A thermodynamically-consistent 3D constitutive model for shape memory polymers

M. Baghania a, R. Naghdabadi a,b,* , J. Arghavani a,c, S. Sohrabpour a,d

a Department of Mechanical Engineering, Sharif University of Technology, Tehran, Iran
b Institute for Nano-Science and Technology, Sharif University of Technology, Tehran, Iran
c Department of Mechanical Engineering, Golpayegan University of Technology, Golpayegan, Iran
d The Academy of Sciences of IR Iran, Tehran, Iran

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The ever increasing applications of shape memory polymers have motivated the development of appropriate constitutive models for these materials. In this work, we present a 3D constitutive model for shape memory polymers under time-dependent multiaxial thermomechanical loadings in the small strain regime. The derivation is based on an additive decomposition of the strain into six parts and satisfying the second law of thermodynamics in Clausius-Duhem inequality form. In the constitutive model, the evolution laws for internal variables are derived during both cooling and heating thermomechanical loadings. The viscous effects are also fully accounted for in the proposed model. Further, we present the time-discrete form of the evolution equations in the implicit form. The model is validated by comparing the predicted results with different experimental data reported in the literature. Finally, using the finite element method, we solve two boundary value problems e.g., a 3D beam and a medical stent made of shape memory polymers.

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1. Introduction

Shape memory materials are a class of multi-phase smart materials that have the ability to return from a deformed state (temporary shape) to their original (permanent) shape called as shape memory recovery. The shape memory recovery is typically induced by an external stimulus such as heat, electricity or magnetism. This behavior has been observed in metals, ceramics and polymers (Lendlein and Langer, 2002; Gall et al., 2009; Gao et al., 2011; Diani et al., 2006).

Shape memory materials have been researched, developed, and utilized in a wide range of applications such as advanced technologies in the aerospace, medical and oil exploration industries (Lendlein and Behl, 2009; Small IV et al., 2010; Leng et al., 2009). Among all smart materials, we focus on shape memory polymers (SMPs). In contrast to other smart materials such as shape memory alloys, SMPs possess the advantages of large elastic deformation, low energy consumption for shape programming, low cost, low density, potential biocompatibility, biodegradability and excellent manufacturability (Leng et al., 2009; El Feninat et al., 2002). Because of these characteristics, SMPs have attracted a great deal of interest for their potential applications. Moreover, SMPs have a promising future for application in sensors, actuators and smart devices (Monkman, 2000; Poilane et al., 2000; Tey et al., 2001; Saf, 2010).

Although constitutive modeling of polymers has been carried out in several works (see e.g., Khan and Lopez-Pamies (2002), Reese (2003), Khan et al. (2006), Hasanpour et al. (2009) and Long et al. (2010) among others), but due to complicated
behavior of different polymers, this field of research is still under progress, especially in the study of SMPs. In addition to experimental efforts attempted to characterize the behavior of SMPs (Tobushi et al., 1997, 1998; Lendlein and Langer, 2002; Abrahamsson et al., 2003; Gall et al., 2004; Liu et al., 2004, 2006; Baer et al., 2007; Atlı et al., 2009; Kolesov et al., 2009; Kim et al., 2010; Volk et al., 2010a,b), considerable part of the research has focused on the prediction and description of the SMP behavior through the development of constitutive models.

There have been several attempts to properly reproduce SMP features such as shape memory effect (SME) and time-dependent behavior in a predictive modeling frame (see e.g., Liu et al. (2006), Diani et al. (2006), Kim et al. (2010), Srivastava et al. (2010) among others). In order to develop new constitutive models for SMPs, two general approaches have mainly been adopted: micro modeling and macro modeling. Description of micro-scale features, such as cross-linking, chain mobility, interface motion and entanglement of polymer molecules, is the main focus of micro models. They are useful for understanding the fundamental phenomena, although they are not easily applicable to the structural scale (Xu and Li, 2010; Nguyen et al., 2010). Macro approaches, on the other hand, phenomenologically describe the material behavior and, in general, they are appropriate for being utilized within numerical methods, such as the finite element method (FEM), in an efficient manner (Voyiadjis et al., 2010; Arghavani et al., 2010). In the following, we present a brief review on some constitutive models of SMPs, available in the literature. After introducing the SMPs in early 90s, researchers tried to model the characteristic behavior of these materials. Most of the earlier modeling efforts (Tobushi et al., 1997, 2001; Lin and Chen, 1999; Bhattacharyya and Tobushi, 2000; Abrahamsson et al., 2003; Morshedian et al., 2005) have adopted rheological models consisting of spring, dashpot, and frictional elements in one-dimensional constitutive models. While such models seem to be simple, they have limitations in certain classes of constitutive relations and usually lead to predictions that agree only qualitatively with experiments.

To describe the behavior of the SMPs, several macro or phenomenological constitutive models (Liu et al., 2006; Diani et al., 2006; Chen and Lagoudas, 2008a; Qi et al., 2008; Kim et al., 2010; Reese et al., 2010; Xu and Li, 2010; Baghani et al., 2012), as well as micro or physical based ones (Barot et al., 2008; Nguyen et al., 2008, 2010; Kafka, 2008; Srivastava et al., 2010) have been proposed in recent years.

One of the first phenomenological constitutive models for thermoset SMPs within the small deformation regime has been proposed by Liu et al. (2006). They have adopted a first-order phase transition concept and modeled the SMP as a continuum mixture of a glassy and a rubbery phase. This model additively decomposes the strain into thermal, elastic, and a stored term. The stored strain has been introduced to identify the strain storage and release mechanisms. However, their model simplifies the SMP as a special elastic material hence does not consider the time-dependency of the material behavior. Moreover, the model does not present the mathematical evolution law upon heating (Chen and Lagoudas, 2008a,b). Based on this model, Chen and Lagoudas (2008a,b) developed a 1D constitutive model to capture the characteristics of SMP behavior in the large deformation regime.

Constitutive equations of crystalline SMPs have been formulated by Barot et al. (2008) where the interaction between an original amorphous phase and a semi-crystalline phase is analyzed. Nguyen et al. (2008) have investigated the SMP behavior through structural and stress relaxation mechanisms. They proposed that the shape memory effect in the SMPs is primarily initiated by the drastic change of molecular chain mobility induced by the glass transition. The chain mobility underpins the ability of the chain segments to rearrange locally to bring the macromolecular structure to equilibrium, suggesting that the structure returns instantaneously to the equilibrium state at a high temperature but responds considerably more slowly in cooling process. Such modeling approach macroscopically freezes the material at a low temperature in a non-equilibrium configuration and allows the material to store a temporary shape. Increasing the temperature, the mobility is restored and the shape recovery happens. This approach can be used to physically interpret the mechanisms responsible for the SME. However, the utilization of this approach requires taking advantage of some elaborate physically-based hypotheses e.g., the free energy activation parameter in the Adams–Gibbs model is assumed to be independent of the temperature and pressure which is still questionable (Andreozzi et al., 2004; Xu and Li, 2010).

