Modeling Strategy for Enhanced Recovery Strength and a Tailorable Shape Transition Behavior in Shape Memory Copolymers

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ABSTRACT: By integrating the Fox−Flory equation and the rubber elasticity principle, a phenomenologically constitutive model was proposed in this study to describe high mechanical recovery strength and a tailorable shape transition behavior of shape memory polymer (SMP) copolymers. The thermodynamics of different monomers in the copolymers were formulated by considering their influences on glass-transition temperatures (T_g) and elastic moduli based on the Fox−Flory and Gordon−Taylor equations. Effects of the T_g, weight fraction, molecular weight, storage modulus, and rubbery modulus of various monomers on thermomechanical and shape recovery behaviors of the SMP copolymers were theoretically investigated and discussed. Working principles of enhanced mechanical strength and a tailorable shape transition behavior of the SMP copolymers have been well-described using this newly proposed model, which offers an effective strategy for designing SMPs with high mechanical strength and a desirable shape memory behavior. Furthermore, molecular dynamics simulations were used to predict the glass-transition temperature from a molecular scale and the experimental results fit well with our modeling results.

1. INTRODUCTION

Shape memory polymers (SMPs) are one of the key stimulus-responsive materials with the ability to regain their permanent shape from a temporary one in the presence of external stimuli, including heat,1,2 solvent,3,4 light,5 and electrical and magnetic fields.6,7 This feature is defined as the shape memory effect (SME), which has found a myriad of practical applications in biomedical devices,8,9 aerospace deployable and periodic structures,10,11 sensors, and actuators.12 In comparison with the conventional shape memory alloys and ceramics, SMPs present many unique advantages, such as a large recovery strain, low cost, and a simple manufacturing process.13−16 However, their relatively low recovery strengths severely limit their practical and potential applications.17−19

To overcome this issue, fiber-reinforced SMP composites and high-enthalpy SMPs have been made, and their rubbery moduli can be as high as 17−20 MPa. However, their shape recovery performance is often undesirable because it is difficult to control the rearrangements of macromolecules at the molecular scale. Therefore, photopolymerized SMP copolymers, that is, MMA-co-PEGDMA (methyl methacrylate (MMA) and poly(ethylene glycol) dimethacrylate (PEGDMA))20,21 and tBA-co-PEGDMA (tert-butyl acrylate (tBA) and poly(ethylene glycol) dimethacrylate (PEGDMA)),22,23 were synthesized to achieve both good mechanical recovery strength and tailorable glass-transition temperatures (T_g) by controlling the weight fraction and molecular weight of the PEGDMA monomers.

Recently, several theoretical models have been proposed to describe the working mechanism and shape memory behaviors of SMPs. Liu et al. formulated a model by combining the phase-transition theory and viscoelasticity to characterize the viscoelastic properties at different prestrains.24 Furthermore, the working mechanisms of temperature- and time-dependent SMEs in SMPs have been well-described using their proposed...
models. On the other hand, structural relaxation, multi-SMP, and thermochemical SME have also been well-investigated using multibranched models. However, it is critically needed to develop theoretical models to describe the working mechanisms of these SMP copolymers with high mechanical recovery strengths. This paper will develop a phenomenological model for the unique characteristics of the SMP copolymers with high mechanical recovery strength and a tailorable shape-transition behavior. The stored mechanical energy is initially obtained and used to link with the high recovery strength in SMP copolymers. The Fox–Flory equation and the Gordon–Taylor equation are then combined to characterize the effects of molecular weight and weight fraction of the PEGDMA monomer on the $T_g$ of the SMP copolymer. Furthermore, the rubbery elasticity theory is then employed to formulate a thermomechanically constitutive model to investigate the fundamental working mechanism of SMP copolymers with their high mechanical recovery strengths. Finally, both the Weibull statistics model and the phase-transition theory are used to investigate the tailorable shape recovery behaviors of the SMP copolymers. The simulation results have been compared with the experimental results to verify the proposed model.

2. MODELING OF MECHANICAL RECOVERY STRENGTH

Mechanical recovery stress is the driving force for the shape recovery of SMPs in their rubbery states. This stress originates from the release of stored mechanical energy in the preloading and deformation processes. When the SMPs are heated to above their transition temperature, the stored mechanical energy and stress are released from the SMPs. Here, the mechanical recovery stress is used to link with the recovery stress and rubbery modulus in the shape recovery process of the SMP copolymer.

