To better illustrate the physics and the mechanics, we use an incremental approach; schematics are attached in the Supplementary materials. Considering at time \( t = t_0 \) all fiber crystals are melted, and mechanical deformation gradient is \( F_{0} \).
Since only the matrix carries load at this moment, $F_{\text{Mx}} = F_0$, and

$$
\sigma_{\text{total}}^0 = \mathbf{v}_{\text{Mx}} \sigma_{\text{Mx}}^0(F_0).
$$

(17)

At time $t = t_0$, crystallization starts. At $t = t_0 + \Delta t$, a small amount of crystalline phase has formed from the fiber melt with a volume fraction $\Delta \nu_j^c$. As stated above, we assume that this newly formed crystalline phase is initially undeformed and stress-free. Simultaneously, a mechanical deformation may occur. One reason for this mechanical deformation could be due to mechanical loading change during crystallization. For example, in a shape memory cycle, the crystallization process can easily extend into S3, the unloading step at the temperature below the crystallization temperature. Another reason could be attributed to the modulus change of the matrix due to its dependence on temperature (entropic elasticity). The deformation and load transfer from the matrix to polymer crystals is complicated (Ma and Negahban, 1995a, b; Negahban, 1993; Negahban and Wineman, 1992); for example, they may depend on the shape and spatial distribution of the crystals. Here, we simplify this deformation transfer by assuming both the matrix and fiber crystals undergo the same small incremental deformation gradient $\Delta \mathbf{F}_1$. Then, the deformations in the matrix and the fiber crystal become

$$
F_{\text{Mx}} = \Delta \mathbf{F}_1 F_0, \quad F_{\text{FbC}} = \Delta \mathbf{F}_1 F_{\text{FbC}},
$$

(18)

and the total stress is

$$
\sigma_{\text{total}}^1 = \mathbf{v}_{\text{Mx}} \sigma_{\text{Mx}}^1(F_{\text{FbC}}) + \mathbf{v}_{\text{FbC}} \Delta \nu_j^c \sigma_{\text{FbC}}(\Delta \mathbf{F}_1).
$$

(19)

Here, the subscript in $F_{\text{FbC}}$ represents the deformation gradient at the time of the 1st time increment for the crystalline phase formed during the 1st time increment. As the crystallization proceeds, more small volume fractions of crystals form. Each of them has no deformation in its new-born state but deforms after its birth due to the reasons discussed above. Following the above discussion, at time $t = t_0 + m \Delta t$, the deformation gradient in the crystalline phase formed at time $t = t_0 + i \Delta t$ can be expressed as

$$
F_{\text{FbC}} = \left( \prod_{j=1}^{m} \Delta \mathbf{F}_j \right) F_0 = F_{\text{FbC}}(i \Delta t).
$$

(20)

where $I_{\text{FbC}}(i \Delta t)$ means the multiplicative operation goes toward left, or $I_{\text{FbC}}(i \Delta t) = (\lambda_1 \cdots \lambda_i)$. $\Delta \mathbf{F}_j$ is the incremental deformation gradient at $t = t_0 + j \Delta t$ when the $j$-th crystal forms; $F_{\text{FbC}}$ represents the deformation gradient at time $t = t_0 + j \Delta t$ for the crystals formed at time $t = t_0 + i \Delta t$. Note that $\Delta \mathbf{F}_j$ has its reference configuration occupying the spatial configuration at time $t = t_0 + (i-1) \Delta t$, so does $F_{\text{FbC}}$. The deformation gradient in the matrix is

$$
F_{\text{Mx}} = \left( \prod_{j=1}^{m} \Delta \mathbf{F}_j \right) F_0 = F_{\text{Mx}}(i \Delta t).
$$

(21)

The total stress is

$$
\sigma_{\text{total}}^m = \mathbf{v}_{\text{Mx}} \sigma_{\text{Mx}}^m(F_{\text{Mx}}(i \Delta t) F_0) + \mathbf{v}_{\text{FbC}} \sum_{i=1}^{m} \Delta \nu_j^c \sigma_{\text{FbC}}(\Delta \mathbf{F}_1).
$$

(22)

Note that Eq. (22) can also be applied to the case where there is no new crystalline phase is formed by simply setting $\Delta \nu_j^c = 0$.

