Recent Advance on Constitutive Models of Thermal-Sensitive Shape Memory Polymers

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ABSTRACT: Shape memory polymers (SMPs) are a novel class of shape memory materials which can store a deformed (temporary) shape and recover an original (permanent) shape under a shape memory thermomechanical loading–unloading cycle. The deformation mechanisms of SMPs are very complicated, but the SMPs also have a lot of advantages and the widespread application value and prospect. So developing proper constitutive models that describe thermomechanical properties of SMPs and the shape memory effect is very challenging and of great theoretical and application value. Based on the deformation mechanisms and considerable experimental investigations of SMPs, researchers have developed many constitutive models. This article investigates the deformation mechanism and introduces the recent research advance of the constitutive models of thermal-sensitive SMPs. Special emphases are given on the micromechanical constitutive relations in which the deformation is considered being based on the microstructure of the SMPs. Finally, the lack of research and prospects for further research are discussed. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1502–1508, 2012

Key words: stimuli-sensitive polymers; constitutive modeling; thermomechanical properties

INTRODUCTION

Shape memory polymers (SMPs) are a new family of smart materials. As a kind of stimuli-responsive materials,[1–3] they can store a deformed (temporary) shape and recover an original (permanent) shape under appropriate stimulus such as temperature,[1,2] moisture,[4–7] light,[8–10] electric field,[11,12] magnetic field,[13,14] and so forth. SMPs belong to the family of shape memory materials, which also includes shape memory alloys (SMAs) and shape memory ceramics. Compared to SMAs and shape memory ceramics, SMPs have the advantages[2,3,15] of light weight, low cost, good manufacturability, high shape deformability, high shape recoverability, biodegradability, and tailorable switch temperature. However, SMPs also have the limitations[2,3,15] such as low strength, low stiffness, low recovery stress, electric insulation, and so on. Although the deficiencies put them at a disadvantage, the excellent characteristics makes it attractive and promising in broad applications area such as in aerospace industry,[15,16] biomedical engineering,[17–19] microsystems,[20–22] smart textile products,[23,24] and numerous other areas.

Among stimulus-sensitive SMPs, the thermal-sensitive SMPs have been most widely studied and used by academic and industrial researchers. Thermoresponsive SMPs are those which are capable of changing their shapes from a temporary shape to a permanent shape on application of an external thermal stimulus. Developing proper constitutive models that describe the thermomechanical behavior of SMPs is critical and urgent, and of great theoretical and application value. Based on the deformation mechanism[1–3] and considerable experimental investigations[25–34] of thermal-sensitive SMPs, researchers have developed many constitutive models. Especially in the past few years, modeling of thermal-sensitive SMPs have witnessed significant advances. The main focus of this review article is mainly on the constitutive models of thermoresponsive SMPs, which are also of great reference value for other types of stimulus-sensitive SMPs.

This article first investigates the deformation mechanism of thermosensitive SMPs, then introduces the recent research advance of the constitutive models of thermosensitive SMPs and gives the main characteristics of the models. Special emphases are given on the micromechanical constitutive relations in which the deformation are considered being based on the microstructure of the materials. Finally, the article discusses the lack of research and the prospects for further research.

Shape memory mechanism of thermoresponsive SMPs

Although having found "shape memory" effects in polymers in 1941 in a United States patent,[35] until 1980s, people just come to realize the importance of SMPs. Many kinds of polymer materials were designed and synthesized mainly in industrial fields, and the main focus was preparation of these new materials for various end applications.[36] Recently, SMPs, being regarded as a novel class of smart materials, have aroused interests for a very broad, additional spectrum of possible applications. Up to now, scientists have prepared large quantity of SMPs and carried out extensive researches to the characteristics of microstructure and thermomechanical properties. The work accommodates basic knowledge and understanding of the special deformation mechanism of shape memory polymer (SMP). As Behl and Lendlein[1] state, "the shape memory effect (SME) is not related to a specific material property of single polymers; it rather results from a combination of the polymer structure and the polymer morphology, together with the applied processing and programming technology." The macroscopic deformation or the SME of thermal-sensitive SMPs depends on the combined actions of the molecular structure, the morphology, and the particular thermomechanical loading–unloading cycle.