The glass-transition temperature ($T_g(s)$) of the PEGDMA monomer as a function of the molecular weight ($M_n$) in the MMA-co-PEGDMA copolymer can be obtained according to the Fox–Flory equation as follows

$$T_g(s) = T_{g0}(s) - \frac{k_s}{M_n}$$

where $T_{g0}(s)$ is the glass-transition temperature of the PEGDMA monomer, whereas the molecular weight is infinity, and $k_s$ is a given parameter.

The $T_g$ of the SMP copolymer can be determined by those of PEGDMA and MMA monomers, and is ruled by the Gordon–Taylor equation

$$T_g = \frac{T_g(h) + (KT_g(s) - T_g(h))W_g}{1 + (K - 1)W_g}$$

where $T_g(h)$ is the glass-transition temperature of the MMA monomer in the SMP copolymer, $W_g$ is the weight fraction of PEGDMA, and $K$ is the Gordon–Taylor constant.

Combining eqs 1 and 2, we can obtain the $T_g$ of the SMP copolymer as a function of the weight fraction of the PEGDMA monomer

$$T_g = \frac{T_g(h) + \left(KT_{g0}(s) - k_s\frac{k_s}{M_n} - T_g(h)\right)W_g}{1 + (K - 1)W_g}$$

Calculation results using eq 3 are plotted in Figure 1, which is also compared with experiment data of the MMA-co-PEGDMA polymer network reported in ref. The parameter values of eq 3 are presented in Table 1. It is found that the $T_g$ value is gradually increased with the decrease of $M_n$ at the given weight fraction of the PEGDMA monomer. On the other hand, the weight fraction of PEGDMA also shows a critical influence on the $T_g$ value of the SMP copolymer, which is gradually decreased with an increase in the weight fraction of the PEGDMA monomer. Combining the influences of the above two parameters, it is found that the decrease rate of $T_g$ is much smaller with the increase of the weight fraction of PEGDMA than the decrease rate of the $T_g$ value of PEGDMA monomer. When the $T_g$ value of PEGDMA monomer is closer to that of the MMA, the effect of the weight fraction of PEGDMA on the $T_g$ of the SMP copolymer becomes smaller. Practically, we can use the molecular design to change $T_g$ values of the SMP copolymer.

Meanwhile, the stored mechanical energy in the MMA-co-PEGDMA SMP copolymer is released when the SMP is heated above its $T_g$ thus triggering the shape recovery. Therefore, the recovery strength of the SMP copolymer is determined by its rubbery modulus. Here, effects of the weight fraction ($W_g$) and copolymer molecular weight ($M_n$) of the PEGDMA monomer on the rubbery modulus of the SMP copolymer ($E_r$) should be studied to identify their constitutive relationships with the mechanical recovery strength. For MMA-co-PEGDMA molecules, their rubbery modulus is incorporated into the MMA and PEGDMA monomers in a series connection to resist an external loading, which can be described using the following equation

$$E_r = E_{hs}(1 - W_g) + E_r W_g$$

where $E_{hs}$ and $E_r$ are the rubbery moduli of the MMA and PEGDMA monomers, respectively. The rubbery modulus of the
MMA monomer is assumed to be a constant because the molecular weight is kept constant. Therefore, the rubbery modulus of the SMP copolymer is determined by the PEGDMA monomer with a variety of molecular weights ($M_n$). Based on the rubbery elasticity theory, the rubbery modulus of PEGDMA ($E_r$) is given as

$$E_r = 3N_cRT$$

(5)

where $R$ is the gas constant ($R = 8.314$ J/(mol K)) and $T$ is the temperature of polymers in their rubber states. $N_c$ (with a unit of mol/cm$^3$) is defined as the molar number of the crosslinking points of the PEGDMA monomer ($n_c$) per cubic centimeter and $n_c$ is set as $c$ times of the molar number of the monomer. We can further obtain the following equation

$$N_c = n_c/V = \frac{amW_s}{M_n} = \frac{c\rho W_s}{M_n}$$

(6)

where $\rho$ is the density, $m$ is the weight, and $V$ is the volume of the SMP copolymer.

