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A phenomenological approach for the chemo-responsive shape memory effect in amorphous polymers

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In this work, we present a phenomenological approach to study the state transition and working mechanism of the chemo-responsive shape memory effect (SME) in shape memory polymers (SMPs). The thermodynamics of polymer solution and free-energy theory are initially applied to quantitatively identify the factors that trigger a chemo-responsive SME. After this, a field theory is developed to couple the chemical potential, stress and relaxation time in a polymer system with free-energy functions. Furthermore, by means of combining together and utilizing the Gordon–Taylor (GT) theory and Free-Volume (FV) theory, the intrinsic plasticizing effect and generalized plasticizing effect are decoupled and quantitatively determined as the driving forces for the chemo-responsive SME in SMPs. In addition, the influence of the intrinsic plasticizing effect and generalized plasticizing effect on the glass transition temperature (T_g) is consequently numerically modeled using the GT and FV equations, respectively. Finally, the theoretical model is verified by the available experimental data reported in the literature and then compared with the simulation results of a semi-empirical model. This phenomenological approach is expected to provide a powerful simulation tool for extracting the transition temperature parameter, theoretical prediction and experimental substantiation of the response of chemo-responsive SME in amorphous SMPs.

1 Introduction

SMPs are fascinating materials, with promising potential in a range of applications as actively moving materials, which can change their shape in a predefined manner in the presence of the correct stimulus,[1,2] such as heat,[3,4] electricity,[5–7] light,[8] or water/solvent.[9–12] SMPs are characterised by their SME, in which the temporary shape can be held virtually forever unless shape recovery is triggered. Meanwhile, they are able to alter other properties, such as stiffness, natural frequency, damping, and other thermo-mechanical characteristics, in a pre-determined manner in response to the applied stimulus. In an SMP, there are always two or more segments (or domains). One is always elastic, while the others are able to significantly alter their stiffnesses, depending on whether or not the right stimulus is presented. This multi-component system is essential for enabling the SME in a polymer.[13] As one of the most popular actively moving materials, SMPs are attracting great research interest at present and we have seen good progress in their development for engineering applications, due to their light weight, capability for a high magnitude of elastic strain, ease of manufacturing and tuning for tailored properties to precisely meet the need(s) of a particular application.[14] Furthermore, their excellent chemical stability, biocompatibility, and even biodegradability make SMPs the right candidate for many biomedical applications.[15] Both the fundamental properties and potential engineering applications of SMPs have therefore been investigated extensively. Meanwhile, some of them have been implemented in some real engineering applications.

As pointed out by Prof. J. C. Tiller and Prof. W. M. Huang *et al.*,[16,17] essentially all SMPs fall into four categories according to the nature of its corresponding stimulus: namely, thermo-responsive SMPs, photo-responsive SMPs, chemo-responsive SMPs and mechano-responsive SMPs.[18,19] Although a cooling-responsive SME has been achieved recently,[20] it should be pointed out that, almost by default, thermal response is traditionally meant only for shape recovery induced by heating, including indirect heating by means of resistive joule heating, light heating (from ultraviolet to infrared), ultrasonic/acoustic heating, *etc.* In order to achieve a photo-responsive SME (*i.e.*, without any apparent temperature fluctuation), polymers should have a special chemical structure that reacts to light by means of altering the molecular structure.[7] In general, the chemo-responsive SME in a SMP is essentially the same as that of the thermo-responsive SME. However, instead of heating to above the transition temperature to trigger the thermo-responsive SME, in a more general sense the approach to trigger the chemo-responsive SME is through decreasing the interactive forces among macromolecules. This approach is expected to increase the flexibility of macromolecular chains, and hence inductively lowers the transition temperature of the polymer by

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means of softening, swelling or dissolving.[21] The key issue is to soften (reducing the transition temperature) or even remove (dissolving) the transition components. The mechanism behind this is the decrease in transition temperature and the energy storing capability in the polymer network.

A few polyurethane SMPs that respond to water/moisture have been initially studied and investigated.[9,12,16] Consequently, it has been found that a polystyrene-based SMP can also be induced by a *N*,*N*-dimethylformamide solvent or toluene solvent through a plasticizing effect.[10,11] Recently, an exciting work has explored the fact that a crystallized natural rubber SMP responds within seconds to the presence of solvents.[16] Meanwhile, studies on the theoretical framework for the chemo-responsive SME have been conducted, *i.e.* based on the theory of polymer solution, free-cavity volume theory, Flory–Huggins (FH) theory and relaxation theory.[21] Originating from polymer physics, the chemical plasticizing effect and physical swelling effect have been identified to quantitatively separate the effect of water/solvent on the chemo-responsive SME in SMPs.[10,11] However, a good first step towards quantitatively understanding the chemo-responsive SME in SMPs is the prediction of (phase) transition temperature lines in the state diagram.[22] We therefore present an effective theoretical approach to studying the state transition and working mechanism of the chemo-responsive SME in SMPs in this study. Initially, the thermodynamics of polymer solutions and free-energy theory were employed to quantitatively identify the factors that trigger the chemo-responsive SME. A field theory was then developed to couple chemical potential, stress, and relaxation time of the polymer system with free-energy functions. Furthermore, by the combination of GT theory and FV theory, the intrinsic plasticizing effect and generalized plasticizing effect were separated and quantitatively identified as the driving force for the chemo-responsive SME in SMPs. Meanwhile, the influence of an intrinsic plasticizing effect and a generalized plasticizing effect on T_g in an SMP were numerically modeled. Finally, the theoretical model has been validated against available experimental data, and then by comparing it with a semi-empirical model. An effective theoretical approach is expected to provide a powerful tool for extracting the transition temperature parameter, theoretical prediction and experimental substantiation of the response of chemo-responsive SME in amorphous SMPs.

