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A modified phase-based constitutive model for shape memory polymers

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ABSTRACT

Constitutive models used for predicting the thermomechanical behavior of shape memory polymers (SMPs) are critical for the development of SMP applications. Among the existing models, the phase transition concept attracts wide attention due to its good predictive capacity and great convenience. However, most of the present phase transition models for SMPs have limitations or deficiencies in considering the effect of temperature change rate on the thermomechanical behavior of SMPs. In this paper, based on the kinetics of phase transitions, we propose a constitutive model in which the temperature change rate is incorporated into the phase evolution function to consider the effect of the temperature change rate on the thermomechanical properties of SMPs. Then experimental data under different recovery conditions for two different types of SMP materials are used to validate the predictive capacity and versatility of the present model. The predicted results agree quite well with the experimental observations, which demonstrates that the present model is robust enough to predict the complex thermomechanical behavior for different SMPs. In addition, through experiments and model predictions, we find that the shape free recovery curves at different heating rates can be easily predicted by just moving a reference recovery curve along the horizontal direction by a distance whose value is calculated through the proposed equation.

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Keywords: smart material; shape memory polymer; constitutive model; phase transition; temperature change rate

INTRODUCTION

Shape memory polymers (SMPs) are a type of smart materials that are able to fix a temporary shape and then return to their permanent shape by an external stimulus¹ such as temperature, light, electricity and humidity.²⁻⁴ Compared to shape memory ceramics and shape memory alloys, SMPs have many special advantages, e.g. low density, low cost, easily tailored properties and large deformation recovery capacity.^{5,6} These novel properties have drawn increasing attention for utilizing SMPs in many potential applications, such as deployable structures, biomedical devices, smart textiles and self-healing composite systems.^{7–13}

SMPs triggered by temperature are known as possessing a thermally induced shape memory effect. In general, the typical thermomechanical cycle of thermally induced SMPs can be described as follows: deform the SMP under an external force at a high temperature; decrease the temperature while maintaining the deformation; remove the external force; reheat the SMP with or without the constraints.^{8,14,15} In last two decades, several thermomechanical constitutive models have been proposed to describe the deformational behavior of SMPs. Typically these models can be classified in two categories: rheological models and phenomenological models.^{16–20}

The early rheological models proposed by Tobushi *et al.*²¹ and Lin and Chen²² using linear rheology elements (spring elements and dashpot elements) are based on the inherent viscoelasticity of SMPs. One major shortcoming of these early models is that they can qualitatively but not quantitatively predict the deformational behavior of SMPs. To more accurately describe the thermomechanical behaviors of SMPs, the rheological models are improved by increasing the number of linear or nonlinear elements,^{23–27} which leads to the fact that most of the present rheological models have many parameters. For example, more than 31 parameters in the model of Diani *et al.*²⁸ 42 in the model of Yu *et al.*²⁹ and up to 45 in the model of Srivastava *et al.*³⁰ need to be determined through specific experiments and complex calibration processes, such as a series of dynamic frequency sweep tests and constrained nonlinear multiparameter regression analysis.³¹

The phenomenological model based on the phase translation concept was first introduced by Liu et al.¹⁴ who considered that the epoxy-based SMP was a mixture of frozen phase and active phase, and the volume fraction of the two phases changed according to the temperature. It is the strain stored in the frozen phase that controls the evolution of the shape storage and recovery. Under these considerations, they developed a constitutive model which could effectively predict the thermomechanical behavior of the SMPs under small strains. Due to its straightforwardness, ease of obtaining the parameters and high predictive capability, the phase transition concept has gradually been adopted by many researchers to develop constitutive models to improve the predictive capability and extend their application scope.^{17,32} In the work of Wang et al.³³ a crystallization theory was applied to describe the frozen process of SMPs and the retardant time was introduced to the phase transition model. Yang and Li¹⁷ treated SMPs as a composite

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with frozen phase matrix and active phase inclusions and used the Mori–Tanaka theory to describe the deformation properties. Qi *et al.*³⁴ developed a 3D large deformation constitutive model based on the phase transition concept and experimental observations. Chen and Lagoudas³⁵ developed a model for finite deformation which combined the phase concept with a neo-Hookean rubber elasticity model. Kim *et al.*³⁶ added one more phase (hard phase) to the classic phase model to predict the behavior of shape memory polyurethanes under large strains.

