A constitutive model for amorphous shape memory polymers based on thermodynamics with internal state variables

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A B S T R A C T

Shape memory polymers (SMPs) are a class of smart materials which can recover a large pre-deformed shape in response to external stimulus. A thermoviscoelastic finite deformation constitutive model incorporated with structural and stress relaxation to capture the material behavior in the vicinity of the glass transition is developed for thermally activated amorphous SMPs in the paper. The incorporation of the Adam–Gibbs model for structure relaxation and the modified Eyring model for viscous flow into a thermoviscoelastic finite deformation modeling framework is the main feature of the model. Differing from the traditional phenomenological fictive temperature modeling approach, an internal state variable modeling approach developed recently based on thermodynamics is used in the model. Besides, the temperature dependence of the model parameters is studied in the research. Comparisons between the simulation results and the experimental data show good agreement. Furthermore, the predictability of the model is examined by a parametric study and the results also demonstrate the validity of the model.

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1. Introduction

Shape memory polymers (SMPs) have drawn considerable attention for their capability to recover their original shape even after undergoing significant deformation, upon exposure to external stimuli, such as temperature (Small et al., 2010), electricity (Liu et al., 2009), light (Lu et al., 2014), water (Wang et al., 2014), solvent (Lu and Du, 2014; Xiao et al., 2015), radiation (Michal et al., 2013) or magnetic field (Leng et al., 2007; Mohr et al., 2006). SMPs have many advantages over shape memory metallic alloys (SMAs) and shape memory ceramics, such as low cost, light weight, high shape deformability, potential biocompatibility, biodegradability and excellent manufacturability (Heuvers et al., 2013; Hoeber et al., 2013). Therefore, SMPs could be applied in broad areas, ranging from clothing manufacturing, sensors and actuators, intelligent medical devices to self-deployable structures in spacecraft, etc (Leng et al., 2011; Zhao et al., 2015; Hu et al., 2012).

For the shape memory effects (SMEs) of the thermally activated SMPs can be easily triggered and well controlled by temperature, they are the most widely studied class of SMPs and may have more potential applications than other SMPs. In order to describe and predict the thermomechanical behavior of the SMPs, it is critical to develop constitutive models for the thermally activated SMPs. The constitutive models for the thermally activated SMPs could be classified as phase transition models and thermoviscoelastic models. In the phase transition models, the material can be divided into two or more phases, and the mechanism of SMEs could be explained by the transition between different phases. The first two-phase model was proposed by Liu et al. (2006) to describe the shape storage and recovery mechanism of the amorphous SMPs, in which the material was split into frozen and active phases. In order to account for the finite deformation SMEs of the amorphous SMPs, the phase transition modeling approach was further developed by Qi et al. (2008), Reese et al. (2010), Guo et al. (2015) and Park et al. (2016). Based on the theory of multiple natural configurations, a phased transition model for the semicrystalline SMPs was proposed by Barot et al. (2008). Similar modeling approaches were proposed by Westbrook et al. (2010) and Ge et al. (2012) to describe the SMEs of the shape memory elastomeric composites which consist of an elastomeric matrix reinforced by a semicrystalline polymer fiber network. Based on the phase transition approach, a new one-dimensional (1D) phenomenological constitutive model was developed by Scalet et al. (2015) to describe the...
behavior of semicrystalline SMPs in a fixed range of temperatures between the glass transition and the melting temperatures.

It should be noted that the phase transition models are physically based for semicrystalline SMPs, but are phenomenological for amorphous SMPs, because of their different molecule network morphologies. The first 3D finite deformation thermoviscoelastic constitutive model for the amorphous SMPs was developed by Diani et al. (2006), based on a physical understanding of the material behavior. It should be noted that the model is an extension of the three element standard linear rheological solid model in nature. To describe the multitude of relaxation processes, a 3D multi-branch model proposed by Westbrook et al. (2011) was used to model the time-dependent thermomechanical behaviors of amorphous SMPs. In fact, the model could be regarded as a thermal expansion element in series with an extension of the generalized viscoelastic model to some extent. Thereafter, Yu et al. (2012) reduced the model to the 1D form and predicted the free recovery behavior of the amorphous SMPs. Besides, Yu et al. (2014) developed a more general multi-branch modeling frame to model the SMEs of the amorphous SMPs. The model parameters could be identified by a set of routine tests. On the other side, thermoviscoelastic models incorporated with the effect of a single or multiple discrete structural and stress relaxation processes were proposed by Nguyen et al. (2008, 2010) and further developed by Xiao et al. (2013). In the framework for the models, the fictive temperature \( \theta_0 \) is used as an internal variable to describe the nonequilibrium structure during the glass transition of amorphous SMPs, which is also the main difference between these models and the other thermoviscoelastic constitutive models mentioned above which also include the relaxation process.

