A VISCOELASTIC-PLASTIC CONSTITUTIVE MODEL OF SHAPE MEMORY POLYMER

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ABSTRACT

It is of practical significance to develop a constitutive model which is able to predict the thermo-mechanical behaviors of the shape memory effect occurring in a shape memory polymer (SMP) accurately. The mechanism of shape memory effect of SMP is explained based on the assumption that SMP is composed by two phases, reversible phase and stationary phase. Especially the different flow elements are respectively added to the reversible phase and stationary phase in order to express the plastic behavior of SMP. There are two springs in series, one dashpot and one flow element in the reversible phase. There are two springs in parallel, one dashpot and one flow element in the stationary phase. A constitutive equation is developed to express the thermo-mechanical behaviors of shape memory effect in the SMP based on viscous-elastic mechanics and plastic theory. An internal variable, frozen ratio, is defined to follow the shape memory process in SMP, and the material properties are described as the functions of frozen ratio based on phase transition theorem. The developed constitutive model, which includes above constitutive equation and material parameter functions, is used to numerically simulate the thermo-mechanical behaviors of SMP under various load cycles. Results show that the developed constitutive model can not only predict the shape memory process of SMP accurately, but also express the rate-dependent behaviors of SMP effectively.

Keywords: Shape memory polymer; viscoelastic-plasticity; constitutive model.

1. INTRODUCTION

Shape memory polymer, which is developed after shape memory alloy and shape memory ceramic, is a type of smart material that possesses the ability to revert to their original shape from the temporary shape by external stimulus [1]. External stimulus such as temperature, light, electricity, magnetism, humidity and PH are capable of causing shape memory effect of different SMP [2], in particularly, the kind of thermal-stimuli responsive SMP is investigated as a typical one [3]. The shape memory process of the thermal-stimuli responsive SMP can be classified into deforming process at high temperature, stress freezing process, unloading process at low temperature and shape recovery process [4]. Comparing with other shape memory materials, there are lots of promising characteristics on SMP like biocompatibility, light weight, high dimensional deformability, durability and low cost [5]. Therefore, SMP has a wide range of applications, especially the thermal-stimuli responsive SMP, which has covered the fields of textile, medicine, aviation, aerospace and microelectronics [6].

Constitutive equations for SMP have been developed to

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demonstrate the mechanical behaviors while wide range of engineering applications require them to describe the shape memory effect of SMP effectively. Tobushi *et al.* [7] developed a one-dimensional linear viscoelastic constitutive model by introducing a non-recoverable slip element to the viscoelastic model with spring and dashpot. Based on the one-dimensional linear viscoelastic constitutive model above, Tobushi *et al.* [8] developed a one-dimensional nonlinear constitutive model, which involved a slip element owing to internal friction and taking account of thermal expansion. Liu *et al.* [9] developed a one-dimensional shape memory polymer constitutive model which can effectively describe the thermodynamic [10] behavior of SMP under simple stress conditions, using the theory of solid phase transition [11]. According to this model, the shape memory effect of SMP is formed by the mutual transformation of the activated phase and the frozen phase under the combined effect of temperature and stress [9]. Based on the work of Liu [9], Chen *et al.* [12] developed two micro-mechanical three-dimensional constitutive models for the sake of large deformation and small deformation respectively.

A UMAT subroutine of SMP, which can be called by the finite element method software, was developed by Zhou *et al.* [4] and then used couple with finite element method software to numerically simulate the thermo-mechanical behaviors of SMP. With the wide applications of shape memory polymer in engineering practice, the mechanical properties of shape memory polymer under complex stress conditions have been gradually studied. Zhou *et al.* [13] established a three-dimensional macroscopic mechanical constitutive model, which can effectively describe the thermo-mechanical behaviors of SMP under complex stress conditions, based on the theory of viscoelasticity. A three-dimensional constitutive model is established by Baghani *et al.* [14] for SMP, which is exposed to time-dependent multiaxial thermo-mechanical loadings and under small deformations. As recorded in the literature, SMP is a class of typical rate-dependent material, which means that the loading rates as well as the temperature change rates have a significant influence on the mechanical behavior of SMP[15]. Guo *et al.* [16] established a viscoelastic one-dimensional constitutive model with parallel viscoelastic structure in rheological presentation of constitutive model and explained shape memory polymer microstructure using a composite system composed of activated phase and frozen phase [18].

The purpose of this article is to develop a three dimensional constitutive model with nonlinear plastic properties for SMP. The constitutive model, which is expected to describe the mechanical properties of thermal-stimuli responsive SMP, includes the explanation for micro-mechanism, the rheological presentation for constitutive model, constitutive equations and material parameter functions. Nowadays, more and more engineering applications involve kinds of SMP evolving from small deformation to large deformation, so that the plastic properties of SMP are required to be demonstrated. It is of necessity to investigate the nonlinear plastic properties of SMP from the viewpoint of practical application, since there are lots of viscoelastic models for SMP but little involve the plastic properties. Therefore we will unify an exponential function, which can describe the nonlinear plastic properties, with a viscoelastic model into one equation to describe the thermo-mechanical circle of SMP. Based on the change of micro-mechanism in the shape memory process of SMP, the concept of frozen ratio will be proposed to establish the material parameter functions to describe the variation of material parameters. Then comparing the numerical simulation results of developed constitutive model with the test data [8] to verify the precision of the proposed model in predicting the shape memory behavior. In addition, in order to provide an effective operation basis for the practical application of the project, we analyze the rate-dependence between stress, strain and temperature based on the numerical simulation under different loading rate, cooling rate and heating rate.

2. VISCOELASTIC-PLASTIC CONSTITUTION MODEL

2.1 Micro-mechanism of SMP

This paper is mainly focused on the thermal-stimuli responsive type of SMP, whose mechanical properties and material parameters change with both the changing of temperature and external loads. Thermal-stimuli responsive SMP will exhibit shape memory effect while undergoing proper conditions of temperature and loads because of the transition of two inter-penetrating phases, reversible phase and stationary phase. According to crystallization theory [19], polymers consist of lots of molecule chains changing between random forms and neatly arranged forms along the change of temperature, and the change of molecule chains will influence the mechanical properties of polymers. Analogous to molecule chains, the reversible phase will transform between activated state and frozen state when the temperature changes, therefore we use linear structures to act as reversible phase in the schematic diagram of microstructure for SMP, as shown in Fig.1. And the stationary phase, which is used to memorize the initial shape due to its constant mechanical properties, is represented by particles in the schematic diagram of microstructure, as shown in Fig.1. The schematic diagram of microstructure for SMP can not only demonstrate the macroscopic shape changes of SMP during the shape memory process, but also describe the phase transition process of SMP.

