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Citation: Liu, Chang, Lu, Haibao, Li, Guoqiang, Hui, David and Fu, Yong Qing (2019) A 'cross-relaxation effects' model for dynamic exchange of water in amorphous polymer with thermochemical shape memory effect. *Journal of Physics D: Applied Physics*, 52 (34). p. 345305. ISSN 0022-3727

Published by: IOP Publishing

URL: <https://doi.org/10.1088/1361-6463/ab2860> <<https://doi.org/10.1088/1361-6463/ab2860>>

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A ‘cross-relaxation effect’ model for dynamic exchange of water in amorphous polymer with thermochemical shape memory effect

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Abstract: Dynamic exchange of water has been shown to effectively trigger thermally responsive shape memory effect (SME) in shape memory polymer (SMP) at room temperature. However, the working mechanism of cross-relaxation effects, which are generated simultaneously from two stimulus fields of water and temperature, has not been understood. In this study, a ‘cross-relaxation effect’ model was formulated for describing water-induced relaxation, thermomechanical behavior and strain recovery of amorphous SMPs. Based on Maxwell’s principle, the ‘cross-relaxation effect’ model was firstly proposed to quantitatively separate the effect of dynamic exchange of water on the thermochemical SME in SMP. Then the water-induced relaxation and strain recovery have been simulated and predicted using this model. Finally, experimental data were used to verify the proposed model, and the numerical results were found to fit well with the experimental ones. This ‘cross-relaxation effect’ model is expected to

provide an effective tool for precise design and control of water-induced SME and shape memory behaviors by means of the dynamic exchange of water.

Keywords: shape memory polymer, cross-relaxation effects, dynamic exchange

1. Introduction

Shape memory polymer (SMP) is a class of smart materials capable of fixing a temporary shape and then regaining the permanent shape triggered by external stimuli, such as temperature, magnetic field, light and moisture, *etc.* [1,2]. For amorphous SMPs, their shape memory effect (SME) is originated from glass transition and they show a temperature-activated shape recovery behavior [3,4]. In the last three decades, the SMPs have attracted great attention due to their potential applications and tailorable properties [5]. However, heating the SMPs to trigger the SME is regarded to be inconvenient for most of biomedical applications [6,7], whereas hygrothermal actuation has a great potential for these applications and thus has attracted significant interests recently [8].

In 2004, Huang et al. [4] experimentally demonstrated that the SME of commercial polyurethane SMP can be triggered when it is immersed into water instead of external heating, and the glass transition temperature (T_g) is found to decrease upon absorption of water. Fourier transformation infrared (FTIR) measurements showed that the hydrogen bonding between water and polyurethane SMP played a key role in determining the water-driven shape recovery behavior [9]. Furthermore, Chen et al. [10] synthesized a novel polyurethane SMP with an excellent water absorption capability and a fast shape recovery speed. Not limited to these polyurethane materials, some other types of SMPs also showed SMEs triggered by water or organic solvents [11-13]. For examples, Lu et al. found that the solvent-driven SME of a styrene-based SMP can be

achieved after being immersed into N,N-Dimethylformamide [11] or toluene [12], while Du et al. investigated effects of hydrogen bonding strength on the solvent-induced SME in poly(vinyl alcohol) SMP [13]. Meanwhile, many types of SMP composites with not only water-driven SMEs but also higher mechanical strength have also been reported, such as polyurethane SMP composite filled with carbon black [14], rigid cotton cellulose nanowhiskers (CNWs) [15] or the polyvinyl alcohol (PVA) SMP filled with graphene oxide (GO) [16].

Diffusion of small solvent molecules into polymers is generally ruled by Fick's second law [17,18]. Marquardt [19] and Ghobadi [20] have studied the diffusion of water, acetone, and ethanol into polyurethane SMP matrix, respectively. It is found that the T_g of polymers is decreased owing to the increased mobility of polymer chains which can be explained either by swelling effect [21-24] or by plasticizing effect [12,25] according to thermodynamics of the polymer solution.

In practical applications, it is critical to develop constitutive models capable of accurately predicting the water-induced shape recovery behaviors of SMPs [25-31]. Generally, the constitutive models are classified into two categories: one is thermo-viscoelastic model [26,27] while the other is phenomenological model [28,29]. Xiao et al. [30] proposed a thermo-viscoelastic model to describe the thermomechanical properties of the amorphous SMP. Luo et al. [31] proposed another thermo-viscoelastic model for polyimine-based covalent adaptable networks (CANs) based on the relaxation time superposition principle [32]. Meanwhile, a phenomenological model [25] has also been formulated to predict the water-induced shape recovery behaviors based on the free energy function. Although these studies provide effective approaches to describe the water-induced shape recovery behavior, they cannot be used to precisely design the new SMPs. While the phenomenological model only presents an effective

approach to simulate the experimental results. There is normally little information of physical and chemical interactions which can be obtained from the experimental results, thus resulting in these working mechanism being not explored. In this study, a ‘cross-relaxation effect’ model is formulated for the SMPs with water-induced SME. The proposed model was firstly used to characterize the thermo-viscoelastic relaxation behavior of amorphous SMPs, according to the Maxwell’s multi-branch model. Then the dynamic exchange of water was introduced into the model in order to investigate the cross-relaxation effects of water and temperature on the relaxation and strain recovery of SMPs. Finally, simulation results of the proposed model were compared with the experimental data of both a polyurethane SMP and a sodium dodecyl sulfate/epoxy composite SMP for further verifications. The working mechanism of the cross-relaxation effects of two stimulus fields of water and temperature on water-induced SME has been explored and discussed.

