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Selective entanglement coupling of nanoparticles in polymer nanocomposite with high shape recovery stress

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Abstract: Nanoparticles have been widely used to enhance mechanical properties of polymer matrix, however, the complex mechanisms of interfacial entanglements, coupled confinements and coordinative motions among the polymer macromolecules and nanoparticles have not been well understood. In this study, we develop a coupling model to describe the thermodynamic entanglements and confinement effects within nanoparticle reinforced shape memory polymer (SMP) nanocomposites. We found that thermodynamic relaxation of the SMP nanocomposite is determined by cooperative effects of sub-entanglement and topological entanglement of macromolecule chains, which selectively enhance the relaxation behaviors and enable a high recovery stress of SMP nanocomposites. Finally, the effectiveness of this model is demonstrated by applying it to predict the constitutive relationships and shape memory behaviors, and this fundamental approach can reveal toughening mechanisms of shape recovery strength in the SMP nanocomposites by nanoparticles.

Keywords: Polymer-matrix composites; topological entanglement; coupling model

1. Introduction

Shape-memory polymers (SMPs) are one of the key smart materials which can be programmed to change into a temporary shape and subsequently regain their permanent shapes under certain stimulus [1-5]. This phenomenon is originated from their intrinsically molecular features, which enable the SMPs with a good shape

memory effect (SME) [6]. In comparison with conventional shape memory alloys and ceramics, SMPs have received tremendous attention recently due to their large deformation strain, low density, designable and tunable properties [7]. They have potential applications in various fields, such as textiles [8], biomedical devices [9,10], sensors and actuators [11]. However, their relatively low recovery stresses, as low as 1-10 MPa, become a limiting factor in many practical applications in comparison with their metallic counterpart [11]. To overcome this drawback, various reinforcement fillers have been added inside to form SMP composites and achieve a good mechanical performance, and these fillers include carbon nanotube (CNT), carbon nanofiber, SiO₂ particle and nanoclay [12-15]. Many experimental results showed that the recovery strengths of the SMPs can be significantly increased due to the nano-sized effects of the nanoparticle fillers [16]. However, the interfacial reactions, coupled confinements and coordinative motions of nanoparticles within the polymer matrix have not been fully understood [17,18]. A micromechanical model was previously utilized to study the interphase influences on the mechanical behavior of SMP nanocomposite, and the environmental conditions were considered in the modelling process [19,20]. Monte Carlo simulation was also used to study the percolation behavior of SMP nanocomposite reinforced by carbon black [21].

Based on the internal entanglement model [22], both the sub-entanglement of polymer-to-polymer chains and topological entanglement of polymer-to-nanoparticle determine the coupling confinements and coordinative motions within the SMP nanocomposite as shown in Fig. 1. They both play essential roles to determine the relaxation and shape recovery behaviors of the SMP nanocomposites. Sub-entanglement is attributed to the weak interactions between adjacent segments in macromolecule chains [23]. While the topological entanglement, of which the coupling motion is geometrically restricted, is originated from the interactions of macromolecule chains and nanoparticles [24,25]. The coupling effect between sub-entanglement and topological entanglement is expected to play a cooperative role in determining the recovery strength of the SMP nanocomposites, resulting from the coupling confinement, coordinative motion and thermodynamic relaxation of

macromolecule chains. Meanwhile, the SME is achieved by the thermodynamic phase transition and relaxation of macromolecule chains.

In this study, a coupling model was proposed to describe the thermodynamic entanglements and confinements of nanoparticle reinforced SMP nanocomposites with high recovery stress. An extended Adam-Gibbs model [26] was initially formulated based on the confinement entropy, interaction entropy and mixing entropy [27-29]. Then the constitutive relationships among glass transition temperature (T_g), recovery stress, stored strain and selective entanglement effects were established to characterize and predict thermodynamic relaxation and shape recovery behavior of the SMP nanocomposite. Finally, the effectiveness of the newly proposed models was validated using the experimental results reported in literature [14,30,31].

Fig. 1. Illustration of sub-entanglement and topological entanglement of macromolecule chains with nanoparticles in SMP nanocomposite.