Now being widely accepted that the thermal-sensitive SMPs could be a thermoplastic elastomer or elastic polymer network, crosslinked chemically or physically.[2,37,38] Although having some imperceptible differences in molecular structures and morphology, they are both considered being consisting of molecular switches and "netpoints" on the molecular level and both have a transition of morphology as the temperature changes termed glass transition or melting. The netpoints that determine the permanent shape of the polymer network can be of a chemical (covalent bonds) or physical (intermolecular interactions) nature. For the physically crosslinked polymer network, the domains related to the highest thermal transition temperature act as netpoints (a hard segment), whereas chain segments in domains with the second highest thermal transition act as molecular switches (a switching segment), which determine the temporary shape of the polymer network.

The SME for most of thermal-sensitive SMPs is obtained by a precisely designed thermomechanical loading–unloading cycle. A typical temperature/loading cycle for shape memory and recovery consists of four steps: loading at constant high temperature, cooling at constant prestrain or constant deformation gradient, unloading at constant low temperature, and heating at zero stress. The process is shown schematically in Figure 1.
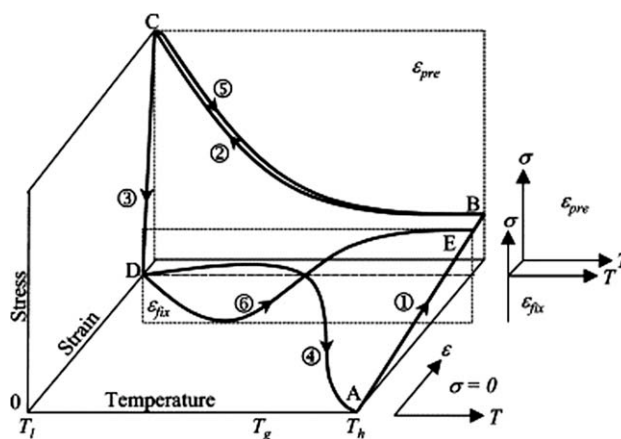

Figure 1 A typical temperature/loading cycle.[39]

The transition of thermal-sensitive SMPs between a state dominated by entropic energy (rubbery state) and a state dominated by internal energy (glassy state) as the temperature changes provides the basic thermodynamical explanations of the SME. In the amorphous state, the flexible polymer chains take up a completely random distribution and can undergo large random conformational changes only under the limitation of the netpoints. Applying a longtime external load could bring in plastic irreversible deformation due to the slipping and disentangling of the polymer chain from each other and reduce the possible configuration and the configurational entropy of the macromolecular chains. The removal of the external load at current temperature will increase its entropy of the materials and recover the undeformed shape defined by the spatial arrangement of the netpoints. However, if the temperature reduces, which will cause the glass transition or formation of crystallite phase, the mobility of macromolecular chains will be significantly reduced by the reduction in free volume, the flexibility of the entire segments is limited, cooperative conformational change of neighboring chains becomes dominant, and deformation thus requires much higher energy. The transition from the rubber-elastic state to glassy state stores the deformation in the crosslinking structure by cooling the polymer below its switch transition temperature. In the glassy state, all movements of the polymer segments are frozen, and hence, the permanent shape of SMP is retained. In the following uploading at low temperature, only a small amount of shape recovery appears. Most of the shape recovery is invoked by heating the polymer above the switch transition temperature and the thermal-sensitive SMP recovers its permanent shape as a result of releasing internal stress stored in the crosslinking structure. Figure 2 shows the molecular mechanism of thermal-sensitive SME.
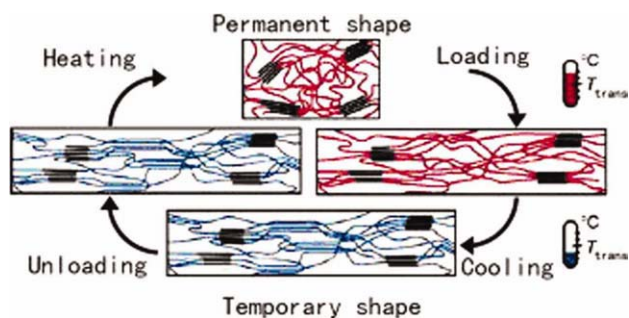
Figure 2 Molecular mechanism of thermal sensitive shape-memory effect.[1] [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Constitutive models of SMPs

SMPs are being attracting increasing attention of researchers all over the world due to its unique structure and excellent properties. To design SMP components and devices, developing appropriate constitutive models that can seize the key molecular characteristics and describe thermomechanical properties of SMPs is an important aspect. The thermomechanical behaviors of thermal-sensitive SMPs are close to the microstructure of the materials and the specific thermomechanical loading–unloading cycle; for this reason, developing constitutive models that describe the SME of SMPs is very complicated. The intensive constitutive models for polymer materials,[40–44] which describe the thermomechanical properties of polymers in the past have been developed. However, these models cannot be applied to SMPs because of the lacking of the underlying mechanism for SMEs. The constitutive models for SMAs[45,46] developed in the past also cannot be applied to SMPs because of the fundamental differences in the underlying mechanism for SMEs between SMPs and SMAs. However, researchers have developed many constitutive models based on the deformation mechanisms and considerable experimental investigations of thermal-sensitive SMPs.