From a macroscopic point of view, SME can be characterized in a stress–strain-temperature diagram as illustrated in Fig. 1. The thermomechanical cycle starts at a strain- and stress-free state while the temperature is \( T_h \) (high temperature) (point \( \circ \), permanent shape). At this point, a purely mechanical loading is applied to SMP and the material demonstrates a rubbery behavior up to point \( \circ \). At point \( \circ \), strain is held fixed and the temperature is decreased until the rubber-like polymer drastically turns into a glassy polymer at the low temperature \( T_l \) (point \( \odot \), fixed shape). In fact, in the neighbourhood of the transition temperature \( T_s \), SMP exhibits a combination of rubbery and glassy behaviors. Subsequently, the material is unloaded. Regarding much higher stiffness of the glassy phase in comparison to the rubbery phase, after unloading, strains change slightly (point \( \odot \)). Finally, the temperature is increased up to \( T_h \). It is seen that the strain will relax and the original permanent shape can be recovered (point \( \circ \)). It is noted that based on the quality of the SMP, in some practical cases, some residual strain may remain in the SMP (point \( \bigcirc \)) (Volk et al., 2010a). This cycle is called stress-free strain recovery in SMP applications. In practice, other types of recoveries may happen. If at point \( \odot \), the strain is fixed and the temperature is increased, the fixed-strain stress recovery (point \( \bigcirc \)) happens. The dotted line in Fig. 1. illustrates the mentioned behavior schematically.

In this study, we present a 3D constitutive model for thermoset SMPs, based on the continuum thermodynamic considerations. We focus on a phenomenological or macro-modeling approach, which is able only to give an average representation of the phenomena occurring at the material micro-mechanical level (Xiao et al., 2006; Voyiadjis et al., 2010). Recently, with the aim of improving the SMP mechanical properties, e.g., strength and stiffness, hard particles (e.g., glass microballoons) are
dispersed in SMP matrices (Li and Nettles, 2010). To capture the behavior of this family of composites, we assume the material as a mixture of a hard segment and an SMP matrix. Using the rule of mixture, we then incorporate the effect of hard segment in the constitutive model. As the stiffness of the hard segment is much higher than the stiffness of the rubbery or glassy phases (Li and Nettles, 2010), the obtained composite generates a higher value of stress in the fixed-strain stress recovery which is a desirable feature in engineering applications. Moreover, taking into account the importance of time-dependent behavior in modeling of polymer materials, three tensorial internal variables (corresponding to the rubbery, glassy and hard phases) are incorporated into the presented constitutive model.

The article is organized as follows. In Section 2, a three-dimensional thermodynamically-consistent constitutive model of a thermoset SMP-based material is developed in the small strain regime. In Section 3, time-discrete form of the introduced model is presented within the finite element framework. In Section 4, we apply the proposed constitutive model to several examples and investigate the ability of the model to reproduce the features of the SMPs. In Section 5, using the proposed finite element model, two boundary value problems, i.e., a 3D beam and a medical stent are simulated. Finally, in Section 6, we present a summary and draw conclusions.

2. Constitutive model development

2.1. Kinematic description

In this study, we separate the material domain into shape memory polymer and hard segments. Further, we divide the shape memory polymer segment into glassy and rubbery phases. In this regard, we introduce the equivalent representative volume element (RVE) of the material as schematically illustrated in Fig. 2.

Assuming small strains, we decompose the total strain additively into four parts; shape memory polymer, hard, irreversible and thermal parts. This decomposition has already been applied in one-dimensional modeling of SMP based foams by Xu and Li (2010).

![Fig. 1. Stress–strain-temperature diagram illustrating the thermomechanical behavior of a pre-tensioned shape memory polymer under different strain or stress recovery conditions.](image)

![Fig. 2. Equivalent representative volume element for shape memory polymer and hard segments: dots represent the hard segment in all cases. Left: at $T = T_g$, dominant glassy phase. Middle: at $T = T_c$, combination of all phases. Right: at $T = T_r$, dominant rubbery phase.](image)
\[ \varepsilon = \varepsilon^p + \varepsilon^g + \varepsilon^e + \varepsilon^T \]  

(1)

where subscripts \( p \) and \( h \) stand for the SMP and hard segments, respectively. Also, \( \varepsilon^e \) and \( \varepsilon^T \) are the irreversible and thermal strains, respectively, while \( \varepsilon^p \) describes the strain in SMP segment of the RVE. \( \phi_p \) and \( \phi_h \) denote the volume fractions of the SMP and hard segments of the RVE, respectively with the constraint \( \phi_p + \phi_h = 1 \).

Further, the strain in the SMP segment is decomposed into two components. Such a decomposition has already been applied in other works (Liu et al., 2006; Chen and Lagoudas, 2008a; Kim et al., 2010).

\[ \varepsilon^p = \phi_p \varepsilon^e + \varepsilon^g \]  

(2)

where subscripts \( r \) and \( g \) stand for the rubbery and glassy phases, respectively. \( \varepsilon^C \) represents the total strain in the glassy phase. Also, \( \phi_r \) and \( \phi_g \) are volume fractions of the rubbery and glassy phases, respectively with \( \phi_r + \phi_g = 1 \). It is assumed that \( \phi_p \) and \( \phi_h \) are constants, while \( \phi_r \) and \( \phi_g \) are functions of temperature.

2.1.1. Strain storage and recovery

We now consider the phase transformation (rubbery to glassy and vice versa) in the representative volume element (RVE). Assuming temperature decreasing, the strain in the newly generated glassy phase, already been in the rubbery phase, had experienced the \( \varepsilon^r \) previously. Then \( \phi_g \varepsilon^C \) is defined as:

\[ \phi_g \varepsilon^C = \phi_g (\varepsilon^e + \varepsilon^i) = \phi_g \left( \varepsilon^e + \frac{1}{V_g} \int_{V_g} \varepsilon^e d\nu \right) = \phi_g \varepsilon^e + \frac{1}{V_p} \int_{V_p} \varepsilon^e d\nu \]  

(3)

where \( V_g \) and \( V_p \) are volumes of the glassy phase and the SMP segment, respectively. In (3), strain in the glassy phase is divided into two parts: strain in the old glassy phase, \( \varepsilon^g \), and strain in the newly generated glassy phase, \( \varepsilon^i \). We now recast (3) as:

\[ \phi_g \varepsilon^C = \phi_g \varepsilon^g + \int \varepsilon^e d\phi_g = \phi_g \varepsilon^g + \varepsilon^s \]  

(4)