2. Thermodynamic model of entanglement coupling

T_g is an essential parameter to determine the thermodynamic relaxation and shape recovery behavior of SMP. Here, a molecular thermodynamics model [27] is initially used to predict the T_g of SMP nanocomposite based on the configurational entropy model [28] and Flory-Huggins theory [29]. It has the following expression,

$$\ln \frac{T_g}{T_{g0}} = \omega \left[\left(1 - \gamma_i \ln \left(\frac{m-1}{e} \right) \right) \left(\frac{\phi_p}{r_p} \ln \phi_p + \frac{\phi_n}{r_n} \ln \phi_n \right) + \frac{\phi_n}{r_n} \left(\ln \phi_n + \tanh \left(\frac{\sigma_n}{\sigma_p} - 1 \right) \frac{4\phi_n - 3\phi_n^2}{\phi_p^2} \right) \right] \quad (1)$$

where ω is the fitting parameter, T_{g0} is the glass transition temperature of original amorphous polymer, γ_i is defined as a proportionality constant representing the specific interactions between polymer matrix and nanoparticle, m is the lattice

coordination number, ϕ_p and ϕ_n are the weight concentrations of polymer and nanoparticle, respectively. r_p and r_n are the volume ratios of polymer and nanoparticle [32], respectively. σ_p and σ_n are the diameter of polymer and nanoparticle based on the quasi-lattice theory [32], respectively. Meanwhile, it is noteworthy that equation (1) is not suitable to predict the thermodynamic behavior of SMP nanocomposite with hybrid nanoparticle system [33,34], since this model cannot capture the synergistic enhancement characteristics [35,36] among different kinds of nanoparticles. These works have been presented in Fig. S1.

Fig. 2 plots the analytical results of T_g based on equation (1) as a function of weight concentration of nanoparticle (ϕ_n). All the parameters used in equation (1) are listed in Table 1. Six groups of experimental data of polymer nanocomposites [14,19,30,31,37,38] have been used to compare the analytical results. As presented in Fig. 2(a), the T_g is gradually decreased from 338.4 K to 333.2 K, from 319.3 K to 311.2 K and from 231.2 K to 227.1 K for the nanocomposites of PLAE/silica (PLAE: polylactide), PVA/Ag (PVA: polyvinyl alcohol) and PS/silica (PS: polystyrene), respectively, where the fitting parameter $\omega > 0$. On the other hand, as shown in Fig. 2(b), the T_g is increased from 410.0 K to 442.0 K, from 293.8 K to 310.3 K and from 342.5 K to 362.5 K for the nanocomposites of epoxy/silica, PU/GNPs (PU: polyurethane, GNPs: graphene nanoplatelets) and PU/CNTs (CNTs: carbon nanotubes), respectively, where the fitting parameter $\omega < 0$. Comparisons of analytical and experimental results show that the fitting parameter (ω) plays a critical role to determine the T_g of the nanocomposite. Based on these results, we can assume that if the fitting parameter $\omega > 0$, the nanoparticle will work as a plasticizer to promote the relaxation motions of macromolecule chains, and result in the T_g of nanocomposite decreased. Whereas if the fitting parameter $\omega < 0$, the nanoparticle will have a strong interaction with the macromolecule chains and restricts the

relaxation motions, which will result in an increased T_g value of the nanocomposite.

Table 1. Values of parameters used in equation (1).

Nanocomposite	ω	$1-\gamma_i \ln((m-1)/e)$	r_p/r_n	σ_n/σ_p	$T_{g0}(K)$
PLAE/silica	4×10^{-4}	-0.49	1.1×10^5	0.97	338.4
PS/silica	5×10^{-4}	-0.29	0.9×10^5	0.76	231.2
PVA/Ag	2×10^{-4}	0.02	3.5×10^6	0.98	317.8
Epoxy/silica	-1.4×10^{-3}	-2.97	5.6×10^5	0.89	410.0
PU/GNPs	-1.2×10^{-3}	-2.89	2.1×10^5	0.89	293.8
PU/CNTs	-3.1×10^{-3}	-2.78	1.2×10^5	0.87	342.5

Fig. 2. Comparisons of analytical results and experimental data [14,19,30,31,37,38] for the T_g with respect to weight concentration of nanoparticles for different types of polymer nanocomposites.