We assume that the rubber state is dominant when the temperature ($T$) is higher than $T_g$ and their temperature difference is $\theta$ (K). Therefore, we can further rewrite eq 3 as follows

$$T = \frac{T_g(h) + \left(KT_{g0}(s) - Kk_M - T_g(h)\right)W_s}{1 + (K - 1)W_s} + \theta$$

(7)

By substituting eqs 6 and 7 into eq 5, we can obtain the following equation

$$E_r = 3N_cRT$$

$$= \frac{3c\rho W_s}{M_n} \left[\frac{1}{1 + (K - 1)W_s} + \theta\right]$$

(8)

Combining eq 8 with (eq 4), we can obtain the expression of the rubbery modulus ($E_r$) as a function of the weight fraction ($W_s$) and the molecular weight ($M_n$) of the PEGDMA as follows

$$E_r = E_{rs}(1 - W_s) + \frac{3c\rho W_s^2}{M_n} \left[\frac{1}{1 + (K - 1)W_s} + \theta\right]$$

(9)

To verify eq 9, simulation results based on the proposed model were plotted and then compared with the experimental data reported in ref 20, and the results are shown in Figure 2, in which both the weight fraction and the molecular weight of the PEGDMA are varied to study their effects on the rubber modulus of the SMP copolymer. The obtained fitting data are presented in Table 1. It is found that the rubbery modulus is increased with an increase in the weight fraction (or decrease in the molecular weight) of the PEGDMA monomer. Clearly, these simulation results are slightly larger than those of the experimental results because during experiments the MMA and PEGDMA monomers in a series connection will resist an external loading. Indeed, the connection modes of the MMA and PEGDMA monomers are complex in the SMP copolymer. With different types of connection modes, the contributions of the MMA and PEGDMA monomers to the rubbery modulus of the SMP copolymer are quite different, thus causing the differences between the simulation result (of series connection mode) and the experimental data, as shown in Figure 2.

Molecular dynamics (MD) simulation is further used to predict the glass-transition temperature with respect to the change of the weight fraction of the PEGDMA monomer. The MD approach has been used in the literature to predict the $T_g$ of polymer systems, and the results agreed well with the experimental findings. The atomic models of the MMA monomer and PEGDMA crosslinkers, and the copolymer systems with the corresponding weight fractions of PEGDMA ($W_s = 20, 40, 60$, and $80\%$), are constructed as shown in Figure 3. The interactions in the polymer systems are described by the consistent valence force field. The partial charges of different types of atoms are calculated using the bond-increment method. The nonbonded interactions, including van der Waals and Coulombic interactions, are calculated with a cutoff of 10 Å. The particle–particle and particle–mesh solver is used to account for the long-range Coulombic interactions. A time step of 1 fs is used in MD simulations. Periodic boundary conditions are applied to all of the directions. The original polymer structures are first equilibrated at a temperature of 450 K and a pressure of 1 atm under the NPT ensemble (constant particle number ($N$), constant pressure ($P$), and constant temperature ($T$)) for 1 ns. Then, the systems are gradually cooled down to 250 K at a step of $1 \times 10^{10}$ K s$^{-1}$. All MD simulations are carried out using a large-scale atomic/molecular massively parallel simulator.

Figure 4 shows the $T_g$ values obtained from the intersections of the two linear fittings of the glassy and rubbery regions in the plots. We can deduce that $T_g = 393.5$ K for the case of $W_s = 20\%$, $T_g = 381.4$ K for the case of $W_s = 40\%$, $T_g = 364.3$ K for the case of $W_s = 60\%$, and $T_g = 357.6$ K for the case of $W_s = 80\%$. All of these are close to the modeling results of $T_g = 399.59$, 384.88, 370.73, and 358.54 K obtained using eq 3. This indicates clearly that the prediction of the $T_g$ from the molecular scale is applicable.

