

Qualitative separation of the effect of the solubility parameter on the recovery behavior of shape-memory polymer

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Abstract

For the thermal response of shape-memory polymer (SMP) it has been experimentally demonstrated that the actuation can be achieved using interactive solvent. In this paper, the effect of the solubility parameter of the interactive solvent on the shape recovery behavior and glass transition temperature of polystyrene SMP was investigated experimentally. The effect of the solubility parameter on the activation energy was separated and qualitatively identified, as expected from the relaxation theory and Eyring equation. This approach should be applicable to other SMPs and their composites and many extension applications and achievements could be based on this outcome.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Shape-memory polymers (SMPs) derive their name from their inherent ability to return to their original 'memorized' shape after undergoing a shape deformation [1]. SMPs can be deformed to any desired shape above their transition temperatures. And they must remain below, or be quenched to below, the transition temperature while being maintained in the desired thermoformed shape to 'lock' in the deformation. Once the deformation is locked in, the polymer network cannot return to a relaxed state due to thermal barriers. The polymer will hold its deformed shape indefinitely until it is heated above its transition temperature, whereupon the stored mechanical strain is released and it returns to its original state [2–4].

SMP is one of the most attractive shape-memory materials that can change shape in response to an external stimulus. However, SMPs have a number of advantages over shape-memory alloys (SMAs), such as wider range of shape recovery temperatures from -70 to 120 °C, larger recoverable strain (up to 400%), lower density and cost [5]. Unlike SMAs, in particular NiTi SMA, which can be actuated by passing an

electrical current directly, SMPs are rather complicated to heat, since they are normally non-conductive in nature. Although the most recent development in the actuation technique of thermo-responsive SMPs can be realized by filling functional fillers into the polymer, i.e., mixed with electrically conductive filler [6, 7], magnetic particles [8–12], or by applying an alternating electric, magnetic field. However, the generation of a strong functional field requires an additional bulky system.

In this study, a new approach has been explored for triggering the recovery of thermo-responsive styrene-based SMP. Instead of heating, the polystyrene SMP can be made to recover its original shape by immersing it into dimethylformamide (DMF) at room temperature. The recovery is due to the strong influence of molecular solvent absorbed upon immersing in DMF, which can reduce the glass transition temperature (T_g) of the SMP. Hence, instead of heating the material to over its T_g , the shape recovery can be initiated by the drop of T_g of the polymer [13, 14]. This finding also provides a simple and convenient approach for use in studying SMP with a view to bio-related applications, in particular for minimally invasive surgery; e.g., laser-activated SMP microactuators which are used for thrombus removal

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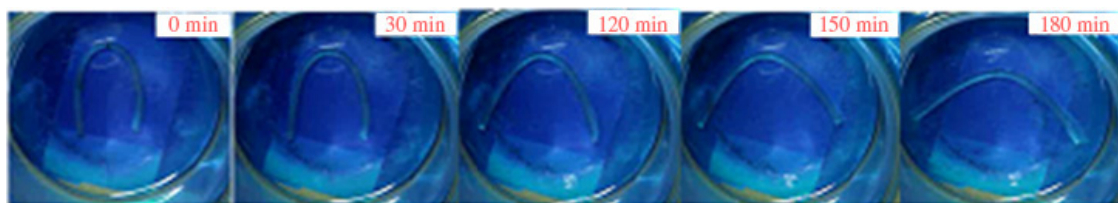


Figure 1. Shape recovery of a 2.88 mm diameter SMP wire in DMF. The wire was bent into 'n'-like shape.

following ischemic stroke can be realized using solvent driven SMP microactuators [15], when the SMP has an interactive response to the blood.

2. Experimental details

The SMP used in this study is thermosetting styrene-based resin from Cornerstone Research Group (CRG) Inc., USA. It was prepared from styrene-based resin, methacrylic acid and hexadiene. The glass transition temperature (T_g) of this material can be tailored to meet the requirements of particular applications. The SMPs were prepared by following various procedures, and had a nominal T_g of 62 °C. Several rectangular sheets were prepared with the dimension of samples as 50 cm × 1.0 cm × 1.0 cm. After being dried in a vacuum oven at 100 °C for 12 h, the samples were immersed into solvents (DMF, ethyl acetate and ethyl formate) at the temperature of 35 °C for different durations, i.e., 15, 30, 45, 60, 75 and 90 min. After the immersion, the samples were dried in the oven at the temperature of 80 °C (higher than the boiling point of solvents), again to identify the effect of solvent molecules that are not involved into chemical interaction, then cut into small pieces for FT-IR (AVATAR 360, Nicolet) and differential scanning calorimetry (DSC) (DSC 2920, TA Instruments) tests.