### 3.3.3. Mechanics during melting

During melting, the crystalline phases vanish gradually. According to the kinetic description of the melting process, the portion of crystalline domains that grow at a later time melts first (as they are closer to the melt–crystal boundary). Assuming at the time when melting starts ($t = t_{\text{ms}}$), the total number of crystalline phases (which is equal to the total number of time increments during crystallization) is $m_\text{e}$, at time $t = t_{\text{ms}} + \Delta t$, $\Delta \nu_j^\text{melt}$, melts. Here, for the sake of brevity, we assume that within $\Delta t$, $\Delta \nu_j^\text{melt}$ volume fraction of crystals melt. Concurrently with melting, a small incremental deformation gradient $\Delta \mathbf{F}_1^\text{melt}$ is induced. This deformation, for example, could be due to shape recovery in the heating step of a shape memory cycle. Following the same assumption for mechanical deformation during crystallization, we assume that the incremental deformation gradient $\Delta \mathbf{F}_1^\text{melt}$ is applied to all the phases, except of $m_\text{e}$-th crystalline phase, which just melted and cannot carry load. Therefore, the total stress is

$$
\sigma_{\text{total}} = \mathbf{v}_{\text{Mx}} \sigma_{\text{Mx}}^m(\Delta \mathbf{F}_1^\text{melt} F_{\text{Mx}}(i \Delta t) F_0) + \mathbf{v}_{\text{FbC}} \sum_{i=1}^{m_\text{e}-1} \Delta \nu_j^c \sigma_{\text{FbC}}(\Delta \mathbf{F}_1^\text{melt} F_{\text{FbC}}(i \Delta t)).
$$

(23)

Note in real simulations, in $\Delta t$ time period, the amount of crystals that melt generally is not equal to $\Delta \nu_j^\text{melt}$. However, this can be treated by conducting interpolation between two time increments. The treatment is arithmetical and therefore is not discussed here.
Following the same argument, at time $t = t_m + n\Delta t$, the crystal with volume fraction $\Delta v^c_{m+1}$ melts and the deformation gradient is increased by $\Delta F^\text{melt}\!_n$. The total stress is

$$\sigma^\text{total} = F_{\text{M}}\sigma^{\text{M}}(F^\text{melt}\!_{1-m}F_{1-m}F_0) + F_{\text{FB}}\sum_{i=1}^{m-n} \Delta v^f_i \sigma^{\text{FB}}(F^\text{melt}\!_{1-m}F_{1-m}), \quad F^\text{melt}\!_{1-m} = \prod_{i=1}^{n} \Delta F^\text{melt}\!_i. \quad (24)$$

Depending on the boundary conditions, Eq. (24) can be solved for $\Delta F^\text{melt}\!_n$ if a constant stress is applied (load control), or for $\sigma^\text{total}$ if $\Delta F^\text{melt}\!_n$ is prescribed (displacement control).

### 3.3.4. Effective phase model (EPM)

The mechanics discussed above is computationally expensive as it requires the deformation gradient in each fraction of crystals to be updated during each time increment and is stored as internal variables. This can quickly exhaust computer CPU time and memory resources. In order to enhance computational efficiency, Long et al. (2010) developed an effective phase model (EPM) to capture the mechanics of a material with evolving phases. In the EPM, the behavior of the new phases formed at different times are combined into an effective phase with an effective deformation. The effective phase and its effective deformation are continuously updated to account for the response of each new phase.