Consequently in a cooling process \( \varepsilon^s \) is defined as:

\[ \varepsilon^s = \int \varepsilon^e d\phi_g \]  

(5)

Such a strain storage in the cooling process has previously been introduced by Liu et al. (2006). In contrast to the cooling process, in a heating process, the stored strain in the glassy phase should be relaxed. This can be mathematically shown as:

\[ \phi_g \varepsilon^C = \phi_g (\varepsilon^g + \varepsilon^i) = \phi_g \left( \varepsilon^g + \frac{1}{V_g} \int_{V_g} \varepsilon^g d\nu \right) = \phi_g \varepsilon^g + \frac{1}{V_p} \int_{V_p} \varepsilon^g d\nu \]  

(6)

We may write (6) in a more compact form as:

\[ \phi_g \varepsilon^C = \phi_g \varepsilon^g + \int \frac{\varepsilon^i}{\phi_g} d\phi_g = \phi_g \varepsilon^g + \varepsilon^s \]  

(7)

As a result, in a heating process \( \varepsilon^s \) is defined as:

\[ \varepsilon^s = \int \frac{\varepsilon^i}{\phi_g} d\phi_g \]  

(8)

We remark that the strain storage/release occurs only in the glassy phase. However, by definition, \( \varepsilon^s \) is assigned to the whole RVE. As a result, a division by \( \phi_g \) appears in the integrals of Eqs. (6)–(8). From (5) and (8), it is concluded that \( \varepsilon^s \) is a fully thermal-driven variable. Moreover, we combine (5) and (8) to obtain:

\[ \varepsilon^s = k_1 \int \varepsilon^e d\phi_g + k_2 \int \frac{\varepsilon^i}{\phi_g} d\phi_g; \begin{cases} k_1 = 1, & k_2 = 0; \quad \dot{T} < 0 \\ k_1 = 0, & k_2 = 1; \quad \dot{T} > 0 \\ k_1 = 0, & k_2 = 0; \quad \dot{T} = 0 \end{cases} \]  

(9)

where \( \dot{\theta} = \partial / \partial t \) represents the derivative with respect to time. Also, \( k_1 \) and \( k_2 \) are constants to be utilized to identify the heating and cooling processes.

Based on the experimental observations, time-dependent effects are of importance in constitutive modeling of polymeric materials (see e.g., Khan and Zhang (2001), Huber and Tsakmakis (2000) and Reese (2003) among others). Experimental observations also reveal that the storage/release process is a highly temperature-driven phenomenon (see e.g., Diani et al. (2011) and Volk et al. (2010a, among others). It is noted that although some SMPs may show time-dependent storage during the cooling process (Li and Xu, 2011) but this is beyond the scope of this paper.
In fact, to capture the viscoelastic behavior of SMPs in each phase, another decomposition should be employed. In this work, we assume that the material in all three phases behaves viscoelastically. Utilizing the small strain assumption, we may additively decompose strains in the glassy, rubbery and hard phases as:

$$\varepsilon^\beta = \varepsilon^{\beta e} + \varepsilon^{\beta i} \quad \beta = r, g, h$$

(10)

where the superscripts $\varepsilon^\beta$ and $i\beta$ denote the elastic and inelastic (viscous) parts of the strain in all phases, respectively. For instance, $\varepsilon^e$ and $\varepsilon^i$ denote elastic and inelastic (viscous) strains in the rubbery phase. Such a decomposition in the rubbery and glassy phases has been previously utilized in one-dimensional constitutive modeling of SMP behavior by Kim et al. (2010) and will be used in the following. We emphasize that the viscoelastic internal variables $\varepsilon^{\beta} \,(\beta = r, g, h)$, are employed to describe just the material time-dependent behavior and are not able to describe the storage and release mechanisms in SMPs.

A schematic rheological illustration as shown in Fig. 3 could be helpful to follow the derivation of the equations in this Section. We remark that the total strain is the weighted summation of the strain in each phase (weights have been shown on the left hand side of each element in Fig. 3).

### 2.2. Free-energy density function for the RVE

We now express the convex free-energy density function $\Psi$ for an amorphous SMP material. Based on the mixture rule, we express the following form for the energy function:

$$\Psi(\varepsilon, T, \phi_g, \phi_h, \varepsilon^r, \varepsilon^g, \varepsilon^h) = \phi_h \Psi_h(\varepsilon^h) + \Psi_T(T) + \phi_r \Psi_r(\varepsilon^r) + \phi_g \Psi_g(\varepsilon^g, \varepsilon^g)$$

(11)

where $\Psi_h, \Psi_g$ and $\Psi_r$ are Helmholtz free-energy density functions of the rubbery, glassy and hard phases, respectively. Also, $\Psi_T$ denotes the thermal energy and temperature is represented by $T$.

In order to enforce the kinematic constraints (1) and (2) in the formulation, we use the method of Lagrange multipliers and add the following term $\Psi_\lambda$ to the free energy (11) (see e.g., Arghavani et al. (2010) and Zaki (2007) among others:

$$\Psi_\lambda = \lambda : \varepsilon - \phi_h (\varepsilon^h + \varepsilon^g) - \phi_r \varepsilon^r$$

(12)

where $\lambda$ is the (tensorial) Lagrange multiplier. Therefore, the free energy function is re-expressed as follows to consider the kinematic constraints (1) and (2) in the formulation:

$$\Psi = \Psi + \Psi_\lambda = \phi_h \Psi_h + \Psi_T + \phi_r \Psi_r + \phi_g \Psi_g + \Psi_\lambda$$

(13)

We also define:

$$\Psi_g(\varepsilon^g, \varepsilon^{eq}) = \Psi^{equiv}(\varepsilon^g), \quad \beta = r, g, h$$

(14)

where the superscripts $eq$ and $neq$ stand for equilibrium and non-equilibrium parts of $\Psi_g(\varepsilon^g, \varepsilon^{eq})$. In the present model, it is emphasized that the internal variables are $\varepsilon^g, \varepsilon^r, \varepsilon^{eq}$, $\varepsilon^i$ and $\varepsilon^e$. Thus, we should define evolution equations for the internal variables in the context of continuum thermodynamics. It is noted that we use a prescribed evolution equation for $\phi_g$. This equation is derived using the unconstrained strain recovery of the material as a function of temperature (see the Appendix A).