3. Results and discussion

As reported in [13], it is demonstrated that the DMF solvent has a strong influence on the glass transition temperature and dynamic mechanical properties of the styrene-based SMP. The characteristic peaks of C=O groups were involved in interaction with the polar solvent. In figure 1, the shape recovery of styrene-based SMP is produced by immersing into DMF solvent for about 180 min; the SMP can recover from the pre-deformed 'n' shape, sequentially, at room temperature. However, the effect of electrostatic interactions of different solvents on the peak shift remains unknown. The following sections will present the mechanism behind the effect of the solubility parameter on the recovery behavior of SMP, particularly the interaction of different solvents with the styrene-based SMP.

3.1. The FT-IR test

In this study, FT-IR spectroscopy was used to study the interaction between the SMP and its interactive solvents and qualitatively study the effect of the solubility parameter on the shape recovery behavior. The samples used for the FT-IR test

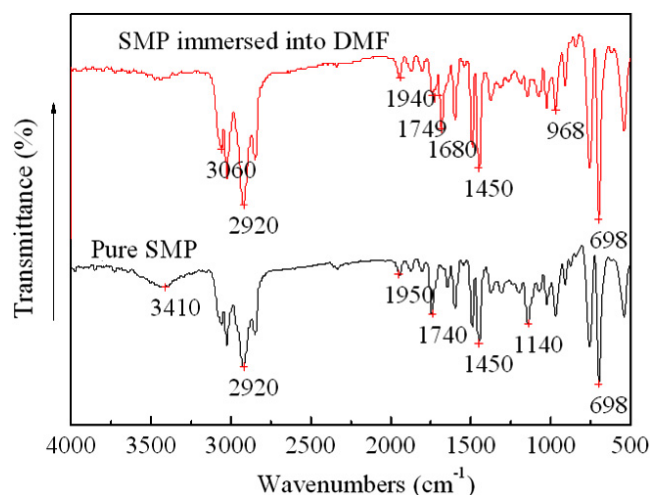


Figure 2. FT-IR spectra of pure styrene-based SMP and the sample (90 min of immersion).

were thin rectangular sheets with a thickness of 1.0 mm. The FT-IR spectra were collected by averaging 128 scans at 4 cm⁻¹ in a reflection mode from a FT-IR spectrometer.

The full FT-IR spectra of the SMPs (at the temperature of 20 °C) after different immersions for 90 min in DMF solvent are shown in figure 2. The characteristic peaks that were relevant to this study were marked out. As we can see, the polar bonding was evident in the styrene-based SMP where the infrared band of the bonded C=O stretching occurred at 1740 cm⁻¹, while that of SMP immersed into DMF solvent occurred at 1749 cm⁻¹.

The infrared band of C=O stretching against immersion time and solubility parameter after immersing into interactive solvents is presented in figure 3. Both immersion time and solubility parameter had a remarkable effect on the C=O infrared band shift, which is coincident with the infrared band shift in figure 2. Furthermore, with increase of the solubility parameter the infrared band intensity of the bonded C=O stretching became more obvious in comparison with that of pure polymer, which indicated that a stronger solubility parameter resulted in more C=O groups being involved in polarization interaction.

3.2. Supramolecular electrostatic interactions of C=O

On the basis of experimental results shown in figure 3, the mechanism behind the polar interaction is seen to be the electrons of polar solvent molecules being absorbed by the

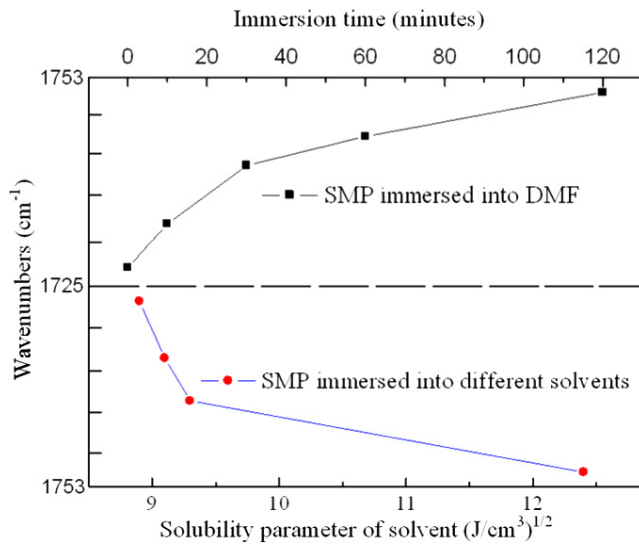


Figure 3. Infrared band of bonded C=O stretching versus immersion time and solubility parameter.