The variations of the two phases and the shape during shape memory process are exhibited in the schematic diagram of the microstructure for SMP. The linear structures are arranged neatly while the reversible phase is in frozen state at a low temperature, and the SMP is in the original shape as state 1 shows in Fig.1. Process ① makes it happened that the SMP is heated to a state at high temperature as state 2 shows in Fig.1, during which the

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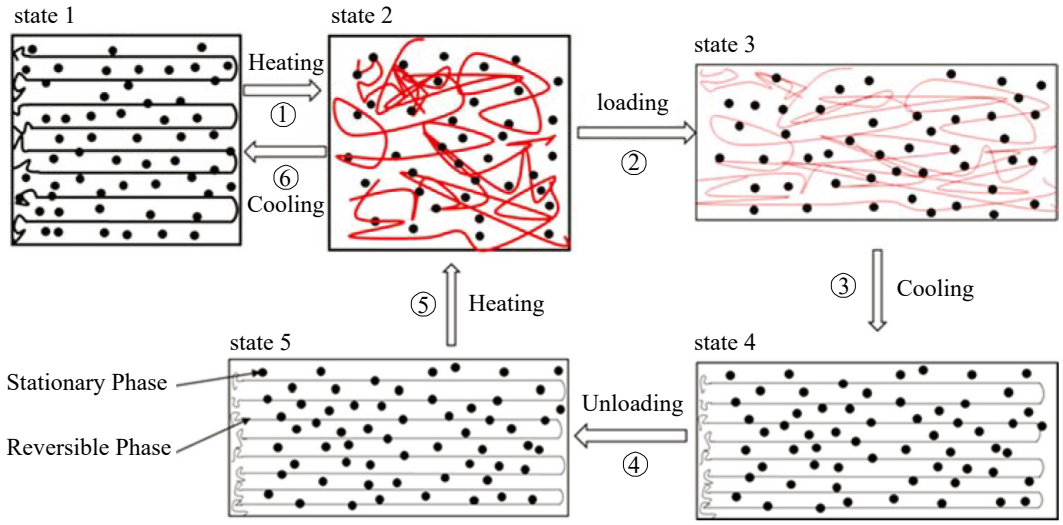


Fig. 1 Schematic diagram of the microstructure for SMP with a two-phase composite structure

stationary phase does not change and the reversible phase transforms from the frozen state to the activated state. The mechanical properties of the SMP, which include elasticity modulus, viscosity coefficient, delay time and plastic modulus, has changed while the shape of the SMP is constant. Loading at the heated SMP in process ②, so that the shape, stress as well as strain of SMP changed to state3. During process ③, that keeping the shape of the SMP unchanged and decreasing the temperature will lead the stress of the SMP to increase gradually with the decreasing of temperature. This due to that the transition from activated state to frozen state of reversible phase result in the change of mechanical properties of SMP. The SMP is unloaded in process ④, during which the SMP has a slight shape recovery and the value of stress revert to zero. In process ⑤, the transition of reversible phase from frozen state to activated state, causing by heating the SMP, results in the change of material parameters as well as the recovery of the shape. Finally, cooling the SMP to revert to the original state and the above is a complete shape memory process. Broad application of SMP result in the demand to develop new kinds of SMP that is superior to the present for thermo-mechanical performance, which require us to investigate the micro-mechanism of SMP.

2.2 Constitutive Equations of SMP

In order to describe the mechanical behavior of SMP, the rheological presentation for constitutive model, which is able to illustrate the viscoelastic-plastic properties qualitatively and intuitively, is developed and showed in Fig.2. According to the schematic diagram of the micro-mechanism for SMP showed in Fig.1, the stationary phase and reversible phase will not influence each other in the process of producing shape memory effect, so we use parallel structure to relate the two phases in the constitutive model as shown in Fig.2. E_{s1}, E_{s2}, μ_{s1} and P_{s2} which are exhibited by springs, dashpot and flow element, in the rheological presentation for constitutive model, represent

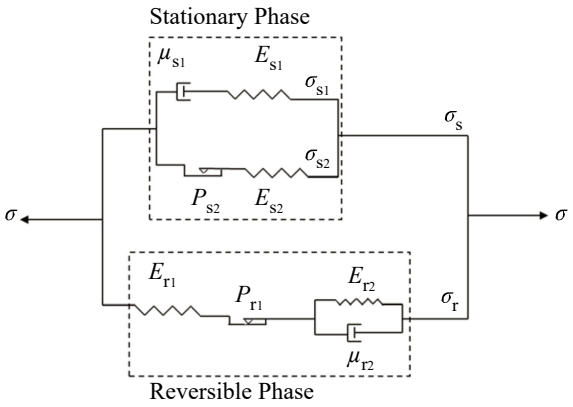


Fig. 2 A schematic diagram of the rheological presentation for constitutive model of SMP

elastic modulus, viscous coefficient and plastic hardening modulus respectively and build a parallel four-element system of stationary phase. Based on phase transition theory, the reversible phase will perform little effect on the mechanical properties of SMP when it is in activated state. So it is of rationality to propose a concept of frozen ratio represented as ϕ to describe the proportion of reversible phase that is in frozen state. E_{r1}, E_{r2}, μ_{r2} and P_{r1} represent the elastic modulus, viscous coefficient and plastic hardening modulus of reversible phase respectively and also build a tandem four-element system that is unified to a whole with the parallel four-element system of stationary phase by the frozen ratio with respect to stress. In short, the schematic diagram of the rheological presentation for constitutive model displays the simplified relationship of the two phases and gives a theoretical basis to deduce the mechanical constitutive equations for SMP.

As showed in Fig. 2, the total stress σ_{ij} is made up of the stationary phase stress σ_{ij}^{s} and the reversible phase stress σ_{ij}^{r}, which is expressed as

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$$\sigma_{ij} = \sigma_{ij}^{s} + \sigma_{ij}^{r} \tag{1}$$