### 2.3. Thermodynamic considerations

The intrinsic mechanical dissipation in the Clausius–Duhem form is defined as (Haupt, 2002; Lubarda, 2001):

$$D^{mech} = \sigma : \dot{\varepsilon} - (\Psi + \eta \dot{T}) \geq 0$$

(15)

where $\eta$ is the entropy. Substituting (13) and (14) into (15) leads to the following inequality:
Furthermore, the Clausius–Duhem inequality (16) is reduced to:

\[\lambda - \eta \dot{T} > 0\]

where \(\dot{\gamma} = \partial \gamma / \partial T\) denotes the derivative with respect to temperature. Regarding (9), the evolution equation of \(\dot{\varepsilon}^r\) in the rate form, is obtained as:

\[
\dot{\varepsilon}^r = \phi_g \dot{T} \left( k_t \varepsilon^r + k_n \varepsilon^h \right)
\]

(17)

It is noted that stored strain \(\varepsilon^s\) inherently consists of thermal-driven time-dependent parts. For example, we may decompose \(\varepsilon^s\) in the form of \(\varepsilon^s = \varepsilon^s_1 + \varepsilon^s_2\) where \(\varepsilon^s_1\) and \(\varepsilon^s_2\) denote the stored strains related to the elastic and viscous effects during the storage process, respectively, with the following evolution equation laws:

\[
\begin{align*}
\dot{\varepsilon}^s_1 & = \phi_g \dot{T} \left( k_t \varepsilon^r + k_n \varepsilon^h \right) \\
\dot{\varepsilon}^s_2 & = \phi_g \dot{T} \left( k_t \varepsilon^r + k_n \varepsilon^h \right)
\end{align*}
\]

(18)

However, Eq. (18) are consistent with Eq. (17) which does not consist of the elastic or viscous terms. Since we did not require the components of the stored strain \(\varepsilon^r_1\) and \(\varepsilon^r_2\), we may alternatively combine these equations and arrive at Eq. (17).

Inequality (16) must be fulfilled for arbitrary thermodynamic processes, i.e. for arbitrary \(\varepsilon, \dot{\varepsilon}, \varepsilon^r, \varepsilon^h, \dot{\varepsilon}^r, \dot{\varepsilon}^h, \lambda\) and \(T\). For arbitrary choices of the variables \(\varepsilon, \dot{\varepsilon}, \varepsilon^r, \varepsilon^h, \lambda\) and \(T\), we may conclude (Coleman and Gurtin, 1967):

\[
\begin{align*}
\sigma & = \lambda + \phi_p \frac{\partial \psi^{\text{meq}}}{\partial \varepsilon^r} + \phi_g \frac{\partial \psi^{\text{meq}}}{\partial \varepsilon^h} - \phi_p \frac{\partial \psi^{\text{meq}}}{\partial \varepsilon^r} + \phi_g \frac{\partial \psi^{\text{meq}}}{\partial \varepsilon^h} \\
\varepsilon & = \phi_p \left( \varepsilon^r + \varepsilon^h \right) + \phi_g \left( \varepsilon^s_1 + \varepsilon^s_2 \right) + \varepsilon^r + \varepsilon^h \\
\eta & = -\dot{T} - \phi_p \frac{\partial \psi^{\text{meq}}}{\partial \varepsilon^r} + \phi_g \frac{\partial \psi^{\text{meq}}}{\partial \varepsilon^h} + \phi_p \left( \varepsilon^s_1 + \varepsilon^s_2 \right) + \varepsilon^r \\
\end{align*}
\]

(19)

Furthermore, the Clausius–Duhem inequality (16) is reduced to:

\[
\phi_p \left( \frac{\partial \psi^{\text{meq}}}{\partial \varepsilon^r} + \phi_g \frac{\partial \psi^{\text{meq}}}{\partial \varepsilon^h} \right) + \phi_p \frac{\partial \psi^{\text{meq}}}{\partial \varepsilon^r} + \phi_g \frac{\partial \psi^{\text{meq}}}{\partial \varepsilon^h} = \dot{\varepsilon}^r + \dot{\varepsilon}^h + \sigma \geq 0
\]

(20)

In accordance with the viscoelastic behavior of polymers, the following evolution equations are sufficient conditions for satisfaction of (20):

\[
\begin{align*}
\dot{\varepsilon}^r & = \frac{1}{\eta_r} \frac{\partial \psi^{\text{meq}}}{\partial \varepsilon^r}, \\
\dot{\varepsilon}^h & = \frac{1}{\eta_h} \frac{\partial \psi^{\text{meq}}}{\partial \varepsilon^h}, \\
\dot{\varepsilon}^s_1 & = \frac{1}{\eta_n} \frac{\partial \psi^{\text{meq}}}{\partial \varepsilon^s_1}, \\
\dot{\varepsilon}^s_2 & = \frac{1}{\eta_n} \frac{\partial \psi^{\text{meq}}}{\partial \varepsilon^s_2}
\end{align*}
\]

(21)

where \(\eta_r, \eta_h, \eta_n\) and \(\eta_l\) are positive viscous coefficients of the rubbery, glassy, hard and irreversible parts, respectively.

We now summarize the constitutive equations in the time-continuous frame in Table 1.

### 3. Time-discrete form of the constitutive model

In this section, we investigate the numerical solution of the constitutive model derived in Section 2 and summarized in Table 1, with the final goal of using it within a finite element program. The main task is to apply an appropriate numerical time-integration scheme to the evolution equations of the internal variables. It is noted that, in general, implicit schemes are preferred because of their stability at larger time step sizes. Moreover, the present section provides some details about the stress update and the computation of the consistent tangent matrix. These are two main points where the material model is directly connected to the finite element solution procedure. We treat the non-linear problem described in Section 2 as an implicit time-discrete deformation-driven problem. Accordingly, we subdivide the time interval of interest \([0, T]\) in sub-increments and solve the evolution problem over the generic interval \([t_n, t_{n+1}]\) with \(t_{n+1} > t_n\). To simplify the notation, we indicate with the subscript \(n\) a quantity evaluated at time \(t_n\), and with no subscript a quantity evaluated at time \(t_{n+1}\) (Arghavani et al., 2011). Further, we show the increment of time by \(\Delta t\). Assuming to know the solution and the strain \(\varepsilon_n\) at time \(t_n\) as well as the stress \(\sigma\) at time \(t_n\), the stress and the internal variables should be updated from the deformation history.