Generally, the current state of the material can not be characterized by the current values of stress and strain, if the material exhibits a history-dependent behavior. In order to address such issues, fictive temperature (Huang and Richert, 2009; Kamrin and Bouchbinder, 2014; Xiao and Nguyen, 2015), order parameters (Lesikar and Moynihan, 1980; Pedersen et al., 2008) or other internal variables (Lion and Yagimi, 2009; Coleman and Gurtin, 1967) which could be used to describe the deviation of the current state from the equilibrium state should be introduced into the constitutive model of the material. The fictive temperature approach was firstly introduced by Tool (1946) to model the structural relaxation in glasses. Whereas the order parameter approach follows irreversible process thermodynamics and uses the Gibbs free energy as thermodynamic potential (see Gutzow et al., 2007 or Lesikar and Moynihan 1980). Based on thermodynamics with internal state variables, Lion et al. (2010) proposed a 3D model to capture the material thermomechanical behavior in the vicinity of the glass transition. The model extends the classical theories based on fictive temperature or order parameters in two ways. Firstly, temperature excitations and mechanical loadings are accounted for in a single consistent modeling approach. Second, the basic thermodynamic potential depends on the temperature, the stress and a set of internal variables (Lion et al., 2011). Moreover, each internal variable can exhibit its own relaxation time. In view of these advantages, the internal variables used in the model of Lion et al. (2010), instead of the fictive temperature, will be introduced into the constitutive model for the amorphous SMPs in the paper for the first attempt.

The organization of the paper is as follows. Section 2 introduces the fundamental relations of the finite deformation constitutive model for the amorphous SMPs. Section 3 puts forward the approach for the determination of model parameters at first. Then the comparisons between the model simulations and the test results are presented in the section, together with the prediction capability of the model. The work is reviewed in Section 4, and the main conclusions of the work along with its further potential study are also addressed in this section.

### 2. Constitutive model

In this section, a finite deformation constitutive model based on thermodynamics with internal state variables is developed for the amorphous SMPs. Fig. 1 illustrates the stress-deformation response of the model. It should be noted that the 3D model can be regarded as a thermal component in series with an extension of the three element standard linear rheological solid model in nature.

#### 2.1. Deformations and stresses

The deformation of a material from its reference configuration \( \Omega_0 \) in thermodynamic equilibrium at time \( t_0 \) and temperature \( \theta_0 \) to the current configuration \( \Omega \) can be described by the deformation gradient \( F \). Since many works developed the similar stress-deformation response model (e.g. Boyce et al., 1988, 1989; Qi et al., 2008; Li and Xu, 2011), it is briefly introduced in this paper as follows.

Through a multiplicative decomposition approach, the general deformation gradient of the material could be separated into the thermal part and the mechanical part, followed by a further decomposition of the mechanical part into elastic and viscos components.

\[
\begin{align*}
F &= F_e F_o F_\theta, \\
\end{align*}
\]

where \( F_e, F_o \) and \( F_\theta \) are the elastic, viscous and thermal components of the general deformation gradient, respectively. It is assumed that the material is isotropic, thus the thermal component could be expressed as

\[
F_\theta = \bar{J}^{1/3} I,
\]

where \( \bar{J} \) is the volume ratio of thermal deformation and \( I \) is the second order identity tensor.

The general stress response could be divided into two parts: an equilibrium part and a nonequilibrium time-dependent part. Generally, the material behavior at high temperatures could be captured by the equilibrium part. Here, the eight-chain network model of Arruda and Boyce (1993a) is used to describe the effects of the chain straightening and alignment of the equilibrium part (Westbrook et al., 2011).

\[
\sigma_n = \frac{n k_B \theta}{3 \bar{J}} \frac{\sqrt{N}}{\lambda_{\text{chain}}} L^{-1/2} \left( \frac{\lambda_{\text{chain}}}{\sqrt{N}} \right) B + K(N_0 - 1) I
\]

where \( n \) is the crosslinking density, \( k_B \) is Boltzmann’s constant, \( N \) is the number of Kuhn segments between two crosslink sites and \( K \) is the bulk modulus. \( \lambda_{\text{chain}} \) is the effective stretch on each chain in the eight-chain network, which can be taken out through

\[
\lambda_{\text{chain}} = \sqrt{\frac{\text{tr}(B)}{3}},
\]

where \( \bar{B} = F_e F_o \bar{F}_e \bar{F}_o = J_0^{-1/3} F_\theta \) and \( J_0 = \det(F_e) \)

\[
\dot{B} = \dot{B} - \frac{1}{2} \text{tr}(\dot{B}) I
\]

is the deviatoric component of \( \dot{B} \). \( L \) is the Langevin function which can be defined as

\[
L(\beta) = \coth(\beta) - \frac{1}{\beta}
\]
The stress of the nonequilibrium part can be derived through the elastic contribution \( F_e \) as follows:

\[
\sigma_v = \sigma_e = \frac{1}{J_e} L_e : E_e
\]  

(5)

where \( J_e = \det(F_e) \), \( E_e = \nabla V_e \), and \( L_e \) is the fourth order isotropic elasticity tensor given by

\[
L_e = 2GJ + \lambda J \otimes J
\]

(6)

where \( G \) and \( \lambda \) are Lamé constants, \( J \) is the fourth order identity tensor.