Furthermore, eq 9 provides an effective model to tailor and design the values of $T_g$ and $E_r$ of the SMP copolymer by control...
The simulation results based on the proposed model (eq 9) are presented in Figure 5. As revealed in Figure 5a, the \( T_g \) of the SMP copolymer is essentially determined by the molecular weight \( (M_n) \) of the monomer. It is also found that the \( T_g \) is gradually increased with an increase in the weight fraction \( (W_s) \) when \( M_n = 200 \) \((M_n < 300)\). However, it is gradually decreased with an increase in the weight fraction \( (W_s) \) of the PEGDMA monomer when \( M_n = 400, 500, 600, \) or 700 \((e.g., M_n > 300)\). At a given weight fraction \( (e.g., W_s = 100\%) \), the \( T_g \) values are gradually increased with an increase in the weight fraction \( (W_s) \) when \( M_n = 200 \) \((M_n < 300)\). However, it is gradually decreased with an increase in the weight fraction \( (W_s) \) of the PEGDMA monomer when \( M_n = 400, 500, 600, \) or 700 \((e.g., M_n > 300)\). At a given weight fraction \( (e.g., W_s = 100\%) \), the \( T_g \) values are...
decreased from 543.4 to 269.4 °C when the molecular weight ($M_n$) is increased from 200 to 700. Effects of the weight fraction and molecular weight of the PEGDMA monomer on the rubbery modulus have been further studied, and the results are shown in Figure 5b. The rubbery modulus is found to increase with the weight fraction ($W_s$) and to reach its highest value when $W_s = 100\%$. They are 56.4, 91.2, 127.3, 199.3 and 387.7 MPa when the molecular weights are $M_n = 700$, $M_n = 600$, $M_n = 500$, $M_n = 400$, $M_n = 300$ and $M_n = 200$, respectively. For the SMP copolymer, its shape recovery will occur when it is heated above its $T_g$. This means that the shape recovery process is induced when the SMP is in its rubbery state. Therefore, the mechanical recovery strength of the SMP copolymer is mainly determined by the rubbery modulus. The above simulation results reveal that the rubbery modulus can be significantly increased by decreasing the molecular weight ($M_n$) or increasing the weight fraction ($W_s$) of the PEGDMA monomer, thus increasing the mechanical recovery strength.

The Weibull statistical model is further introduced to characterize the storage modulus, which is a critical parameter to determine the rubbery modulus. The constitutive relationship for the storage modulus ($E(T)$) is given as follows:

$$E(T) = (E_1 - E_2) \exp \left( - \left( \frac{T}{T_\beta} \right)^m \right) + (E_2 - E_1) \exp \left( - \left( \frac{T}{T_f} \right)^m \right) + E_i \exp \left( - \left( \frac{T}{T_f} \right)^m \right)$$

(10)

where $T_\beta$ is the transition temperature of $\beta$ relaxation in the monomer, $T_f$ is the flow temperature of the polymer chains, and $m$ is the Weibull modulus. Both $E_1$ and $E_2$ are the stiffness values of the MMA and PEGDMA monomers in the SMP copolymer, respectively.

According to eq 10, a constitutive relationship among the storage modulus ($E(T)$), temperature ($T$), glass-transition temperature ($T_g$), and rubbery modulus ($E_r$) can be obtained by the following equation

$$E(T) = (E_2 - E_1) \exp \left( - \left( \frac{T}{T_g} \right)^m \right) + E_i$$

(11)

By substituting eqs 3 and 9 into eq 11, the influences of the weight fraction and molecular weight of the PEGDMA monomer on the storage modulus of the SMP copolymer can be obtained as follows. Figure 6a provides the numerical results of the rubbery moduli as a function of the weight fraction of the PEGDMA monomer, thus increasing the mechanical recovery strength.

Table 2. Experimental Data of tBA-co-PEGDMA Copolymers in Reference 22

<table>
<thead>
<tr>
<th>$M_n$ (g/mol)</th>
<th>$E_r$ (MPa)</th>
<th>$T_g$ (°C)</th>
<th>$W_s$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>2.4</td>
<td>280</td>
<td>10%</td>
</tr>
<tr>
<td></td>
<td>5.2</td>
<td>306</td>
<td>20%</td>
</tr>
<tr>
<td></td>
<td>12.8</td>
<td>312</td>
<td>40%</td>
</tr>
<tr>
<td></td>
<td>67.5</td>
<td>322</td>
<td>100%</td>
</tr>
<tr>
<td>750</td>
<td>1.6</td>
<td>242</td>
<td>10%</td>
</tr>
<tr>
<td></td>
<td>3.08</td>
<td>278</td>
<td>20%</td>
</tr>
<tr>
<td></td>
<td>7.2</td>
<td>298</td>
<td>40%</td>
</tr>
<tr>
<td></td>
<td>38.2</td>
<td>313</td>
<td>100%</td>
</tr>
</tbody>
</table>