#### 3.1. Time integration scheme

In this section, we introduce quadratic forms for the free-energy density functions as follow:
Regarding (17), the discrete form of the evolution equation for the stored strain is obtained as:

\[ e^{is}_n = e^{is}_{n-1} + \Delta \phi_s \left( k_{s1} e^r + k_{s2} \frac{e^{is}}{\phi_s} \right) \]  

where \( \Delta \phi_s = \phi_s - \phi_{0s} \). Consequently, we obtain:

\[ e^{is} = \left( 1 - \Delta \phi_s \frac{k_{s3}}{\phi_s} \right)^{-1} \left( e^{is}_{n-1} + \Delta \phi_s k_{s1} e^r \right) \]  

Finally, we conclude:

\[
\begin{cases}
  e^{is} = k_{s1} e^r + k_{s4} e^r \\
k_{s3} = (1 - \Delta \phi_s \frac{k_{s2}}{\phi_s})^{-1} \\
k_{s4} = k_{s1} k_{s3} \Delta \phi_s 
\end{cases}
\]
3.2. Consistent tangent matrix

In this section, we report the construction of the tangent matrix. Using the discrete form of (19)\textsubscript{1}, we may write:

\[ \sigma = \kappa_p^{\text{eq}} : \varepsilon^p + \kappa_{\text{pl}}^{\text{eq}} : (\varepsilon^p - \varepsilon_0^p) ; \quad \beta = r, g, h \]  

(29)

Moreover, we have:

\[ \sigma = \kappa_p^{\text{eq}} : \varepsilon^p + \frac{\eta_r}{\Delta t} (\varepsilon^p - \varepsilon_n^p) = \left( \kappa_p^{\text{eq}} + \frac{\eta_r}{\Delta t} \right) : \varepsilon^p + \frac{\eta_r}{\Delta t} (\varepsilon^p - \varepsilon_n^p) \]  

(30)

We now recast (30) in a more compact form as:

\[ \sigma = \varepsilon^p : \varepsilon^p + \mathbf{Q}_n^p \]  

(31)

where

\[ \varepsilon^p = \kappa_p^{\text{eq}} + \frac{\eta_r}{\Delta t} \varepsilon^p, \quad \mathbf{Q}_n^p = \frac{\eta_r}{\Delta t} (\varepsilon^p - \mathbf{1}) : \varepsilon_n^p ; \quad \beta = r, g, h \]  

(32)

We now write strains \( \varepsilon^e, \varepsilon^h \) and \( \varepsilon \) in terms of \( \varepsilon^r \) as:

\[ \varepsilon^e = \varepsilon^e + \varepsilon \]  

(33)

\[ \varepsilon^h = \varepsilon^h + \varepsilon \]  

(34)

Substituting (33) and (34) into (19)\textsubscript{2}, we obtain:

\[ \varepsilon = \phi_p (\phi_s \varepsilon^e + \varepsilon^h - \mathbf{Q}_n^p + \phi_s \varepsilon^r + k_{\text{pl}} \varepsilon_0^r + k_{\text{pl}} \varepsilon^r) + \phi_h \varepsilon^h + \phi_h \varepsilon^r + \frac{\Delta t}{\eta_r} (\varepsilon^r : \varepsilon^r + \mathbf{Q}_n^r) \]  

(35)

Solving (35) for \( \varepsilon^r \), we obtain the following relation:

\[ \mathbf{A} : \varepsilon^r = \mathbf{b} \]  

(36)

where

\[ \mathbf{A} = \phi_p \phi_s \varepsilon^e + \phi_h \varepsilon^h + \phi_p \varepsilon^r + \phi_h \varepsilon^r + \frac{\Delta t}{\eta_r} \varepsilon^r + \left( \phi_s + k_{\text{pl}} \right) \mathbf{I} \]  

\[ \mathbf{b} = \varepsilon - \phi_p (\phi_s \varepsilon^e + \phi_h \varepsilon^h + k_{\text{pl}} \varepsilon_0^r + k_{\text{pl}} \varepsilon^r) - \phi_h \varepsilon^h - \phi_h \varepsilon^r - \frac{\Delta t}{\eta_r} \mathbf{Q}_n^r \]  

(37)

Now, we can find an expression for stress using (30). We may write:

\[ \sigma = \varepsilon^p + \frac{\eta_r}{\Delta t} \varepsilon^p + \phi_h \varepsilon^h : \varepsilon^h + \phi_h \varepsilon^r + \frac{\Delta t}{\eta_r} \varepsilon^r + \left( \phi_h + k_{\text{pl}} \right) \mathbf{I} \]  

(38)

Also, the consistent tangent matrix is calculated as follows:

\[ C^\text{Tan} = \frac{d\sigma}{d\varepsilon} = \varepsilon^p + \frac{\eta_r}{\Delta t} \varepsilon^p + \phi_h \varepsilon^h + \phi_h \varepsilon^r + \frac{\Delta t}{\eta_r} \varepsilon^r \]  

(39)

For more details and discussions on the numerical solution, we refer to Baghani (2012).

**Remark.** In most engineering applications, SMP components are used to provide a force over some large displacement via the shape memory effect e.g., in artery stents. Structural components such as beams and torque tubes usually exhibit large global displacements with small strains. We should remark that small-strain constitutive models can be successfully applied to the solution of such large displacement problems, where strains are small though rotations can be arbitrarily large. From theoretical point of view, it is done by replacing the Cauchy stress, \( \sigma \), and infinitesimal strain, \( \varepsilon \), tensors by the second Piola–Kirchhoff stress and Green–Lagrange strain tensors, respectively, in the formulation (Crisfield, 1997).

However, the numerical manipulation of this procedure follows a standard approach in the literature (Hartl and Lagoudas, 2009), thanks to the well-known Hughes–Winget algorithm (Hughes and Winget, 1980). In fact, for the large displacement problems (where the updated Lagrangian formulation is employed) the time-discretization of the rate form equations should satisfy the objectivity requirements (such algorithms are called incrementally-objective). For a typical Jaumann objective rate form equation \( \mathbf{A} = \mathbf{F}(t, \mathbf{T}, \mathbf{A}, \ldots) \), the incrementally-objective time-discrete form via Hughes–Winget algorithm is obtained as (Hughes and Winget, 1980):
where \( \mathbf{A} \) and \( \mathbf{F} \) are second order tensor quantities in the current configuration. Also, \( \mathbf{Q} \) is the incremental rotation tensor defined as \( \mathbf{Q} = \mathbf{I} + \frac{1}{2} \mathbf{w} \), where \( \mathbf{I} \) represents the second order identity tensor and \( \mathbf{w} \) is the vorticity tensor (asymmetric part of the velocity gradient tensor).

Finally, we should highlight that, to use a small-strain constitutive model for solution of large displacement problems in software ABAQUS/Standard, the user should activate the option NLGEOM. However, in this case, only stress and strains are automatically rotated incrementally by the software. The rotation of user-defined tensorial internal variables \( (\mathbf{v}^a, \mathbf{v}^b, \mathbf{v}^c, \mathbf{v}^e, \mathbf{v}^f) \) are left to the user, while the tensor \( \mathbf{Q} \) is passed through the UMAT as a 3 × 3 matrix \( \mathbf{D}_{\text{rot}} \).

4. Model verification

The present section deals with several uni-axial and multi-axial loading paths. In particular, Examples 4.1, 4.2.1 and 4.2.2 present the results for uni-axial tests to show the model capability of reproducing basic effects such as shape memory effect and time-dependent behavior in different recovery conditions, comparing them also with experimental data available in the literature. Examples 4.3.1 and 4.3.2 present the results for multi-axial combined tension–torsion tests to show the model ability to predict the material behavior under complicated multi-axial loading paths. Furthermore, the identification of material parameters involved in the constitutive equations is reported in Appendix A.