In order to research the mechanical properties of SMP in detail, the total stress of stationary phase is deposed into viscous stress σ_{ij}^{sv} and elastoplastic stress σ_{ij}^{sep}, which is exhibited as

$$\sigma_{ij}^{s} = \sigma_{ij}^{sv} + \sigma_{ij}^{sep} \tag{2}$$

The same as stationary phase, the total stress of reversible phase is expressed as

$$\sigma_{ij}^{r} = \sigma_{ij}^{rv} + \sigma_{ij}^{rep} \tag{3}$$

In the thermal mechanical cycles of SMP, the viscoelastic properties of SMP are considered when the equivalent stress, which is expressed as σ_{eq}, is less than the yield stress, which is expressed as σ_y. According to the theory of solid mechanics [10] and viscoelasticity [20], the factors affecting the mechanical behavior of SMP can be summarized as elasticity and viscidity. The whole stress of the parallel four-element system of stationary phase for SMP, which is expressed as σ_{ij}^{s}, is decomposed into viscous stress of stationary phase σ_{ij}^{sv} and elastic stress of stationary phase σ_{ij}^{se}, showed as

$$\sigma_{ij}^{s} = \sigma_{ij}^{sv} + \sigma_{ij}^{se} \tag{4}$$

The expressions for viscous stress and elastic stress of stationary phase are obtained by theoretical deriving based on the rheological presentation for constitutive model showed in Fig.2. Therefore the viscous stress and elastic stress of stationary phase in Eq. (4) are respectively represented as

$$\sigma_{ij}^{sv} = \mu_s[\frac{\nu\dot{\varepsilon}_{kk}\delta_{ij}}{(1+\nu)(1-2\nu)} + \frac{\dot{\varepsilon}_{ij}}{(1+\nu)}] - \lambda_s[(1+\nu)\dot{\sigma}_{ij}^{s} - \nu\dot{\sigma}_{kk}^{s}\delta_{ij}] \tag{5}$$

$$\sigma_{ij}^{se} = E_s[\frac{\nu\varepsilon_{kk}\delta_{ij}}{(1+\nu)(1-2\nu)} + \frac{\varepsilon_{ij}}{(1+\nu)}] \tag{6}$$

in which μ_s, E_s and λ_s are the viscosity coefficient, elastic modulus and delay time of stationary phase, and the total stress, viscous stress and elastic stress of stationary phase are respectively expressed as $\sigma_{ij}^{s}, \sigma_{ij}^{sv}, \sigma_{ij}^{se}$. The relationships between the material parameters of the stationary phase of SMP and those of each component in the rheological presentation for constitutive model are defined as

$$\mu_s = \frac{(E_{s2} + E_{s1})\mu_{s1}}{E_{s1}}, E_s = E_{s2}, \lambda_s = \frac{\mu_{s1}}{E_{s1}} \tag{7}$$

where E_{s1} and E_{s2} are the elastic modulus of the spring elements, and μ_{s1} is the viscosity coefficient of dashpot in the parallel four-element system of stationary phase shown in Fig.2. Due to the tandem structure of the four-element system for reversible phase showed in Fig.2, the total stress of reversible phase, which is expressed as σ_{ij}^{r}, is composed of viscous stress σ_{ij}^{rv} and elastic stress σ_{ij}^{re}, expressed as

$$\sigma_{ij}^{r} = \sigma_{ij}^{rv} + \sigma_{ij}^{re} \tag{8}$$

The viscous stress and elastic stress of reversible phase in Eq. (8) are given as

$$\sigma_{ij}^{rv} = \mu_r[\frac{\nu\dot{\varepsilon}_{kk}\delta_{ij}}{(1+\nu)(1-2\nu)} + \frac{\dot{\varepsilon}_{ij}}{(1+\nu)}] - \lambda_r[(1+\nu)\dot{\sigma}_{ij}^{r} - \nu\dot{\sigma}_{kk}^{r}\delta_{ij}] \tag{9}$$

$$\sigma_{ij}^{re} = E_r[\frac{\nu\varepsilon_{kk}\delta_{ij}}{(1+\nu)(1-2\nu)} + \frac{\varepsilon_{ij}}{(1+\nu)}] \tag{10}$$

in which μ_r, E_r and λ_r are the viscosity coefficient, elastic modulus and delay time of reversible phase respectively. The material parameters of reversible phase in Eq. (9) and Eq. (10) are expressed by the parameters of the components showed in the schematic diagram of the rheological presentation for constitutive model, which is showed as

$$\mu_r = \frac{\mu_{r2}E_{r1}}{E_{r1} + E_{r2}}, E_r = \frac{E_{r1}E_{r2}}{E_{r1} + E_{r2}}, \lambda_r = \frac{\mu_{r2}}{E_{r1} + E_{r2}} \tag{11}$$

where E_{r1} and E_{r2} are the elastic modulus of the spring elements and μ_{r2} is its viscosity coefficient of the four-element system for reversible phase.

The SMP will undergo plastic deformation process, when the equivalent stress σ_{eq} is greater than or equal to the yield stress σ_y, so the plasticity of SMP in thermo-mechanical cycles is considered at this paper. The constitutive relation of SMP in plastic hardening process is deduced based on the Levy-Mises flow law [21] and the Prandtl-Reuss flow law [21] in the theory of solid mechanics. Levy-Mises flow law can describe the plasticity of SMP better, whereas the Prandtl-Reuss flow law, which argues that elastic deformation follows the generalized Hooke's law, considers both the elastic deformation process and the plastic deformation process. Therefore, the combination of the two flow law can accurately describe the viscoelastic-plastic mechanical properties of SMP during the thermo-mechanical process, the relationship between stress and strain of the Prandtl-Reuss flow law is expressed as

$$d\varepsilon_{ij}^{ep} = \frac{1-2\nu}{E}d\sigma_m\delta_{ij} + \frac{1}{2G}dS_{ij} + d\gamma S_{ij} \tag{12}$$

Levy-Mises flow law takes the isotropic plastic-

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hardening process into account, where $d\gamma$ is defined as

$$d\gamma = \frac{3d\varepsilon_{eq}^{P}}{2\sigma_{eq}} \tag{13}$$

in which ε_{eq}^{p} is the equivalent plastic strain, and the relationship between stress and strain at this time is in exponential form, which is given as

$$\sigma_{eq} = P(\varepsilon_{eq}^{P})^{\alpha} \tag{14}$$

The expression for the increment of equivalent plastic strain is obtained by differentiating Eq. (14) and showed as

$$d\sigma_{eq} = \alpha P(\varepsilon_{eq}^{P})^{\alpha-1} d\varepsilon_{eq}^{P} \tag{15}$$

where P and α are plastic parameters. Formula (16) is obtained by simultaneous Eqs. (10) and (12), which is expressed as

$$d\gamma = \frac{3d\sigma_{eq}}{2\alpha P(\varepsilon_{eq}^{P})^{\alpha-1}\sigma_{eq}} \tag{16}$$

