A small strain constitutive model for shape memory polymers

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Abstract

The present paper proposes a 3D small strain constitutive model for thermo-responsive shape memory polymers (SMPs). The model is based on the laws of thermodynamics and derived through a phase transition approach which assumes SMPs consisting of two phases (rubbery phase and glassy phase). The total strain of SMPs is decomposed into four parts and the fulfillment of Clausius-Duhem inequality for arbitrary thermodynamic process is checked. To validate the developed constitutive model, complete shape memory cycles are simulated with ABAQUS and the simulation results are compared with experimental data. At last, a numerical test is conducted to assess the effectiveness of the constitutive model in complicated boundary conditions.

Keywords: Shape memory polymers; Constitutive model; Simulation; Thermodynamics

Introduction

Shape memory polymers (SMPs) are a class of smart materials, because SMPs have the ability to recover the original shape upon a stimulus. Compared with other shape memory materials, SMPs possess the advantages of large elastic deformation, low energy consumption for shape programming, low cost, low density, potential biocompatibility, biodegradability and excellent manufacturability [1]-[2]. The increasing applications motivate the development of constitutive models for SMPs. Qi, Nguyen [3] developed a constitutive model in the large strain regime considering the yield behavior of the material at low temperature. Srivastava, Chester [4] formulated a thermo-mechanically coupled constitutive model. Nguyen, Jerryqi [5] developed a viscoelastic constitutive model incorporating structure and stress relaxation. Park, Harrison [6] developed a constitutive model considering the time-dependent and inelastic behavior of the material through viscoelastic and viscoplastic strains. Though the developed large strain constitutive models can reproduce the comprehensive shape memory behaviors well, most of these models are complicated and require many experiments to obtain the material parameters.

In practical large deformation engineering problems, there are many situations where the strain is small but the rigid motion is large. In these situations, a constitutive model within the small strain regime is enough. The earlier constitutive models within the small strain regime are based on the combination of rheological elements, such as spring, dashpot, and frictional elements [7]-[8]. While these models are simple to use, they usually lead to predictions that are only consistent with experiments qualitatively. Liu, Gall [9] developed the first phase transition-based constitutive model which introduces an internal state variable named storage strain upon cooling only. Baghani, Naghdabadi [10] developed a constitutive model which presents evolution law of storage strain during both cooling and heating, but it introduces other internal state variables and makes the parameters determination and application in the finite element simulation difficult again. Motivated by these considerations, the present paper aims to introduce a small strain constitutive model which has only a few parameters that can be quickly identified and simple formulation that can be easily applied into the numerical simulations.

Model development

Kinematic description

Within the small strain regime the total strain of SMPs can be additively decomposed into four parts: the elastic strains of the rubbery phase and glassy phase, the storage strain, and the thermal strain.

$$\boldsymbol{\varepsilon} = \phi_r \boldsymbol{\varepsilon}_r + \phi_g \boldsymbol{\varepsilon}_g + \boldsymbol{\varepsilon}_s + \boldsymbol{\varepsilon}_T,\ \phi_r + \phi_g = 1 \tag{1}$$

where ϕ_r and ϕ_g denote volume fractions of the rubbery phase and the glassy phase, respectively. It is assumed that they are functions of temperature only. Also, $\boldsymbol{\varepsilon}_s$ and $\boldsymbol{\varepsilon}_T$ are the storage and thermal strains, respectively. And it is assumed that the corresponding stresses in the two different phases are equal.