2. ‘Cross-relaxation effects’ model for the water-induced SME

For the diffusion of water molecules into polymer, it is assumed that: (1) the polymer is homogeneous and the diffusion coefficient D remains a constant during the diffusion process. (2) The concentration gradient varies only along a space coordinate direction and belongs to a one-dimensional diffusion case. (3) The diffusion process is governed by the Fick's second law [17,18].

According to the Fick's second law, the governing equation is:

$$\frac{\partial u(z,t)}{\partial t} = D \cdot \frac{\partial^2 u(z,t)}{\partial z^2} \quad (1)$$

where z is the space coordinate along the direction of diffusion, t is the immersion time, $u(z,t)$ represents the water concentration and D is the diffusion coefficient [33].

According to Marquardt's work [19], the diffusion coefficient D follows the equation:

$$D(T) = D_0 \cdot \exp\left(\frac{-Q_{Diff}}{RT}\right) \quad (2)$$

where $R=8.314 \text{ J}/(\text{mol}\cdot\text{K})$ is the gas constant, T is the absolute temperature; D_0 is a constant, and Q_{Diff} represents the activation energy of diffusion. For the dynamic exchange of water in the polyurethane SMP, it is determined that $\log D_0 = -1.86 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$ and $Q_{Diff} = 57.58 \text{ kJ} \cdot \text{mol}^{-1}$ [19].

Assuming that water content in the whole polymer is u_0 before immersion, the initial condition can be expressed as:

$$u(z, t)|_{t=0} = u_0 \quad (3)$$

Here, a rectangular SMP specimen with its thickness much thinner than the other two directions is considered. Assuming a symmetrical diffusion, the boundary condition for the middle plane is:

$$\frac{\partial u(z, t)}{\partial z} \Big|_{z=l/2} = 0 \quad (4)$$

where l is the thickness of the specimen. Another boundary condition of the specimen at the surface contacting the water is:

$$D \cdot \frac{\partial u(z, t)}{\partial z} \Big|_{z=0} = h \cdot [u(z, t)|_{z=0} - u_{out}] \quad (5)$$

where h is the convection coefficient and u_{out} represents the water concentration.

On the other hand, a multi-branch thermo-viscoelastic model is used to describe the viscoelastic behavior of SMPs [34,35]. As shown in Figure 1, the model consists of a thermal expansion element and a mechanical element, thus, the total strain ε is the sum of the thermal strain ε_T and the mechanical strain ε_M :

$$\varepsilon = \varepsilon_T + \varepsilon_M \quad (6)$$

[Figure 1]

In the model, the coefficient of thermal expansion can be considered to follow the bilinear equation [34,35], thus, thermal strain ε_T can be expressed as:

$$\varepsilon_T = \int \alpha_i^{Ther} dT, \quad (i = r, g) \quad (7)$$

where α_r^{Ther} and α_g^{Ther} represent the coefficients of thermal expansion of the SMP in the rubbery and glassy states, respectively.

The mechanical element is represented by an equilibrium branch and n numbers of nonequilibrium branches. The strain can then be written as:

$$\varepsilon_M = \varepsilon_{eq} = \varepsilon_M^i \quad (8)$$

where ε_{eq} represents the strain in the equilibrium branch and ε_M^i is the strain of the i th nonequilibrium branch which consists of one spring and one dashpot element,

$$\varepsilon_M^i = \varepsilon_i^d + \varepsilon_i^e \quad (9)$$

$$\sigma_M^i = \sigma_i^d = \sigma_i^e \quad (10)$$

where σ_i^d (σ_i^e) is the stress and ε_i^e (ε_i^d) is the strain. For the viscoelasticity model, the dashpot and spring follow Newton's flow law ($\sigma_i^d = \eta_i \cdot \dot{\varepsilon}_i^d$) and Hooke's law ($\sigma_i^e = E_i \cdot \varepsilon_i^e$), respectively, where η_i is the viscosity of the dashpot and E_i is the elastic modulus of spring in the i th nonequilibrium branch.

Based on the Boltzmann superposition principle [32], the total stress of the model σ is:

$$\sigma = E_{eq} \cdot \varepsilon_M(t) + \sum_{i=1}^n E_i \cdot \varepsilon_i^e \quad (11)$$

where the ε_i^e can be described using the following equation:

$$\varepsilon_i^e = \int_0^t \frac{d\varepsilon_M(s)}{dt} \exp\left(-\int_s^t \frac{dt'}{\tau_i(t')}\right) ds \quad (12)$$

where τ_i denotes the relaxation time in the i th nonequilibrium branch.

As is known, relaxation time plays an essential role to determine the thermo-viscoelastic properties of the SMP, and temperature and water play similar roles to influence the relaxation time of the SMPs [31]. Therefore, the cross-relaxation effects, which are generated simultaneously from two stimulus fields of water and temperature, have been considered. While the cross-relaxation effects of water and temperature on the relaxation time τ_i are obtained according to the Boltzmann superposition principle [32], i. e.:

$$\tau_i = \tau_i^{ref} \cdot \alpha_T(T) \cdot \alpha_w(u) \quad (13)$$

where α_T and α_w are the shift factors, depending on the temperature and water content, respectively. Whereas $\alpha_T(T)$ is the ‘cross-relaxation effects’ shifting factor, which can be written as:

$$\ln \alpha_T(T) = -\frac{C_1(T - T_M)}{C_2 + (T - T_M)}, \quad T \geq T_g \quad (14a)$$

$$\ln \alpha_T(T) = -\frac{AF_C}{k_b} \left(\frac{1}{T} - \frac{1}{T_g} \right), \quad T < T_g \quad (14b)$$

Equation (14a) is a Williams-Landel-Ferry (WLF) equation [36], where C_1 and C_2 are material constants and T_M is the reference temperature. Equation (14b) is an Arrhenius-Type equation [37], where A is the material constant, F_C is the configurational energy, k_b is Boltzmann’s constant and T_g is the glass transition temperature of the SMP.