2 Theoretical basis and analysis

In 2004, water-driven polyurethane SMPs had been demonstrated and had opened an era of studying the chemo-responsive SME in SMPs. Another essential point made for polyurethane SMPs driven by water or moisture is that the absorbed water is quantitatively separated into two parts, namely, the bound water and the free water. It should be pointed out that research on the water-driven polyurethane SMP has made tremendous progress in the history of the chemo-responsive SMPs. Consequently, an essential point for chemo-responsive SMPs is provided in a constructive review: "indirect actuation of the shape-memory effect has been realized to low transition temperature by diffusion of low molecular weight molecules into the polymer, which works as a plasticizer".[23] Based on the theory of polymer solution, the T_g of polymers decreases when the solvent molecules are mixed with the macromolecules. Solvent molecules absorbed into the polymer networks in order to make it softer and more flexible at ambient temperatures are known as plasticizers. As detailed, the solvent molecule has a plasticizing effect on the polymer network first, followed by chemical or physical interactions, resulting in a decrease in the transition temperature. However, the plasticizing effect plays a more important role than the chemo-physical interaction in influencing transition temperature. Therefore free-energy function, relaxation theory, GT theory and FV theory, which are fundamental to the plasticizing effect, are employed to identify the factors that have influenced the chemo-responsive SME in SMPs.

3 Modeling and experimental verification

3.1 Free-energy function

As is known, when a polymer is subject to a solvent, there are four contributions to the free-energy density of the blending system: the free-energy of stretching W_s, free-energy of mixing W_m, free-energy of polarization W_p, and free-energy of mobile ions transport W_i,[24]

$$W = W_s + W_m + W_p + W_i \tag{1}$$

The free-energy of mixing is taken to be (Flory, 1942; Huggins, 1941),[25]

$$\begin{cases} W_s = \dfrac{3}{2}NkT\left(\lambda^2 - 1 - 2\log\lambda\right) \\ W_m(C) = -\dfrac{kT}{\nu}\left[\nu C\log\left(1+\dfrac{1}{\nu C}\right) + \dfrac{\chi}{1+\nu C}\right] \end{cases} \tag{2}$$

where N is the number of chains in the polymer, λ is the stretching ratio. C is the nominal concentration of the solvent molecules in the polymer network, and ν is the volume per solvent molecule. k ($k = 1.38 \times 10^{-23}$) is the Boltzmann constant. χ is the FH interaction parameter. And T is the absolute temperature.

For the free-energy of polarization, it is assumed that the polymer has a dielectric energy with a constant permittivity ε.[24]

$$W_p = \frac{1}{2}\varepsilon(C)E^2 \tag{3}$$

The permittivity ε_p of the polymer in general is a function with respect to the solvent concentration, as $\varepsilon_p(C)$, the true electric field is E. A simple estimate would be the volumetric average among the solvent and the polymer:

$$\varepsilon(C) = \frac{\varepsilon_p + \nu C\varepsilon_s}{1+\nu C} \tag{4}$$

where ε_s is the permittivity of the solvent.

Combining eqn (3) and (4), the free-energy of polarization is

$$W_p = \frac{1}{2}\frac{\varepsilon_p + \nu C\varepsilon_s}{1+\nu C}E^2 \tag{5}$$

Previous studies have experimentally demonstrated the chemo-responsive SME in the styrene-based SMP by dimethylformamide (DMF).[11] This is a kind of extension of the water-induced

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polyurethane SMPs. It has also been experimentally demonstrated that there is no volume change or ions transported in the process of the polyurethane SMP being mixed with water or the styrene-based SMP with DMF solvent, resulting in the free-energy of stretching (W_s) and free-energy of mobile ions transport (W_i) being 0. Therefore, combining eqn (1), (2) and (5), we get,

$$\begin{aligned} W &= W_m + W_p \\ &= -\frac{kT}{v}\left[vC\log\left(1+\frac{1}{vC}\right)+\frac{\chi}{1+vC}\right]+\frac{1}{2}\frac{\varepsilon_p+vC\varepsilon_s}{1+vC}E^2 \end{aligned} \quad (6)$$