Eventually, the general stress \( \sigma \) can be obtained by

\[
\sigma = \sigma_n + \sigma_e
\]

(7)

2.2. Structural relaxation and thermal deformation

It should be noted that all amorphous SMPs are featured by their relaxation behavior above and below the switching transition temperature and the transition phenomena could be characterized by a variety of approaches (Lu and Huang, 2013). As demonstrated previously, the nonequilibrium structure of the polymer in

**Table 1** Parameters of the model.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \theta_f ) (( \beta )-transition temperature)</td>
<td>22.2 °C</td>
</tr>
<tr>
<td>( \theta_e ) (Glass transition temperature)</td>
<td>32 °C</td>
</tr>
<tr>
<td>( \theta_i ) (Temperature at the beginning of the flow region)</td>
<td>142.5 °C</td>
</tr>
<tr>
<td>( E_1^s ) (Material stiffness at the beginning of ( \beta )-transition)</td>
<td>2552.9 MPa</td>
</tr>
<tr>
<td>( E_2^s ) (Material stiffness at the beginning of glass transition)</td>
<td>3876.3 MPa</td>
</tr>
<tr>
<td>( \mu_1, \mu_2, \mu_3 ) (Weibull moduli)</td>
<td>19.3, 58.4, 177.6</td>
</tr>
<tr>
<td>( \mu_4 ) (Poisson’s ratios of the frozen phase)</td>
<td>0.35</td>
</tr>
<tr>
<td>( \mu_5 ) (Poisson’s ratios of the active phase)</td>
<td>0.499</td>
</tr>
<tr>
<td>( \theta_n ) (Reference temperature for phase transition)</td>
<td>27.3 °C</td>
</tr>
<tr>
<td>( Z ) (Parameter characterizing the width of the phase transition zone)</td>
<td>7</td>
</tr>
<tr>
<td>( K ) (Bulk modulus)</td>
<td>1000 MPa</td>
</tr>
<tr>
<td>( k_b ) (Boltzmann’s constant)</td>
<td>( 1.38 \times 10^{-23} ) J K(^{-1} )</td>
</tr>
<tr>
<td>( n ) (Crosslinking density)</td>
<td>( 1.3 \times 10^{20} ) m(^{-3} )</td>
</tr>
<tr>
<td>( N ) (Number of kuhn segments between two crosslinks)</td>
<td>1.3</td>
</tr>
<tr>
<td>( s_0 ) (Initial value of athermal shear strength)</td>
<td>20 MPa</td>
</tr>
<tr>
<td>( s_1 ) (Saturation value of athermal shear strength)</td>
<td>16 MPa</td>
</tr>
<tr>
<td>( h ) (Slope of the yield variation with respect to plastic strain)</td>
<td>150 MPa</td>
</tr>
<tr>
<td>( Q ) (Activation parameter for viscous flow)</td>
<td>3500 °C</td>
</tr>
<tr>
<td>( \eta_{sl} ) (Reference shear viscosity)</td>
<td>12 MPa/s</td>
</tr>
<tr>
<td>( \theta_{sl} ) (Temperature of thermodynamic equilibrium reference state)</td>
<td>25 °C</td>
</tr>
<tr>
<td>( S_{ent} ) (Specific entropy of thermodynamic equilibrium reference state)</td>
<td>6 J/kg K</td>
</tr>
<tr>
<td>( T_{ent} ) (Uniaxial stress of thermodynamic equilibrium reference state)</td>
<td>−5 MPa</td>
</tr>
<tr>
<td>( c_{sf} ) (Specific heat)</td>
<td>50 J/kg K</td>
</tr>
<tr>
<td>( k_0 ) (Thermal expansion coefficient)</td>
<td>( 1.4 \times 10^{-4} ) °C</td>
</tr>
<tr>
<td>( d ) (Parameter for internal variable perturbations)</td>
<td>1.5 \times 10^{-11} ) J/kg</td>
</tr>
<tr>
<td>( \varepsilon, \mu_s, \nu_s ) (Parameter for influence of coupling)</td>
<td>( 1.5 \times 10^{-3} ) J/kg K</td>
</tr>
<tr>
<td></td>
<td>( 1 \times 10^{-6} ) m(^3)/kg</td>
</tr>
<tr>
<td></td>
<td>( 5 \times 10^{-6} ) m(^3)/kg</td>
</tr>
<tr>
<td>( B_s ) (Activation parameter for structural relaxation)</td>
<td>20,000 J/kg</td>
</tr>
<tr>
<td>( \tau_{rel} ) (Reference value of structural relaxation time)</td>
<td>( 3 \times 10^{-6} ) s</td>
</tr>
<tr>
<td>( \rho ) (Density of the material)</td>
<td>1050 kg/m(^3)</td>
</tr>
</tbody>
</table>