The shift factor $\alpha_w(u)$ can be defined as [25]:

$$\alpha_w(u) = \exp\left(\frac{m(u) \cdot \Delta E(u)}{RT}\right) \quad (15)$$

where $\Delta E(u)$ is the stored mechanical energy and m is defined as the reciprocal of polymer volume in the diffusion process:

$$m(u) = \frac{1}{V(u)} \quad (16)$$

According to the Flory-Huggins solution theory, the chemical potential of the polymer can be described by,

$$\mu_1 = -\frac{\partial W(C)}{\partial C} \quad (17)$$

where $W(C)$ represents the free energy of the polymer solution [38].

However, it was reported that the volume change for the water-driven polyurethane SMPs is too small to be identified in the experiments [4]. Therefore, the free energy is considered to be mainly determined by the mixing free energy [39], e.g.:

$$W(C) = W_m(C) = \frac{k_b \cdot T}{v} \left[v \cdot C \cdot \log\left(1 + \frac{1}{vC}\right) - \frac{\chi}{1 + vC} \right] \quad (18)$$

where v is the volume of one water molecule and χ is the Flory-Huggins interaction parameter. Therefore, the chemical potential of the polyurethane SMPs can be obtained using equation (19):

$$\mu_1 = -\frac{\partial W_m}{\partial C} = -k_b \cdot T \left[\log\left(1 + \frac{1}{vC}\right) + \frac{\chi}{(1 + vC)^2} - \frac{1}{1 + vC} \right] \quad (19)$$

3 Simulation, validation and discussion

3.1 Simulation of thermomechanical properties

According to the one-dimensional multi-branch thermo-viscoelastic model [34,35],

the storage modulus E_s , loss modulus E_l and $\tan \delta$ can be expressed using:

$$E_s = E_{eq} + \sum_{i=1}^n \frac{E_i \cdot \omega^2 \cdot (\tau_i)^2}{1 + \omega^2 \cdot (\tau_i)^2} \quad (20)$$

$$E_l = \sum_{i=1}^n \frac{E_i \cdot \omega \cdot \tau_i}{1 + \omega^2 \cdot (\tau_i)^2} \quad (21)$$

$$\tan \delta = \frac{E_l}{E_s} \quad (22)$$

where ω is the loading frequency in the thermoviscoelastic model.

In the constitutive models, the parameters that need to be identified can be divided into four different types: e.g., (1) the parameters in the equations (14a) and (14b) for calculating the ‘cross-relaxation effects’ shifting factor; (2) the elastic modulus and the reference relaxation time in the Maxwell branches; (3) the coefficients of thermal expansion of polymer; and (4) the diffusion model parameters. According to Yu et al. [34,35], the first two types of parameters can be determined by fitting the material’s DMA experiment data. The fitting process was implemented by using the nonlinear regression method [40]. Figures 2(a) and 2(b) show the comparisons between the simulation results and experimental ones for a polyurethane SMP (MM 5520) [41] and a sodium dodecyl sulfate/epoxy composite SMP (20% SDS-ER) [42], respectively. The obtained slopes ($2.16 \times 10^{-4} K^{-1}$ and $1.18 \times 10^{-4} K^{-1}$) of the curves below and above T_g can be taken as the coefficients of thermal expansion in rubbery and glassy states, respectively [34,35,43]. Tables 1 and (in Appendix A.1) summarize all the used parameters in the constitutive model of equations (20), (21) and (22) for the above-mentioned two types of SMPs, respectively.

[Table 1]

[Figure 2]

Figure 3 plots the numerical results of the storage modulus, loss modulus and $\tan \delta$ as a function of temperature (T) with different water contents of $u=0.4 \text{ mol} / \text{m}^3$, $0.3 \text{ mol} / \text{m}^3$, $0.2 \text{ mol} / \text{m}^3$, $0.1 \text{ mol} / \text{m}^3$ and $0 \text{ mol} / \text{m}^3$, respectively. As shown in Figure 3(a), the water content has a significant influence on the T_g , which is increased from -56.4°C to 50.4°C when the water content is reduced from $0.4 \text{ mol} / \text{m}^3$ to $0 \text{ mol} / \text{m}^3$. The $\tan \delta$ curve, of which the pick value is defined as the T_g in this study, is also influenced by the water content as shown in Figure 3(b). Simulation results reveal that the T_g is increased from -52.3°C to 55.0°C with the water content is decreased from $0.4 \text{ mol} / \text{m}^3$ to $0 \text{ mol} / \text{m}^3$. These simulation results can be therefore employed to account for the water-induced shape recovery behavior of the polyurethane SMP. With more water absorbed by the SMP, the glass transition temperatures are gradually decreased, resulting in the SME triggered by the water at ambient temperature.