During crystallization at time $t = t_0 + m\Delta t$, there are $m$ crystalline phases during crystallization beginning at $t = t_0$. In the EPM, it is assumed that the mechanical deformation in these $m$ crystalline phases can be represented by an effective phase with a combined volume fraction of $v^c_m = \sum_{i=1}^{m} \Delta v^c_i$ and an effective deformation gradient $F_m$. The total stress in the SMEC is therefore:

$$\sigma^\text{total}_m = F_{\text{M}}\sigma^{\text{M}}(F_m) + F_{\text{FB}}v^f_m \sigma^{\text{FB}}(F_m). \quad (25)$$

At time $t = t_0 + (m+1)\Delta t$, a new crystalline phase with volume fraction $\Delta v^c_{m+1}$ is formed. Accompanying this new crystalline phase, the composite undergoes a further deformation with $\Delta F^\text{melt}\!_{m+1}$ and the total stress is now calculated as

$$\sigma^\text{total}_{m+1} = F_{\text{M}}\sigma^{\text{M}}(\Delta F^\text{melt}\!_{m+1}F_m) + F_{\text{FB}}\left[v^f_m \sigma^{\text{FB}}(\Delta F^\text{melt}\!_{m+1}F_m) + \Delta v^c_{m+1} \sigma^{\text{FB}}(\Delta F^\text{melt}\!_{m+1})\right]. \quad (26)$$

Applying Eq. (25) to the time $t = t_0 + (m+1)\Delta t$, we have

$$\sigma^\text{total}_{m+1} = F_{\text{M}}\sigma^{\text{M}}(F_{m+1}) + F_{\text{FB}}v^f_{m+1} \sigma^{\text{FB}}(F_{m+1}), \quad (27)$$

where $F_{m+1} = \Delta F^\text{melt}\!_{m+1}F_m$ and $F_{m+1} = \Delta F^\text{melt}\!_{m+1}F_m$. Comparing Eqs. (26) and (27), we have

$$v^f_{m+1} \sigma^{\text{FB}}(\Delta F^\text{melt}\!_{m+1}F_m) = v^f_m \sigma^{\text{FB}}(\Delta F^\text{melt}\!_{m+1}F_m) + \Delta v^c_{m+1} \sigma^{\text{FB}}(\Delta F^\text{melt}\!_{m+1}), \quad (28)$$

For a given $\Delta F^\text{melt}\!_{m+1}$ and with a calculation of Jacobian, Eq. (28) can be solved using a Newton–Raphson scheme for the deformation increment in the effective phase $\Delta F^\text{melt}\!_{m+1}$. The same process can be applied to melting. In order to help readers better understand the EPM theory, schematics are presented in Supplementary material.

### 3.4. Thermal deformation

Thermal deformation of the SMEC arises from contributions from the matrix and fiber network. The latter includes thermal contraction/expansion of the crystalline phase as well as a volume change that accompanies the melt–crystal phase transformation. Here, we assume that the thermal contraction/expansion is always isotropic, therefore:

$$C^T = j^T1 = (\lambda^T)^T1, \quad (29)$$

where $\lambda^T$ is the linear stretch ratio due to thermal contraction/expansion.

Based on the thermal contraction/expansion experiment in Section 2.4, there are three regions of the thermal deformation: (i) the high temperature linear regime characterized by a linear coefficient of thermal expansion ($\lambda_T$), where the fibers are completely melted; (ii) the nonlinear strain drop or rise ($\Delta \lambda_P$) region corresponding to the melt–crystal transition of the fibers; (iii) the low temperature linear deformation ($\lambda_L$) regime where the fibers are crystallized.

At high temperatures, where the fibers melt completely and the SMEC contracts or expands linearly with $\lambda_L$, the thermal stretch is:

$$\lambda^T = 1 + \lambda_L(T - T_H), \quad (30)$$

where $T_H$ is the temperature where the experiment starts.