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_r = \boldsymbol{\sigma}_g \tag{2}$$

The storage strain is influenced by the phase transformation and changes with temperature only. When the temperature decreases, the rubbery phase transforms to the glassy phase and the strain of the rubbery phase stores in the glassy phase as storage strain. It is assumed that the newly generated storage strain is in proportion to the strain of the rubbery phase:

$$d\boldsymbol{\varepsilon}_s = d\phi_g \boldsymbol{\varepsilon}_r \tag{3}$$

Then, the average storage strain of the whole SMP generated in the cooling process can be obtained by integrating Eq. (3) as follows:

$$\boldsymbol{\varepsilon}_s = \int \boldsymbol{\varepsilon}_r d\phi_g \tag{4}$$

When the temperature increases, the glassy phase transforms to the rubbery phase and the storage strain will be released. It is assumed that the released storage strain is in proportion to the storage strain of the glassy phase generated in the cooling process:

$$d\boldsymbol{\varepsilon}_s = d\phi_g \boldsymbol{\varepsilon}_s^g / \phi_g \tag{5}$$

Then, the average storage strain of the whole SMP in the heating process can be obtained by integrating Eq. (5) as follows:

$$\boldsymbol{\varepsilon}_s = \int \frac{\boldsymbol{\varepsilon}_s}{\phi_g} d\phi_g \tag{6}$$

Thermodynamic considerations

The Helmholtz free-energy density function of the whole SMPs can be expressed as follows:

$$\Psi\left(\boldsymbol{\varepsilon}_r, \boldsymbol{\varepsilon}_g, \phi_g, T\right) = \phi_r \Psi_r\left(\boldsymbol{\varepsilon}_r\right) + \phi_g \Psi_g\left(\boldsymbol{\varepsilon}_g\right) + \Psi_T\left(T\right) + \Psi_\lambda \tag{7}$$

where Ψ_r and Ψ_g represent Helmholtz free-energy density functions of the rubbery phase and glassy phase, respectively. Ψ_T denotes the term caused by the variation of temperature. Ψ_λ denotes Lagrange multiplier term which enforces the kinematic constraints in the formulation. Ψ_λ is expressed as follows:

$$\Psi_\lambda\left(\boldsymbol{\varepsilon}_r, \boldsymbol{\varepsilon}_g, \phi_g, T, \boldsymbol{\varepsilon}\right) = \boldsymbol{\lambda} : \left[\boldsymbol{\varepsilon} - \left(\phi_r \boldsymbol{\varepsilon}_r + \phi_g \boldsymbol{\varepsilon}_g + \boldsymbol{\varepsilon}_s + \boldsymbol{\varepsilon}_T\right)\right] \tag{8}$$

where $\boldsymbol{\lambda}$ is the Lagrange multiplier. The Helmholtz free energy must satisfy the Clausius-Duhem inequality:

$$\boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} - \left(\dot{\Psi} + \eta \dot{T}\right) - \mathbf{q} \cdot \nabla T / T \geq 0 \tag{9}$$

where η is the entropy and $\mathbf{q}$ is the heat flux vector. The symbol ∇ represents the gradient operator and $-\mathbf{q} \cdot \nabla T / T$ gives the thermal dissipation. Working with the Fourier's law

$\mathbf{q} = -k\nabla T$ with $k > 0$ is defined. Substituting Eq. (7) and Eq. (8) into Eq. (9) leads to the following expression:

$$(\boldsymbol{\sigma}-\boldsymbol{\lambda}):\dot{\boldsymbol{\varepsilon}}+\phi_r\left(\boldsymbol{\lambda}-\frac{\partial\Psi_r}{\partial\boldsymbol{\varepsilon}_r}\right):\dot{\boldsymbol{\varepsilon}}_r+\phi_g\left(\boldsymbol{\lambda}-\frac{\partial\Psi_g}{\partial\boldsymbol{\varepsilon}_g}\right):\dot{\boldsymbol{\varepsilon}}_g-\dot{\boldsymbol{\lambda}}:\left[\boldsymbol{\varepsilon}-(\phi_r\boldsymbol{\varepsilon}_r+\phi_g\boldsymbol{\varepsilon}_g+\boldsymbol{\varepsilon}_s+\boldsymbol{\varepsilon}_T)\right]+$$

$$\boldsymbol{\lambda}:\left\{\begin{matrix}\left[\left(\boldsymbol{\varepsilon}_g+c_1\boldsymbol{\varepsilon}_r+c_2\dfrac{\boldsymbol{\varepsilon}_s}{\phi_g}-\boldsymbol{\varepsilon}_r\right)\dfrac{\partial\phi_g}{\partial T}+\dfrac{\partial\boldsymbol{\varepsilon}_T}{\partial T}\right]- \\ \dfrac{\partial\Psi_T}{\partial T}-\left(\Psi_g-\Psi_r\right)\dfrac{\partial\phi_g}{\partial T}-\eta\end{matrix}\right\}\dot{T}\geq 0 \tag{10}$$