As discussed in Ref. [27], the topological confinement entropy (S_c) and specific interaction entropy (S_i) of nanoparticles are the major contributions to the decrease in relaxation motions of macromolecule chains, while the mixing entropy (S_{mix}) will increase their relaxation motions. By introducing the nanoparticles, these three entropy expressions can be linked using the following forms [27],

$$\begin{cases} S_c = -R \frac{\phi_n}{r_n} \left[\ln \phi_n + \tanh \left(\frac{\sigma_n}{\sigma_p} - 1 \right) \frac{4\phi_n - 3\phi_n^2}{\phi_p^2} \right] \\ S_i = R \gamma_i \ln \left(\frac{m-1}{e} \right) \left(\frac{\phi_p}{r_p} \ln \phi_p + \frac{\phi_n}{r_n} \ln \phi_n \right) \\ S_{mix} = -R \left(\frac{\phi_p}{r_p} \ln \phi_p + \frac{\phi_n}{r_n} \ln \phi_n \right) \end{cases} \quad (2)$$

where R is the gas constant.

Therefore, the change in configurational entropy (ΔS) per mole macromolecule chain has the following form as a function of weight concentration of nanoparticle,

$$\Delta S = S_c + S_i + S_{mix} = -R \left(\frac{\phi_n}{r_n} \left(\ln \phi_n + \tanh \left(\frac{\sigma_n}{\sigma_p} - 1 \right) \frac{4\phi_n - 3\phi_n^2}{\phi_p^2} \right) + \left(1 - \gamma_{spe} \ln \left(\frac{m-1}{e} \right) \right) \left(\frac{\phi_p}{r_p} \ln \phi_p + \frac{\phi_n}{r_n} \ln \phi_n \right) \right) \quad (3)$$

The Adam-Gibbs theory [26] is then employed to characterize the thermodynamic relaxation of polymer nanocomposites.

$$S_c(T) = s^* \frac{T^*}{T^* - T_0} \frac{T - T_0}{T} \quad (4)$$

where T_0 is the low-limit temperature, and T^* is the high-limit temperature where the configurational entropy reaches to the maximum value (s^*).

The thermodynamic model has been fundamentally introduced for the configurational entropy of polymer nanocomposite using the Adam-Gibbs equation [26]. A constitutive relationship between configurational entropy and weight fraction of nanoparticle is obtained by substituting equation (3) into (4):

$$S_c(T, \phi_n) = \Delta S + S_c(T) = s^* \frac{T^*}{T^* - T_0} \frac{T - T_0}{T} - R \left(\frac{\phi_n}{r_n} \left(\ln \phi_n + \tanh \left(\frac{\sigma_n}{\sigma_p} - 1 \right) \frac{4\phi_n - 3\phi_n^2}{\phi_p^2} \right) + \left(1 - \gamma_{spe} \ln \left(\frac{m-1}{e} \right) \right) \left(\frac{\phi_p}{r_p} \ln \phi_p + \frac{\phi_n}{r_n} \ln \phi_n \right) \right) \quad (5)$$

With the increase of temperature, the domain size (z , e.g., the number of conformers in one domain) is decreased [39]. The domain size (z) has been introduced in literature with a function as [26],

$$z = s^* / S_c \quad (6)$$

In combination of equations (5) and (6), we can the domain size (z) as functions of temperature (T), diameter (σ_n) and weight concentration of nanoparticles (ϕ_n),

$$z(T, \phi_n) = \frac{T^* - T_0}{T^*} \frac{T}{T - T_0} - \frac{s^*}{R} \left(\frac{\phi_n}{r_n} \left(\ln \phi_n + \tanh \left(\frac{\sigma_n}{\sigma_p} - 1 \right) \frac{4\phi_n - 3\phi_n^2}{\phi_p^2} \right) + \left(1 - \gamma_{spe} \ln \left(\frac{m-1}{e} \right) \right) \left(\frac{\phi_p}{r_p} \ln \phi_p + \frac{\phi_n}{r_n} \ln \phi_n \right) \right) \quad (7)$$

Additionally, the relaxation time (τ) has a relationship with domain size (z) and can be expressed by the following equation [26],

$$\ln(\tau / \tau_o) = \frac{\Delta\mu}{R} \left(\frac{z}{T} - \frac{1}{T^*} \right) \quad (8)$$

where $\Delta\mu$ is the active energy per macromolecule chain to be relaxed independently and τ_o is the relaxation time at a temperature of T^* .