Although the above phase transition constitutive models are widely adopted in the SMP community, most of the present phase transition models are not able to consider the effect of temperature change rate on the thermomechanical behavior of SMPs. This lack of consideration has a great limitation on designing and optimizing the application of SMPs, as different temperature change rates are very common in practical applications.³⁷ To the authors' knowledge, there are only a few studies that intended to indirectly or directly take this effect into consideration; however, these studies have their own limitations. Wang et al.³³ introduced a retardant time to the phase transition model and they pointed out that the retardant time was dependent on the temperature change rate. In previous work of our group,³⁷ a unique phase-based constitutive model was developed by introducing a time factor to take the strain release rate into account. Nevertheless, these two models do not give the expression between the temperature change rate and the introduced time-dependent parameters. That is, when changing the temperature change rate, the introduced parameters have to be determined by additional corresponding experiments. In Yang and Li's work,¹⁷ a physics-based phase evolution model which contained the heating rate effect was developed. However, in the parametric study part, the effect of the heating rate on the frozen volume fraction was quite different from the experimental observations existing in other publications. In addition, all the studies provide experiments with only one heating rate for comparison. Therefore, it is still indispensable to develop models that could reflect the effect of the temperature change rate on the thermomechanical behavior of SMPs. In the present study, we try to overcome these problems and develop a phase-based constitutive model for SMPs in which the effect of the temperature change rate is considered.

The paper is organized as follows. The next section presents the overall thermomechanical constitutive model and the derivation of the expression of the phase evolution function considering the temperature change rate. In the following section the parameter determination methods are introduced. Then, two groups of comparisons between the model predictions and experimental tests are presented. Finally, the main conclusions are drawn.

CONSTITUTIVE MODEL

Basic thermomechanical constitutive model

Based on the work of Liu *et al.*¹⁴ we make the basic assumptions that a SMP is a two-phase (active phase and frozen phase) composite and that the stress is uniform within the composite. Thus the basic thermomechanical constitutive equation can be summarized as follows:¹⁴

$$\sigma = \frac{1}{\varphi_{\rm f}/E_{\rm f} + (1 - \varphi_{\rm f})/E_{\rm a}} \left(\varepsilon - \varepsilon_{\rm s} - \int_{T_0}^T \alpha {\rm d}T\right) \tag{1}$$

where σ is the total stress, φ_f is the volume fraction of the frozen phase, E_f and E_a are Young's modulus of the frozen and active

phase domains, respectively, ε is the total strain, T_0 is the initial temperature, ε_s is the stored strain and α is the coefficient of thermal expansion. The derivative of the stored strain with respect to temperature can be written as¹⁴

$$\frac{\mathrm{d}\varepsilon_{\mathrm{s}}}{\mathrm{d}T} = \frac{\varepsilon - \varepsilon_{\mathrm{s}} - \int_{T_{0}}^{T} \alpha \mathrm{d}T}{E_{\mathrm{a}} \left[\varphi_{\mathrm{f}}/E_{\mathrm{f}} + \left(1 - \varphi_{\mathrm{f}}\right)/E_{\mathrm{a}}\right]} \frac{\mathrm{d}\varphi_{\mathrm{f}}}{\mathrm{d}T}$$
(2)