**Fig. 2.** Parameter fitting for storage modulus.
the glass transition and the vicinity of the process can be well described by the internal variable approach. In the works of Nguyen et al. (2008, 2010) and Xiao et al. (2013), the fictive temperature is used as the internal variable to describe the structural relaxation of the SMPs. In comparison with the fictive temperature approach and order parameter approach, the approach developed by Lion et al. (2010) which is based on thermodynamics with internal state variables has the advantages of good applicability and more definite physics-based description. Therefore, it is used here to model the structural relaxation of the amorphous SMPs.

While the material is in a thermodynamic equilibrium reference state, the values of the temperature $\theta$, the stress tensor $T$, the strain tensor $E$, the specific entropy $s$ per unit mass and the set of internal variables tensor $\alpha_1, \alpha_2, \ldots, \alpha_m$ can be regarded as the reference values, i.e., $\theta_{ref}, T_{ref}, E_{ref}, S_{ref}$ and $\alpha_{1ref}, \alpha_{2ref}, \ldots, \alpha_{mref}$. In the model, if the values of the temperature $\theta$ and the stress $T$ reach $\theta_{ref}$ and $T_{ref}$, respectively, and remain constant for an infinite duration, other variables will relax asymptotically to time-independent equilibrium values in the reference state. The vicinity of the reference state can be defined by the sufficient small fluctuations of the variables. It should be pointed out that the model is only valid in the neighbourhood of the reference state. Here, the values of the variables in the current state can be calculated as follows:

$$\theta = \theta_{ref} + \vartheta(t)$$

$$T = T_{ref} + \Sigma_1(t)$$

$$E = E_{ref} + \Gamma_1(t)$$

$$s = s_{ref} + \eta(t)$$

$$\alpha_k = \alpha_{k,ref} + \delta_k(t)$$
Influence expressed through evolution works, where
\[ \eta = \frac{\partial}{\partial \psi} \phi \]
for the specific entropy, together with the evolution equations for the internal state variables can be derived from the Clausius-Duhem inequality as follows:
\[ \{ \delta \} = D_0 \{ \Sigma \} + k_0 \partial - \rho w \{ \delta \} \]  \hspace{1cm} (10a)
\[ \eta = \frac{c_p \rho}{\theta_{ref}} \phi - e \cdot \{ \delta \} + \frac{1}{\rho} k_0 \cdot \{ \Sigma \} \]  \hspace{1cm} (10b)
\[ \{ \delta \} = -A(d \{ \delta \} + e \rho + w^T \{ \Sigma \}) \]  \hspace{1cm} (10c)
where \( c_p \) is the specific heat of the material, \( \rho \) is the density of the material, and \( k_0 \) and \( e \) are the parameter vectors that can be expressed as
\[ k_0 = [ k_0 \quad k_0 \quad k_0 \quad 0 \quad 0 \quad 0 ]^T \]  \hspace{1cm} (11)
\[ e = [ e \quad e \quad e \quad 0 \quad 0 \quad 0 ]^T \]  \hspace{1cm} (12)
where \( k_0 \) is the thermal expansion coefficient and \( e \) describes the influence of coupling between the internal variables and the temperature. \( D_0 \) is the compliance of the isotropic material in the glassy state and can be written as
\[ D_0 = \frac{1}{E} \left[ \begin{array}{cccccc}
1 & -\mu & -\mu & 0 & 0 & 0 \\
-\mu & 1 & -\mu & 0 & 0 & 0 \\
-\mu & -\mu & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 2(1 + \mu) & 0 & 0 \\
0 & 0 & 0 & 0 & 2(1 + \mu) & 0 \\
0 & 0 & 0 & 0 & 0 & 2(1 + \mu)
\end{array} \right] \]  \hspace{1cm} (13)
where \( E \) and \( \mu \) are the Young’s modulus and Poisson’s ratio of the material, respectively. The influence of the internal variable perturbations on the basic thermodynamic potential can be represented by material parameter matrix \( d \).
\[ d = d_0 \]  \hspace{1cm} (14)
where \( d \) is the material parameter and \( d_0 \) is the \( 6 \times 6 \) identity matrix. \( w \) is the matrix of additional material parameters \( w_i, v_i \), and \( w_s \), in which the influence of the coupling between the internal variables and the stress is incorporated.
\[ A = A_0 \]  \hspace{1cm} (16)
where \( A \) is related to the structural relaxation time \( \tau \) with the expression as follows:
\[ \tau = \frac{1}{Ad} \]  \hspace{1cm} (17)
Therefore, Eq. (10c) can be rewritten as
\[ \{ \delta \} = -\frac{1}{\tau} \left( \{ \delta \} + e_d \rho + w_t^T \{ \Sigma \} \right) \]  \hspace{1cm} (18)
As demonstrated previously, \( \tau \) can be well described by the Adam–Gibbs model (Adam and Gibbs, 1965).
\[ \tau = t_0 \exp \left( \frac{B_1}{T_0} \right) \]  \hspace{1cm} (19)
where \( \tau_0, B_1 \) and \( S_c \) are the reference value of the structural relaxation time, the activation parameter and the configurational entropy, respectively. Through the dimensional analysis, Eq. (19) can be rewritten as