Substituting formula (16) into the Prandtl-Reuss flow law (12) to get the constitutive equation of elastoplastic material, the elastoplastic strain rate is expressed as,

$$\dot{\varepsilon}_{ij}^{ep} = \frac{1-2\nu}{E}\dot{\sigma}_m\delta_{ij} + \frac{1}{2G}\dot{S}_{ij} + \frac{3\dot{\sigma}_{eq}}{2\alpha P(\varepsilon_{eq}^{p})^{\alpha-1}\sigma_{eq}}S_{ij} \tag{17}$$

where,

$$\sigma_m = \frac{1}{3}\sigma_{kk}, \quad G = \frac{E}{2(1+\nu)} \tag{18}$$

Substituting the material parameters of the stationary phase showed in Eq. (7) into Eq. (17), the elastoplastic strain rate of the stationary phase is obtained as

$$\dot{\varepsilon}_{ij}^{sep} = \frac{1-2\nu}{E_s}\dot{\sigma}_m^s\delta_{ij} + \frac{1}{2G_s}\dot{S}_{ij}^s + \frac{3\dot{\sigma}_{eq}^s}{2\alpha P_s(\varepsilon_{eq}^{p})^{\alpha-1}\sigma_{eq}^s}S_{ij}^s \tag{19}$$

Introducing the parametric Eq. (11) into Eq. (17) to obtain the elastoplastic strain rate of the reversible phase, which is showed as

$$\dot{\varepsilon}_{ij}^{rep} = \frac{1-2\nu}{E_r}\dot{\sigma}_m^r\delta_{ij} + \frac{1}{2G_r}\dot{S}_{ij}^r + \frac{3\dot{\sigma}_{eq}^r}{2\alpha B_r(\varepsilon_{eq}^{rp})^{\alpha-1}\sigma_{eq}^r}S_{ij}^r \tag{20}$$

Based on the viscoelastic theory and the rheological presentation for constitutive model showed in Fig.2, deriving the relationship of the stress and strain for the stationary and reversible phases of SMP by referencing Eq.(5)as well as Eq.(6) , and the viscous strain rates are obtained as

$$\dot{\varepsilon}_{ij}^{sv} = \frac{1}{\mu_s}[(1+\nu)\sigma_{ij}^s - \nu\sigma_{kk}^s\delta_{ij}] - \frac{E_s}{\mu_s}[\frac{\nu\varepsilon_{kk}\delta_{ij}}{(1+\nu)(1-2\nu)} + \frac{\varepsilon_{ij}}{(1+\nu)}] \tag{21}$$

$$\dot{\varepsilon}_{ij}^{rv} = \frac{1}{\mu_r}[(1+\nu)\sigma_{ij}^r - \nu\sigma_{kk}^r\delta_{ij}] - \frac{E_r}{\mu_r}[\frac{\nu\varepsilon_{ij}\delta_{ij}}{(1+\nu)(1-2\nu)} + \frac{\varepsilon_{ij}}{(1+\nu)}] \tag{22}$$

The total strain rate of SMP is made up of the viscous strain rate and the elastoplastic strain rate, which is expressed as

$$\dot{\varepsilon}_{ij} = \dot{\varepsilon}_{ij}^{s} = \dot{\varepsilon}_{ij}^{sv} + \dot{\varepsilon}_{ij}^{sep} \tag{23-a}$$

$$\dot{\varepsilon}_{ij} = \dot{\varepsilon}_{ij}^{r} = \dot{\varepsilon}_{ij}^{rv} + \dot{\varepsilon}_{ij}^{rep} \tag{23-b}$$

All in all, based on the variation of mechanical properties of SMP, the schematic diagram of microstructure for SMP, which has explained the phenomenon of shape memory effect and given a clear explanation of phase transition, is showed in Fig.1. Then the relationship between stationary phase and reversible phase in shape memory process is obtained refer to the crystallization theory and showed in Fig.2, which give a basis to derive the constitutive equations of SMP. Finally, the constitutive equations, which describe the viscosity, elasticity and plasticity of SMP, are established according to the viscoelastic theory and plastic theory. The constitutive equations established in this paper can effectively describe the thermodynamic behaviors of SMP and provide a theoretical basis for the practical applications of SMP. The change law of material parameters plays an important role in producing shape memory effect, so it is of necessity to establish clear functions for material parameters which change with the changing of temperature.

2.3 Material Parameters Functions

The transitions of reversible phase, which is between the frozen state and the activated state during the process of changing temperature, affect the material parameters and thus result in the shape memory effect. Based on the crystallization theory of the semicrystalline polymer, a concept of frozen ratio, which changes with temperature and is related to the temperature change rate, is proposed to describe the transitions of reversible phase. So the relationship between the frozen ratio, the temperature and the temperature change rate is given as

$$1-\phi = \exp\left[-F(T)/\beta^{n}\right] \tag{24}$$

where ϕ is the frozen ratio, β is the temperature change rate, $F(T)$ is the cooling function. The relationship between the cooling function $F(T)$ and the crystallization rate constant $K(T)$ is different between the cooling process

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and the heating process, and the relationship between $F(T)$ and $K(T)$ during cooling process is expressed as

$$F(T)=\left[-\frac{1}{n}\int_{T_0}^{T}K(T)dT\right]^n \tag{25-a}$$

The relationship between $F(T)$ and $K(T)$ during heating process is expressed as

$$F(T)=\left[\frac{1}{n}\int_{T_0}^{T}K(T)dT\right]^n \tag{25-b}$$

in which $\ln F(T)$ has the empirical relationship with temperature, showed as

$$\ln F(T)=aT+b \tag{26}$$

$$T=T_0+i\Delta T \tag{27}$$

Substituting Eq. (26) into Eq. (25) gives the expression for the crystallization rate constant expressed as

$$K(T)=-a\exp[(aT+b)/n] \tag{28-a}$$

$$K(T)=a\exp[(aT+b)/n] \tag{28-b}$$

The material parameters of the reversible phase, which include elastic modulus, viscosity coefficient, plastic hardening modulus and delay time, change with the frozen ratio during the process of producing shape memory effect. Therefore, the material parameters during the process of transforming state of reversible phase are expressed as

$$E'_r(T)=\sum_{i=1}^{t}E_r(\phi(i)-\phi(i-1)) \tag{29-a}$$

$$\mu'_r(T)=\sum_{i=1}^{t}\mu_r(\phi(i)-\phi(i-1)) \tag{29-b}$$

$$P'_r(T)=\sum_{i=1}^{t}P_r(\phi(i)-\phi(i-1)) \tag{29-c}$$

$$\lambda'_r(T)=\sum_{i=1}^{t}\lambda_r(\phi(i)-\phi(i-1)) \tag{29-d}$$

where the time taken for the SMP to raise or lower the temperature from the initial temperature to the current temperature is expressed by t, and the relationship between t and temperature is

$$t=\frac{T-T_0}{\beta} \tag{30}$$

The total stress of SMP is the sum of reversible phase stress and stationary phase stress, the stress of reversible phase change gradually during the shape memory process, which is the same as the changing of the linear structure showed in Fig.1. So the relationship between the total stress, the reversible phase stress and the stationary phase stress is

$$\sigma_{ij}=\sigma_{ij}^{s}+\sum_{i=1}^{t}\sigma_{ij}^{r}(\phi(i)-\phi(i-1)) \tag{31}$$

Substituting Eq. (2) and Eq. (3) into Eq. (31) yields the relationship of material parameters between stationary phase and reversible phase as

$$E=E_s+E'_r \tag{32-a}$$

$$\mu=\mu_s+\mu'_r \tag{32-b}$$

$$P=P_s+P'_r \tag{32-c}$$

$$\lambda=\lambda_s+\lambda'_r \tag{32-d}$$

in which the material parameters of E, μ, P, λ are functions of temperature T.