We denote this free-swelling stretch by λ, which relates to the chemical potential μ as discussed in previous work.[24] Considering a cubic solvent-swollen polymer to be stretched in three directions without constraint, and setting the stretches of the polymer to a fixed value, namely $\lambda_1 = \lambda_2 = \lambda_3 = \lambda$, thus the $1 + vC$ can be calculated by inputting λ into eqn (6), namely $1 + vC = \lambda^3$. Eqn (6) can be rewritten as

$$W = -\frac{kT}{v}\left[\left(\lambda^3-1\right)\log\left(\frac{\lambda^3}{\lambda^3-1}\right)+\frac{\chi}{\lambda^3}\right]+\frac{1}{2}\frac{\varepsilon_p+\left(\lambda^3-1\right)\varepsilon_s}{\lambda^3}E^2 \quad (7)$$

It should be noted that the differential change in chemical potential of the polymer is equal to the negative value of that of the solvent. For example, in the case of "a", the molar numbers of polymer and solvent are x_p^a and x_s^a in the polymer system (where $x_p^a + x_s^a = 1$), respectively. In the case of "b", the molar numbers of polymer and solvent are $x_p{}^b$ and $x_s{}^b$ in the polymer system (where $x_p^b + x_s^b = 1$), respectively. From case "a" to "b", the change in the mole of solvent in polymer system is $x_s^b - x_s^a = \Delta C$. While the change in the mole of the polymer is $x_p^b - x_p^a = (1 - x_s^b) - (1 - x_s^a) = -(x_s^b - x_s^a) = -\Delta C$. So the change in chemical potential of the polymer μ_p can be expressed as,

$$\begin{aligned} \mu_p &= \frac{\partial W}{\partial(-C)} = -\left(\frac{\partial W_m}{\partial C}+\frac{\partial W_p}{\partial C}\right) \\ &= -kT\left[\log\frac{\lambda^3-1}{\lambda^3}+\frac{1}{\lambda^3}+\frac{\chi}{\lambda^6}\right]-\frac{1}{2}\frac{vE^2}{\lambda^6}\left(\varepsilon_s-\varepsilon_p\right) \end{aligned} \quad (8)$$

A representative value of the volume per solvent molecule is $v = 10^{-28}$ m^3.[24] At room temperature, $kT = 4 \times 10^{-21}$ J, and $kT/v = 4 \times 10^7$ Pa, $(\varepsilon_s - \varepsilon_p)$ is approximately taken as 80 (for example the permittivity of water is 78 F m^{-1} and that of polyurethane SMP is 1.8 F m^{-1} at room temperature) and χ is the FH interaction parameter. In the numerical examples below, the parameter χ is a dimensionless parameter used to measure the change in enthalpy upon mixing, with representative value χ ranging from 0 to 0.8. The chemical potential as a function of χ and E is respectively shown in Fig. 1(a) and (b).

For such a plot, χ ranges from 0 to 0.8, and E ranges from 800 to 1200 V m^{-1}. Note that increasing χ or E is equivalent to making it more difficult to mix the polymer with the solvent, resulting in a significant change in the chemical potential of the polymer.

On the other hand, the stress in a polymer system can be expressed by:

$$S = \frac{\partial W}{\partial \lambda_i} \ (i = 1, 2, 3) \quad (9)$$

Combining eqn (7) and (9), and taking $\lambda_1 = \lambda_2 = \lambda_3 = \lambda$ into the equation, the stress of the polymer system can be rewritten as,

$$S = \frac{\partial W}{\partial \lambda} = -\frac{kT}{v}\left[3\lambda^2\log\left(\frac{\lambda^3}{\lambda^3-1}\right)-\frac{3}{\lambda}-\frac{3\chi}{\lambda^4}\right]+\frac{3}{2}\frac{\left(\varepsilon_s-\varepsilon_p\right)}{\lambda^4}E^2 \quad (10)$$

Fig. 2(a) and (b) characterize the relationship between the stress function S and the stretching ratio λ. For a given parameter of $\chi = 0$, the S function increases sharply till it reaches a constant maximum value, then the external stress is applied to make the polymer stretch to a proper size. While further stretching the polymer, the S function gets smaller as the given stretch ratio is reached. On the other hand, with a respective increase in the interaction parameter χ or the electric field parameter E, the maximum value of the S function is shifted to a higher value, due to the difficulty in mixing the polymer with the solvent. The stress S applied on the polymer system is increased, indirectly resulting from the increase in Gibbs free-energy, as shown in eqn (7).