According to eq 10, the storage modulus of the tBA-co-PEGDMA copolymer reported in ref 22 are also plotted in Figure 6a for a comparison. Tables 2 and 3 list the experimental data and the fitted data used in eq 12, respectively. It is found that the simulation results are in good agreement with the experimental data. With the molecular weight increased from 550 to 750, the rubbery modulus of the SMP copolymer is increased from 7.2 to 12.8 MPa at a given weight fraction of $W_s = 40\%$. This confirms that the rubbery modulus of the tBA-co-PEGDMA copolymer is strongly determined by the molecular weight of the PEGDMA monomer.
There are de
from two monomers, that is, PEGDMA and
PEGDMA, for example, this SMP copolymer is incorporated
of a frozen phase (fraction, and
other words, the storage modulus of the SMP copolymer can be
by the molecular weight, weight fraction, and
experimental results. The storage modulus is mainly determined
results obtained from the theoretical model shown in eq 14 has therefore been veri
Based on eq 13, the recovery strain is determined by the transition temperature (T_h), which is mainly determined by the T_c. Here, we set T_h = T_c + \theta' (\theta' is the difference between T_h and T_c) and eq 13 is therefore rewritten as follows
\[ \varepsilon(T)/\varepsilon_{\text{pre}} = 1 - \varepsilon_1 = 1/(1 + c_T(T_h - T))^{n} \] (14)
Equation 15 is then employed to predict the free recovery process of the MMA-co-PEGDMA copolymer with T_h = 349 and 365 K, which have been reported in ref 20. The obtained simulation results are c_T = 4.01 \times 10^{-8}, n = 4.64, and \theta' = 12.71 K. As shown in Figure 7, the simulation results of the free recovery strain as a function of temperature fit well with the experimental data obtained using the same parameters. The proposed model shown in eq 14 has therefore been verified by the experimental results and provides an effective approach to predict the free shape recovery of the MMA-co-PEGDMA copolymer.
Combining eq 3 with eq 14, the effects of the molecular weight and weight fraction on the free recovery strains are further investigated using M_w = 300 (400, 500, 600, or 700) and W_f = 0.8. As presented in Figure 8a, the obtained results show that the free recovery curves are gradually shifted to the higher temperature side, for example, to 309, 322, 345, 375.3, and 429.5 K with an increase in the molecular weight M_w from 300, 400, 500, 600, and 700 g/mol, respectively, at a given weight fraction of the PEGDMA monomer W_f = 0.8. On the other hand, the numerical results shown in Figure 8b reveal that the free recovery curves are gradually shifted to the higher temperature side to 324.2, 346.7, 362, 382, and 402.3 K with a decrease in the weight fraction of W_f = 1.0, 0.8, 0.6, 0.4, and 0.2, respectively. These simulation results clearly show the significant effects of both the molecular weight and the weight fraction of the PEGDMA monomer on the free recovery strain of the MMA-co-PEGDMA copolymer. The tailorable shape recovery behavior originates from the effects of the molecular weight and weight

### Table 3. Parameter Values Used in eq 12

<table>
<thead>
<tr>
<th>E_0 (MPa)</th>
<th>\alpha_p (g/cm³)</th>
<th>T_c (K)</th>
<th>K</th>
<th>T_{fi} (K)</th>
<th>K_f</th>
<th>\theta (K)</th>
<th>m_f</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.23</td>
<td>5.95 (4.55)</td>
<td>339.87</td>
<td>1.882</td>
<td>233.18</td>
<td>-58.72</td>
<td>15</td>
<td>23.21</td>
</tr>
</tbody>
</table>

\[
T = T_c(h) + \left(\frac{KT_{fi}(h) - K}{M_s} - T_c(h)\right)\frac{W_f}{1 + (K - 1)W_f} + \theta
\]

\[
E_s = E_n(1 - W_f) + \frac{3\alpha_pRW_f}{M_s} \left[ T_c(h) + \left(\frac{KT_{fi}(h) - K}{M_s} - T_c(h)\right)\frac{W_f}{1 + (K - 1)W_f} \right]
\]

\[
E(T) = (E_s - E_f) \exp\left(\frac{T}{T_h}\right) + E_f
\]