The frozen ratio is defined to describe the variation of material parameters with temperature, which can not only reveal the change rule of material parameters, but also explain the relationship between stationary phase and reversible phase. The new model reflects the mechanical properties of stationary phase and reversible phase of SMP, especially demonstrate the plastic properties of the SMP in a new form during the large deformation process. The description of plastic properties has been improved in this paper, exponential relations are used to describe the relationship between stress and strain during plastic deformation process. The proposed three-dimensional mechanical constitutive equations can accurately describe the mechanical properties of shape memory polymers, and it can be used to develop UMAT function to do numerical simulations for SMP.

3. NUMERICAL SIMULATION EXAMPLES.

3.1 Validation study

In order to investigate the correctness of the developed constitutive model, we conduct numerical simulations and compare the results with the test data of Tobushi [8]. The coefficients used in the numerical simulations are deduced to fit the developed constitutive equations from the coefficients in the experiment of Tobushi [8], which are showed in table.1.

Table 1 Material parameters of SMP

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μ_{r2} (GPs)	E_{r1}(MPa)	E_{r2}(MPa)	P_r(MPa)	λ_r (s)	α	a	n
1004	1600	2000	1280	279	0.28	-0.3	3
μ_s(GPs)	E_{s2}(MPa)	E_{s1}(MPa)	Ps(MPa)	λ_s (s)	ν	b	
1.27	27.7	45.6	720	27.8	0.25	93.8	

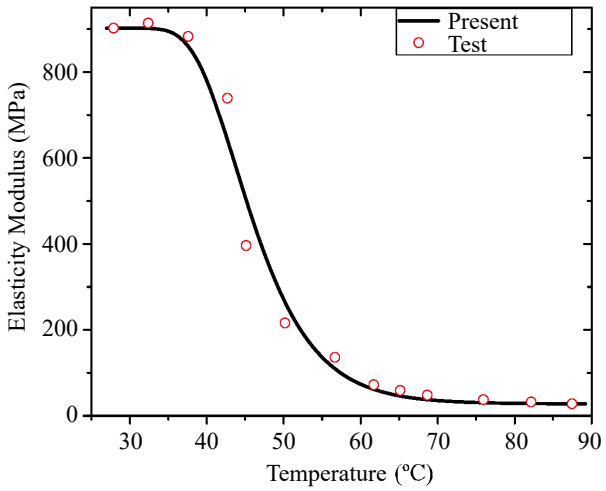


Fig. 3 The elastic modulus-temperature curves obtained by Tobushi's experiment and the calculation of the new model

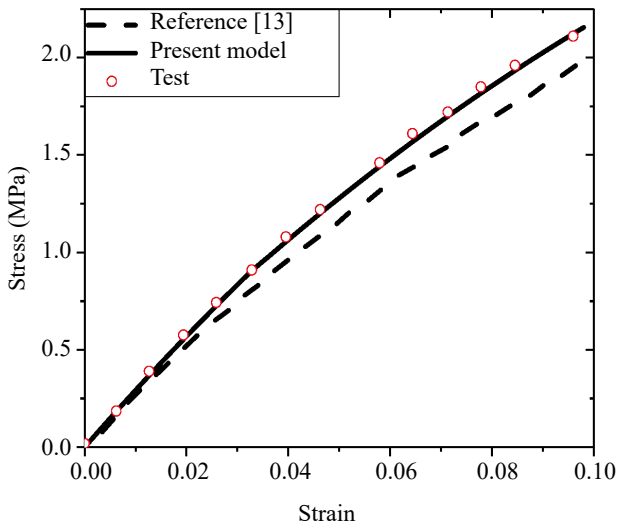


Fig. 4 The stress-strain curves during loading process

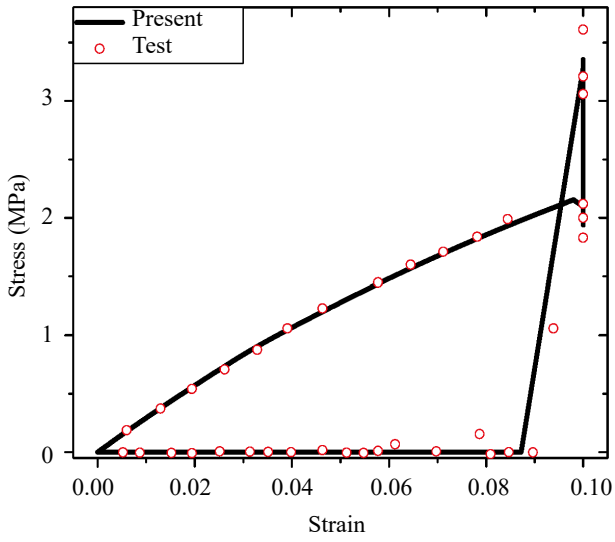


Fig. 5 The stress-strain curves obtained by Tobushi's experiment and the calculation of new model

Fig. 3 exhibits the curves between elastic modulus and temperature, which are obtained by Tobushi's experiment and the calculation of the new model respectively. As shown in Fig. 3, the red circles represent the test data of Tobushi [8] whereas the black solid line stand for the calculation results of the new model. The calculation results of the elastic modulus are in accord with those experimental data of Tobushi [8], which illustrate the fact that the developed material parameter functions can describe the effect of temperature on elastic modulus preferably. The elastic modulus increases nonlinearly with the decreasing of temperature and become unchanged at a high temperature, which due to the change of state of reversible phase as showed in Fig. 1. In term of crystallization theory, the value of the elastic modulus, which is in the state that molecular chains of polymers are ordered, will be bigger than that is in the state with messy molecular chains of polymers. Hence, the value of elastic modulus with lower temperature is bigger than that with higher temperature. The reversible phase of SMP with a low temperature is in the frozen state and the morphology of molecular chains is ordered, while it is in the activated state and the morphology of molecular chains is messy with a high temperature.