To evaluate polyurethane series, SMP's characteristic of shape memory and recovery, Tobushi[47] proposed a four-element linear constitutive modeling involving a slip mechanism by adding a slip element due to internal friction to the linear viscoelastic equation, which well expressed the overall thermomechanical properties of SMPs. The stress–strain relationship is expressed as follows:

$$\dot{\varepsilon} = \frac{\dot{\sigma}}{E} + \frac{\sigma}{\mu} - \frac{\varepsilon - \varepsilon_s}{\lambda} + \alpha\dot{T} \tag{1}$$

$$\varepsilon_s = S\varepsilon_c \tag{2}$$

where σ, ε, ε_c, ε_s, and T denote stress, strain, creep strain, irrecoverable strain and temperature, respec-

tively. The material parameters E, μ, λ, and α, which are expressed as functions of temperature represent modulus of elasticity, viscosity, retardation time, and coefficient of thermal expansion.

To express the behavior of large deformation, Tobushi[48] revised the model above to build a nonlinear equation of SMPs by adding two nonlinear terms expressed by power functions of stress to the elastic term and the viscous term, respectively. Equation (1) became

$$\dot{\varepsilon} = \frac{\dot{\sigma}}{E} + m\left(\frac{\sigma - \sigma_y}{\kappa}\right)^m \frac{\dot{\sigma}}{\kappa} + \frac{\sigma}{\mu} + \frac{1}{b}\left(\frac{\sigma}{\sigma_c} - 1\right)^n$$
$$- \frac{\varepsilon - \varepsilon_s}{\lambda} + \alpha\dot{T} \tag{3}$$

And eq. (2) became $\varepsilon_s = S(\varepsilon_c + \varepsilon_p)$. σ_y, σ_c denoted proportional limits of stress in the time-independent term and the viscous term and ε_p presented plastic strain. Because of deficiency of internal mechanism of strain storage and recovery, the model had limited predictive effectiveness.

Liu[39] systematically investigated the thermomechanics of shape storage and recovery of an epoxy resin for small strains (within $\pm 10\%$) in uniaxial tension and uniaxial compression. Based on the experimental results and the molecular mechanism of SMPs, they developed a three-dimensional small-strain internal state variable linear-elastic constitutive model. The constitutive model assumes that the polymer model is a mixture of two kinds of extreme phases: the "frozen phase" and the "active phase." The shape memory behavior in a thermomechanical cycle mainly is obtained by the frozen fraction, which represents the volume fraction of the frozen phase and being used to describe the extent of the glass transition and the state of polymer, and the storage and release of the entropic strain energy, which is used to explain the strain that is stored (memorized) in the material during freezing. The overall constitutive equation for the polymer in a thermomechanical cycle is:

$$\sigma = (\phi_f \mathbf{S}_i + (1 - \phi_f)\mathbf{S}_e)^{-1} : (\varepsilon - \varepsilon_s - \varepsilon_T) \tag{4}$$

where σ, ε, ε_s, and ε_T denote stress, strain, stored strain, and thermal strain. $\mathbf{S}_i$, $\mathbf{S}_e$, and ϕ_f represent the fourth-order elastic compliance tensor corresponding to the internal energetic deformation, the elastic compliance fourth-order tensor corresponding to the entropic deformation and frozen fraction respectively. In the article, the free energy function of the model is also developed, which is proved being compatible with the second law of thermodynamics in the sense of the Clausius–Duhem inequality. Although the model can be used to investigate

the strain and stress recovery responses under various external constraints, the range of application was limited because of its framework of small strain.