Figure 6b,c plot the numerical results of the storage moduli as a function of temperature for the SMP copolymer with the molecular weight of the PEGDMA monomer M_w = 550 and 750, respectively. The experimental data obtained from ref 22 of the tBA-co-PEGDMA are also collected and plotted for comparisons. At a given weight fraction and a given T_{fi} the numerical results obtained from the theoretical model fit well with the experimental results. The storage modulus is mainly determined by the molecular weight, weight fraction, and T_c of the PEGDMA monomer in the tBA-co-PEGDMA copolymer. In other words, the storage modulus of the SMP copolymer can be tailored and designed by adjusting the molecular weight, weight fraction, and T_c of the monomers inside. Taking tBA-co-PEGDMA, for example, this SMP copolymer is incorporated from two monomers, that is, PEGDMA and tBA monomers. There are definite differences in the T_c and thermomechanical properties between the PEGDMA and tBA monomers. With an increase in the molecular weight or weight fraction of the PEGDMA monomer, the T_c and thermomechanical properties of the tBA-co-PEGDMA copolymer are decreased. Therefore, the T_c and thermomechanical properties of the tBA-co-PEGDMA copolymer can be tailored and designed by adjusting the molecular weight and weight fraction of the PEGDMA monomer. Meanwhile, other types of monomers can also be selected, but not the PEGDMA monomer, to tailor and design the SMP copolymer based on the different T_c values and thermomechanical properties of the monomers.

### 3. Modeling of the Shape Transition Behavior

Based on the phase-transition theory, the volume fraction ratio of a frozen phase (\phi_1) is equal to the normalized unrecovered strain. Therefore, the constitutive relationship between the recovery strain (\varepsilon(T)) and the frozen phase \phi_1 can be written as follows
\[
\varepsilon(T)/\varepsilon_{\text{pre}} = 1 - \phi_1 = 1/(1 + c_T(T_h - T))^{n} \] (13)
where \phi_1 and n are material constants, T_h is the transition temperature, and \varepsilon_{\text{pre}} presents the pre-deformed strain. As is well-known, the phase-transition model is generally limited to cases with a small strain (<10%), wherein the nonlinearity of rubbery elasticity of a polymer is often ignored. It should be noted that the SMP presents a viscoelastic shape deformation with a strain larger than 10%. Here, the phase-transition model is employed to characterize the shape recovery behavior, where the strain of the SMP is larger than 10%. On the other hand, the phase-transition model should be combined with the viscoelasticity of the SMP to characterize its large deformation under tensile loading (e.g., the strain is larger than 10%).

The obtained simulation results are c_T = 4.01 \times 10^{-8}, n = 4.64, and \theta' = 12.71 K. As shown in Figure 7, the simulation results of the free recovery strain as a function of temperature fit well with the experimental data obtained using the same parameters. The proposed model shown in eq 14 has therefore been verified by the experimental results and provides an effective approach to predict the free shape recovery of the MMA-co-PEGDMA copolymer.
fraction on the $T_g$ of the SMP copolymer. With an increase in the $T_g$, the free recovery stress is induced at a higher temperature as shown in Figure 8. These simulation results verify that the proposed model in eq 14 provides an effective and critical approach to design the $T_g$ of the SMP copolymer to achieve its tailorably shape transition behavior.

To further investigate the mechanical recovery strength, it is necessary to study the shape recovery stress of the SMP copolymer. In certain applications, the recovery stress is often used to estimate the actuation capability of the shape memory polymers.35,36 According to eqs 11 and 14, the recovery stress as a function of the rubbery modulus ($E_r$) and $T_g$ can be written as follows

$$\sigma(T) = E(T) \cdot \varepsilon(T)$$

where $\varepsilon(T)$ is the strain, $E(T)$ is the modulus, and $\sigma(T)$ is the stress. The larger value of the recovery stress is obtained when the temperature is over the glass-transition temperature. This is mainly because of the increase of the degree of crosslinking in the SMP copolymer when the molecular weight of PEGDMA is decreased.

The parameters used in eq 15 are shown in Table 4.