4.1. Example 1: reproduction of stress-free strain recovery and fixed-strain stress recovery

In order to show the ability of the model to show the shape memory effect in different strain and stress recovery paths, we ignore the time-dependent effects as well as the hard segment of the equivalent RVE (\( \phi_h = 0 \)). We use the experiments done by Liu et al. (2006) and adopt the material parameters reported in Table 2. As shown in Fig. 4, the model is able to reproduce the characteristic shape memory effect in stress-free strain recovery as well as in fixed-strain stress recovery.

4.2. Time-dependent aspects in modeling of SMP behavior

4.2.1. Example 2: according to experiments done by Li and Nettles (2010)

To show the validity and accuracy of the model in time-dependent regimes of thermomechanical loadings, we simulate experiments reported by Li and Nettles (2010) already used by Xu and Li (2010).

During the experiment, an SMP-based syntactic foam sample is compressed under a constant stress \( \sigma_0 = \) 263 kPa at \( T_h \), held for 30 min. Then the sample is cooled down to \( T_l \) while the stress is held constant. The cooling rate is determined by Newtons law of cooling: \( \frac{dT}{dt} = 4.6 \times 10^{-5} (T - 293) \). Once the temperature reaches \( T_l \) (at \( t = 1256 \) min), the load is removed and the sample is heated up to \( T_h \) in a stress-free manner with heating rate \( = 0.3 \frac{\text{K}}{\text{min}} \). Corresponding material parameters are presented in Table 3. The strain–time behavior is illustrated in Fig. 5 (left). These results show good correlation between experimental results and numerical simulation. Now, if the recovery happen in a fixed-strain stress recovery, the stress–temperature behavior of the material will be obtained as shown in Fig. 5 (right). As results show, in spite of some discrepancy, the overall trend is in good agreement with the experimental data.

4.2.2. Example 3: according to experiments done by Volk et al. (2010a,b)

Recently, Volk et al. (2010a,b) have performed a series of time-dependent experiments on Veriflex™. They have also calibrated the model presented previously by Chen and Lagoudas (2008a, 2008b). This model has been developed for fully thermo-elastic loadings. Therefore, it does not consider irreversible strains in an SMP stress-free strain recovery cycle. The test conditions (time and temperature dependency of the test) was fully reported in work done by Volk et al. (2010b) for the case of heating rate \( = 2 \frac{\text{K}}{\text{min}} \). Corresponding material parameters are presented in Table 4. Fig. 6 shows the strain-temperature relationship during a stress-free strain recovery in two different prescribed strains \( \varepsilon_0 \). It is observed that the proposed model can successfully predict the time-dependency and the amount of irreversible strains. In order to compare model predictions, results predicted by Chen and Lagoudas (2008a) are also illustrated in Fig. 6.

4.3. Multiaxial loadings

4.3.1. Example 4: multiaxial loading-path 1

In this section, we simulate a multiaxial loading path. We use the material parameters reported in Table 3 except that \( \phi_h = 0.33 \). First, at \( T = T_h \), we apply a strain \( \varepsilon_0 = 0.1 \) for \( \Delta T = 50 \) min. Then, we hold the normal strain constant and apply a shear strain \( \varepsilon_{12} = \varepsilon_{13} = 0.15 \) for \( \Delta T = 50 \) min. Holding the strains fixed, we let the material relax the viscous effects for...
Table 2
Material parameters adopted from experiments reported by Liu et al. (2006).

<table>
<thead>
<tr>
<th>Material parameters</th>
<th>Values</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{eq}$, $E_{eq}^g$</td>
<td>8.8, 813 MPa</td>
<td>[MPa]</td>
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<tr>
<td>$\phi_r, \phi_g$</td>
<td>0, 0</td>
<td>[-]</td>
</tr>
<tr>
<td>$v_r, v_g$</td>
<td>0.4, 0.3</td>
<td>[-]</td>
</tr>
<tr>
<td>$T_l, T_g, T_h$</td>
<td>273, 343, 358 [K]</td>
<td>[-]</td>
</tr>
<tr>
<td>$\mu$</td>
<td>$(-3.14 \times 10^{-4} (T - T_h) + 0.7 \times 10^{-6} (T^2 - T_h^2))$</td>
<td>[-]</td>
</tr>
<tr>
<td>$\rho_{\phi}$</td>
<td>$1/(1 + 2.76 \times 10^{-5} (T_h - T)^4)$</td>
<td>[-]</td>
</tr>
</tbody>
</table>

Fig. 4. Reproduction of the shape memory effect: stress-free strain recovery (left), fixed-strain stress recovery (right).

Table 3
Material parameters adopted from experiments reported by Li and Nettles (2010).

<table>
<thead>
<tr>
<th>Material parameters</th>
<th>Values</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{eq}$, $E_{eq}^g$</td>
<td>1.3, 15.7, 0.2, 247, 1000 MPa</td>
<td>[MPa]</td>
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<tr>
<td>$\eta_\tau, \eta_\gamma, \eta_\phi$</td>
<td>$5, 30 \times 10^5, 30 \times 10^5$ MPa min</td>
<td>[-]</td>
</tr>
<tr>
<td>$\phi_h$</td>
<td>0.4</td>
<td>[-]</td>
</tr>
<tr>
<td>$v_r, v_g, v_h$</td>
<td>0.4, 0.3, 0.3</td>
<td>[-]</td>
</tr>
<tr>
<td>$T_l, T_g, T_h$</td>
<td>296, 344, 353 [K]</td>
<td>[-]</td>
</tr>
<tr>
<td>$\mu$</td>
<td>$0.5542 \times 10^{-3} T - 0.01083456 - 7 \times 10^{-7} T^2$</td>
<td>[-]</td>
</tr>
<tr>
<td>$\rho_{\phi}$</td>
<td>$1/\exp(-\Delta_{\phi}/T)$</td>
<td>[-]</td>
</tr>
</tbody>
</table>

Fig. 5. Reproduction of the shape memory effect: stress-free strain recovery (left), fixed-strain stress recovery (right). Experiments reported by Li and Nettles (2010).
We now decrease the temperature down to $T_{l}$ for $D_{t} = 100$ min. After that, we unload the stresses and allow the system to relax for $D_{t} = 100$ min. In this step, the material is in temporary shape. Finally, the temperature is increased to $T_{h}$ for $D_{t} = 50$ min. Increase of the temperature leads to recovery of the strain, thus the material recovers its initial shape.

Fig. 7a–d present the time and temperature histories of stress and strain components, respectively.