Diani[49] proposed a 3D thermoviscoelastic constitutive model to describe the thermomechanical behavior of SMPs under large strain deformations. This model is based on thermodynamic considerations for the viscoelastic behavior of crosslinked SMP networks and is formulated in a finite strain framework and the stress evolution of the material in a thermomechanical cycle is derived from the Helmholtz free energy. The total Cauchy stress including the portion due to the entropy change and the portion due to the internal energy change can be expressed as follows:

$$\sigma = \frac{E^r}{3}\frac{T}{T_h}\mathbf{B} - p\mathbf{I} + \mathbf{L}^e[\ln(\mathbf{V}^e)] \tag{5}$$

where σ, $\mathbf{B}$, and $\mathbf{V}^e$ denote Cauchy stress, the left Cauchy-Green tensor, and left stretch tensor; E^r and $\mathbf{L}^e$ denote the Young's modulus of the material, the fourth-order elastic constant tensor; and T, p, and $\mathbf{I}$ characterize the temperature, Lagrange multiplier, and unit tensor, respectively. This model can capture critical features of SMP deformation and provide very favorable prediction of experimental results especially in the estimation of the remaining strain during stress release and in the prediction of the overall material behavior in compressive prestrain. However, the stress–temperature curves during constrained thermomechanical recovery of SMPs show obvious discrepancy with experiment data, so the evolution equation between glassy and rubbery state of the material needs to be precisely chosen to obtain better agreement with the experimental observations.

Rao et al.[50–53] had done symmetric investigations for the constitutive modeling of crystallizable polymers. Based on the studying of the crystallization in polymers and on the theory of multiple natural configurations, Rao et al.[54] developed a constitutive equation to model the thermomechanical behavior of crystallizable SMPs in 2006 and the stress for the semicrystalline phase can be given by:

$$\begin{aligned}\mathbf{T} &= -p\mathbf{I} + (1-\alpha)2\rho\mathbf{F}_{\kappa_a}\frac{\partial\psi_a}{\partial C_{\kappa_a}}\mathbf{F}_{\kappa_a}^T + \alpha 2\rho\mathbf{F}_{\kappa_c}\frac{\partial\psi_c}{\partial C_{\kappa_c}}\mathbf{F}_{\kappa_c}^T \\ &= -p\mathbf{I} + (1-\alpha)\hat{\mathbf{T}}_\mathbf{a} + \alpha\hat{\mathbf{T}}_\mathbf{c} \end{aligned} \tag{6}$$

where $\mathbf{T}$ is the average stress of the entire material, $\hat{\mathbf{T}}_a$ is the stress in amorphous phase, $\hat{\mathbf{T}}_c$ is the stress in crystallite phase, p is the Lagrange multiplier due to the constraint of incompressibility, C_{κ_0} and C_{κ_c} is the right Cauchy-Green tensor, $\mathbf{F}_{\kappa_0}$ is the deformation gradient measured from fixed configuration κ_a

associated with the amorphous phase, and $\mathbf{F}_{\kappa_c}$ is the deformation gradient measured from configuration κ_c associated with the crystalline phase. ψ is the Helmholtz potential, α is the volume ratio of the crystalline phase. In a typical thermomechanical cycle, the model described the process of shape memory and shape recovery by using the formation of the crystalline phase, which is used to retain the temporary shape and the melting of the crystalline phase, which is used to recover its original shape, respectively. The behaviors of a homogenous deformation of uniaxial cycle and an inhomogeneous deformation of circular shear of a hollow cylinder were investigated by using the model and the uniaxial cycle of deformation demonstrates good agreement with experiments.

Applying the general mesomechanical concept,[55] which is based on the assumption of existence of a continuous substructure that remains elastic throughout the SM process, Kafka[56] formulated a mescoscopic constitutive equation with tensorial internal variables for small strains of SMPs. The constitutive modeling is based on a description of two 3D continuous elastic substructures in the SM process. One of the 3D continuous substructures, which cause the recovery of shape on the macroscale is assumed to remain elastic throughout the SM process, while the others deform in an elastic–plastic–viscous way. The macroscopic differential constitutive equation in the form of the deviatoric and isotropic parts is as follows:

$$\dot{\varepsilon}_{ij} = \dot{e}_{ij} + \delta_{ij}\dot{\bar{\varepsilon}} = \bar{\mu}\dot{\tilde{S}}_{ij} + v_n(\mathbf{M}_n S_{ijn} + \mathbf{M}'_n S'_{ijn})\dot{h}_n + \delta_{ij}\bar{\alpha}\dot{T} \tag{7}$$

In the continuation of their model, the article gives the description of uniaxial time- and temperature-independent elastic–plastic process and uniaxial time- and temperature-dependent viscous process and the method of determination and optimization of the model parameters, respectively. The constitutive modeling can successfully represent the material's deformation in response to a complicated loading path, and also provides good agreement with experimental data.