bonded C=O of the polymer, leading to the infrared band shifting to a higher frequency, slightly. This reveals that the C=O bonds of solvent molecules have direct influence on the C=O bonds in the styrene-based SMP, which can be explained by the model in figure 4, where R, R' and R'' present alkyl, and OR' also can be displaced by formamide. However, the absorbed solvent molecules can form two types of interaction (the electronic absorption effect and conjugate effect) with C=O groups. Due to the former interaction, the infrared band shifted up to a higher frequency while the interaction at the site 'latter' brings it down to a lower frequency. There, two interactions may work together and counteract each other. According to the previous research [16], solvent in the site 'latter' is more firmly bounded than that in the site 'former', largely determined by the spatial block interaction of C=O in solvent molecules. Consequently, the infrared band of C=O increases.

3.3. Modeling

In the process of interaction between solvent and polymer, both the temperature and air pressure being kept constant, the essential factor of change in the Gibbs free energy must be satisfied when mixing, namely

$$\Delta F_M = \Delta H_M - T \Delta S_M < 0, \quad (1)$$

where ΔH_M is known as the change in enthalpy, ΔS_M presents the change of entropy, T is the absolute temperature, and ΔF_M is the free energy. The equation indicates that mixing will occur when the ΔF_M has a negative value [17, 18].

On the basis of the Hildebrand equation, the change in enthalpy can be written as

$$\Delta H_M = V \phi_1 \phi_2 [(\Delta E_1/V_1)^{1/2} + (\Delta E_2/V_2)^{1/2}]^2. \quad (2)$$

where ϕ represents the volume fraction, ΔE is the activation energy of chain mobility, V is the total volume of mixture,

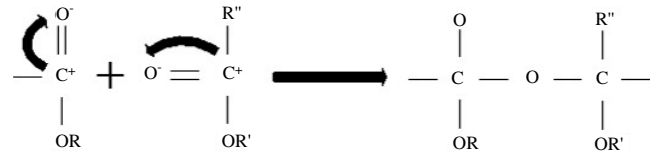


Figure 4. Effect of electron absorption on the C=O bands in polymer.

and $\Delta E/V$ is defined as the cohesive energy density, while labels 1 and 2 represent that the corresponding parameter is for solvent or polymer, respectively. From the above equation, it is obviously obtained that the different cohesive energy density results in a change of enthalpy. When the δ^2 (δ is the solubility parameter) is defined as the cohesive energy density, the Hildebrand equation can be expressed as

$$\Delta H_M = V \phi_1 \phi_2 [\delta_1 - \delta_2]^2. \quad (3)$$

The polymer used in this study is a polar polymer; thus the above equation should be amended as

$$\Delta H_M = V \phi_1 \phi_2 [(\omega_1 - \omega_2)^2 + (\Omega_1 - \Omega_2)^2] \quad (4)$$

where ω represents the solubility parameter of the polarity part, Ω represents the solubility parameter of non-polarity part, and 1, 2 represent solvent and polymer, respectively. Before discussing the effect of the solubility parameter on the shape recovery behavior, the relaxation theory and Eyring equation should be addressed. As we know, the shape recovery behavior obeys the relaxation theory, and the relationship between recovery time and activation can be expressed using the Eyring equation, as [19]

$$\tau = \tau_0 \exp(\Delta E/RT) \quad (5)$$

where τ is the relaxation time (which is defined as the shape recovery time in this study), ΔE is the activation energy of the chain mobility, R is the gas constant, and τ_0 is a constant. From this equation, the relaxation time can be shortened by decreasing the activation energy or increasing the temperature. Thus, in this study, the effect of the solvent and the solubility parameter on the shape recovery behavior may be attributed to the former.