As one may see, due to time-dependent behavior of SMPs, applying a strain produces an over-stress in the material as depicted in Fig. 7a. Besides, holding strains fixed during cooling leads to an increase in normal stresses which happens due to negative thermal strains and glassy-rubbery phase transformation. Moreover, even after heating and recovery, some irreversible strains remain in the material as shown in Fig. 7b and d.

4.3.2. Example 5: multiaxial loading-path 2

In this section, we simulate another multiaxial loading path. The structure is initially under an external load $\sigma_{33} = 500$ kPa. First, at $T = T_{h}$, we apply a strain, $\epsilon_{11} = 0.1$ in $D_{t} = 50$ min. Then, we hold the normal strain $\epsilon_{11}$ constant and apply strain $\epsilon_{22} = 0$ in $D_{t} = 50$ min. Holding the strains ($\epsilon_{11} = 0.1, \epsilon_{22} = 0$) and stress ($\sigma_{33} = 500$ kPa) fixed, we allow the structure to relax the viscous effects for $D_{t} = 150$ min. We now decrease the temperature to $T_{l}$ in $D_{t} = 100$ min. Subsequently, we unload the stresses (by removing the external constraints and loads) and let the system relax for $D_{t} = 100$ min. In this stage, the system is in a temporary shape. Finally, the structure is heated up to $T_{h}$ in $D_{t} = 50$ min. Fig. 7(a, b, c, d) present the time and temperature history of stress and strain components, respectively. We use the material properties reported in Table 2 except that $\phi_{h} = 0.33$.

Similar to previous example, because of time-dependent behavior of the SMP, applying a strain produces an over-stress in the material as shown in Fig. 8a. Also, holding strains fixed during cooling leads to an increase in normal stresses which happens due to negative thermal strains and glassy-rubbery phase transformation. Furthermore, after shape recovery, some irreversible strains remain in the material as illustrated in Fig. 8b and d.

5. Boundary value problems

In this section, we solve two boundary value problems to validate the proposed model as well as the numerical solution procedure. A 3D beam and a medical stent are simulated to show the model capability of capturing the shape memory effect.

<table>
<thead>
<tr>
<th>Material parameters</th>
<th>Values</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{eq}$, $E_{eq}$, $E_{eq}$, $E_{eq}$</td>
<td>0.39, 1100, 0.02, 150</td>
<td>[MPa]</td>
</tr>
<tr>
<td>$\eta_{r}, \eta_{g}, \eta_{r}$</td>
<td>1, 4000, 10000</td>
<td>[MPa min]</td>
</tr>
<tr>
<td>$\phi_{h}$</td>
<td>0.0</td>
<td>[-]</td>
</tr>
<tr>
<td>$\nu_{r}, \nu_{g}$</td>
<td>0.4, 0.3</td>
<td>[-]</td>
</tr>
<tr>
<td>$T_{l}, T_{g}, T_{h}$</td>
<td>298, 345, 363</td>
<td>[K]</td>
</tr>
<tr>
<td>$e^{I}$</td>
<td>$(\phi_{r} \alpha_{r} + \phi_{g} \alpha_{g})(T - T_{a})I$</td>
<td>[-]</td>
</tr>
<tr>
<td>$x_{r}, x_{g}$</td>
<td>$0.7 \times 10^{-4}, 5.9 \times 10^{-5}$</td>
<td>[K]</td>
</tr>
<tr>
<td>$\phi_{g}$</td>
<td>$\tanh((T_{h}/C_{0} - T_{g})/b) - \tanh((T_{l}/C_{0} - T_{g})/b)$</td>
<td>$b = 7.33$</td>
</tr>
</tbody>
</table>

Fig. 6. Reproduction of the shape memory effect: stress-free strain recovery. Experiments reported by Volk et al. (2010b).
5.1. 3D SMP beam with distributed force on upper surface: shape memory effect test

In this example, a 3D SMP beam is simulated. To this end, a beam with 100 mm length, 12.5 mm width and 10 mm height has been modeled under fully clamped boundary conditions along one end. The history of the applied distributed force on the upper surface and temperature are illustrated in Fig. 9 (left). Owing to the low temperature, while the external load is removed, the beam remains in a deformed state. The structure is in the temporary shape at $t = 600$ min. However, the initial shape is recovered after heating. Fig. 10 illustrates the steps of the shape memory effect in a stress-free strain recovery cycle. Moreover, the displacement-temperature behavior of the upper middle node at the free end of the beam is shown in Fig. 9 (right). Further, to have a better comparison among different steps of an SMP cycle, the two dimensional illustration of the beam is plotted in Fig. 11. It can be obviously seen that the beam recovers its original shape.

5.2. Medical SMP stent: shape memory effect test

In this example, an SMP stent is simulated. Initial configuration of the stent has been shown in Fig. 12-left. Due to the symmetry of the problem in our simulation, we considered only a quarter of the stent geometry. The stent has a length of 20 mm, an inner radius of $R_i = 4.8$ mm and an outer radius of $R_o = 5$ mm. The diameter of the holes is $d = 0.5$ mm. At $T = T_h$, during $t_1 = 200$ min, a displacement $u_y = -5$ mm along line AB is applied to the stent while the displacement $u_z = 2$ mm is applied on the face C simultaneously. We now let the stent relax up to $t_2 = 300$ min. Between $t_2$ and $t_3 = 500$ min, the stent is being cooled down to $T = T_l$. Consequently, during $t_3$ and $t_4 = 500$ min the whole structure is abruptly being unloaded. The temporary shape of the stent is shown in Fig. 12-right. As shown in Fig. 13, in spite of removing the external loads, the stent memorizes its temporary shape. In this step we let the system relax prior to $t_5 = 700$ min. This step is followed by heating the stent up to $T = T_h$ until $t_6 = 1000$ min. The contours in Fig. 13 refer to the von-Mises stress at different steps of a stress-free strain recovery cycle.

6. Summary and conclusions

In this paper, we presented a 3D constitutive model for shape memory polymers which reasonably captures the essential features of the shape memory behavior under time-dependent multiaxial loadings. In many applications shape memory
polymers are used in accompanying with another material such as glass particles as a reinforcing phase. In order to capture the behavior of this family of composites, a hard segment was incorporated into the proposed constitutive model. For this purpose, assuming small strains, we used an additive decomposition of the strain into six parts using a first order mixture rule. In fact, the material was considered as a mixture of rubbery, glassy and hard phases. It was also assumed that the volume fraction of the hard phase was constant while the rubbery and glassy phases were able to be transformed to each other through external stimuli of heat. The evolution laws for internal variables were derived in an arbitrary thermomechanical loading. Moreover, the polymer in each phase (the rubbery, glassy or hard phase) was considered as a viscoelastic material.

Fig. 8. Reproduction of the shape memory effect: stress-free strain recovery.