Clausius–Duhem inequality must be fulfilled for arbitrary thermodynamic processe, so we may conclude:

$$\begin{cases}\boldsymbol{\sigma}=\boldsymbol{\lambda}=\dfrac{\partial\Psi_r}{\partial\boldsymbol{\varepsilon}_r}=\dfrac{\partial\Psi_g}{\partial\boldsymbol{\varepsilon}_g} \\ \boldsymbol{\varepsilon}=\phi_r\boldsymbol{\varepsilon}_r+\phi_g\boldsymbol{\varepsilon}_g+\boldsymbol{\varepsilon}_s+\boldsymbol{\varepsilon}_T \\ \eta=\boldsymbol{\lambda}:\left[\left(\boldsymbol{\varepsilon}_g+c_1\boldsymbol{\varepsilon}_r+c_2\dfrac{\boldsymbol{\varepsilon}_s}{\phi_g}-\boldsymbol{\varepsilon}_r\right)\dfrac{\partial\phi_g}{\partial T}+\dfrac{\partial\boldsymbol{\varepsilon}_T}{\partial T}\right]-\dfrac{\partial\Psi_T}{\partial T}-\left(\Psi_g-\Psi_r\right)\dfrac{\partial\phi_g}{\partial T}\end{cases} \tag{11}$$

Based on the small-strain assumption, the quadratic forms for the Helmholtz free-energy density functions are introduced as follow:

$$\Psi_r=\frac{1}{2}\boldsymbol{\varepsilon}_r:\mathbf{K}_r:\boldsymbol{\varepsilon}_r,\ \Psi_g=\frac{1}{2}\boldsymbol{\varepsilon}_g:\mathbf{K}_g:\boldsymbol{\varepsilon}_g \tag{12}$$

where $\mathbf{K}_r$ and $\mathbf{K}_g$ are the fourth-order stiffness matrices of rubbery phase and glassy phase, respectively.

Model verification

The proposed constitutive model is demonstrated with the experiment data in Liu, Gall [9]. The material parameters are determined and the shape memory cycles are simulated with ABAQUS by implementing the model within a user-defined subroutine.

The determination of material parameters

From the DMA data, the glass transition temperature is found to be 343K. And the transformation temperature range is chosen from 273 K to 358 K. The elasticity modulus of the rubbery phase is assumes as a function of the absolute temperature:

$$E_r = 3NKT \tag{13}$$

where K is the Boltzmann’s constant, T is the absolute temperature, N is the cross-link density. The elasticity modulus of the glassy phase is assumes as a constant. $N = 9.86\times10^{-4}\mathrm{mol/\ cm^3}$ and $E_g = 750\mathrm{MPa}$ are obtained by fitting the uniaxial stress-strain curves. Poisson’s ratios of rubbery phase and glassy phase are assumed as 0.499 and 0.4, respectively.

A second order polynomial expression is used here to capture the nonlinear relation between the thermal strain and temperature as follows:

$$\boldsymbol{\varepsilon}_T=\left(aT^2+bT+c\right)\mathbf{I} \tag{14}$$

where $\mathbf{I}$ is the symmetric second-order identity tensor. *a*, *b* and *c* are calculated through curve fitting as $a = 7.19\times10^{-7}\,\mathrm{K}^{-2}$, $b = -3.20\times10^{-4}\,\mathrm{K}^{-1}$, $c = 2.24\times10^{-2}$.