3.2 Qualitative separation of the effect of plasticizing effect on T_g

Against this background, the polymer physics on glass transition could be employed to verify terms made in eqn (6).[25] As presented in polymer physics, the T_g of a polymer can always be influenced by four major factors: the copolymerization interaction, the cross-linking interaction, the molecular weight, and the plasticizing effect. Here, the two factors of the copolymerization interaction and the plasticizing effect are considered to account for the water-/moisture-driven chemo-responsive SME in polyurethane SMPs. On one hand, the copolymerization interaction can be introduced for the effect of bound water on the polyurethane SMP, as there are hydrogen bonds between polymer and solvent molecules. Looking back to the theory of glass transition, it is known that GT theory is always used to quantitatively separate the effect of the copolymerization interaction on the T_g of a polymer.[26]

$$T_g^{(p)} = \frac{T_{gp} + \left(\mathrm{K}T_{gs} - T_{gp}\right)W_s}{1 + (\mathrm{K} - 1)W_s} \quad (11)$$

where T_{gp} and T_{gs} are the glass transition temperature of polymer and solvent, respectively; K is a constant; W_s is the mass fraction of the solvent in a blended system, and T_g is the glass transition temperature of the blended system. Eqn (11) can be rewritten in terms of the molar weight as,[26]

$$T_g^{(p)} = \frac{T_{gp} + \left(\mathrm{K}T_{gs} - T_{gp}\right)n_s M_s}{1 + (\mathrm{K} - 1)n_s M_s} \quad (12)$$

where n_s and M_s are the molar weight and molecular weight of the solvent, respectively. Then, eqn (12) is normalized as,

$$T_g^{(p)} = \frac{T_{gp} + \left(\mathrm{K}T_{gs} - T_{gp}\right)\phi_s M_s}{1 + (\mathrm{K} - 1)\phi_s M_s} \quad (13)$$

where ϕ_s is the molar weight fraction of the solvent. The relationship between dT_g and dϕ_s can be expressed as,

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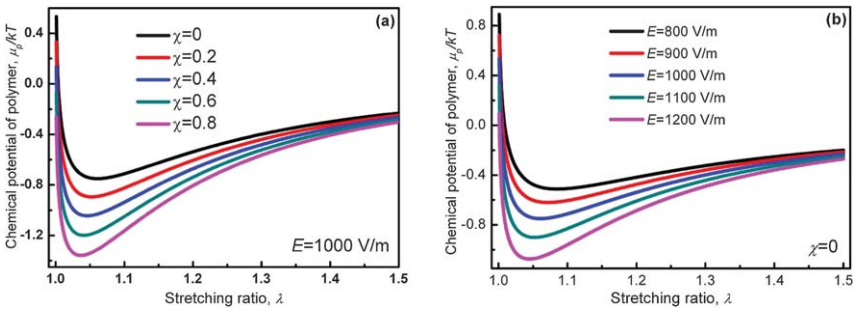

Fig. 1 (a) Dependence of chemical potential in polymer as a function of χ, and (b) dependence of chemical potential in polymer as a function of E.

$$\mathrm{d}T_{\mathrm{g}}^{(\mathrm{p})} = \frac{(T_{\mathrm{gs}} - T_{\mathrm{gp}})\phi_{\mathrm{s}} M_{\mathrm{s}}}{[1 + (\mathrm{K} - 1)\phi_{\mathrm{s}} M_{\mathrm{s}}]^2}\,\mathrm{d}\phi_{\mathrm{s}} \tag{14}$$

On the other hand, here the FV theory is employed to quantitatively separate the effect of the plasticizing effect on the T_{g} of the polymer.

$$T_{\mathrm{g}}^{(\mathrm{m})} = \frac{a_{\mathrm{fp}}(1 - \phi_{\mathrm{s}})T_{\mathrm{e}} + a_{\mathrm{fs}}\phi_{\mathrm{s}}T_{\mathrm{gs}}}{a_{\mathrm{e}}(1 - \phi_{\mathrm{s}}) + a_{\mathrm{fs}}\phi_{\mathrm{s}}} \tag{15}$$

where a_{fp} and a_{fs} are the thermal expansion coefficients of the polymer and solvent, respectively. Therefore, the relationship between $\mathrm{d}T_{\mathrm{g}}^{(\mathrm{m})}$ and $\mathrm{d}\phi_{\mathrm{s}}$ can be expressed as follows

$$\mathrm{d}T_{\mathrm{g}}^{(\mathrm{m})} = \frac{a_{\mathrm{fp}}a_{\mathrm{fs}}(T_{\mathrm{gs}} - T_{\mathrm{gp}})}{[a_{\mathrm{fp}}(1 - \phi_{\mathrm{s}}) + a_{\mathrm{fs}}\phi_{\mathrm{s}}]^2}\,\mathrm{d}\phi_{\mathrm{s}} \tag{16}$$

Combining eqn (14) and (16), the effect of the copolymerization interaction and the plasticizing effect on the polymer can be expressed as

$$\mathrm{d}T_{\mathrm{g}}^{(\mathrm{p})} + \mathrm{d}T_{\mathrm{g}}^{(\mathrm{m})} = \left\{\frac{(T_{\mathrm{gs}} - T_{\mathrm{gp}})\phi_{\mathrm{s}} M_{\mathrm{s}}}{[1 + (\mathrm{K} - 1)\phi_{\mathrm{s}} M_{\mathrm{s}}]^2} + \frac{a_{\mathrm{fp}}a_{\mathrm{fs}}(T_{\mathrm{gs}} - T_{\mathrm{gp}})}{[a_{\mathrm{fp}}(1 - \phi_{\mathrm{s}}) + a_{\mathrm{fs}}\phi_{\mathrm{s}}]^2}\right\}\mathrm{d}\phi_{\mathrm{s}} \tag{17}$$