[Figure 3]

Furthermore, it is necessary to investigate the effect of diffusion time on thermodynamic properties of the SMP in order to identify the working mechanism of hydrogen bonding in the water-induced SME. Before simulating, some initial conditions are listed as follows: (1) the SMP sample is dry at the beginning, namely, $u_0=0 \text{ mol} / \text{m}^3$ in equation (3); (2) the diffusion coefficient is $D=6.45 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$ in equation (2); (3) the SMP sample is a rectangular strip with a dimension of 15.0 mm in length, 3.0 mm in width and 0.5 mm in thickness; (4) the water molecules are diffused along the thickness direction of the SMP. A schematic illustration of 1D diffusion model is shown in Figure 4, where M is the number of elements in SMP sample, $e_i (i=1 \dots M)$ represents the i th discrete element, e_M is the middle element and $u_i (i=1 \dots M)$ is the water content in the i th element.

[Figure 4]

Figure 5 presents the simulation results of the water concentrations as a function of immersion time and convection coefficient between polymer and water ($h=11\times 10^{-15} m\cdot s^{-1}$). It is found that the water content is decreased gradually from outside to inside before reaching an equilibrium value in the sample. As discussed in the previous study [31], the storage modulus and $\tan \delta$ start to change as the water molecules are being diffused into the center of the tested sample. Therefore, it is assumed that the water content in the middle plane of the sample determines the thermomechanical properties of the sample, thus the following simulations are all focused on water content in the middle plane of the sample.

[Figure 5]

Figure 6 plots the dependences of water content, chemical potential, storage modulus and $\tan \delta$ on immersion time at various given parameters h , where h is a convection coefficient between polymer surface and external water. As revealed from Figure 6(a), the water content in the SMP is gradually increased with an increase in the immersion time at a given parameter h . With an increase of h from $3\times 10^{-15} m\cdot s^{-1}$ to $11\times 10^{-15} m\cdot s^{-1}$, the water content is increased at a given immersion time. These simulation results reveal that the water content is increased owing to the increased convection coefficient between polymer and water. On the other hand, both the storage modulus and $\tan \delta$ are decreased with an increase in the immersion time, as shown in Figure 6(b) and 6(c), respectively. With the increase in the immersion time, water content is increased, thus resulting in the decreases of both storage modulus and $\tan \delta$. In comparison with the previous experimental DMA results [31], these numerical results reveal that the immersion time plays a similar role to the temperature in terms of determining the thermomechanical properties of the SMP.

[Figure 6]

3.2 Simulation of the strain recovery behavior

To further verify the constitutive model, the water-induced strain recovery behavior by means of water diffusion needs to be investigated. Based on Yang et al.'s study [41], the shape programming step of the polyurethane SMP was recorded as follows: (1) the polyurethane SMP sample was initially heated from room temperature 22°C (T_r) to the programming temperature of 65°C (T_d) with a heating rate of 10°C/min; (2) it was held for 5 minutes at 65°C; (3) then stretched to a targeted strain of 20% (e_{\max}) at a constant strain rate of 0.005/s; (4) held for another 5 minutes at 65°C and 20% in the constant strain; (5) cooled from 65°C to 22°C at a cooling rate of 10°C/min while holding the strain constant; (6) holding further for 5 minutes; (7) removing the external loading. Figure 7 shows the simulation results of strains in the programming step. In the last, the fixed strain is kept at 19.74% which is basically consistent with the results reported in the literature [41].

[Figure 7]

After the programming step, the sample was then placed in room temperature water (22°C) for the full recovery. Here, the time-dependent strain recovery ratio R_r can be defined as [44]:

$$R_r = 1 - e(t) / e_r \quad (23)$$

where $e(t)$ represents the time-dependent strain in the recovery process, and e_r ($e_r = 19.74\%$) is the fixed strain after the programming step.

Figure 8(a) presents the simulation results of the recovery ratio as a function of immersion time at various convection coefficients of $h = 3 \times 10^{-15} \text{ m} \cdot \text{s}^{-1}$, $5 \times 10^{-15} \text{ m} \cdot \text{s}^{-1}$, $7 \times 10^{-15} \text{ m} \cdot \text{s}^{-1}$, $9 \times 10^{-15} \text{ m} \cdot \text{s}^{-1}$ and $11 \times 10^{-15} \text{ m} \cdot \text{s}^{-1}$. With an increase in the immersion

time, more water molecules are absorbed in the polyurethane SMP, resulting in an increase in the strain recovery ratio. Meanwhile, it is found that the convection coefficient (h) of SMP sample plays a critical role in influencing the water-induced strain recovery ratio. With an increase in the convection coefficient from $3 \times 10^{-15} \text{ m} \cdot \text{s}^{-1}$ to $11 \times 10^{-15} \text{ m} \cdot \text{s}^{-1}$, the SMP sample completes the full recovery at a much shorter immersion time of 17.7 hours. Owing to the large convection coefficient, more water is absorbed by the SMP sample, the relaxation time is therefore reduced, whereas the strain recovery ratio reaches to 100%.

Furthermore, the experimental data in reference [41] are also plotted in Figure 8(b) for comparisons with the numerical results (where the convection coefficient of the SMP sample is $h = 8.6 \times 10^{-15} \text{ m} \cdot \text{s}^{-1}$). It is found that the simulation results are in good agreements with the experimental ones. With an increase in the immersion time, the strain recovery ratio of polyurethane SMP is gradually increased until reaching its maximum value of 20%. However, the recovery strain is not completed for the tested SMP sample in the experiment. The sample might be too soft to overcome the environmental pressure, thus resulting in an experimental error of the strain recovery ratio. The simulation results also confirm that the strain recovery ratio is strongly determined by the immersion time, and the constitutive model of equation (23) can well predict the experimental results.