Phase evolution function

For the phase transition approach, the volume fraction of the frozen phase φ_f plays an essential role in predicting the thermomechanical behavior of the SMPs. Varieties of frozen phase evolution functions have been put forward by researchers and a good summary of them can be found in reference.¹⁷ As stated in the introduction, the existing models have deficiencies and limitations in considering the effect of temperature change rate on the thermomechanical behavior of SMPs. Therefore, in this study we are aiming to improve the phase transition model by introducing the rate effect into the frozen phase evolution function. The basic frozen phase evolution function is expressed as³⁴

$$\varphi(T) = 1 - \frac{1}{1 + \exp\left[-\left(T - T_0\right)/b\right]}$$
(3)

where T_0 and b are constants; thus it cannot be used under different temperature change rate conditions. By analyzing the experimental results and the properties of Eqn (3), we find that T_0 is almost the same as the phase transition temperature T_{tr} where the temperature derivative of the volume fraction of the frozen phase reaches an extreme. This tells us that an improved phase transition model will have the ability to predict the thermomechanical properties of SMPs under different temperature change rates if we find how the temperature change rate affects T_{tr} . Mathematically, the frozen phase evolution function in the present model can be expressed as

$$\varphi\left(T,\dot{T}\right) = 1 - \frac{1}{1 + \exp\left\{-\left[T - T_{\rm tr}\left(\dot{T}\right)/b\right]\right\}} \tag{4}$$

where \dot{T} is the time derivative of temperature T or the temperature change rate.

The aim of this section is to explore the expression of the specific relation between $T_{tr}(\dot{T})$ and \dot{T} , and between $\varphi(T, \dot{T})$ and T, \dot{T} , based on the kinetics of phase transitions. The basic theory is mainly based on the work of Moynihan et al.³⁸⁻⁴⁰ In the kinetics of phase transition theory, they consider that the evolution of temperature with respect to time at a constant temperature change rate is a series of instantaneous and sufficiently small temperature jumps ΔT , after which there is an isothermal hold of time duration Δt (isothermal relaxation process). According to the thermodynamics, the transition temperature can be defined by the point of inflection of the enthalpy-temperature curve under a certain temperature change rate. The following assumptions about the evolution of the enthalpy H during the isothermal relaxation process are made. First, during the heating process, the isothermal relaxation is considered as a series of n independent processes and the rate of enthalpy H_i change is associated with a time and temperature dependent relaxation time τ_i such that

$$\left(\frac{\partial H}{\partial t}\right)_{T} = \sum_{i=1}^{n} \left(\frac{\partial H_{i}}{\partial t}\right)_{T} = -\sum_{i=1}^{n} \frac{H_{i} - H_{ei}}{\tau_{i}}$$
(5)

where $H_{\rm ei}$ is the equilibrium value of enthalpy at the present temperature.

Second, the relaxation time at temperature T is assumed to be⁴⁰

$$\tau_i = f_i \exp\left(-gT\right) \exp\left[-k\left(H - H_e\right)\right] \tag{6}$$

where f_{i} , g and k are constants and $g = -\Delta h^*/RT^2$, R is the ideal gas constant and Δh^* is a material parameter corresponding to the activation enthalpy of the relaxation process.

Third, the differences between the heat capacities at two extreme temperatures where the SMPs are made up of only active phase and only frozen phase for different temperature change rates are unchanged.

Due to the fact that the enthalpy is a function of time as well as temperature, the following equation holds:

$$\frac{\mathrm{d}H}{\mathrm{d}T} = \left(\frac{\partial H}{\partial T}\right)_t + \left(\frac{\partial H}{\partial t}\right)_T \frac{\mathrm{d}t}{\mathrm{d}T} \tag{7}$$

Combining Eqns (5)–(7) and considering the relationship between enthalpy and heat capacity, we have the following formula:

$$d\ln\left|\dot{T}\right|/d\left(1/T_{\rm tr}\right) = -\Delta h^*/R \tag{8}$$

If the phase transition temperature is expressed as $T_{tr}(\dot{T}_r)$ at the reference temperature change rate \dot{T}_{rr} then the phase transition temperature $T_{tr}(\dot{T})$ at the temperature change rate \dot{T} will be expressed as

$$T_{\rm tr}\left(\dot{T}\right) = \frac{T_{\rm tr}\left(\dot{T}_{\rm r}\right)}{1 - cT_{\rm tr}\left(\dot{T}_{\rm r}\right)} \tag{9}$$

where

$$c = \frac{R}{\Delta h^*} \ln \left| \frac{\dot{T}}{\dot{T}_r} \right|$$
(10)

Thus far, the specific expression of the effect of the temperature change rate on the phase transition temperature has been obtained. According to Eqns (1), (2), (4) and (9), the new phase-based constitutive model can take the effect of the temperature change rate into consideration.