The change in T_{g} of the polymer in the polymer/solvent system can therefore be expressed as

$$\Delta T_{\mathrm{g}} = \frac{(T_{\mathrm{gs}} - T_{\mathrm{gp}})\mathrm{K}\phi_{\mathrm{s}} M_{\mathrm{s}}}{[1 + (\mathrm{K} - 1)\phi_{\mathrm{s}} M_{\mathrm{s}}]} + \frac{(T_{\mathrm{gs}} - T_{\mathrm{gp}})\phi_{\mathrm{s}} a_{\mathrm{fs}}}{[a_{\mathrm{fp}}(1 - \phi_{\mathrm{s}}) + a_{\mathrm{fs}}\phi_{\mathrm{s}}]} \tag{18}$$

Based on eqn (18), we can quantitatively separate the effect of the copolymerization interaction and the plasticizing effect on the T_{g} in SMPs. Generally, K is kept as a constant of 0.28 in the GT equation.[26] In the numerical examples below, the parameter ϕ_{s} ranges from 0 to 1. The decrease in the T_{g} of the polymer as a function of $(T_{\mathrm{gs}} - T_{\mathrm{gp}})$ and $a_{\mathrm{fs}}/a_{\mathrm{fp}}$ is presented in Fig. 3(a) and (b), respectively. Fig. 3(a) plots the relationship between the T_{gp} and the molar weight fraction of the solvent ϕ_{s}. For given values of $(T_{\mathrm{gs}} - T_{\mathrm{gp}})$, such as $T_{\mathrm{gs}} - T_{\mathrm{gp}} = 30$, $T_{\mathrm{gs}} - T_{\mathrm{gp}} = 40$, $T_{\mathrm{gs}} - T_{\mathrm{gp}} = 50$, $T_{\mathrm{gs}} - T_{\mathrm{gp}} = 60$ and $T_{\mathrm{gs}} - T_{\mathrm{gp}} = 70$, T_{gp} gradually decreases as the molar weight fraction of the solvent ϕ_{s} increases. This numerical pattern reveals that T_{gp} does indeed gradually decrease during the process of mixing the polymer with the solvent. Fig. 3(b) plots the relationship between the T_{gp} function and the molar weight fraction of the solvent ϕ_{s}. For given values of $a_{\mathrm{fs}}/a_{\mathrm{fp}}$, such as $a_{\mathrm{fs}}/a_{\mathrm{fp}} = 1$, $a_{\mathrm{fs}}/a_{\mathrm{fp}} = 1/2$, $a_{\mathrm{fs}}/a_{\mathrm{fp}} = 1/3$, $a_{\mathrm{fs}}/a_{\mathrm{fp}} = 1/4$ and $a_{\mathrm{fs}}/a_{\mathrm{fp}} = 1/5$, the T_{gp} function gradually decreases as the molar weight fraction of the solvent ϕ_{s} increases. This trend reveals that as the molar weight fraction of the solvent ϕ_{s} becomes larger, T_{gp} decreases more rapidly as $(T_{\mathrm{gs}} - T_{\mathrm{gp}})$ (from copolymerization interaction part) increases, or as $a_{\mathrm{fs}}/a_{\mathrm{fp}}$ (from plasticizing effect part) decreases.

3.3 Prediction of chemo-responsive recovery of SMP by Arrhenius equation

Since T_{g} for the SMP can be reduced by the plasticizing interaction with the solvent, we can utilize this to design functionally controllable chemo-responsive SMPs. The basic idea is to lower the T_{g} in the SMP by immersing it into interactive solvents

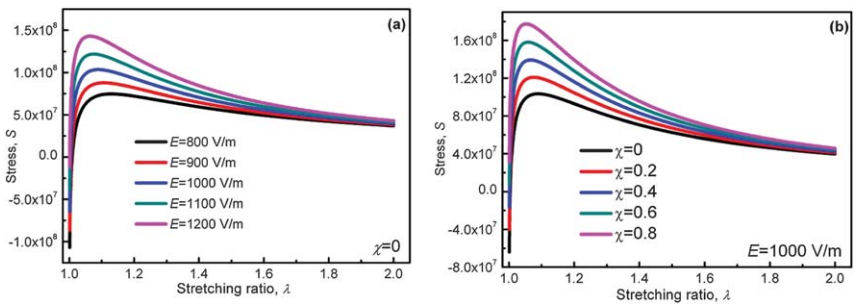

Fig. 2 Numerical results for the free swelling of SMP immersed in a solvent. (a) Relation of S as a function of λ for a given parameter $\chi = 0$. (b) Relation of S as a function of λ for a given parameter $E = 1000$ V m^{-1}.