As equation (5) presented, the relaxation time can be shortened by increasing the temperature or decreasing the activation energy. Thus, the effect of the activation energy on the relaxation time will be investigated instead of that of temperature. To compare the relationship between the solubility parameter and relaxation time, the experimental temperature is always considered as a constant. As equations (4) and (5) presented, the solubility parameter has a direct relation with the activation energy which has an effect on the relaxation time. Thus an indirect relationship between the solubility parameter and the relaxation can be constructed as follows:

$$\tau = \tau_0 \exp\left(\frac{\Delta E - \Delta H}{RT}\right). \quad (6)$$

If equations (4) and (6) are combined, we can relate the recovery time to the solubility parameter as follows:

$$\tau = \tau_0 \exp\left(\frac{\Delta E}{RT}\right) \times \exp\left(-\frac{V\phi_1\phi_2[(\omega_1 - \omega_2)^2 + (\Omega_1 - \Omega_2)^2]}{RT}\right) \quad (7)$$

where $\tau_0 \exp(\frac{\Delta E}{RT})$ is constant. That is to say, the recovery time is determined by the solubility parameter completely. The above equation can be simplified as

$$\tau = A \exp\left(-\frac{V\phi_1\phi_2[(\omega_1 - \omega_2)^2 + (\Omega_1 - \Omega_2)^2]}{RT}\right) \quad (8)$$

where $A = \tau_0 \exp(\frac{\Delta E}{RT})$ is a constant, R is the gas constant, $[(\omega_1 - \omega_2)^2 + (\Omega_1 - \Omega_2)^2]$, V and T are known constants when the experimental factors are determined. So the linear relationship between $\ln \tau$ and $\phi_1\phi_2$ can be obtained. As we know, with immersion time increase the absorption of solvent molecules increases until saturation occurs. $\phi_1\phi_2$ is just determined by the absorption of solvent molecules, while the absorption of solvent molecules has a direct influence on the transition temperature reduction of polymer based on the plastic effect:

$$\Delta T = \beta n \quad (9)$$

where n presents the mole number of solvent molecules, and β is defined as a proportionality factor. Thus, the mole number of solvent molecules absorbed into the polymer can be obtained from the above equation. Finally, $\phi_1\phi_2$ can be calculated as

$$\phi_1\phi_2 = \phi_1(1 - \phi_1) = \frac{n}{n + n_p} \left(1 - \frac{n}{n + n_p}\right) = \frac{nn_p}{(n + n_p)^2} \quad (10)$$

where n_p is the mole number of polymer, and can be considered as a known constant in the process of the plastic effect.

On the basis of the aforementioned, the effect of the solubility parameter on the shape recovery behavior can be obtained and calculated using the following equations:

$$\Delta T = \beta n$$

$$\phi_1\phi_2 = \phi_1(1 - \phi_1) = \frac{n}{n + n_p} \left(1 - \frac{n}{n + n_p}\right) = \frac{nn_p}{(n + n_p)^2} \quad (11)$$

$$\tau = \tau_0 \exp\left(\frac{\Delta E}{RT}\right) \times \exp\left\{-\frac{V\phi_1\phi_2[(\omega_1 - \omega_2)^2 + (\Omega_1 - \Omega_2)^2]}{RT}\right\}$$

ΔT can be obtained from the DSC test; then n can be calculated from the second equation in this group of equations. Then on n being input into the third equation, $\phi_1\phi_2$ is obtained. Finally, $\phi_1\phi_2$ is input into the first equation, and the effect of the solubility parameter on the shape recovery behavior is qualitative separated.

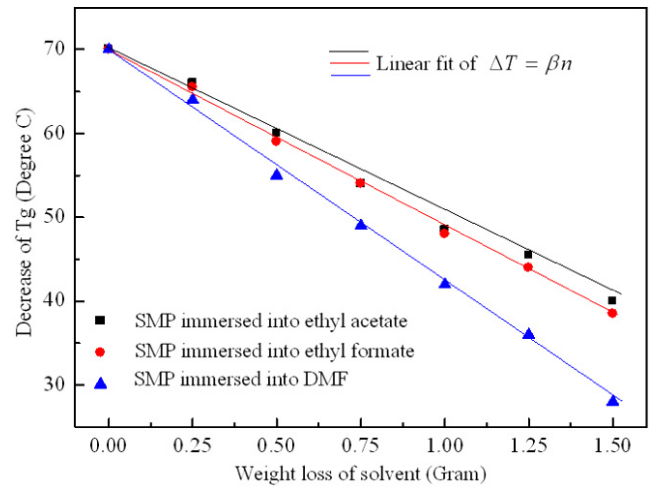


Figure 5. The effect of solvent molecule absorption on the glass transition temperature.