PARAMETER DETERMINATION

In this section, we present the process of determining the parameters. $E_{\rm f}$ is the modulus corresponding to the frozen phase and is assumed constant while $E_{\rm a}$ is the modulus of the active phase which is temperature dependent and is expressed as

$$E_{\rm a} = 3NkT \tag{11}$$

where N is the crosslink density of the SMP and k is Boltzmann's constant. Therefore, the modulus at any temperature T can be expressed as

$$E = \frac{1}{\varphi_{\rm f}/E_{\rm f} + \left(1 - \varphi_{\rm f}\right)/3NkT} \tag{12}$$

Considering two extreme values of modulus calculated from the uniaxial tension curve, at temperature $T_{\rm h}$, $\varphi_{\rm f} = \varphi_{\rm h}$, $E = E_{\rm h}$, and at temperature $T_{\rm I}$, $\varphi_{\rm f} = \varphi_{\rm I}$, $E = E_{\rm I}$, according to Eqn (12) two equations can be formulated. Solving these two simultaneous equations, the crosslink density of the polymer and $E_{\rm f}$ can be easily obtained. The coefficient of thermal expansion (CTE) is determined by calculating the slope of the thermal deformation curve under no external force.

As stated by Liu *et al.*¹⁴ the phase evolution parameter *b* is determined by fitting the normalized free recovery experimental curve using Eqn (4) at a certain temperature heating rate, i.e.

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$$\varphi\left(T,\dot{T}\right) = 1 - \frac{1}{1 + \exp\left\{-\left[T - T_{\rm tr}\left(\dot{T}\right)\right]/b\right\}} = \frac{\varepsilon\left(T\right)}{\varepsilon\left(T_{0}\right)}$$
(13)

where $\varepsilon(T)$ and $\varepsilon(T_0)$ are the strain at temperature T and at the temperature of the start of heating, respectively.

Two phase transition temperatures (the temperature derivative of $\varphi_{\rm f}$ reaches an extreme or the second order temperature derivative of $\varphi_{\rm f}$ equals zero) can be obtained at two different heating rates; then, according to Eqns (9) and (10), $R/\Delta h^*$ is obtained.

MODEL VERIFICATION AND DISCUSSION

Thus far, all the parameters of the model can be obtained by relevant experimental data. In order to verify the predictive capacity and versatility of the proposed model, the predicted results were compared with experimental data for two different kinds of SMPs. One set of experimental data for a polystyrene-based SMP was obtained from our own experiments, while the other was found from Arrieta *et al.*⁴¹ for an acrylate polymer network.

Case 1: Model validation for a polystyrene-based SMP *Materials*

The SMP material used in this case is a styrene-based polymer, which has been studied by several groups.⁴² All the materials were obtained from Sigma-Aldrich (St. Louis, MO, USA) and were used without any purification. In the synthesis process, the styrene (analytical reagent), butyl acrylate (analytical reagent), divinylbenzene (analytical reagent) and benzoyl peroxide (analytical reagent) were first mixed in a mass ratio of 65:35:2:2; then the mixture was stirred and cast into a glass mold. Finally, it was cured in an oven at 70 °C for 24 h. After curing, the SMP sample was machined into rectangular shaped specimens with dimensions 20 mm \times 5 mm \times 0.50 mm.