\[
\tau = \tau_0 \exp \left( \frac{B_2 \theta}{\beta s} \right)
\]

(20)

where \( B_2 \) is the activation parameter, and \( s \) can be calculated by Eqs. (8d) and (10b).

Under the condition of \( \{ \Sigma \} = \{ 0 \} \), the thermal strain \( \{ \varepsilon_\theta \} \) can be derived from Eqs. (10a) and (10c) as follows:

\[
\{ \varepsilon_\theta \} = k_0 \theta - \rho \{ \delta \}
\]

(21)

By taking Eqs (11), (15) and (21) into account, the thermal volume strain \( \varepsilon_{\theta,\text{vol}} \) can be obtained by the sum of the three normal strains of \( \{ \varepsilon \} \).

\[
\varepsilon_{\theta,\text{vol}} = 3k_0 \theta - \rho (w_1 + 2v_1) (\delta_1 + \delta_2 + \delta_3)
\]

(22)

Here, the thermal volume strain at the beginning of the thermomechanical process is given by

\[
\varepsilon_{\theta,\text{vol}}^0 = 3k_0 (\theta_0 - \theta_{\text{ref}}) - \rho (w_1 + 2v_1) (\delta_0^1 + \delta_0^2 + \delta_0^3)
\]

(23)

where \( \theta_0 \) is the initial temperature, \( \delta_0^1, \delta_0^2 \) and \( \delta_0^3 \) are the initial values of the internal variables. Therefore, the thermal deformation \( J_\theta \) in the thermomechanical process can be given by

\[
J_\theta = 1 + \varepsilon_{\theta,\text{vol}} - \varepsilon_{\theta,\text{vol}}^0
\]

(24)

2.3. The viscous flow rule

Since the molecular process of a viscous flow is to overcome the shear resistance of the material for local rearrangement, the viscoplastic stretch rate \( D_v \) of the nonequilibrium part can be constitutively prescribed by the plastic shear strain rate \( \dot{\gamma}_V \) as follows (Arruda and Boyce, 1993b):

\[
D_v = \dot{\gamma}_V n
\]

(25)
where \( \mathbf{n} = \mathbf{a}'_{\mathbf{v}}/\|\mathbf{a}'_{\mathbf{v}}\| \) is the direction of the flow stress and \( \sigma' = \sigma_{\mathbf{v}} - 1/3\text{tr}(|\sigma_{\mathbf{v}}|)I \) is the deviatoric component of \( \sigma_{\mathbf{v}} \). As demonstrated previously, the Eyring model can be used to characterize the temperature-dependent, stress-activated nature of viscoplastic flow behavior for the polymers in the glassy state.

\[
\dot{\gamma}_{\mathbf{v}} = \frac{s_{\mathbf{y}}}{\eta_{\text{ref}}} \frac{\theta}{Q} \exp\left(-\frac{E_{0}}{k_{B}T}\right) \sinh\left(\frac{Q}{\theta} \frac{\bar{\tau}}{s_{\mathbf{y}}} \right)
\]

where \( \eta_{\text{ref}} \) is the reference shear viscosity, \( Q \) and \( E_{0} \) are the activation parameters, \( s_{\mathbf{y}} \) is the yield stress which denotes the resistance to the viscoplastic shear deformation of the material, and \( \bar{\tau} = \|\mathbf{a}'_{\mathbf{v}}\|/\sqrt{2} \) is the equivalent shear stress.

In order to extend the viscoplastic flow rule for the glassy state to the glass transition and the vicinity of the process, Eq. (20) is applied to modify Eq. (26) as:

\[
\dot{\gamma}_{\mathbf{v}} = \frac{s_{\mathbf{y}}}{\eta_{\text{ref}}} \frac{\theta}{Q} \exp\left(-\frac{B_{2}}{\theta s_{\mathbf{y}}}\right) \sinh\left(\frac{Q}{\theta} \frac{\bar{\tau}}{s_{\mathbf{y}}} \right)
\]

In the paper, the evolution rule for athermal shear strength developed by Boyce et al. (1989) is used to characterize the post-yield strain softening behavior as follows:

\[
\dot{S}_{\mathbf{y}} = h\left(1 - \frac{S_{\mathbf{y}}}{S_{\text{sat}}}\right) \dot{\gamma}_{\mathbf{v}}
\]

where \( s_{\text{sat}} \) is the saturation value of \( s_{\mathbf{y}} \), \( s_{0} \) is the initial value of \( s_{\mathbf{y}} \), and the softening effect can only be described on the condition that \( s_{0} > s_{\text{sat}} \). \( h \) is the slope of the yield variation with respect to plastic strain.