Based on the experimental observations and an understanding of the underlying physical mechanism of the shape memory behavior, Qi[37] developed a three-dimensional (3D) constitutive model to describe the finite deformation thermomechanical response of SMPs. In the models, the SME of an SMP is considered consisting of two concurrent processes: the transition from rubbery behavior dominated by entropic energy at high temperatures to glassy behavior dominated by internal energy at low temperatures, and the storage of the deformation incurred at high temperatures during cooling.

Based on the assumption above, the change in Helmholtz energy is used to describe the transition of energy, and the model develop Liu's assumption of two phases of SMPs to three phases by dividing the glassy phase into two phases: frozen glassy phase (FGP), which is vital in capturing the SMEs and initial glassy phase. The total Helmholtz energy and the total stress, therefore, are written, respectively, as:

$$\mathbf{H}_{total} = f_r \mathbf{H}_r + f_{g0} \mathbf{H}_{g0} + f_T \mathbf{H}_T \qquad (8)$$

$$\mathbf{T} = f_r \mathbf{T}_r + f_{g0} \mathbf{T}_{g0} + f_T \mathbf{T}_T \qquad (9)$$

The evolution rule for volume fractions is defined, the Langevin chain based Arruda–Boyce eight-chain model is used to capture the hyperelastic behavior of rubbery phase and the behavior of glass phase is characterized by applying a viscoplastic model in which the continuity of overall deformation of frozen glass phase is considered. The ultimate constitutive equations are summarized in the article.[37] This model considers separate material behaviors at temperatures above and below of T_g and hence, other type of models for rubbery behavior and glassy behavior is allowed to be used to capture the SME. The definition of the FGP, which causes the new deformation due to the redistribution of overall deformation, make unnecessary the introduction of a 3D finite deformation equivalent "stored strain," which was used in a Liu's small deformation constitutive model.[37]

Based on the idea in the work of Liu[39] and on the framework of nonlinear thermoelasticity, Chen[38] developed a three-dimensional nonlinear constitutive theory for large deformations of SMPs. The average deformation gradient is expressed as follows:

$$\mathbf{F}(t) = [1 - \phi(\theta(t))]\hat{\mathbf{F}}_a(t)(\mathbf{S}(t), \theta(t))$$
$$+ \int_0^t \hat{\mathbf{F}}_f(t)(\mathbf{S}(t), \theta(t))\hat{\mathbf{F}}_f^{-1}(\mathbf{S}(\tau), \theta(\tau))\hat{\mathbf{F}}_a(\mathbf{S}(t),$$
$$\times \theta(t))\phi'(\theta(\tau))\dot{\theta}'(\tau)d\tau \qquad (10)$$

The theory considers glass transition as the underlying mechanism of SME, and defines the frozen region function to describe the freezing process of a SMP. After the derivation of the constitutive equation for individual material points in which the frozen reference configuration is applied to ensure the continuity of deformation in the process of glass transition, the constitutive equation for the whole material, which gives the relation between the overall deformation and the stress is derived by the integration of the constitutive equations of the coexisting phases. The theory can describe thermomechanical properties of the active and frozen phases of the material, as well as the corresponding

phase transitions and can be used to examine the thermomechanical behavior of the SMP in an arbitrary temperature/loading process. In the continuation of their model, Chen et al.[57] also derived a linear constitutive model by considering small deformations and compared the predictions of this model with experimental measurements.

In 2008, Rao et al.[58] extended the constitutive eq. (6), which was developed within a mechanical setting to a full thermodynamic framework. The changes of morphology of the SMP in a typical cycle are considered consisting of four different processes namely: loading, cooling/crystallization, unloading, and heating/transition to the amorphous phase. Constitutive equations for rubbery phase (the amorphous phase), the semicrystalline phase and the transition between the semicrystalline phase and the amorphous phase are formulated. The specific formation of the constitutive modeling, respectively, for the above mentioned morphology can be found in the article.[58]

Based on the assumption that structural and stress relaxation are the primary molecular mechanisms of the SME and its time-dependence, Nguyen[59] developed a thermoviscoelastic constitutive model for the finite-deformation, time-dependent thermomechanical behavior of thermally active amorphous SMPs. This constitutive model incorporates the nonlinear Adam–Gibbs model of structural relaxation and a modified Eyring model of viscous flow into a continuum finite–deformation thermoviscoelastic framework and includes structural relaxation in the glass-transition region, viscoelasticity in the rubbery and transition regions, and viscoplasticity in the glassy region. Comparisons with experiments show that the model can explain the temperature dependence and time dependence of the shape memory phenomena.