Experimental tests

The CTE was measured by capturing the strain of the SMP specimen under no external force using a dynamic mechanical analysis (DMA) tester (DMA Q800, TA Instruments, New Castle, DE, USA).⁴³ To measure the CTE, first an SMP specimen was heated to 75 °C and equilibrated at that temperature for 10 min. Then the sample was cooled to 15 °C. Meanwhile, the strain during the cooling step was recorded. Figure 1 shows the thermal strain evolution during cooling from 75 to 15 °C. The CTE α is defined by the slope of the thermal strain curve. From Fig. 1, the CTE is 3.2×10^{-5} °C⁻¹ at temperatures below 38 °C while its value is 2.1×10^{-4} °C⁻¹ at temperatures above 38 °C.

The uniaxial tension tests at a low and a high temperature under a strain rate of 2% min⁻¹ were carried out using the DMA tester and the tension curves are shown in Fig. 2. The moduli are determined by the slope of the stress–strain curves. The values of the modulus at 20 and 65 °C are 874.5 and 1.01 MPa, respectively.

The cycle of the shape memory free recovery test was conducted on the DMA tester as well. In the first step, the shape memory rectangular specimen was first deformed to a predefined strain under a strain rate of 2% min⁻¹ at 65 °C. Subsequently, the deformed specimen was cooled to 20 °C at the temperature decreasing rate of \dot{T} (1, 2, 3 and 4 °C min⁻¹) while maintaining the total strain unchanged. Then the external force was removed and the temporary



Figure 1. Thermal expansion strain as a function of temperature.

(deformed) shape was retained. Finally, the SMP was reheated to 75 °C at the same rate \dot{T} . The frozen phase evolution function was fitted using the normalized free recovery experimental curve at a heating rate of 2 °C min⁻¹ (shown in Fig. 3), and *b* was determined to be 2.53 K. The transition temperatures at a heating rate of 2 and 3 °C min⁻¹ were 52 and 56 °C, respectively. According to Eqns (9) and (10), the value of $R/\Delta h^*$ is calculated to be 9.226 × 10⁻⁵ K⁻¹.

Model predictions for free recovery behaviors

In order to show the capability of the proposed model in predicting the thermomechanical properties of SMPs, experiments on shape memory free recovery for a polystyrene-based SMP with different heating rates (1, 2, 3 and 4° C min⁻¹) conducted above were adopted for comparison. First all the parameters were obtained according to the methods mentioned in the section Parameter Determination and the aforementioned experimental data. They are listed in Table 1 for further predictions.

The transition temperatures at different heating rates obtained by the model predictions and the experiments are shown in



Figure 3. Frozen phase evolution with respect to temperature derived from fitting the shape memory free recovery curve.

Table 1. Material parameters for the polystyrene-based SMP			
Material parameter	Value	Unit	
E _f	874.5	MPa	
Ν	118.7	mol m ⁻³	
Ь	2.53	K	
R/∆h*	9.226×10^{-5}	1 K ⁻¹	
α	3.2×10^{-5} for $T < 311$ K 2.1 × 10 ⁻⁴ for $T > 311$ K	1 K ⁻¹	

Fig. 4(a). The results show that the model of the kinetics of phase transitions can be used in predicting the phase transition of SMPs. Figure 4(b) shows comparisons between the modeling results and experimental tests for shape memory free recovery at different heating rates. The results show that the predictions of the present model are in excellent agreement with the experimental



10



Figure 4. (a) Comparison of the transition temperatures at different heating rates between experiments and model predictions. (b) Shape memory free recovery curves at different heating rates.



Figure 5. Master curves obtained (a) by experiments and (b) by model predictions

observations, which demonstrates that the current approach can reasonably account for the effect of heating rate on the thermomechanical properties of SMPs.

Further, we find that if we select a recovery curve under any heating rate as the reference curve and move the others along the horizontal direction (temperature axis) by a distance of

$$d = T_{\rm tr} \left(\dot{T} \right) - T_{\rm tr} \left(\dot{T}_{\rm r} \right) \tag{14}$$

the curves after moving will collapse into a single curve which we define as the master curve, where \dot{T}_r is the heating rate of the reference curve and T_{tr} (\dot{T}) is the phase transition temperature at a heating rate of \dot{T} and can be determined according to Eqn (9). In this study, the recovery curve at a heating rate of 2 °C min⁻¹ is chosen as the reference curve, and the other three curves are moved by a distance calculated according to Eqn (14). The results obtained by the experiments and the present model predictions are shown in Fig 5(a), (b) where the scattered points denote the master curve. This conclusion is quite useful because, if we have one recovery curve at a certain heating rate, then the recovery curves at different heating rates can be obtained by just moving the reference recovery curve along the horizontal direction (temperature axis) by the distance of Eqn (14).