Substituting equation (7) into (8), we can obtain,

$$\ln\left(\frac{\tau}{\tau_o}\right) = \frac{\Delta\mu}{R} \left[\frac{T^* - T_0}{T^*(T - T_0)} - \frac{s^*}{RT} / \left(\frac{\phi_n}{r_n} \left(\ln \phi_n + \tanh\left(\frac{\sigma_n}{\sigma_p} - 1\right) \frac{4\phi_n - 3\phi_n^2}{\phi_p^2} \right) + \left(1 - \gamma_{spe} \ln\left(\frac{m-1}{e}\right) \right) \left(\frac{\phi_p}{r_p} \ln \phi_p + \frac{\phi_n}{r_n} \ln \phi_n \right) \right) - \frac{1}{T^*} \right] \quad (9)$$

The relationship among the recovery stress (σ), relaxation time and temperature can be obtained using the Kohlrausch-Williams-Watts (KWW) equation [40],

$$\sigma = \sigma_0 \exp\left[-(t / \tau(T))^\beta\right] \quad (10)$$

where σ_0 is the initial recovery stress at a relaxation time of $t=0$, and β ($\beta=0.226$) is the stretching constant [40].

Fig. 3. Comparisons between the analytical results and experimental data [14] of the recovery stress with respect to relaxation time, at a temperature of $T=333\text{ K}$.

Based on the equations (9) and (10), analytical results of recovery stress as a function of relaxation time for the PLA0/silica nanocomposites incorporated of 0%, 1%

and 3% weight concentration of silica are obtained, as shown in Fig. 3. With an increase in the weight concentration of silica, the relaxation time (τ) is gradually decreased from 25 min, 20 min to 18 min. At a temperature $T=333\text{ K}$ and relaxation time $t=23.7\text{ min}$, the recovery stress is increased from 0.27 MPa, 0.35 MPa to 0.44 MPa with an increase in the weight concentration of silica from 0%, 1% to 3%, respectively. These analytical results fit well with the experimental data [14] of PLAE/silica nanocomposites. Furthermore, the constitutive relationship of recovery stress and relaxation time has also been well predicted by the proposed model.

3. Thermodynamic behavior

Meanwhile, storage modulus is another important parameter to characterize the thermodynamics of SMP nanocomposite, it is critical to investigate the working mechanism of these thermodynamic behaviors. A statistical model [41] is employed to model the constitutive relationship of storage modulus ($E_m(T)$) with respect to the transition temperatures, which has the following form,

$$E_m(T) = (E_1 - E_2) \exp\left(-\left(\frac{T}{T_\beta}\right)^{m_1}\right) + (E_2 - E_3) \exp\left(-\left(\frac{T}{T_g}\right)^{m_2}\right) + E_3 \exp\left(-\left(\frac{T}{T_f}\right)^{m_3}\right) \quad (11)$$

where E_1 , E_2 and E_3 are the moduli of the polymer matrix for β transition, glass transition and flow transition, respectively; T_β , T_g and T_f are the temperatures for the β transition, glass transition and melting transition, respectively. The parameters m_i ($i=1, 2, 3$) are the Weibull moduli [41].

For SMP, the SME is originated from the T_g , which is far from the melting temperature. Equation (11) can be then rewritten as,

$$E_m(T) = (E_1 - E_2) \exp\left(-\left(\frac{T}{T_\beta}\right)^{m_1}\right) + (E_2 - E_3) \exp\left(-\left(\frac{T}{T_g}\right)^{m_2}\right) + E_3 \quad (12)$$

By substituting equation (1) into (12), the storage modulus can be expressed as,

$$E_m(T) = (E_1 - E_2) \exp \left(- \left(\frac{T}{T_\beta} \right)^{m_1} \right) + (E_2 - E_3) \cdot \exp \left(- \left(\frac{T}{T_{g0}} / \exp \left\{ \omega \left[\left(1 - \gamma_i \ln \left(\frac{m-1}{e} \right) \right) \left(\frac{\phi_p}{r_p} \ln \phi_p + \frac{\phi_n}{r_n} \ln \phi_n \right) \right] \right\} \right)^{m_2} \right) + E_3 \quad (13)$$

where σ_n and ϕ_n are the diameter and weight concentration of nanoparticles, respectively.

According to the Halpin-Tsai rule [42], the storage modulus ($E(T)$) of nanocomposites can be then obtained,

$$E(T) = E_m(T) \left(1 + f \phi_n \frac{E_n / E_m(T) - 1}{E_n / E_m(T) + f} \right) / \left(1 - \frac{\phi_n (E_n / E_m(T) - 1)}{E_n / E_m(T) + f} \right) \quad (14)$$

where E_n is the modulus of nanoparticle, f ($f = \exp(a - b\phi_n)$) function is used to correct the effect of nanoparticle on the modulus of nanocomposite.