During the melt–crystal phase transition, where $\nu^c$ increases from 0 to the saturated crystallinity $H_s$, the thermal deformation can be expressed by combining the linear and nonlinear thermal behavior:

$$\lambda^T = 1 + \lambda_{L}T_H + \Delta \lambda_P(T/T_H), \quad (31)$$

where $T_H$ is the equilibrium melting temperature in Eq. (13) where crystallization or melting starts, and $H_s$ is the saturated crystallinity in Eq. (15).
At low temperatures, where the fibers crystallize completely and \( v^e = H_{\alpha} \), the SMEC contracts or expands linearly with \( \alpha_2 \) and the thermal stretch is:

\[
\lambda^T = 1 + \alpha_1(T_m^0 - T_r) + \alpha_2(T - T_r) + \Delta \lambda_{PT}
\]

where \( T_r \) is a reference temperature corresponding to the time increment where the crystallinity reaches \( H_{\alpha} \).

Fig. 8 shows the comparison between experimental data and simulation. Overall, the model captures the thermal deformation reasonably well. The largest error occurs during heating from 10 to 50 °C: The model predicts a linear expansion whilst the experiment shows a slightly nonlinear behavior.

4. Results

4.1. Mechanical behaviors under uniaxial loading with a neo-Hookean solid

To begin we briefly describe results of our above model with simple material behaviors and uniaxial loading conditions. For the Sylgard matrix, the maximum stretch of the sample was 1.15 and the stress-strain behavior did not exhibit non-Gaussian behavior. For the PCL semicrystalline polymer, as will be shown later, the strain was low. For the sake of brevity, we assume that both Sylgard and the PCL semicrystalline polymer can be described by an incompressible neo-Hookean model with the strain energy functions (Treloar, 1958):

\[
W_{Mx} = \frac{1}{2} N k T (\lambda^2 + \lambda_2^2 + \lambda_3^2 - 3),
\]

\[
W_{FbC} = \frac{1}{2} \mu (\lambda^2 + \lambda_2^2 + \lambda_3^2 - 3),
\]

where \( \lambda_i \) are the applied stretches in the three principal directions, \( N \) is the chain density, \( k \) is Boltzmann’s constant, \( T \) is temperature, \( \mu \) is the shear modulus of the semicrystalline PCL. When subject to uniaxial loading, the Cauchy stress of each phase is

\[
\sigma_{Mx} = \lambda \frac{\partial W_{Mx}(\lambda)}{\partial \lambda} = N k T, \quad \sigma_{FbC} = \lambda \frac{\partial W_{FbC}(\lambda)}{\partial \lambda} = \mu (\lambda^2 - 1/\lambda)
\]

Here, we enforce material incompressibility, \( \lambda \) is the mechanical stretch in the uniaxial stretching direction and it is defined as \( \lambda = 1 + \varepsilon \), and \( \varepsilon \) is the strain. Note that for the Sylgard matrix, the stress is also a function of temperature \( T \). In addition, the total stretch of the material should include the thermal contraction/expansion, i.e., \( \lambda_{total} = \lambda^T \).

The mechanical stretch \( \lambda \) during a shape memory cycle can be simulated using either the general model or the EPM theory which improves the computational efficiency. Details are listed in the Supplementary material.

4.2. Comparison between model simulations and experiments

4.2.1. Free recovery

The thermomechanical model we have developed is complex and requires a number of input parameters that must be determined. Specifically, it requires 18 parameters; they are summarized in Table 2 along with their values and sources. Of the 18, 12 are determined by independent experiments and reasonable literature values and the other 6 are determined by fitting the experimental curve of a single shape memory cycle at an imposed stress of 0.15MP and a heating/cooling rate of
2°C/min (details about how to identify these parameters are presented in Supplementary material). Fig. 9 shows the results of the parameter fitting; the excellent agreement between model simulation and experiment validates the ability of the model to adequately capture the physical phenomena underlying the shape memory behavior.