The glassy phase volume fraction can be determined from the unconstrained recovery data with reasonable accuracy, and a power function of temperature is used here:

$$\phi_g = 1 - \frac{1}{1 + f_1\left(T - T_h\right)^{f_2}} \tag{15}$$

where f_1 and f_2 are obtained from curve fitting as $f_1 = 2.76\times10^{-5}\,\mathrm{K}^{-4}$ and $f_2 = 4$.

Finite element simulation results and comparison with experiment

At the first step in this shape memory cycle, 9.1% tensile pre-strain and -9.1% compressive pre-strain are applied at 358K. Tensile strain and compressive strain give the linear stress-strain plot as shown in Fig. 1.

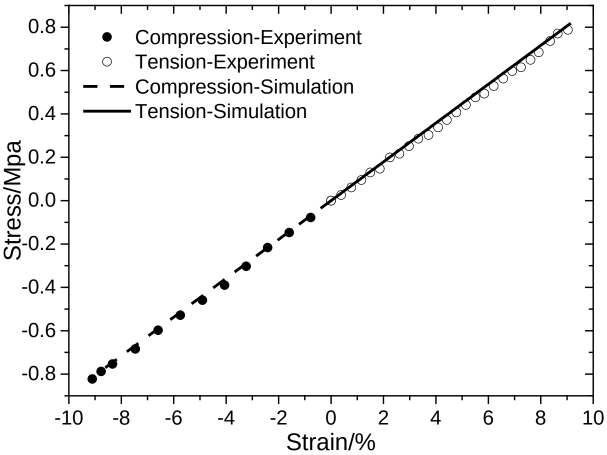

Figure 1. Isothermal stress-strain response at 358K

In the second step, the temperature decreases to 273K with the strains maintained. The stress responses with temperature for various strain levels are shown in Fig. 2. When the temperature decreases, thermal contraction takes place. Because of the constrained strains, thermal stress develops and provides a positive contribution to the total stress.

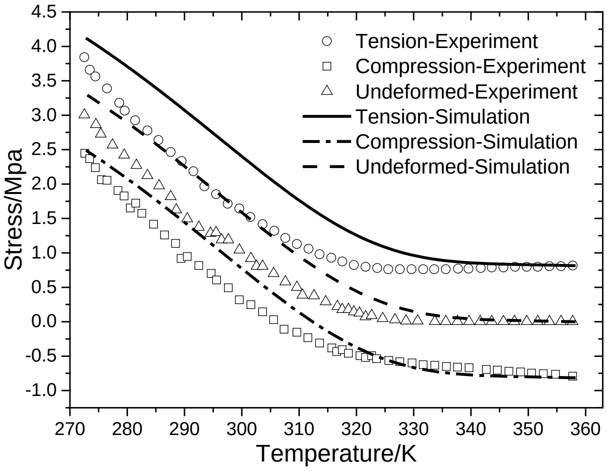

Figure 2. Evolutions of stresses during cooling for different pre-strains

After unloading at 273K, the SMP is in a stress-free condition and the temporary shape is fixed due to the storage strain. In the heating process, glassy phase transforms to rubbery phase resulting in the shape recovery as shown in Fig. 3. When the temperature is far below 343K, thermal strain is the predominant one, which leads to the slight increment of strain.

When the temperature approaches to 343K, storage strain decreases dramatically, which leads to the shape recovery.