Fig. 4 exhibits the curves between stress and strain during loading process, and the black dotted line represents the calculation results of the model in a separate paper [13], the black solid line represents the calculation results of the model developed in this paper, and the red circles represent the experimental results of Tobushi [8]. It can be seen from the figure that the black solid line is nearly straight when the value of strain is greater than 1

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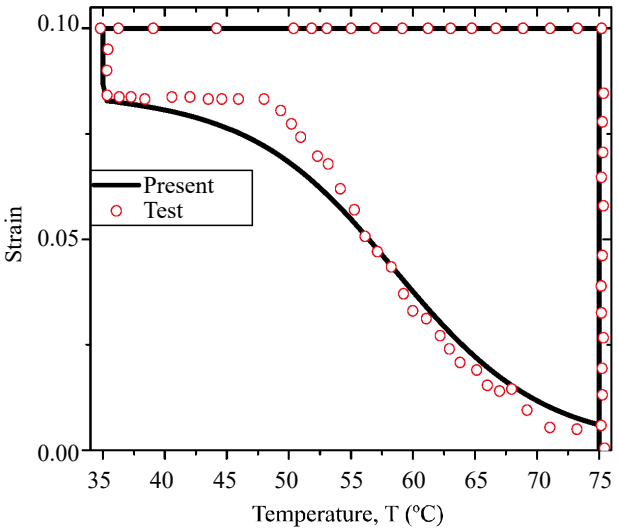


Fig. 6 The strain-temperature curves obtained by Tobushi's experiment and the calculation of the new model

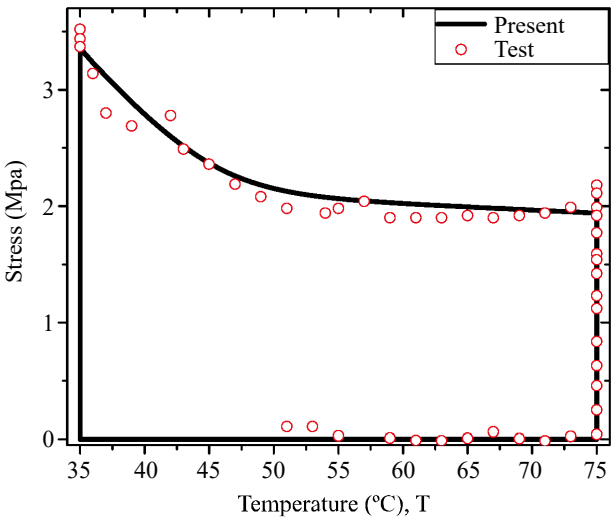


Fig. 7 The stress-temperature curves obtained by Tobushi's experimentation andthe calculation of the new model

while the black solid line is bent when the value of strain is smaller than or equal to 1, which makes it happened that the calculation results of the new model is in accord with the test data. The coherence with the test data for the new model should owe to that the plastic deformation has been considered and expressed accurately by the exponential function. Therefore the proposed exponential formula between stress and strain for plastic deformation can be adapted to illustrate the mechanical properties of SMP.

Fig. 5 shows the curves between stress and strain obtained by Tobushi's experimental data and the calculation results of new model for the shape memory process. The comparison between the experimental results curve of Tobushi [8] and those calculated results curve of the proposed constitutive model indicates that the calculation results have a preferable propensity to the experimental results. Although there is a tiny difference during unloading process, which can be explained by the precision of controlling temperature as different temperature corresponds to different values of material parameters. The curves have verified the accuracy and practical applicability of the proposed constitutive model which has the ability to describe the relation of stress and strain accurately during the shape memory process.

Fig. 6 shows the curves between strain and temperature obtained by Tobushi's experimental data and the calculation results of the new model, and the red circles represent the experimental data [8] while the black solid line represents the calculation results of the new model. It can be seen from Fig. 6 that the calculated results of the developed constitutive model have good propensity to Tobushi's experimental results, which have presented the same strain value at the maximum of the temperature as the experimental data. That means the new model is able to provide reference for controlling temperature to reach the expected shape of SMP in the practical application.

Fig. 7 shows the curves between stress and temperature obtained by Tobushi's experimental data and the calculation results of the new model. It can be seen from
Fig. 7 that the curve of the calculation results for the new model is in accord with the experimental data of Tobushi[8], especially in the stress-frozen process during which the stress decrease with the increasing of temperature. This owes to the frozen ratio proposed by considering the micro mechanism of SMP to help describe the changing rule of material parameters based on the crystallization theory. The curves reflect a fact that the proposed constitutive equations can give a great performance on predicting the mechanical behavior of SMP and it is indicated that the frozen ratio proposed in this paper can be used to predict the values of material parameters in practical applications.

Based on the comparisons above, it is obvious that the proposed model have a good performance in predicting the process of conducting the shape memory effect, so that the proposed three dimensional equations as well as the parameter functions can be used to design programs for calling by finite element method software. And the model is also able to act as a reference to direct the practice applications for different kinds of thermal-stimuli responsive SMP or do further investigations to research more properties of SMP.

3.1 Rate correlation of SMP

The results, which is from the numerical simulation using the three-dimensional constitutive model established in this paper for the shape memory process of SMP, are compared with the numerical results of the three-dimensional constitutive model established in a separate paper [13]. For the sake of investigating the property of rate-dependence for SMP, we use the developed three-dimensional constitutive model to analyze the effect of different strain rate on stress in loading at high temperature process, the effect of different cooling rate on stress in stress freezing process and the influence of different heating rate on strain in the shape recovery process. The material parameters used in this numerical simulation are shown in table 2, which are based on the material parameters in the literature [13] and obtained by calculating and necessary assumption.