[Figure 8]

For the sodium dodecyl sulfate/epoxy composite SMP mentioned in Section 3.1, according to Wang et al. published experimental results [42], it is nearly fully restored to its initial shape in water (due to the addition of the sodium dodecyl sulfate, a polyelectrolyte, the SMP has better water absorption). Figure 9 shows the simulation results of the SMP free recovery process in water with convection coefficient h

$=8.6 \times 10^{-15} \text{ m} \cdot \text{s}^{-1}$ (the parameters used in the model and the shape programming steps are shown in Appendix A.1 and A.2, respectively.). It can be seen that the proposed model can predict the whole process of free shape recovery very well, which further verifies the validity of the newly proposed model.

[Figure 9]

4. Conclusion

In this study, we proposed a ‘cross-relaxation effect’ model to investigate the water-induced SME, relaxation and strain recovery of amorphous SMP. The cross-relaxation effects of water and temperature on the relaxation time have been identified as the key driving force for the water-induced SME in SMPs. The proposed model has further been used to simulate the thermomechanical and shape recovery behaviors of the SMP, and the numerical results fit well with the experimental ones. Finally, the effects of immersion time, thickness and water content on the dynamic exchange of water were investigated in order to quantitatively identify their roles in influencing water-induced SME in SMPs. These are useful to precisely design and control water-induced shape memory behaviors using dynamic exchange of water.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (NSFC) under Grant No. 11672342 and 11725208.

Appendix

A.1. Parameter table for the sodium dodecyl sulfate/epoxy composite SMP [42]

[Table A1]

A.2. *The shape programming step simulation for the sodium dodecyl sulfate/epoxy composite SMP* [42]

Based on Wang et al.'s study [42], the shape programming step of the sodium dodecyl sulfate/epoxy composite SMP was recorded as follows: (1) the SMP sample (a rectangular strip with dimensions of 55.0 mm in length, 5.0 mm in width and 1.0 mm in thickness) was initially heated from room temperature 25°C (T_r) to the programming temperature of 115°C (T_d) at a heating rate of 10°C/min; (2) it was held for 5 minutes at 115°C; (3) then bent into a “U”-like shape around a mandrel at a constant strain rate of 10°/s, and the targeted strain is considered to be 100% (e_{\max}) here; (4) and then held for another 5 minutes at 115°C and 100% in the constant strain; (5) cooled from 115°C to 25°C at a cooling rate of 10°C/min while holding the strain constant; (6) holding for 5 minutes; (7) removing the external loading. The simulation results of strain in the programming step are shown in Figure A1. In the last, the fixed strain is kept at 98.14% which is basically consistent with the results reported in the literature [42].

[Figure A1]

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Tables caption

Table 1. Parameter values used in equations (20)-(22) for the polyurethane SMP [41]

Table A1. Parameter values used in equations (20)-(22) for the sodium dodecyl sulfate/epoxy composite SMP [42]

Figures caption

Figure 1. 1D multi-branch thermoviscoelastic model, where the total strain (ε) is incorporated of a thermal expansion element (ε_T) and a mechanical element (ε_M). E_{eq} represents the modulus in the equilibrium branch, E_n and τ_n are the modulus and relaxation time of the n th nonequilibrium branch.

Figure 2. Comparisons between the simulation results of equations (20)-(22) and experimental data of the storage modulus and $\tan \delta$ as a function of temperature. (a) For a polyurethane SMP [41]. (b) For the sodium dodecyl sulfate/epoxy composite SMP [42].

Figure 3. Numerical results of thermomechanical properties as a function of temperature for the polyurethane SMP with various water content u of $0.4 \text{ mol} / \text{m}^3$, $0.3 \text{ mol} / \text{m}^3$, $0.2 \text{ mol} / \text{m}^3$, $0.1 \text{ mol} / \text{m}^3$ and $0 \text{ mol} / \text{m}^3$. (a) For storage modulus (the solid line) and loss modulus (the dashed line). (b) For $\tan \delta$.

Figure 4. A schematic illustration of 1D diffusion model

Figure 5. Simulation results of the water concentration field as a function of immersion time and thickness.

Figure 6. Numerical results of the (a) water content, (b) storage modulus, (c) $\tan \delta$ as a function of immersion time at a given convection coefficient between polymer and

water, where $h=3\times 10^{-15} m\cdot s^{-1}$, $5\times 10^{-15} m\cdot s^{-1}$, $7\times 10^{-15} m\cdot s^{-1}$, $9\times 10^{-15} m\cdot s^{-1}$ or $11\times 10^{-15} m\cdot s^{-1}$.

Figure 7. Temperature and strain as a function of time in the whole programming steps for polyurethane SMP.

Figure 8. Free strain recovery of polyurethane SMP in water at room temperature. (a) Numerical results for the strain recovery ratio as a function of immersion time at various convection coefficients of $h=3\times 10^{-15} m\cdot s^{-1}$, $5\times 10^{-15} m\cdot s^{-1}$, $7\times 10^{-15} m\cdot s^{-1}$, $9\times 10^{-15} m\cdot s^{-1}$ and $11\times 10^{-15} m\cdot s^{-1}$. (b) Comparisons between the simulation results and the experimental data [41] of the recovery strain for the polyurethane SMP with a convection coefficient of $h=8.6\times 10^{-15} m\cdot s^{-1}$.

Figure 9. Comparisons between the simulation results of and the experimental data [42] of the recovery strain for the sodium dodecyl sulfate/epoxy composite SMP with a convection coefficient of $h=110\times 10^{-15} m\cdot s^{-1}$.

Figure A1. Temperature and strain as a function of time in the whole programming steps for the sodium dodecyl sulfate/epoxy composite SMP [42].