To verify equation (14), the analytical results of storage moduli as a function of temperature for the PLA/E/silica nanocomposites have been plotted and then compared with the corresponding experimental results reported in literature [14]. Values of all the parameters used in the calculations using equation (14) are presented in Table 2. Fig. 4 plots the analytical results of storage moduli, which are in good agreements with the experimental ones. As shown in Figs. 4(a), 4(b) and 4(c), the storage modulus is initially increased from 1049 MPa, 1151 MPa to 1193 MPa with an increase in the weight concentration of nanoparticle (ϕ_n) from 0%, 1% to 3%. However, it turns to be decreased from 1193 MPa to 825 MPa with a further increase in the ϕ_n from 3% to 5% at 290 K, as shown in Figs. 4(c) and 4(d). These analytical and experimental results indicate that the nanoparticles have strong interactions with the macromolecule chains, which restrict their relaxation motions due to a strong topological entanglement. This has been revealed from the results when the weight concentration of nanoparticle is increased from 0% to 3%. On the other hand, the

topological entanglement of nanoparticle and macromolecular chain is then decreased with a further increase in concentration of nanoparticle from 3% to 5%, resulting in relaxation motions accelerated. These analytical and experimental results are following the percolation rule of nanoparticles in the nanocomposites [21].

Table 2. Values of parameters used in equations (13) and (14) for the PLAE nanocomposites with various weight concentrations of silica.

$E_1(\text{MPa})$	$E_2(\text{MPa})$	$E_3(\text{MPa})$	$E_n(\text{GPa})$	$T_\beta(\text{K})$	a	b	m_1	m_2
1135.1	135.2	19.8	10.2	316.9	2.12	29.93	26.2	45.4

Fig. 4. Comparisons of storage modulus as a function of temperature between the experimental data [14] and analytical results using equation (14). (a) for PLAE0; (b) for PLAE1; (c) for PLAE3 and (d) for PLAE5.

4. Constitutive relationship of recovery stress and stretch ratio

4.1 Below and close to the T_g

For the amorphous SMPs and their nanocomposites, the SMEs are originated from the glass transitions and thermodynamic relaxations of macromolecule chains, undergoing a remarkable change in the recovery stress [7]. A high recovery stress enables the SMP with a good actuation capability [43]. Therefore, many previous studies focused to improve the recovery stress of SMP by means of composite and

nanocomposite technologies [18]. Therefore, it is necessary to propose a theoretical model to explore the working mechanism of the SMP nanocomposites.

For SMP nanocomposites, there is a coupling effect between the sub-entanglement and topological entanglement. Under an external stress, both the sub-entanglement and topological entanglement are changed. We can assume that there is a total number N of the macromolecule chains, in which N_{pp} of them are in sub-entanglement states, and N_{np} macromolecule chains are in topological entanglement state. An expression for N , N_{pp} and N_{np} can thus be obtained,

$$N = N_{pp} + N_{np} \quad (15)$$

Stress-induced elastic free energy (ΔF_{el}) of SMP nanocomposite is written as [44],

$$\Delta F_{el} = \frac{1}{2} NRT (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 - \ln(\lambda_1 \lambda_2 \lambda_3)) \quad (16)$$

where $\lambda_j = l_j / l_{j0}$, ($j=1,2,3$) is the elastic stretch ratio in three directions, l and l_0 are the initial and final lengths of a cubic nanocomposite sample.

During the elastic deformation process, the cubic nanocomposite sample is under a uniaxial tensile loading and the volume is kept a constant, therefore,

$$\lambda_2 = \lambda_3 = 1/\sqrt{\lambda_1} \quad (17)$$

where $\lambda_1 = \lambda$ is the stretch ratio along the tensile stress, $\lambda_2 = \lambda_3$ and $\lambda_1 \lambda_2 \lambda_3 = 1$.

By substituting equation (17) into (16), the elastic free energy (ΔF_{el}) in response to uniaxial stress can be expressed as,

$$\Delta F_{el} = \frac{1}{2} NRT \left(\lambda^2 + \frac{2}{\lambda} - 3 - \ln \lambda \right) \quad (18)$$

With a further increase in tensile stress, a certain amount of mechanical energy is necessary to resist the sub-entanglement of macromolecule chains [44],

$$\Delta W = \begin{cases} \Delta F_{el}, & 0 \leq \lambda \leq \lambda_i \\ \Delta F_{el} + N_{pp} \xi, & \lambda \geq \lambda_i \end{cases} \quad (19)$$

where ΔW is the mechanical energy, λ_i is the maximum stretch ratio of elastic deformation and ξ is the activation energy of sub-entanglement.