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Table 2 Material parameters of SMP

μ_r (GPs)	E_{r1}(MPa)	E_{r2}(MPa)	P_r(MPa)	λr (s)	a	b	n
116	2000	2400	1170	58.94	-0.18	98.8	3
μ_s(GPs)	E_{s1}(MPa)	E_{s2}(MPa)	α	λs (s)	P_s(MPa)	ν	
2.03	100	400	0.3	4.06	700	0.25	

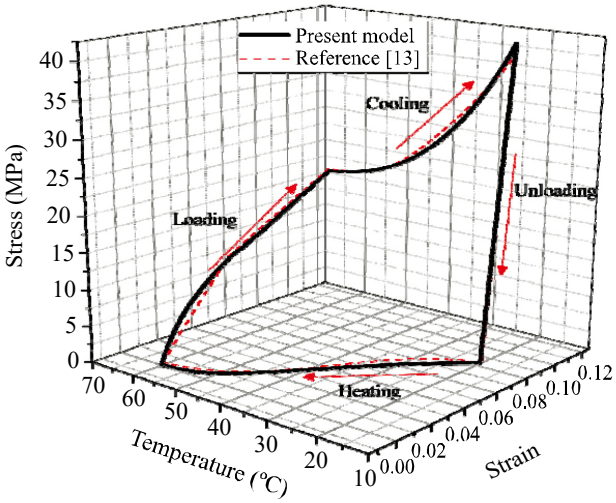


Fig. 8 Three dimensional SMP relational curves of stress, strain and temperature

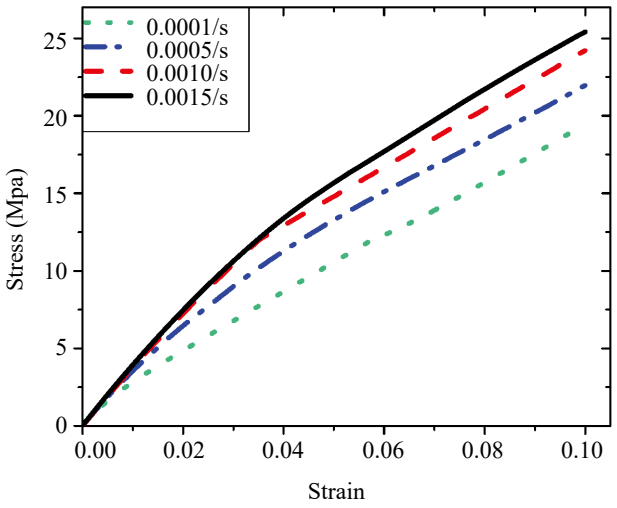


Fig. 9 Stress-strain curves of SMP at different loading rates

The relationship between stress, strain and temperature is revealed and showed by three-dimensional curves in Fig. 8, which is resulted from the simulation for the case in uniaxial stress state utilizing the model belong to Zhou[13] and the model developed by ourselves respectively . As showed in Fig. 8, the simulated results of the two models are relatively close while the solid line represents the simulation results using the developed constitutive model, and the dotted line represents the calculation results using Zhou's constitutive model. The simulated results of the model proposed in this paper is smoother during the process of loading at high temperature, which due to that the non-linear relationship between stress and strain in the plastic deformation stage of SMP has been considered.

The process of producing shape memory effect of the SMP is described in detail as follows. Firstly, the SMP is loaded at the strain loading rate of 0.0005/s at the temperature of 60 ℃, which results in the phenomenon that the stress increases nonlinearly with the increasing of strain. When the strain reaches 0.1, holding the strain constant, at the same time, cooling the SMP from 60 ℃ to 20 ℃, so that the stress increases with the decreasing of temperature and the relationship between stress and temperature are nonlinear. Then the temperature is kept at 20℃, and the SMP is unloaded so that the stress deceases to 0 while the deformation of the SMP recovers a bit, and most of the deformation is held during this process. Finally, the SMP is heated from 20℃ to 60℃ to revert to the original shape, as the elastic modulus, plastic-hardening modulus, viscosity coefficient and retardation time decrease with the increasing of temperature. Fig.8 has given the integrated relation curves of stress, strain and temperature, which is able to act as an integral reference for predicting the shape memory effect in practical applications.

The established three-dimensional constitutive model is used to numerically simulate the SMP in loading at high temperature process with different loading rates. Fig.9 shows the stress-strain relationship at a temperature of 60 °C with strain rate of 0.0001 / s, 0.0005 / s, 0.001/s, and 0.0015 /s respectively. It can be seen from Fig. 9 that the stress increases with the increasing of strain at high temperature, and the relationship between stress and strain are nonlinear, which due to the synergistic effect of mechanical properties such as viscoelasticity and plasticity. The required stress for the SMP to reach the

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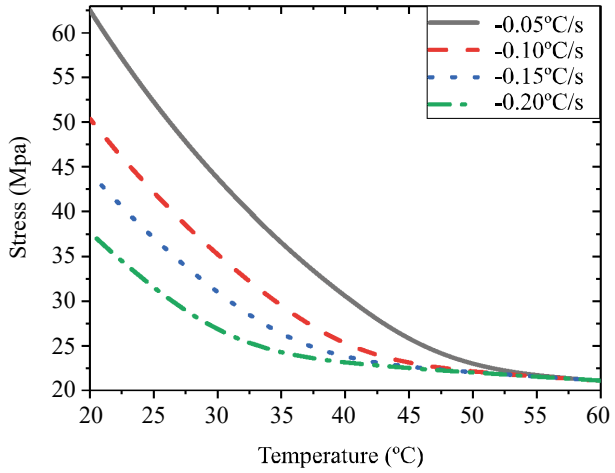


Fig. 10 Stress-temperature curves of the SMP at different cooling rates

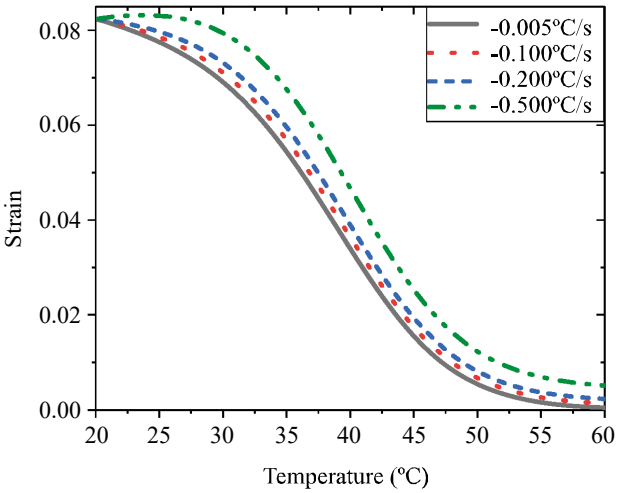


Fig. 11 Strain-temperature curves of SMP at different heating rates

same strain value increases with the increasing of strain rate, which reflects the rate dependence of strain during the loading at high temperature process of SMP. The rule about the rate dependence of strain showed in Fig.9 can be used to direct the practical operation of controlling the strain conditions to reach the required deformation of SMP.

The results of numerical simulation for the stress freezing process during which the SMP is cooled from 60 °C to 20 °C under the cooling rates of -0.05 °C / s, -0.1 °C / s, -0.15 °C / s and -0.2 °C / s respectively by using the proposed three-dimensional constitutive model are showed in Fig.10. As shown in Fig.10, the stress increases nonlinearly with the decreasing of temperature and when the SMP is cooled to the same temperature, the stress decreases with the increasing of the cooling rate, which shows a significant rate dependence property. The rule about the rate dependence of temperature showed in Fig.9 can be used to direct the practical operation of controlling the temperature to reach the required deformation or stress conditions of SMP.