Table 1. Parameter values used in equations (20)-(22) for the polyurethane SMP [41]

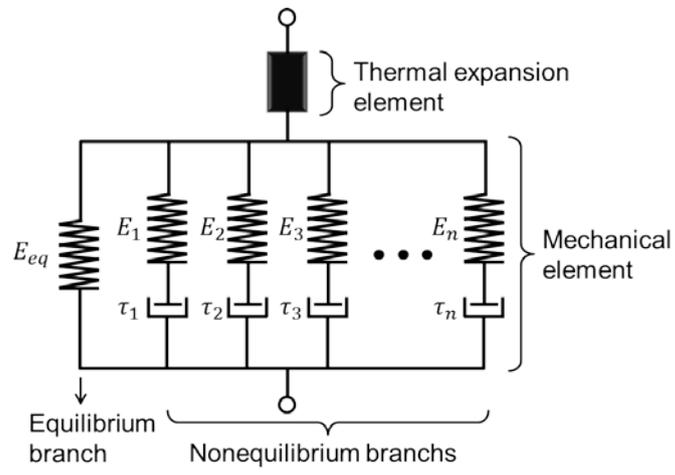
Parameters	Values	Parameters	Values
C_1	15	C_2	60 K
T_M	47 °C	$AF_c k_b^{-1}$	-24500 K
T_g	55 °C	T_s	42.14 °C
n	17	E_{eq}	5.0 MPa
$E_1 \square E_{17}$	(294.41, 280.63, 262.01, 242.44, 214.98, 204.53, 119.13, 109.72, 68.68, 44.27, 23.85, 10.35, 4.85, 1.99, 0.95, 0.76, 0.57) MPa		
$\tau_1^{ref} \square \tau_{17}^{ref}$	(4.1×10^{-2} , 9.0×10^{-2} , 4.5×10^{-1} , 6.3×10^{-1} , 1.0, 3.1, 5.6, 6.0, 1.9×10^1 , 3.5×10^1 , 1.3×10^2 , 5.9×10^2 , 4.2×10^3 , 2.3×10^4 , 5.6×10^4 , 2.5×10^5 , 5.0×10^5) s		
α_r^{Ther}	$2.16 \times 10^{-4} K^{-1}$	α_g^{Ther}	$1.18 \times 10^{-4} K^{-1}$
D	$6.45E-11 m^2 \cdot s^{-1}$	h^*	—
u_0	0 mol / m ³		
ω [41]	1 Hz	χ	0.45

Notes: symbol “*” represents the regulated parameter

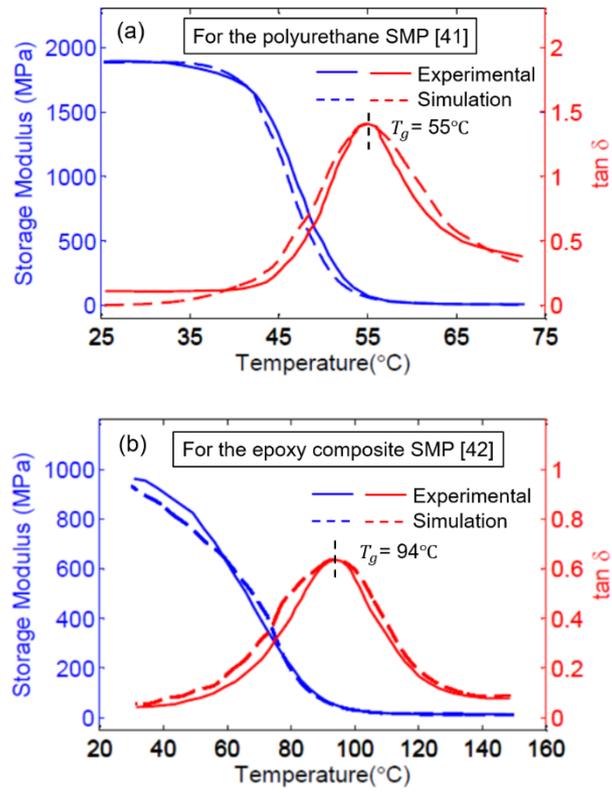
Table A1. Parameter values used in equations (20)-(22) for the sodium dodecyl sulfate/epoxy composite SMP [42]

Parameters	Values	Parameters	Values
C_1	11	C_2	86 K
T_M	84 °C	$AF_c k_b^{-1}$	-23000 K
T_g	94 °C	T_s	72.56 °C
n	22	E_{eq}	11.0 MPa
$E_1 \square E_{22}$	(20.10, 28.52, 50.79, 89.99, 107.23, 140.35, 174.10, 93.72, 70.28, 57.71, 50.55, 29.87, 16.44, 12.07, 11.17, 8.75, 5.33, 1.82, 1.15, 0.70, 0.59, 0.59) MPa		
$\tau_1^{ref} \square \tau_{22}^{ref}$	(9.3×10^{-7} , 1.1×10^{-6} , 3.0×10^{-6} , 2.7×10^{-5} , 2.3×10^{-4} , 2.1×10^{-3} , 1.3×10^{-2} , 6.1×10^{-2} , 1.2×10^{-1} , 3.6×10^{-1} , 1.0, 3.2, 7.0, 1.3×10^1 , 3.0×10^1 , 7.5×10^1 , 3.0×10^2 , 1.6×10^3 , 7.5×10^3 , 7.5×10^4 , 8.0×10^4 , 8.0×10^4) s		
α_r^{Ther}	$2.16 \times 10^{-4} K^{-1}$	α_g^{Ther}	$1.18 \times 10^{-4} K^{-1}$
D	$8.15E-7 m^2 \cdot s^{-1}$	h^*	—
u_0	0 mol / m ³		
ω [42]	1 Hz	χ	0.45