As discussed in Ref. [24], the number of sub-entanglement (N_{pp}) is determined by both the temperature and stretch ratio, which has the following expression,

$$N_{pp}(\lambda, T) = N_{pp}(T) \exp(-\kappa(\lambda_p - 1)) = N_{pp}(T) \exp(-\kappa(\lambda - \lambda_i)) \quad (20)$$

where κ is the constant, $(\lambda_p - 1)$ is the equivalent plastic stretch ratio, which has a function of $\exp(-\kappa(\lambda - \lambda_i)) = 1$ when $\lambda \leq \lambda_i$.

Based on Ref. [23], the $N_{pp}(T)$ can be written as,

$$N_{pp}(T) = N_{pp}(T_g) \exp\left(d\left(\frac{1}{T} - \frac{1}{T_g}\right)\right) \quad (T < T_g) \quad (21)$$

where d is the constant and $N_{pp}(T_g)$ is the number of sub-entanglement at T_g .

By substituting equation (21) into (20), a constitutive relationship among the number of sub-entanglement (N_{pp}), temperature (T) and stretch ratio (λ_i) can be described using the following equation,

$$N_{pp}(\lambda, T) = N_{pp}(T_g) \exp\left(d\left(\frac{1}{T} - \frac{1}{T_g}\right) - \kappa(\lambda - \lambda_i)\right) \quad (22)$$

In combination of equations (15) and (22), the total number of entanglement ($N(T)$) as functions of temperature (T) and stretch ratio (λ) can be obtained,

$$N(T) = N_{pp}(T_g) \exp\left(d\left(\frac{1}{T} - \frac{1}{T_g}\right) - \kappa(\lambda - \lambda_i)\right) + N_{np} \quad (23)$$

By substituting equations (18) and (23) into (19), the mechanical energy (ΔW) can be obtained,

$$\begin{aligned} \Delta W = & \frac{RT}{2} \left(N_{pp}(T_g) \exp\left(d\left(\frac{1}{T} - \frac{1}{T_g}\right) - \kappa(\lambda - \lambda_i)\right) + N_{np} \right) \left(\lambda^2 + \frac{2}{\lambda} - 3 \right) \\ & + \xi N_{pp}(T_g) \exp\left(d\left(\frac{1}{T} - \frac{1}{T_g}\right)\right) (1 - \exp(-\kappa(\lambda - \lambda_i))) \end{aligned} \quad (24)$$

The internal force (f) can be further derived as,

$$f = \left(\frac{\partial \Delta W}{\partial l} \right)_{T,V} = \left(\frac{\partial \Delta W}{\partial \lambda} \right)_{T,V} \left(\frac{\partial \lambda}{\partial l} \right)_{T,V} = \frac{1}{l_0} \left(\frac{\partial \Delta W}{\partial \lambda} \right)_{T,V} \quad (25)$$

The tensile stress (σ) can be obtained using,

$$\sigma = \left(\left(\frac{\partial \Delta W}{\partial \lambda} \right)_{T,V} \right) / V_0 \quad (26)$$

By substituting equation (24) into (26), the constitutive relationship between the tensile stress (σ) and stretch ratio (λ) below T_g can be obtained,

$$\sigma = \frac{RT}{V_0} \left(N_{pp}(T_g) \exp \left(d \left(\frac{1}{T} - \frac{1}{T_g} \right) - \kappa(\lambda - \lambda_i) \right) + N_{np} \right) \left(\lambda - \frac{1}{\lambda^2} \right) + \frac{\kappa N_{pp}(T_g)}{V_0} \exp \left(d \left(\frac{1}{T} - \frac{1}{T_g} \right) - \kappa(\lambda - \lambda_i) \right) \left(\xi - \frac{RT}{2} \left(\lambda^2 + \frac{2}{\lambda} - 3 \right) \right) \quad (27)$$

Table 3. Values of parameters used in equation (27) for PLAE/silica nanocomposites.