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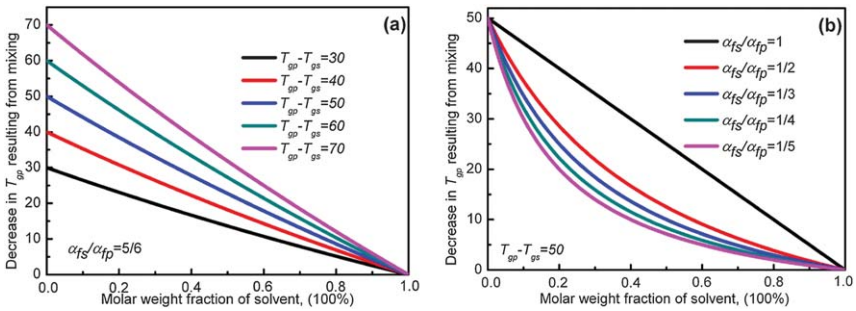

Fig. 3 (a) Dependence of glass transition temperature T_{gp} of polymer on the molar weight fraction of solvent for a given parameter $\alpha_{fs}/\alpha_{fp} = 5/6$. (b) Dependence of glass transition temperature T_{gp} of polymer on the molar weight fraction of solvent for a given parameter $T_{gp} - T_{gs} = 50$.

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which will have a copolymerization interaction with it and a plasticizing effect on it. In order to verify the suggested new features, which can dramatically widen the applications of SMPs, the relaxation theory and the Arrhenius equation should be initially addressed. As we know, the recovery behavior of an SMP obeys the relaxation theory, and the relationship between relaxation time and activation energy can be expressed by using the Arrhenius equation,[24]

$$\tau = \tau_0 \exp\left(\frac{\Delta E}{RT}\right) \tag{19}$$

where τ is the relaxation time which is defined as the recovery time in this study, ΔE is the activation energy of the chain mobility, R is the gas constant, and τ_0 is another constant. From this equation, the relaxation time can either be shortened by decreasing the activation energy or increasing the temperature. Therefore, in determining the recovery time of an SMP, the decrease in activation energy is equivalent to the increase in temperature. Based on the above mentioned qualitative and quantitative analyses, we can summarize that the relaxation theory and the Arrhenius equation help to demonstrate that all thermal SMPs have a chemo-responsive SME. Namely, they can all be induced by their interactive solvent by inductively reducing the activation energy in the polymer.

Here, the effect of temperature on the relaxation time is investigated by combining eqn (13) and (19). At first, the effect of copolymerization interaction on the relaxation time can be quantitatively depicted by combining these two equations and is expressed as,

$$\tau = \exp\left(\frac{\Delta E}{kT}\frac{T_g^p}{T_{gp}}\right) = \exp\left(\frac{\Delta E}{kT}\right) + \exp\left(\frac{1 + \left(\mathrm{K}\frac{T_{gs}}{T_{gp}} - 1\right)\phi_s M_s}{1 + (\mathrm{K} - 1)\phi_s M_s}\right) \tag{20}$$

As shown in Fig. 4(a), the relaxation time, or, in its extension, the recovery time of the SMP/solvent system gradually decreases as the molar weight fraction of the solvent increases. As the T_{gs}/T_{gp} function decreases, the decrease in relaxation (recovery) time becomes sharp. That is to say, the difference between the transition temperature of polymer and solvent determines the change in the transition temperature of the polymer. As the difference becomes larger, the change in the transition temperature of the polymer decreases more sharply. In addition, the effect of molar weight of solvent M_s on the relaxation (recovery) time is depicted in Fig. 4(b). It shows that the decrease in relaxation (recovery) time becomes sharp as the molar weight of solvent M_s increases. This is because the change in internal energy of the polymer would significantly decrease as the molar weight of solvent M_s increases, as the molar weight fraction of solvent remains the same.

On the other hand, the effect of the plasticizing effect on the relaxation time can be quantitatively depicted by combining eqn (15) and (19), and can be expressed as,

$$\begin{aligned}\tau &= \exp\left(\frac{\Delta E}{kT}\frac{T_g^m}{T_{gp}}\right) \\ &= \exp\left(\frac{\Delta E}{kT}\right) + \exp\left(\frac{a_{fp}(1-\phi_s) + a_{fs}\phi_s\left(\frac{T_{gs}}{T_{gp}}\right)}{a_{fp}(1-\phi_s) + a_{fs}\phi_s}\right)\end{aligned} \tag{21}$$

Based on eqn (21), the relaxation time of the SMP as a function of molar weight fraction of solvent for given values of T_{gs}/T_{gp} and a_{fs}/a_{fp} is presented in Fig. 5(a) and (b), respectively. Fig. 5 shows the effect of the molar weight fraction of solvent on the relaxation (or recovery) time. With a fixed value of T_{gs}/T_{gp}, the change in relaxation time gradually decreases as the molar weight fraction of solvent increases. From these curves, it was found that with an increase in the T_{gs}/T_{gp} in the polymer system, the decrease in relaxation (or recovery) time gradually decreased. Alternatively, as the parameter a_{fs}/a_{fp} decreases, the decrease in relaxation (or recovery) time becomes sharp.