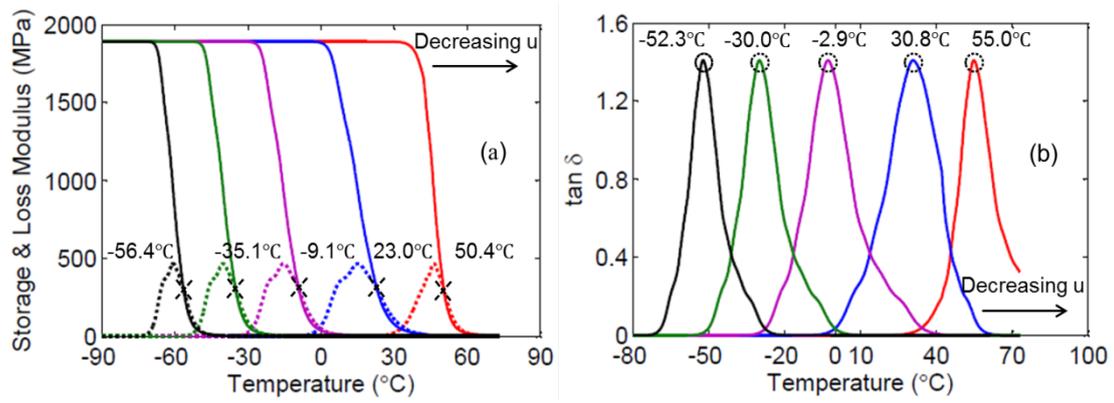
Notes: symbol “*” represents the regulated parameter



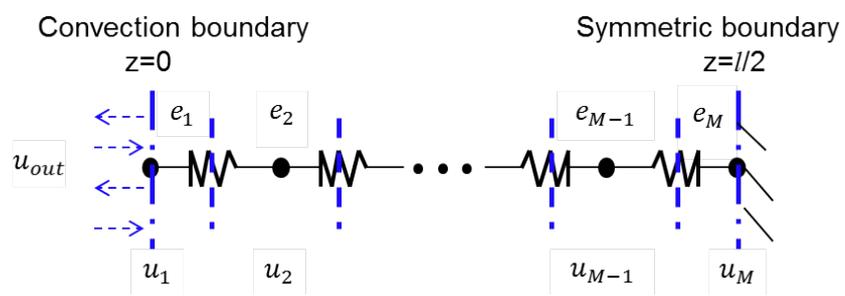
[Figure 1]



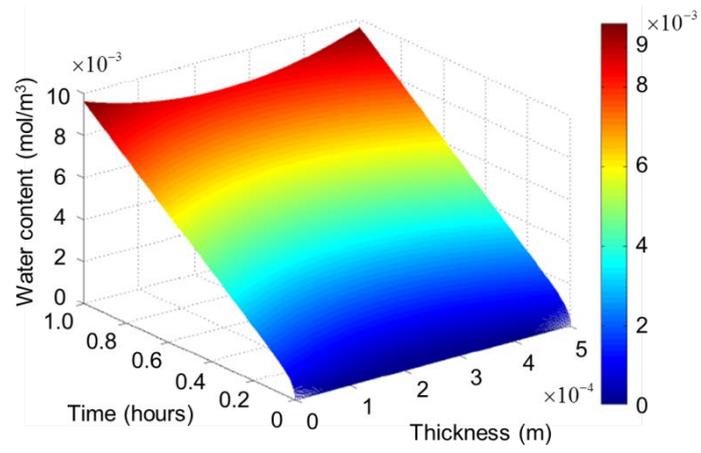
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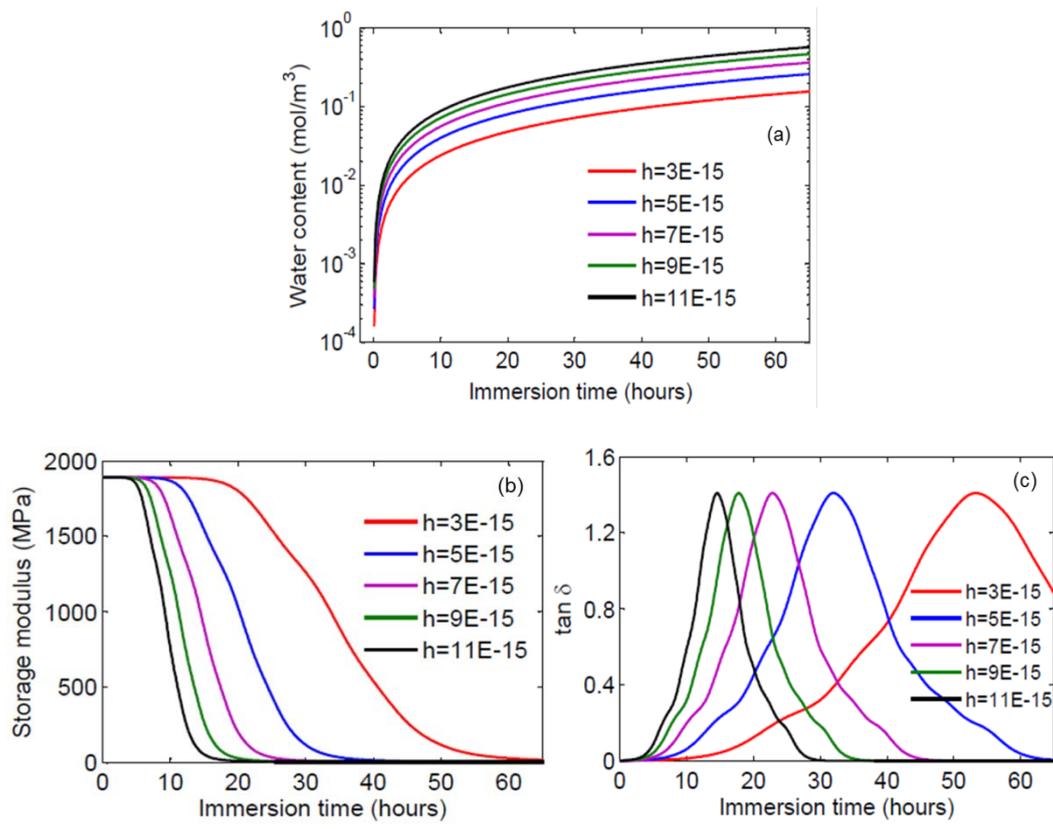
[Figure 3]