Wang[60] proposed a new physical-based, temperature- and time-dependent constitutive model to predict the thermomechanical response of SMPs under different prestrain constraint conditions. In the model, the crystallization theory is applied to the determination of the frozen fraction, and Mori-Tanaka approach,[61] which is a method to determine the effective properties in composites, is used to predict the effective elastic properties of SMPs. The overall constitutive equation is expressed as:

$$\sigma = \widetilde{\mathbf{L}}(\varepsilon - \varepsilon_f^M - \varepsilon_f^T) = \widetilde{\mathbf{L}}\left[\varepsilon^{pre}(1 - \Phi_f^M) + \varepsilon^T(1 - \Phi_f^T)\right] \qquad (11)$$

Kim[62] developed a one-dimensional constitutive model to predict the shape memory behavior of shape memory polyurethanes according to their microstructure. This model separates the material domain into three phases: one hard segment phase

that governs the viscoelastic behavior and two (active and frozen) soft segment phases that undergo a reversible phase transformation. Hyperelastic and viscoelastic equations are applied to describe the thermomechanical behavior of the soft and hard segments in SMPUs. Linking models are built by the series and parallel between the active phase and frozen phase of the soft segments and then connecting the hard segment phase with the soft segment phases. The final series and parallel models can respectively be expressed as follows:

$$\lambda \cong \xi_h(\varepsilon_h(\sigma) + 1) + \xi_{sf}\left(\frac{2C_{01,sf}}{2C_{01,sf} - \sigma}\right)^{1/3}$$
$$+ \xi_{sa}\left(\frac{2C_{01,sa}}{2C_{01,sa} - \sigma}\right)^{1/3} + \lambda_{st} - 1 \tag{12}$$

$$\sigma_h = \sigma_s = \int_t Y(t - \tau)\frac{(d\lambda_h - 1)}{d\tau}d\tau$$
$$= \left[\xi_{sf0}\left[2C_{10,sf}\left(\lambda_s - \lambda_s^{-2}\right) + 2C_{01,sf}\left(1 - \lambda_s^{-3}\right)\right]\right.$$
$$\left. + \xi_{sa}\left[2C_{10,sa}\left(\lambda_s - \lambda_s^{-2}\right) + 2C_{01,sa}\left(1 - \lambda_s^{-3}\right)\right] + \sigma_{sfst}\right]$$
$$/(1 - \xi_n) \tag{13}$$

For modeling of SMP stents, Reese[63] presented a new constitutive approach for the modeling of SMPs. The modeling applies a simple rule of mixture to identify the energy parts of the rubbery and the glassy phases and is assumed that, in the rubbery phase, the frozen deformation is equal to the total deformation, which is then held constant in the glassy phase. Applying the viewpoint of thermodynamics, the article derives the full thermomechanical coupling constitutive equations both in a macromechanical and in a micromechanical format in the framework of large strains. The models have been implemented into the finite element method to investigate two kinds of stent structures.

CONCLUSIONS

SMPs are new stimuli-responsive materials. The specific SME makes it attractive and promising in broad applications areas. SMPs have been made rapid progress in theories and practical applications in the past several years. As the shape memory processes in SMPs are so complicated that any constitutive model can describe them only in some main features. This article first summarized the basic deformation mechanism, and then introduced the new advancement of the constitutive modeling of thermoresponsive SMPs.

Although the advancements lay an important foundation for application of SMPs, so far as I know, the practical application examples are so little that the

new materials are far from the expectation. There are still many problems to solve. (1) As the deformation of polymer is obviously time dependent, now developing viscoelastic constitutive modeling for SMPs still need further research. (2) One of the key problems which limit the practical application is the lower mechanical properties of SMPs. So developing the SMP composites and related research methods is of special significance. (3) Besides the problem of materials itself, how to control the deformation in a thermomechanical cycle to ensure sufficient accuracy especially in microsystems also is very important, especially in complex environmental condition. Up to now, the modeling effort for SMPs is still in its infancy, the further research still needs the coworks of physical, mechanical, and material scientists.

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