3.4. Evolution of the glass transition temperature

On the basis of the data obtained from DSC tests, we can find the relation between the decrease of T_g and the weight loss of solvent which was established. The T_g decreased obviously with solvent molecule absorption increase in figure 5. That can perhaps be attributed to the polar interaction between macromolecules and solvent molecules and the plasticizing effect, while we should also pay attention to the fact that the change of T_g strongly depends on the process of diffusion of the solvent molecules [20]. By comparison of the three curves, there was obviously a quantifiable effect of the solubility parameter on the T_g . The experimental results revealed that the higher the solubility parameter for dispersion between polymer and solvent, the more evident the decrease of T_g , under the condition that the polymer was immersed into the interactive solvent. This can all be demonstrated using the solution theory of polymer physics [21].

3.5. The effect of the solubility parameter on the shape recovery actuation

Since T_g for the styrene-based SMP can be reduced using polar solvent, we can utilize this to design solvent driven functionally controllable SMP. The basic idea is to lower T_g for the SMP by immersing it into interactive solvents. In order to verify the suggested new features, which can dramatically widen the applications of SMPs, the effect of the solubility parameter on the shape recovery behavior was experimentally validated.

The rectangular SMP samples were bent into an 'n'-like shape at 80 °C and retained this shape during cooling back to the temperature of 35 °C. No apparent shape recovery was found after the deformed wires were kept for one day. However, after immersing in 35 °C solvents for about 20–40 min they started to recover gradually. With the increase of the solubility parameter, the shape recovery time decreases remarkably. The dependence of the recovery behavior on the solubility parameter is due to the stronger plasticizing and the polarized effect between the solvent molecules and polymeric

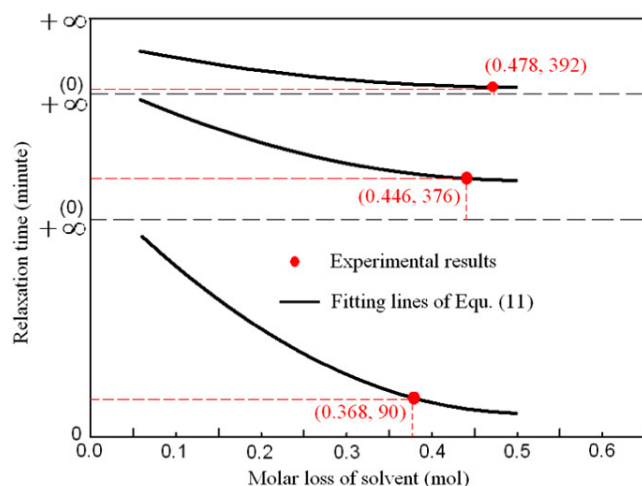


Figure 6. The relationship between relaxation time (recovery time) and molar loss of solvent.

macromolecules. After 392, 376 and 90 min immersion time, it was found that the polymer regained the original shape in the corresponding solvent. As shown in figure 6, it was obvious that the recovery of SMP had taken the shortest time in DMF solvent with the highest solubility parameter.

4. Conclusions

A series of experiments were conducted to study the effects of the solubility parameter on the recovery behavior of styrene-based SMP actuation. The experimental results indicate that the shape recovery behavior of SMP was improved by increase in the solubility parameter. This improvement is more remarkable in SMP actuation with shorter recovery time.

T_g for the SMP can be reduced effectively by immersing in solvent. This phenomenon remains valid until the polymer is saturated by the solvent molecules. It is also found that the decrease in T_g is more dramatic, since the solubility parameter of the solvent is increased.

The effects of the solvent and solubility parameter on T_g for SMP were investigated using a series of FT-IR, DSC tests and relaxation theory. The relationships between T_g and the

immersion time as well as between the solubility parameter and the recovery time for SMP were obtained. It was found that the absorbed solvent molecules have a tendency to reduce T_g . The mechanism is that the activation energy of the polymer chain is reduced during the process of mixing of polymer and solvent, leading to the actuation of SMP.

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