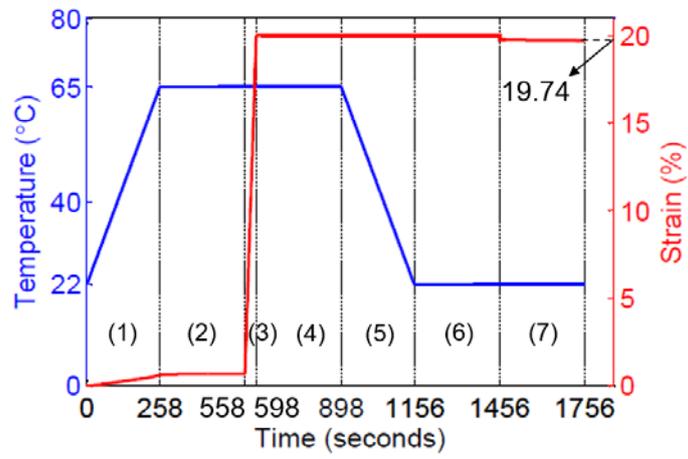
[Figure 4]



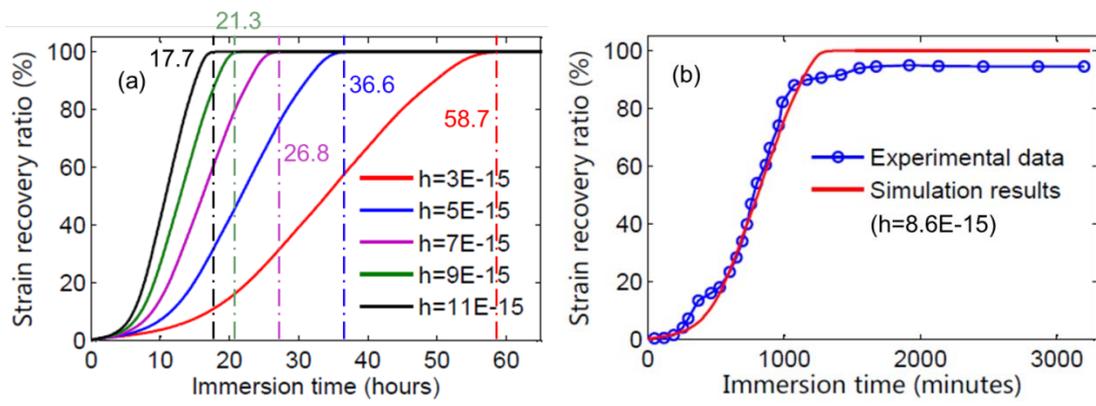
[Figure 5]



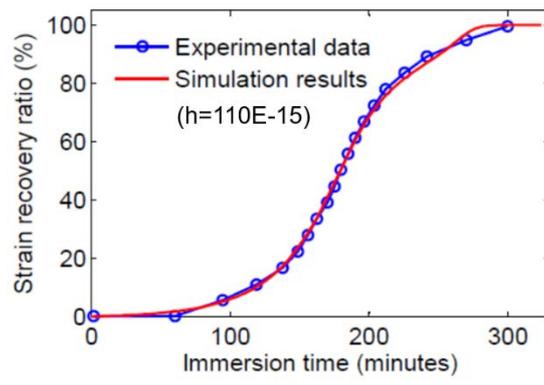
[Figure 6]



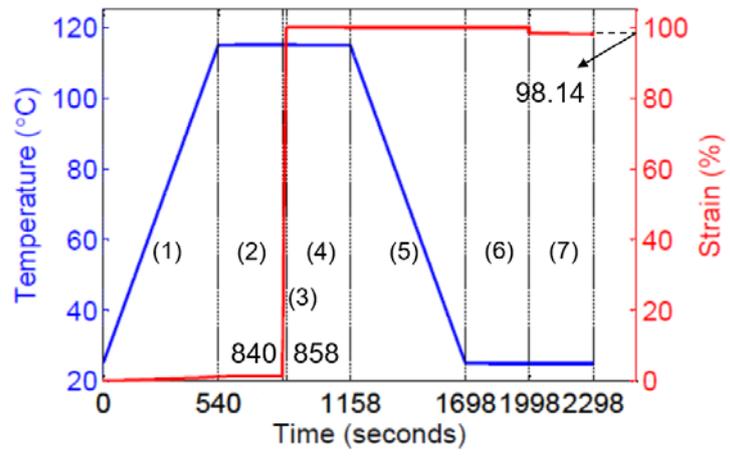
[Figure 7]



[Figure 8]



[Figure 9]



[Figure A1]