There is an essential point behind the chemo-responsive SME in SMPs, which is addressed to provide further clarification of this mechanism. As the internal energy is lowered to a critical level, the stored elastic strain energy in the molecules is subsequently released. As for thermal SMPs, the mechanism of the SME in a polymer originates from the storage and release of elastic strain energy. It is therefore summarized that the thermal SME can also be inductively induced by a chemical interaction through releasing the stored elastic strain energy in the polymer.

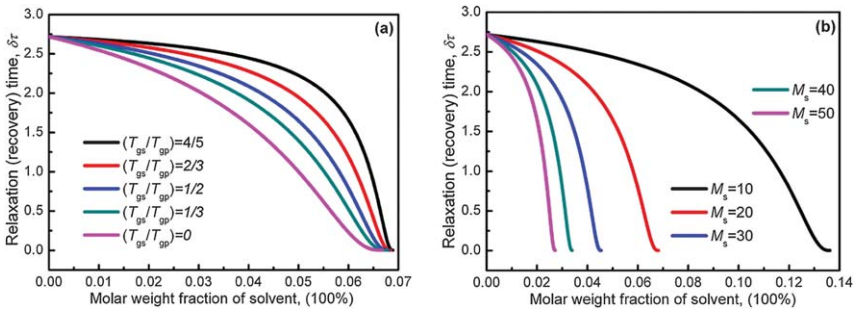

Fig. 4 Numerical results for the effect of copolymerization interaction on the relaxation (or recovery) time. (a) Relation of relaxation time as a function of molar weight fraction of solvent for a given parameter $M_s = 20$. (b) Relation of relaxation time as a function of molar weight fraction of solvent for a given parameter $T_{gs}/T_{gp} = 1/2$.

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3.4 Experimental verification of a water-driven polyurethane SMP

Since the relaxation (or recovery) time of a polymer can be significantly shortened, resulting from the inductive decrease in chemical potential or T_g of the polymer, we can utilize this to design solvent driven SMPs. The basic idea is to lower the chemical potential and transition temperature for the SMP through interaction with the solvent. In order to verify the suggested new features, which can dramatically widen the applications of SMPs, experimental validations are necessary to increase confidence in the modeling. For a chemo-responsive SME in SMPs, the water-driven approach is well known and widely studied.[9,12,27] There are two essential points made by previous research which we address here once more: (1) the absorbed water is quantitatively separated into two parts, the bound water and the free water, and (2) hydrogen bonding is identified as the reason behind water-driven polyurethane SMPs.[28,29] Here, the interaction between bound water and polyurethane SMPs is regarded as the copolymerization interaction. On the other hand, the interaction between the free water and the polyurethane SMP is regarded as the plasticizing effect. Furthermore, the copolymerization interaction and plasticizing effect are regarded as the intrinsic plasticizing effect and generalized plasticizing effect, respectively. The data from experiments on the effect of immersion time on the weight ratio of water to polyurethane SMP is collected here: (1) at 11 h, the total ratio of water to SMP is 1.75%, where the free water is 1.02% and the bound water is 0.73%; (2) at 50 h, the total ratio of water to SMP is 3.84%, where the free water is 2.54%, and the bound water is 1.30%; (3) at 168 h, the total ratio of water to SMP is 4.48%, where the free water is 2.72%, and the bound water is 1.76%, and (4) at 240 h, the total ratio of water to SMP is 4.77%, where the free water is 2.94%, and the bound water is 1.83%.[29] Furthermore, the effect of bound water and free water on the T_g of polyurethane SMP can be quantitatively separated based on the experimental results, as studied in previous work.[29] The experimental data and analytical results have both been presented in Fig. 6 for comparison, where T_{gp} is 310 K, T_{gs} is 273 K, M_s is 18 g mol^{-1}, a_{fp} is 57.6×10^{-6} mK^{-1}, and a_{fs} is 2890×10^{-6} mK^{-1}. As shown in Fig. 6, the correlation between the weight fraction of water and the T_g of the polymer is presented, based on eqn (13), (15) and (18). These simulation results testify that the decrease in the T_g of polyurethane SMP is determined by the weight fraction of water. Consequently, the effects of the intrinsic plasticizing effect and generalized plasticizing effect on the T_g of the SMP are presented. These analytical results provide evidence to support our previous statement and theoretical prediction of the T_g of SMPs in mixing with the solvent. We can utilize these to account for the effects of bound water and free water on the polyurethane SMP. A comparison between the analytical simulation results and the experimental results has therefore been presented. The results from the model and from the trials agree with each other. On the other hand, the decrease in the T_g of the polyurethane SMP