![Fig. 8](image)

Fig. 9. History of the distributed force and temperature applied to the beam (left). Displacement-temperature behavior of the upper middle node at free end of the beam (right). $|u|$, $|u_{\text{max}}|$ and $|P_{\text{max}}|$ denote the magnitude of displacement, maximum magnitude of displacement and maximum distributed force, respectively.

![Fig. 9](image)
Fig. 10. Reproduction of the shape memory effect: stress-free strain recovery at different steps of an SMP cycle. (a) $t = 0$ min, structure at rest at $T_h$; (b) $t = 10$ min, load has been fully applied at $T_h$; (c) $t = 200$ min, beam has been relaxed at $T_h$; (d) $t = 500$ min, system has been cooled down to $T_l$ and relaxed; (e) $t = 510$ min, external load has been removed at $T_l$; (f) $t = 600$ min, system has been relaxed at $T_l$; (g) $t = 770$ min, glass transition at $T_g$; (h) $t = 800$ min, temperature has been increased up to $T_h$; (i) $t = 1000$ min, the structure is relaxed until the permanent shape has been fully recovered at $T_h$.

Fig. 11. Reproduction of the shape memory effect: stress-free strain recovery at different steps of an SMP cycle. Steps are in correspondence with Fig. 10. (a) $t = 0$ min, structure at rest at $T_h$; (b) $t = 10$ min, load has been fully applied at $T_h$; (c) $t = 200$ min, structure has been allowed to relax at $T_h$; (d) $t = 500$ min, system has been cooled down to $T_l$ and relaxed; (e) $t = 510$ min, external load has been removed at $T_l$; (f) $t = 600$ min, system has been relaxed at $T_l$; (g) $t = 770$ min, glass transition at $T_g$; (h) $t = 800$ min, temperature has been increased up to $T_h$; (i) $t = 1000$ min, permanent shape has been fully recovered at $T_h$. 
For the sake of consistency and completeness, free energy function of the model is introduced which is compatible with the second law of thermodynamics, in the sense of the Clausius–Duhem inequality.

We also presented the time-discrete form of the evolution equations in an implicit form and presented the time integration scheme as well as the construction of the tangent matrix which are the two main issues in the finite element modeling of the material behavior. The model was validated by comparing the predicted results with different experimental data available in the literature. It was shown that the model is capable of capturing the main features reported in experimental observations. Implementing the proposed model within a user-defined subroutine (UMAT) in the commercial non-linear finite element software ABAQUS, we solved two boundary value problems e.g., a 3D beam and a medical stent made of shape memory polymers and showed the capability of the proposed constitutive model. In fact, the model is a useful and appropriate computational tool for design, analysis and optimization of structures made of shape memory polymers.

Appendix A

The material parameters used in Sections 4 and 5, as listed in Tables 2–4, were mainly identified using various experimental results reported in the literature (Liu et al., 2006; Li and Nettles, 2010; Volk et al., 2010b). In the following, we present some guidelines on material parameter identification.

- Characteristic temperatures $T_l$, $T_g$ and $T_h$ are measured using DMA (Dynamic Mechanical Analysis) tests (Liu et al., 2006).
- It is observed that the thermal strain (under no external load) exhibits a nonlinear behavior as the temperature traverses through the glass transition region (Liu et al., 2006; Li and Nettles, 2010; Volk et al., 2010a). Different nonlinear relations have been utilized in the literature to capture this effect. Commonly, a second order polynomial expression for the thermal strain gives a good approximation. As an example, such a curve fitting has been performed in the following form for experimental data reported by Liu et al. (2006) as follows:

$$e(T) = a_1(T - T_h) + a_2(T^2 - T_h^2)$$

where $a_1$ and $a_2$ are material parameters and have been calculated using a curve fitting method as $a_1 = -3.14 \times 10^{-4}$ K$^{-1}$ and $a_2 = 0.7 \times 10^{-6}$ K$^{-2}$. Fig. 14 (left) shows the fitted curve and the experimental data reported in Liu et al. (2006) for the thermal strain.

- Volume fractions $\phi_n$ and $\phi_p$ are constant parameters. In order to specify the evolution equation for the volume fraction of the glassy phase $\phi_g$ as a function of temperature, we use the fact that Eq. (17) during heating in a 1D stress-free strain recovery (while the stored strain after unloading is $\varepsilon_0$, corresponding to point $\oplus$ in Fig. 1) reduces to:

$$\dot{\varepsilon}_g^B - \frac{\dot{\phi}_g \varepsilon^B}{\phi_g} = 0, \quad \varepsilon^B|_{\phi_g=1} = \varepsilon_0 \Rightarrow \varepsilon^B = \varepsilon_0 \phi_g$$

Eq. (43) shows that the expression for $\phi_g$ should follow the same trend as stored strain $\varepsilon^B$. Thus using a curve fitting method, we define a function which fits the experimental data in the best way. A combination of exponential or power terms normally leads to a successful curve fitting. For instance, such a curve fitting has been utilized for the experimental data reported by Liu et al. (2006) in Fig. 14 (right). In this case, we used a relation for $\phi_g$ in the following form:

$$\phi_g = 1/(1 + c_1(T_h - T)^{c_2})$$

where $c_1$ and $c_2$ are calculated applying a curve fitting method. The obtained values are $c_1 = 2.76 \times 10^{-5}$ K$^{-1}$ and $c_2 = 4$. 

![Fig. 12. Initial configuration of the simulated medical stent (left). Temporary shape of the stent (right). Due to symmetry, only a quarter of the stent has been modeled.](image-url)
Fig. 13. Stress-free strain recovery at different steps of an SMP cycle. (a) $t = 0$ min, structure at rest at $T_h$; (b) $t = 200$ min, load has been fully applied at $T_h$; (c) $t = 300$ min, system has been relaxed at $T_h$; (d) $t = 500$ min, system has been cooled down to $T_l$; (e) $t = 500$ min, external load has been removed at $T_l$; (f) $t = 770$ min, system has been relaxed at $T_l$; (g) $t = 800$ min, during glass transition; (h) $t = 980$ min, during glass transition; (i) $t = 1000$ min, temperature has been increased up to $T_h$; (j) $t = 1200$ min, we let the system relax until the permanent shape be fully recovered at $T_h$. 

Elastic moduli and viscosity coefficients of each phase is calculated using one-dimensional stress–strain curves. The stress–strain responses of a pure SMP \((\phi_h = 0)\) at \(T_h\) as well as \(T_l\) give the elastic moduli and viscosity coefficients of the rubbery and glassy phases, respectively. These parameters for the hard segment are calculated using stress–strain response of the pure hard segment (before producing the composite and mixing the hard segment in the SMP matrix). Due to the lack of experimental data, we assumed values of 0.4, 0.3 and 0.3 for \(\nu_r\), \(\nu_g\) and \(\nu_h\), respectively.

References