Case 2: Model validation for an acrylate polymer network

In this section, another set of experimental data for an acrylate polymer network conducted by another research group⁴¹ is used to validate the versatility of the present model. The parameters were determined according to the methods described above and the relevant experimental data were obtained from the work of Arrieta *et al.*⁴¹ The frozen phase evolution is fitted using the experimental curve at a heating rate of 1 K min⁻¹, and the results are shown in Fig. 6. The material parameters are listed in Table 2.

Both shape memory free recovery and fixed strain constraint stress recovery tests were used to verify our model. The transition temperatures at different heating rates obtained by the



Figure 6. Frozen phase evolution with respect to temperature derived from fitting the shape memory free recovery curve.

Table 2. Material parameters for the acrylate polymer network		
Material parameter	Value	Unit
E _f	853.9	MPa
N	593.55	mol m ⁻³
Ь	2.61	К
R∕∆h*	2.382×10^{-5}	1 K ⁻¹
α	9.1718 × 10 ⁻⁵ + 1.354 × 10 ⁻⁶ × (T - 293) for \dot{T} = 1 K min ⁻¹ 1.1741 × 10 ⁻⁴ + 1.24 × 10 ⁻⁶ × (T - 293) for \dot{T} = 5 K min ⁻¹	1 K ⁻¹

model predictions and the experiments are shown in Fig. 7(a). Figure 7(b) shows the comparisons between modeling results and experimental tests for the shape free recovery at different heating rates, indicating the good predictive capacity of our model. Figure 7(c) shows the parameter study for a wider range of heating rates.



Figure 7. (a) Comparison of the transition temperatures at different heating rates between experiments and model predictions. (b) Shape memory free recovery curves at heating rates of 1 and 5 °C min⁻¹. (c) Parameter study of free recovery for a wider range of heating rates.



Figure 8. The comparisons between model results and experimental tests for fixed strain constraint stress recovery at different heating rates.

Figure 8 shows the comparisons between the modeling results and experimental tests for the fixed strain constraint stress recovery at different heating rates. An excellent agreement between the present model predictions and the experimental results can be seen from the comparisons. Therefore, we may safely draw the conclusion that the present model is quite robust in predicting the complex thermomechanical behavior of different SMPs.

Both experimental results and theory predictions have a certain significance in guiding researchers and engineers in developing and optimizing SMP applications. In addition, for some SMPs, especially thermoplastics, the recovery behaviors are influenced by the loading conditions. This is the limitation of the work. However, the present model lays a foundation for future models which could take into account the loading condition effect.

CONCLUDING REMARKS

Constitutive models used for predicting the thermomechanical behavior of SMPs are fundamental for the development of SMP applications. In this paper, based on the kinetics of phase transitions, the temperature change rate is incorporated into the phase evolution function to consider the effect of the temperature change rate on the thermomechanical properties of SMPs. The free recovery experiments for a polystyrene-based SMP are used to validate the predictive capacity of the present model. In addition, the free recovery and fixed stress recovery experiments for an acrylate polymer network are also used to test the proposed model's validity and versatility. The comparisons between the predicting results and experimental data are remarkably consistent. This indicates that our model has the ability to predict the strain and stress response with respect to temperature under different recovery conditions for different SMPs.

It should be noted that, if we have obtained one recovery curve at a certain heating rate, then the recovery curves at different heating rates can be obtained by just moving the recovery curve along the horizontal direction by a distance whose value is calculated through a simple equation. We hope our model may provide guidelines for developing and optimizing SMP applications.

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