The material parameters in Table 2 (identified by fitting the 0.15 MPa data) were then used to predict the shape memory behaviors with 0.1 and 0.2 MPa stresses. Fig. 10 shows good agreement between the model prediction and the experiment.

### 4.2.2. Constrained recovery

The numerical simulation of a constrained recovery experiment is shown in Fig. 11 along with experimental results. The model predicts the constrained recovery of the material well, including the existence of two strain peaks at different temperatures that arise from the hysteresis of crystallization and melting.

---

**Table 2**

Material parameters used in simulations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Description (fitting parameters are described in italics)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Composition</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( v_{\text{Mx}} )</td>
<td>0.87</td>
<td>Matrix (Sylgard) volume fraction of (determined by fabrication)</td>
</tr>
<tr>
<td>( v_{\text{Fb}} )</td>
<td>0.13</td>
<td>Fiber (PCL) volume fraction (determined by fabrication)</td>
</tr>
<tr>
<td><strong>Kinetics of crystallization and melting</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( G_0 )</td>
<td>( 4.6 \times 10^5 \text{ m s}^{-1} )</td>
<td>Pre-exponential factor of growth rate (Liu et al., 2010)</td>
</tr>
<tr>
<td>( U )</td>
<td>17.3 kJ mol(^{-1})</td>
<td>Diffusional activation energy (Liu et al., 2010)</td>
</tr>
<tr>
<td>( T_m )</td>
<td>310 K</td>
<td>The equilibrium melting temperature (Kweon et al., 2003)</td>
</tr>
<tr>
<td>( T_e )</td>
<td>193 K</td>
<td>The temperature 30 K lower than ( T_m ) (obtained from DMA)</td>
</tr>
<tr>
<td>( K_c )</td>
<td>35080 K(^2)</td>
<td>Nucleation constant (Liu et al., 2010)</td>
</tr>
<tr>
<td>( N_0 )</td>
<td>( 2.4 \times 10^4 \text{ m}^{-3} )</td>
<td>Pre-exponential factor of nucleation density (fitting parameter)</td>
</tr>
<tr>
<td>( \beta )</td>
<td>0.1349 K(^{-1})</td>
<td>Empirical parameter (Angelloz et al., 2000)</td>
</tr>
<tr>
<td>( C )</td>
<td>( 8.3 \times 10^5 \text{ m s}^{-1} )</td>
<td>The melting contraction rate (fitting parameter)</td>
</tr>
<tr>
<td>( H )</td>
<td>0.25</td>
<td>The saturated crystallinity (Kweon et al., 2003)</td>
</tr>
<tr>
<td><strong>Mechanical behaviors</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \gamma_{\text{Mx}} )</td>
<td>0.51</td>
<td>Stress concentration factor of matrix (Sylgard) (fitting parameter)</td>
</tr>
<tr>
<td>( \gamma_{\text{Fb}} )</td>
<td>4.31</td>
<td>Stress concentration factor of fiber (PCL) (fitting parameter)</td>
</tr>
<tr>
<td>( N )</td>
<td>( 2.16 \times 10^{26} \text{ m}^{-3} )</td>
<td>Polymer crosslinking density (from DMA for neat Sylgard)</td>
</tr>
<tr>
<td>( \mu )</td>
<td>20.69 MPa</td>
<td>PCL crystal phase modulus (fitting parameter)</td>
</tr>
<tr>
<td><strong>Thermal contraction/expansion</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \alpha_1 )</td>
<td>( 2.66 \times 10^{-4} \text{ C}^{-1} )</td>
<td>CTE at high temperature (measured)</td>
</tr>
<tr>
<td>( \alpha_2 )</td>
<td>( 8.27 \times 10^{-5} \text{ C}^{-1} )</td>
<td>CTE at low temperature (measured)</td>
</tr>
<tr>
<td>( \Delta \sigma_{\text{PT}} )</td>
<td>( -1.16 \times 10^{-2} )</td>
<td>Thermal strain due to phase transition (fitting parameter)</td>
</tr>
</tbody>
</table>