Table 4. Parameter Values Used in eq 15

<table>
<thead>
<tr>
<th>$\varepsilon_{pre}$</th>
<th>$c_1$</th>
<th>$\theta'$ (K)</th>
<th>$n$</th>
<th>$E_r$ (MPa)</th>
<th>$E_g$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.014</td>
<td>5.01 x 10^{-6}</td>
<td>19</td>
<td>3.306</td>
<td>2000</td>
<td>1442.72</td>
</tr>
<tr>
<td>1.00</td>
<td>5.01 x 10^{-6}</td>
<td>19</td>
<td>3.306</td>
<td>2000</td>
<td>1442.72</td>
</tr>
</tbody>
</table>

Figure 9 clearly shows that the simulation curves fit well with the experimental data. When the temperature is within the phase-transition temperature region (e.g., from 310 to 355 K), the recovery stress is dramatically increased with respect to temperature, and a larger recovery stress of 10.2 MPa is achieved when the rubbery modulus of the SMP copolymer is 23 MPa. From the numerical analysis of the derivative of the recovery stress as a function of temperature, this value is quite small when the temperature is over the glass-transition temperature ($T_g = 349$ K), which results in insignificant changes of the recovery stress. The larger value of the recovery stress is obtained when the temperature is over the glass-transition temperature. This indicates the significant release of the stored mechanical energy, which is critically determined by the rubbery modulus. The recovery stress can be significantly improved by means of increasing the rubber modulus. Therefore, the proposed model is useful to characterize and predict the mechanical recovery strength of the SMP copolymer.

From the above analysis, the largest value of the mechanical recovery stress is determined by the rubber modulus. From eq 15, the recovery stress is also controlled by the glass-transition temperature $T_g$. As illustrated in Figures 1 and 2, both $T_g$ and $E_r$ are controlled by the molecular design (e.g., weight fraction of PEGDMA ($W_s$) and molecular weight of the PEGDMA monomer ($M_s$)). We further investigate the effects of two molecular design methods of the SMP copolymer on the tailorable recovery strength.

First, the weight fraction of PEGDMA is set as a constant ($W_s = 50\%$), but the molecular weight of the PEGDMA monomer is changed, for example, $M_s = 400, 500, 600$, and 700 as shown in Figure 10a. It is found that a lower value of the molecular weight of PEGDMA results in a higher recovery stress (from 338.4 K at $M_s = 400$ to 381.6 K at $M_s = 400$) and a higher value of recovery stress (from 33.6 MPa at $M_s = 700$ to 57.8 MPa at $M_s = 400$). This is mainly because of the increase of the degree of crosslinking in the SMP copolymer when the molecular weight of PEGDMA is decreased.

Next, we fix the molecular weight of the PEGDMA monomer as a constant ($M_s = 400$) and change the weight fraction of PEGDMA, for example, $W_s = 20, 40, 60$, and 80% as shown in Figure 10b. Results show that although the glass-transition temperature is decreased (e.g., from 401.2 K at $W_s = 20\%$ to...
363.2 K at \( W_s = 80\% \) with the increase of the weight fraction of PEGDMA in the SMP copolymer, the largest value of recovery stress is increased from 33.6 MPa at \( W_s = 20\% \) to 56.9 MPa at \( W_s = 80\% \).

Based on the above discussion, the recovery stress could be significantly changed when the SMP copolymer is in the rubbery state, and a larger value of recovery stress can be obtained with a lower value of the molecular weight of the PEGDMA monomer and a higher value of the weight fraction of PEGDMA.

From the obtained recovery stress and strain, it is possible to characterize the stored mechanical energy (\( W \)), which is the driving force of the SME in shape memory polymers.\(^42,43\) The stored mechanical energy can be obtained from the stress and strain parameters using the following equation

\[
W \equiv \int \sigma(T) \varepsilon \, d\varepsilon = \frac{1}{2} E(T) \varepsilon^2 = \frac{1}{2} \left( E_s - E_g \right) \exp \left\{ - \frac{T}{T_g} \right\} \, \varepsilon^2
\]

(16)

Figure 11 presents the numerical results of stored mechanical energy obtained from eq 17 at temperatures of \( T = 310 \) and 349 K.