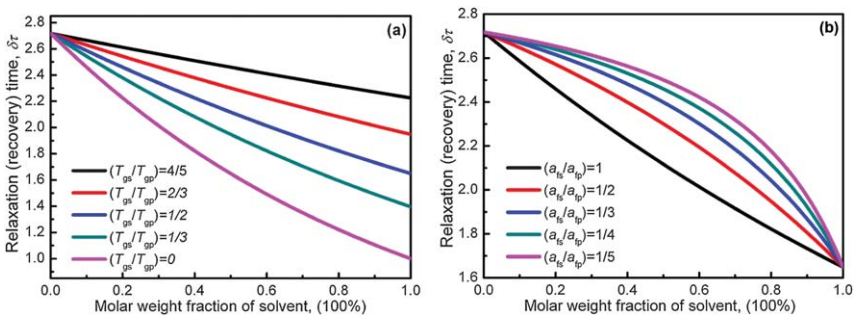

Fig. 5 Numerical results for the effect of plasticizing effect on the relaxation (or recovery) time. (a) Relation of relaxation time as a function of molar weight fraction of solvent for a given parameter $a_{fs}/a_{fp} = 1$. (b) Relation of relaxation time as a function of molar weight fraction of solvent for a given parameter $T_{gs}/T_{gp} = 1/2$.

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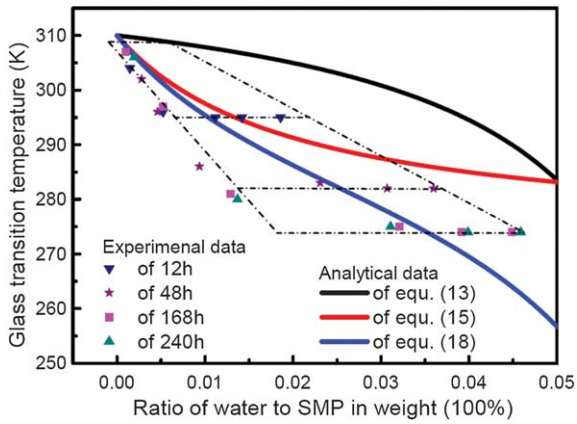

Fig. 6 Glass transition temperature as a function of the ratio of water to SMP in weight percent. The comparison is between the previously experimental data obtained from ref. 25 and the fitting plots of eqn (18) in this study.

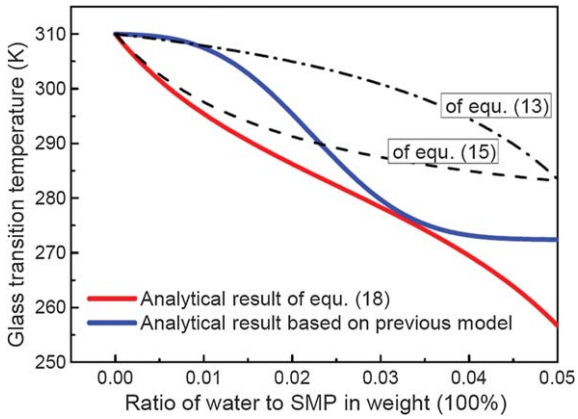

Fig. 7 T_g as a function of the ratio of water to SMP in weight percent. The comparison is between the previous model of ref. 26 and the fitting plots of eqn (18) in this study.

resulting from bound water and free water is in agreement with the analytical results that originated from the corresponding intrinsic plasticizing effect and the generalized plasticizing effect. It should also be noted that the error could be significantly reduced if the given constants were fitted.

To further verify the simulated model, an existing model has been introduced.[29]

$$T_g = 37\exp(-0.06\phi_s^3) - 0.6[1 - \exp(-\phi_s)] + 273 \quad (22)$$

The analytical results obtained from eqn (18) and (22) have been presented and compared in Fig. 7. This comparison further verified the application of the theoretical models originated from the GT theory and FV theory. Not only could we predict the revolutionary change in T_g of the SMP, but we could also qualitatively separate the effects of the solvent on the T_g of the SMP in response to a solvent. These models support the statements in our previous research, that the thermal responsive SMPs can be induced by a solvent either *via* chemical interaction or the physical swelling effect.[10,23]

4 Concluding remarks

In this study, we validated the use of an effective theoretical approach for the determination of state transition in chemo-responsive SMPs. In this method the GT theory and FV theory have both shown that recovery behavior of the SMP can be very well described and predicted. The theoretical approach from GT theory and FV theory provides an effective way to determine the intrinsic plasticizing effect and the generalized plasticizing effect on the T_g of a chemo-responsive SMP. Furthermore, we examined the accuracy of the analytical results based on the experimental results and semi-empirical simulation results. The theoretical approach provides an accurate estimation of the experimental results and semi-empirical simulation results. This effective approach is expected to make it possible to theoretically and/or semi-empirically predict the chemo-responsive SME in amorphous SMPs.

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