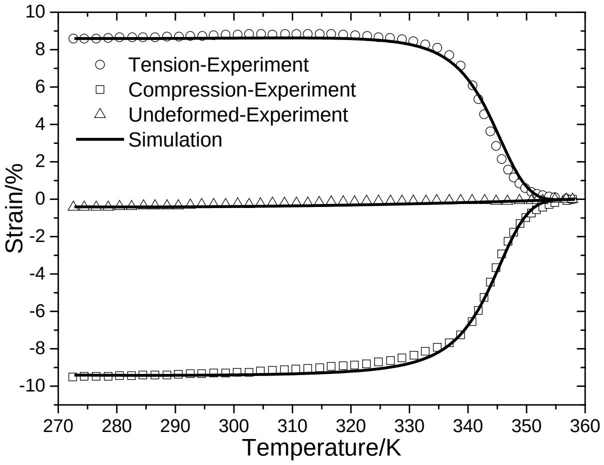

Figure 3. Strains recovery during heating for different pre-strains

In the heating process, if the strain after unloading is maintained, stress will be generated. The evolutions of stresses during heating for different pre-strains are shown in Fig. 4. Since the strains are maintained, compressive stress will develop first because of the thermal expansion. When the temperature further increases and approaches to 343K, storage strain decreases dramatically and the stresses are recovered to the initial states at 358K. From Fig.1-Fig.4, it is seen that the shape memory cycles can be well predicted by the simulations, so the effectiveness of the developed constitutive model is demonstrated.

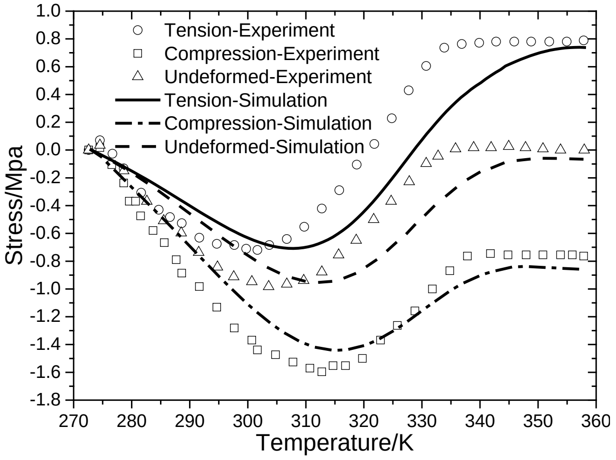

Figure 4. Evolutions of stresses during heating for different pre-strains

Numerical simulation test

In practical engineering problems, the deformation may be complex. To further demonstrate the effectiveness of the constitutive model in solving complex engineering problems, shape memory cycle of cylinder squashing is simulated. The external diameter, inner diameter and length of the cylinder are 99 mm, 98 mm and 99 mm, respectively. At high temperature, the cylinder is squashed. Then, the temperature is decreased holding the squashed shape fixed. After the low temperature is reached, the cylinder is relaxed. At last, the cylinder is heated to high temperature again.

Contour plots of the Von Misses stress distribution at the end of each step are reported in Fig. 5. It can be noted that the squashed shape of the cylinder is fixed after the unloading step and the original shape is almost recovered completely during the heating step. The effectiveness of the constitutive model in solving complex engineering problems is demonstrated further.

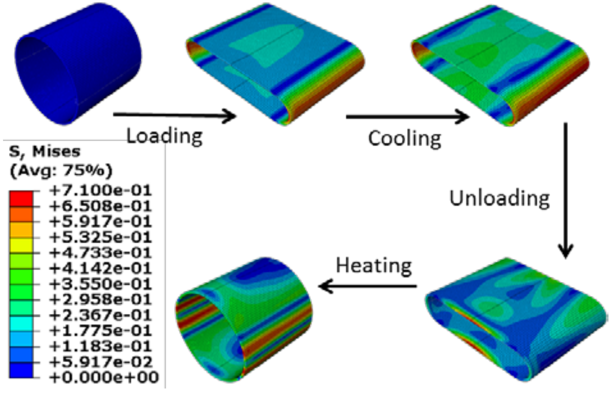

Figure 5. The complete shape memory cycle of cylinder squashing

Conclusions

A small strain constitutive model for thermo-responsive SMPs was developed. It was based on the laws of thermodynamics and derived through a phase transition approach assuming that SMPs consist of rubbery phase and glassy phase. Based on the small-strain assumption, the total strain was decomposed into four parts addictively using a first order mixture rule. The constitutive equations were derived based on the fulfillment of Clausius-Duhem inequality for arbitrary thermodynamic processes. Complete shape memory cycles were simulated with ABAQUS by implementing the model within a user-defined subroutine. And the simulation results were compared with the experimental data to verify the developed constitutive model. A numerical test was also conducted to assess the performance of constitutive model in complex deformation processes.

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