3. Results and discussions

The objective of the paper is to propose a constitutive model that can be used to describe and predict the thermomechanical behavior and the SME of the amorphous SMPs. To date, a large amount of systematic experiments have been done for the amorphous SMPs to test the SME and the relative thermomechanical behaviors, and the experimental data could be easily found in
the literature. In order to demonstrate the validity and accuracy of the model, the constitutive relations are implemented into the C++ program and comparisons between the model results and the thermomechanical experiments carried out in Westbrook et al. (2011) are presented in this section.

3.1. Material properties and model parameters

The SMP material used in the experiments done by Westbrook et al. (2011) is an acrylate-based network polymer and the synthesis follows the procedure in Yakacki et al. (2007). Since extensive experiments were done in their study, the model parameters can either be measured from or fitted to the experimental data as discussed below. The values of model parameters are summarized in Table 1.

Assuming that the SMP material is isotropic, Lamé constants \( G \) and \( \lambda \) are related to Young’s modulus \( E \) and Poisson’s ratio \( \nu \) by \( G = E/[2(1+\nu)] \) and \( \lambda = E\nu/[\{(1+\nu)(1-2\nu)\}] \) (Qi et al., 2008).

Based on the theory of polymers, it is known that the amorphous polymers undergo three main transitions (i.e. \( \beta \)-transition, glass transition and flow), as the temperature changes. In the works of Mahieux and Reifsnider (2001, 2002), the temperature-dependent storage modulus \( E' \) at a constant frequency can be described by

\[
E'(\theta) = \left(E'_1 - E'_2\right) \cdot \exp\left(-\left(\frac{\theta}{\theta_B}\right)^{m_1}\right) + \left(E'_2 - E'_3\right) \cdot \exp\left(-\left(\frac{\theta}{\theta_g}\right)^{m_2}\right) + E'_3 \cdot \exp\left(-\left(\frac{\theta}{\theta_f}\right)^{m_3}\right)
\]

(29)

where \( \theta_B \), \( \theta_g \) and \( \theta_f \) are the \( \beta \)-transition temperature, the glass transition temperature and the temperature at the beginning of the flow region, respectively. The moduli \( E'_1 \), \( E'_2 \), and \( E'_3 \) are the instantaneous stiffnesses of the material at the beginning of each transition. In addition, the parameters \( m_1 \), \( m_2 \) and \( m_3 \) are the Weibull moduli corresponding to the statistics of the bond breakage. Here, the values of the parameters in Eq. (29) can be deter-

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**Fig. 10.** Structural relaxation time as a function of temperature for processes with the same cooling rate of 2.5 °C/min but different heating rates.

**Fig. 11.** Thermal strain as a function of temperature for processes with the same cooling rate of 2.5 °C/min but different heating rates.
Fig. 12. Influences of the cooling rates on the processes of cooling and constrained recovery.

Fig. 13. Thermal strain as a function of temperature for the processes with the same heating rate of 2.5 °C/min but different cooling rates.

The thermal strain of the isotropic material can be given by

$$\varepsilon_\theta = J_\theta^{1/3} - 1$$

in which $J_\theta$ can be derived from Eq. (24) by using the approach based on thermodynamics with internal state variables. Therefore, the proper values of parameters in the approach can be determined by fitting the coefficient of thermal ex-

$$\mu = \mu_g f_g + \mu_r (1 - f_g)$$

(30)

where $\mu_g$ and $\mu_r$ are the Poisson’s ratios of the frozen phase and the active phase, and $f_g$ is the volume fraction of the frozen phase. Generally, the typical values of Poisson’s ratios of the polymer in glassy state and rubbery state are 0.35 and 0.499, respectively. Therefore, the values of $\mu_g$ and $\mu_r$ are equal to 0.35 and 0.499, respectively. As proposed by Qi et al. (2008), $f_g$ is given by

$$f_g = 1 - \frac{1}{1 + \exp[-(\theta - \theta_m)/Z]}$$

(31)

where $\theta_m$ and $Z$ are the reference temperature and the material parameter which characterizes the width of the phase transition zone, respectively.