363.2 K at \( W_s = 80\% \) with the increase of the weight fraction of PEGDMA in the SMP copolymer, the largest value of recovery stress is increased from 33.6 MPa at \( W_s = 20\% \) to 56.9 MPa at \( W_s = 80\% \).

Based on the above discussion, the recovery stress could be significantly changed when the SMP copolymer is in the rubbery state, and a larger value of recovery stress can be obtained with a lower value of the molecular weight of the PEGDMA monomer and a higher value of the weight fraction of PEGDMA.

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W = \int \sigma(T) \varepsilon \, d\varepsilon = \frac{1}{2} E(T) \varepsilon^2 = \frac{1}{2} \left( E_s - E_g \right) \exp \left\{ - \frac{T}{T_g} \right\} \, \varepsilon^2
\]

(16)

Figure 11 presents the numerical results of stored mechanical energy obtained from the eq 17 at temperatures of \( T = 310 \) and 349 K, respectively. It is found that the stored mechanical energy is gradually increased with an increase in the strain. As shown in Figure 11a, the stored mechanical energy is increased from 3550 to 11 671 J when the rubbery modulus is increased from 9.3 to 23 MPa, at a given strain of \( \varepsilon = 5.0 \) and \( T = 310 \) K. Meanwhile, it is increased from 1503 to 4885 J when the rubbery modulus is increased from 9.3 to 23 MPa, at a given strain of \( \varepsilon = 5.0 \) and \( T = 349 \) K, as revealed in Figure 11b. These simulation results clearly reveal that the higher rubbery modulus results in a higher stored mechanical energy. However, the stored mechanical energy is decreased from 11 671 to 4885 J with the temperature increased from 310 to 349 K for the SMP copolymer, and in this case, the rubbery modulus \( E_r = 23 \) MPa and strain \( \varepsilon = 5.0 \). That is to say, a higher temperature results in a lower stored mechanical energy.

As is well-known, shape recovery of the SMP copolymer is a stress relaxation process, which is ruled by the Eyring equation below its \( T_g \), whereas it is ruled by the WLF equation above its \( T_g \).\(^30\) The relaxation time will be significantly shortened when the polymer is heated to a high temperature because the stored mechanical energy can be quickly released.\(^19,30\)

As shown in eq 3, both the weight fraction of PEGDMA (\( W_s \)) and the molecular weight of the PEGDMA monomer (\( M_n \)) have shown significant effects on the glass-transition temperature. A multiple glass-transition process of SMP copolymers could be obtained by mixing different segments with different glass-transition temperatures, which can be controlled by the values of \( W_s \) and \( M_n \). Based on Boltzmann’s superposition principle and the series connection among different segments,\(^33\) the overall response of the recovery strain in multi-SMP copolymers is as follows

\[
\varepsilon = \sum_{i=1}^{n} \left[ \frac{\varepsilon_{pre}(i)}{1 + \varepsilon_{i} (T_{g}(i) + \theta' - T)^{n(i)}} \right]
\]

(17)

where \( n \) is the number of transition segments and the subscript \( i \) represents the \( i \)th transition segment. The simulation results of the segmental relaxation behavior of the multi-SMP copolymer are shown in Figure 12. The values of parameters used are listed in Tables 1 and 4.

4. CONCLUSIONS

In this study, a phenomenological model was formulated to explore the working mechanism and describe the unique
characteristics of the SMP copolymers with high mechanical recovery strengths and a tailorable shape transition behavior. The Fox–Flory equation and the rubber elasticity theory were used to investigate the thermomechanical behaviors of SMP copolymers. Effects of the $T_g$ molecular weight, and weight fraction of monomers on the mechanical recovery strength were systematically studied. Based on the phase-transition theory, effects of molecular structure characteristics on the shape transition behaviors were investigated. From the numerical analysis results using our proposed model, it can be concluded that this new model provides an effective design principle in the molecular scale, which is favorable to achieve high mechanical recovery strength (i.e., elastic modulus, recovery stress, and stored mechanical energy) and tailorable shape recovery behaviors of the SMP copolymers. Finally, experimental data have been employed to verify the proposed model, and the numerical results fit well with the experimental data. This study is expected to provide an essential and effective tool to understand the working mechanism and provide a theoretical strategy for the design of SMP copolymers with high mechanical recovery strength and a tailorable shape transition behavior.

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