Fig. 9. Simulations used to fit model parameters and experimental results for a shape memory cycle with an imposed stress 0.15 MPa: (a) stress–temperature–strain plot; (b) strain–temperature plot.
4.3. Parametric studies

4.3.1. Effect of thermal rates

The constitutive model with parameters in Table 2 is used to investigate the effect of thermal rates on the shape memory performance in Fig. 12. The model predictions are in good agreement with companion experiments. To develop insight into the role of crystallization/melting kinetics on the shape memory behavior, in Fig. 13, we plot the computed crystallinity as a function of temperature for various thermal rates. The crystallinity clearly plays a key role in determining the fixity upon unloading. For the slow cooling, such as 1 and 2 °C/min, crystallization occurs at a faster rate than the cooling rate and the fiber network reaches the saturation crystallinity at or before the low temperature is reached, and therefore the best fixity is achieved. For the faster cooling rates, crystallization occurs at a slower rate than the cooling rate. Thus upon unloading at the low temperature, the crystallinity has only reached 5% and 2%, respectively, leading to a poor fixity: the 5 °C/min case held about 60% of the temporary shape and the 10 °C/min case fixed only about 40%. Interestingly, for the 5 and 10 °C/min cases, the crystallinity keeps increasing during heating, since the temperature is still below the crystallization temperature.
4.3.2 Effect of volume fractions

As mentioned in Section 2.3, the fixing capability of SMEC can be affected by changing the composition, e.g., the volume fraction of fibers. The effect of the fiber (PCL) volume fraction on the ability to fix the temporary shape is studied in Fig. 14 and Table 3.

Fig. 14 shows model predictions of shape memory behavior as the fiber volume fraction is varied from 5% to 30%. At S1, the sample stretch increases with fiber volume fraction since this leads to a softer SMEC at \( T_H \). At S3, upon unloading, increasing the fiber volume fraction yields a smaller strain drop and better fixity. Therefore, the advantage of a higher fiber volume fraction is the better fixity. However, this also leads to softer material behavior at high temperatures. Table 3 lists the fixing ratios \( R_f \) and the strains \( \varepsilon_H \) at \( T_H \), demonstrating the increased fixing ratio along with the increased strain \( \varepsilon_H \) at \( T_H \).

5. Conclusion

We studied the shape memory behavior of a new class of active materials, shape memory elastomeric composites (SMECs). In these materials an elastomeric matrix (Sylgard) provides entropic elasticity and a semicrystalline fiber network (PCL) serves as a reversible “switch phase” due to existence of a melt–crystal transition within the temperature range of operation. This results in a composite system capable of elastomeric response at all temperatures (within the intended range) that can exhibit shape memory behavior. We carried out extensive thermomechanical experiments to characterize and understand the behavior of this SMEC. We also developed a 3D finite-deformation constitutive model to...
describe the complex thermomechanical shape memory behavior. Our constitutive model includes a description of the crystal/melt phase transformation using the Evans theory and Hoffman–Lauritze expression for crystallization. The kinematics of the evolving phases during transformation is tracked based on the assumption that newly formed crystalline phases are undeformed and stress-free. In order to improve the computational efficiency, an effective phase model is adopted to capture the mechanics of material with evolving phases. The model accurately captures the complex shape memory behavior in both free and constrained recovery and provides insight into the role of crystallization kinetics on behavior. We also used the model to explore the effect of fiber volume fraction on shape fixity and showed how the fiber volume fraction impacts the strain at high temperature as well as the shape fixity. While our approach was to incorporate simple descriptions of various phenomena with the goal of reasonably describing the macroscopic thermomechanical response, our framework readily admits the incorporation of more sophisticated models of various phenomena such as crystallization and melting.

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Appendix A. Supporting materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jmps.2011.09.011.

References