$mined from the Dynamic Mechanical Analysis (DMA) experiment by using a nonlinear regularization program of MATLAB, as shown in Fig. 2. Evidently, the model fits well with the experiment. It should be noted that although the SMP may only have the glass transition and no apparent $\beta$-transition can be identified in Fig. 2, the temperature-dependent storage modulus can also be determined by Eq. (29) with the appropriate values of parameters, for the model has the robust property. For the loss modulus is usually much less than the storage modulus, the Young’s modulus $E$ could be chosen to be equal to the storage modulus $E'$ in the paper. Actually it is not easy to determine the temperature dependence of Poisson’s ratio $\mu$ for SMPs during the glass transition. In order to address this issue, the volume fraction model of glassy phase in the phase transition model proposed by Qi et al. (2008) together with the mixture rule are used here, i.e.,
It is assumed that the bulk modulus $K$ is typically 1000 MPa to ensure incompressibility of the SMP. Here, $n$ is regarded as a temperature-independent constant. Since $n k_B \theta$ is equal to the shear modulus of the SMP at high temperatures, the value of $n$ can be derived with a shear modulus value of 0.6 MPa which is obtained from the stress-strain curve of the uniaxial compression experiment carried out at 60°C.

As shown in Fig. 5, the values of parameters $s_0$, $s_1$, $h$, $Q$, $\eta_{ref}$ and $N$ can be given by fitting the stress-strain response of the SMP at 30°C at a compression strain rate of 0.01/s. Specifically, the values of $s_0$ and $s_1$ can be estimated from the yield point and the plateau of the stress-strain curve, respectively. For the parameter $h$ characterizes the rate of post-yield strain-softening, an estimation of $h = 150$ MPa is used here. In addition, the initial values of parameters $Q$, $\eta_{ref}$ and $N$ can be estimated from the relevant researches (Qi et al., 2008; Nguyen et al., 2008; Li et al., 2011). It should be
pointed out that the final values of all these parameters should be subject to fitting the experimental data. The prime reason for the discrepancy between the simulation and the experiment is that the Young’s modulus $E$ calculated by Eq. (29) is a bit higher than the value from experiment.

### 3.2. Model validation

Here, the simulation results are compared with the experimental data obtained from Westbrook et al. (2011) to validate the ability of the constitutive model to reproduce and predict the SMEs and other thermomechanical behaviors of the SMPs. In the work of Westbrook et al. (2011), both constrained recovery and free recovery were explored in the shape memory cycle experiments. In the programming step, a compressive strain of 20% was applied to the specimen at a rate of 0.01/s. After that, the specimen was allowed to relax for 10 min before the temperature was reduced to one at which the temporary shape was fixed, at a rate of 2.5 °C/min. Once the shape fixing temperature was reached, 60 min was given to the specimen for stabilization. It should be noted that the difference between constrained recovery and free recovery occurs at the end of the stabilization step. In the constrained recovery, the compression platen was kept still and the stress evolution was recorded. While the upper compression platen was withdrawn in the free recovery, and the evolution of the shape was measured. The temperature condition for the free and constrained recovery is listed in Table 2.

Table 2: Temperature condition of thermomechanical experiment for the free and constrained recovery.

<table>
<thead>
<tr>
<th>Recovery type</th>
<th>Temperature condition (variation rate $q = 2.5$ °C/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Programming</td>
</tr>
<tr>
<td>Constrained recovery</td>
<td>60 °C</td>
</tr>
<tr>
<td>Free recovery</td>
<td>40 °C</td>
</tr>
</tbody>
</table>

Fig. 6 shows the simulation results for the stress and the temperature separately as a function of time in three steps before the constrained recovery. From the simulation results, it is found that the stress decreases fast in the beginning of the relaxation process (i.e. Step 1(a)) and then reaches the steady state as shown in Step 1(b). The stress continues to decrease in the cooling process until it reaches 0, and then the specimen is detached from the upper compression platen. Similar stress evolution exists in the steps before the free recovery.

Obviously, the investigation of the stress response during recovery is essential for the practical application with the boundary conditions of constrained recovery. The comparison between the simulation results and the experimental data for the thermomechanical shape memory cycle of constrained recovery is shown in Fig. 7.

It is shown that the general evolution rule of the stress-temperature response of the model agrees with the experiment to some extent, although there are some differences between the stress values of the simulation and the experiment at corresponding temperatures. The prime reason for the discrepancies may be that the stress of the model decreases faster in the cooling process, shifting the onset of the stress recovery to a higher temperature. Therefore, the temperature influence on the model needs further refinement.