Fig.11 shows the curves of strain and temperature at different heating rates during the shape recovery process. As shown in Fig .11, when the temperature is raised to the same value, the larger the heating rate, the greater the final strain value, and the less complete the shape recovery is and the strain decreases with the increasing of temperature nonlinearly. This phenomenon due to that the elastic modulus, plastic modulus and viscosity coefficient decrease with the increasing of temperature. The numerical simulation results indicate that the established three-dimensional constitutive model can effectively describe the thermodynamic process and shape memory effect of SMP under complex stress conditions. According to the correlation of the rate verified in this paper, we can adjust the loading rate, the cooling rate and the heating rate to adapt the actual situation in engineering application, and obtain different shape memory processes.

4. CONCLUSIONS

In this paper, a three-dimensional constitutive model of SMP is proposed, including the schematic diagram of the microstructure, the schematic diagram of the rheological presentation for constitutive model, the constitutive equations and parameter functions. The schematic diagram of the microstructure can not only demonstrate the macroscopic shape change of the SMP during the shape memory process, but also explain the micro mechanism of SMP. In order to explain the viscoelastic-plastic properties of SMP we use the method of rheological presentation for constitutive model and add a flow element to it to describe the plastic properties of SMP. According to solid mechanics theory as well as viscoelastic theory, and on analogy with the crystallization process of polymer, we deduced the three-dimensional constitutive equations and material parameter functions. In particularly, a concept of frozen ratio has been proposed to establish the parameter functions and explain the relationship of the two phases, the reversible phase as well as the stationary phase. The three-dimensional constitutive model established in this paper is used to numerically simulate the SMP whose results are compared with the experimental results of Tobushi and the reference [13] to verify the accuracy of the model. Then the numerical simulation, which include the conditions of different loading rates, cooling rates and heating rates, verify the rate dependence between stress, strain and temperature of SMP. All the material parameters in this model can be determined by macroscopical experiment, since the parametric equations developed in this paper are simple and accurate. The three-dimensional constitutive model developed in this paper can describe the mechanical properties and be used in designing programs to simulate the SMP in complex stress states.

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REFERENCES

1. Zhou. T and Tan. H, "Review on constitutive modeling methods of thermally actuated shape memory polymers," *Polymer Materials Science and Engineering* 28(5), pp.165-169. (2012).
2. Chen. S, Hu. J and Zhuo. H, "Properties and mechanism of two-way shape memory polyurethane composites," *Composites Science & Technology* 70 (10), pp. 1437-1443(2010).
3. Guo. X, Liu. L, Liu. Y, Zhou. B and Leng. J, "Constitutive model for a stress-and thermal-induced phase transition in a shape memory polymer," *Smart Material & Structures*, 23 (10), 105019(2014).
4. Zhou. B, Liu. Y and Leng. J, "Finite element analysis on thermo-mechanical behavior of styrene-based shape memory polymers,"*Acta Polymerica Sinica, 6*, pp.525-529(2009).
5. Alberto Belmonte1, Xavier Fernández-Francos and Silvia De la Flor, "Thermomechanical characterization of thiol-epoxy shape memory thermosets formechanical actuators design,"*American institute of physics*, pp.030012-1–030012-12,(2018).
6. Leng. J, Lan. X, Liu. Y and Du. S, "Shape memory polymer composites and their applications in space deployable structures," *Journal of Astronautics*, 31(4), pp.950-956(2010).
7. Tobushi. H, Hashimoto. T, Hayashi. S and Yamada. E, "Thermomechanical constitutive modeling in shape memory polymer of polyurethane series," *Intelligent Material System &structures,* 8 (8), pp.711-718(1997).
8. Tobushi. H, Okumura. K, Hayashi. S and Ito. N, "Thermomechanical constitutive model of shape memory polymer," *Mechanics of Materials, 33* (10), pp.545-554(2001).
9. Liu. Y, Gall. K, Dunn. M, Greenberg. A and Diani. J, "Thermomechanics of shape memory polymers: uniaxial experiments and constitutive modeling," *Plasticity,* 22 (2), pp. 279-313(2006).
10. Huang. K and Huang. Y, "Constitutive relationships of solid," Beijing: Tsinghua University Press, pp.1–35(1999).
11. Ward. I and Hadley. D, *An Introduction to the Mechanical Properties of Solid Polymers*, John Wiley & Sons, LTD, New York. (1993).
12. Chen Y and Lagoudas D, "A constitutive theory for shape memory polymers: part I large deformation," *Journal of the Mechanics &Physics of Solids, 56*, pp.1752—1765 (2008).
13. Zhou. B, Liu. Y and Leng. J, "A macro-mechanical constitutive model for shape memory polymer" *science china,* 53 (12), pp.2266-2273(2010).
14. Baghani M, Naghdabadi R, Arghavani J and Sohrabpour S, "A thermodynamically-consistent 3D constitutive model for shape memory polymers" *International Journal of Plasticity,* 35, pp.13–30(2012)
15. Guo. X, Liu. L, Zhou. B, Liu. Y and Leng. J, "Influence of strain rates on the mechanical behaviors of shape memory polymer," *Smart Materials and Structures*, pp.1-8(2015)
16. Guo. J, Liu. J, Wang. Z, He. X, Hu. L, Tong. L and Tang. X, J. "A thermodynamics viscoelastic constitutive model for shape memory polymers," *Journal of Alloys and Compounds*, 705, pp.146-155(2017)
17. Guo. X, Zhou. B, Liu. L, Liu. Y and Leng. J, "A Stress-induced Phase Transition Model for Semi-crystallize Shape Memory Polymer," *SPIE Smart Structures and Materials,* 905817-905818(2014)
18. Khonakdar. H, Jafari. S, Rasouli. S, Morshedian. J and Abedini. H, "Investigation and modeling of temperature dependence recovery behavior of shape-memory crosslinked polyethylene, Macromol," *Theory Simulations,* 16 (1), pp.43-52. (2007)
19. Tsukada. G, Tokuda. M and Torii. M, "Temperature triggered shape memory effect of transpolyisoprene-based polymer", *Journal of Endodontics*, 40 (10) 1658-1662(2014)
20. Zhang. Y *Theory of thermo-viscoelasticity*. Tianjin: Tianjin University Press, pp.1–15(2002)
21. Basilevsky. M, Petrochenko. S, "Motion of polymer chains in a molecular crystal", *Chemical Physics*, 67 (3), pp.319-335(1982)
22. Ozawa. T "Kinetics of non-isothermal crystallization", *Polymer*, 12(3), pp.150-158(1971).

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