In order to study the influences of the thermal rates on the constrained recovery, comparisons between the simulation results for different thermal rates are presented in the following discussion. Fig. 8 shows the simulation results for different heating rates while undergoing the same cooling process (cooling rate $q_c = 2.5$ °C/min) and stabilization time (60 min). From the simulation results, it is predicted that a faster heating rate results in a higher stress overshoot (a peak stress occurring during constrained recovery that is larger than the final stress) occurring at a higher temperature, which is also demonstrated by Castro et al. (2010) (see Fig. 5(b) in Castro et al. (2010)). Since the internal variable is a critical parameter in the model, its influence on the constrained recovery process is studied here. Fig. 9 shows the variation of the internal variable $\delta_1$ in response to a temperature change for the processes with the same cooling rate $q_c = 2.5$ °C/min but different heating rates. Since the temperature of the beginning of the cooling process is much higher than $T_g$, the internal variable can be assumed to be in its equilibrium state. Therefore, the initial value of $\delta_1$ can be determined on the condition that the derivative of $\delta_1$ in Eq. (18) is equal to 0 in the equilibrium state. It is found that only the internal variable in the range of glass transition can be visibly influenced by the heating rate. Obviously, the values of the internal variable for $q_h = 5$ °C/min is larger than that for $q_h = 2.5$ °C/min at
the same temperature during the glass transition. According to Eq. (20), the corresponding variation of the structural relaxation time is derived and depicted in Fig. 10. Similarly, only the structural relaxation time in the same temperature range can be influenced by the heating rate. It can be seen that the structural relaxation time is longer at a higher heating rate during the glass transition. According to Eq. (27), a longer structural relaxation time could lead to a slower viscous flow and makes the SMP stiffer at the same temperature. This should be the main reason for the phenomenon depicted in Fig. 9. In addition, the thermal deformation is also taken into consideration in the model for accuracy. Fig. 11 shows the thermal strain as a function of temperature for the processes with the same cooling rate of 2.5 °C/min but different heating rates. It is found that thermal recovery strain is smaller at a higher heating rate during the glass transition. Since the SMP is stiffer at a higher heating rate, a larger recovery stress can be generated by a smaller thermal recovery strain, as shown in Fig. 9. Therefore, it can be concluded that the effect caused by the thermal recovery strain on the recovery stress at different heating rates is not evident.

Accordingly, Fig. 12 shows the simulation results at the cooling rates of 2.5 and 5 °C/min with respective hold times of 60 and 70 min, while undergoing the same heating process (heating rate \(q_h = 2.5 \, \text{°C/min}\)). The combinations of cooling rates and hold times give the same total time (80 min) before heating. It is shown that a faster cooling rate shifts the onset of the stress recovery to a higher temperature and reduces the peak stress, which is also predicted by Castro et al. (2010) (see Fig. 9(a) in Castro et al., 2010). Fig. 13 shows the thermal strain as a function of temperature for processes with the same heating rate of 2.5 °C/min but different cooling rates. It is clear that the contrast is not obvious, since the difference between the cooling rates is limited. Here, the structural relaxation time as a function of temperature for the same processes is depicted in Fig. 14. It is found that the structural relaxation time is shorter at a higher cooling rate after the glass transition, making the SMP softer at the same temperature. This should be the main reason for the phenomenon depicted in Fig. 12.

Fig. 15 presents a comparison between the model prediction and the free recovery experiment with a programming temperature of 40 °C and a recovery temperature of 50 °C. Generally, the simulation results fit the experimental data well, except for the slope of the curve of the strain recovery ratio versus time. The main reason may be that the viscous flow in the model triggered by heating is a bit slow during the free recovery process. To reveal the influence of the heating rate on the free recovery process, model predictions with different heating rates \(q_h = 2.5 \, \text{°C/min}\) and \(q_h = 5 \, \text{°C/min}\) are shown in Fig. 16. It is found that a faster heating rate shifts the onset of the strain recovery to a shorter time, but has little effect on the slope of the strain recovery ratio versus time curve. Clearly, the main reason for the phenomenon is that the SMP experiences a shorter time when being heated at a higher rate, before reaching the same temperature. Fig. 17 shows the variation of the structural relaxation time in response to a temperature change from 20 °C to 50 °C at different heating rates during the free recovery process. Obviously, the structural relaxation time for \(q_h = 5 \, \text{°C/min}\) is longer than that for \(q_h = 2.5 \, \text{°C/min}\) during the glass transition. From Fig. 16, it can be concluded that although the recovery strain could be delayed by a longer structural relaxation time caused by the higher heating rate, the delay effect is not obvious.

4. Conclusions

In the paper, a thermoviscoelastic finite deformation constitutive model incorporated with structural and stress relaxation is developed for the thermally activated amorphous SMPs. The main feature of the model is the incorporation of the Adam–Gibbs model for structure relaxation and the modified Eyring model for viscous flow into the thermoviscoelastic finite deformation modeling framework which has been proved to be successful in capturing the thermomechanical behavior for glassy polymers. In order to describe the thermomechanical behavior of the SMPs in the vicinity of the glass transition, an internal state variable modeling approach developed recently based on thermodynamics is used in the study. As demonstrated previously, the modeling approach employed in the paper has the advantages of good applicability and more definite physics-based description compared with the traditional phenomenological fictive temperature approach and the order parameter approach.

The methods for the parameter determination are also presented in the paper. For accuracy, part of model parameters are considered temperature-dependent. To validate the accuracy of the model, the simulation results are compared with the experimental