Sample	$T_g(K)$	$N_{pp}(T_g)$	N_{np}	λ_i	$T_g(K)$	ζ	$V_0(cm^3)$	κ	d
PLAE0	338.4	5	0	1.03	338.4	262.4	1479	1.6	3.7
PLAE1	335.6	4.05	0.59	1.06	231.2	312.0			
PLAE3	334.8	3.1	1.35	1.07	317.8	457.2			
PLAE5	332.9	2.8	1.47	1.08	342.5	725.4

Fig. 5. Analytical and experimental results [14] of recovery stress with respect to stretch ratio of PLAE nanocomposites with various weight concentrations of silica.

To verify the proposed model of equation (27), the analytical results of mechanical stress as a function of stretch ratio for the PLAE/silica nanocomposites were obtained, and plotted in Fig. 5. The parameters used in the equation (27) are listed in Table 3. Experimental data of PLAE/silica nanocomposites reported in Ref. [14] have been

employed for comparisons. At $T=313\text{ K}$ (where $T < T_g$) and stretch ratio of $\lambda = 1.275$, the recovery stress of SMP nanocomposite is gradually increased from 3.1 MPa, 4.1 MPa, 4.3 MPa to 4.9 MPa with an increase in weight concentration of nanoparticle (ϕ_n) from 0%, 1%, 3% to 5%. These analytical results reveal that the recovery stress is significantly increased due to the topological entanglement between macromolecule chains and nanoparticles, whereas the sub-entanglement is depressed with an increase in the weight concentration of nanoparticles in the nanocomposite.

As shown in Fig. 6(a), it is found that the stress is dramatically increased from 2.1 MPa to 5.1 MPa (an increase rate of 242%) as the number of topological entanglement (N_{np}) is increased from 0.5 to 1.5, at a given constant of $N=N_{pp}+N_{np}=5$, $T=313\text{ K}$ and $\lambda=2.0$. Meanwhile, the maximum yield stress is also increased from 5.0 MPa to 5.4 MPa. Effect of temperature on recovery stress has further been obtained as shown in Fig. 6(b). Within the whole temperature range, the analytical results reveal that all the recovery stress values are increased with an increase in number of topological entanglements. At $T=330\text{ K}$ (near to $T_g=333\text{ K}$), the recovery stress is increased from 1.0 MPa to 2.8 MPa (an increase rate of 280%), because the number of topological entanglement (N_{np}) is increased from 0.5 to 1.5.

Fig. 6. Analytical results of the recovery stress with respect to the number of topological entanglement, at a given number of topological entanglement of $N_{np}=0.5$, 0.75, 1, 1.25, 1.5 mol/L and $N_{np} + N_{pp} = 5$ mol/L. (a) For stress and stretch ratio; (b)

For stress and temperature.

4.2 Above the T_g

At the temperature above T_g , the thermodynamic relaxation of SMP nanocomposite is governed by Williams-Landel-Ferry (WLF) equation [45],

$$\ln \alpha_T(T) = -\frac{C_1(T-T_g)}{C_2 + (T-T_g)} \quad (28)$$

where $\alpha_T(T)$ is the time-temperature shift factor, C_1 and C_2 are material constants.

Here, the numbers of sub-entanglement (N_{pp}) and topological entanglement (N_{np}) can be expressed as a function of temperature:

$$\begin{cases} N_{pp}(T) = N_{pp}(T_g) \exp\left(-\frac{C_1^{pp}(T-T_g)}{C_2^{pp} + (T-T_g)}\right) & (T \geq T_g) \\ N_{np}(T) = N_{np}(T_g) \exp\left(-\frac{C_1^{np}(T-T_g)}{C_2^{np} + (T-T_g)}\right) & (T \geq T_g) \end{cases} \quad (29)$$

By substituting equation (29) into (20), the total number of entanglements (N) as functions of temperature (T) and stretch ratio (λ) can be obtained as,

$$N = N_{pp}(T_g) \exp\left(\frac{-C_1^{pp}(T-T_g)}{C_2^{pp} + (T-T_g)} - \kappa(\lambda - \lambda_i)\right) + N_{np}(T_g) \exp\left(\frac{-C_1^{np}(T-T_g)}{C_2^{np} + (T-T_g)}\right) \quad (30)$$

By substituting equations (18) and (30) into (19), the mechanical energy (ΔW) can be obtained using the following form,

$$\begin{aligned} \Delta W = \frac{RT}{2} & \left(N_{pp}(T_g) \exp\left(\frac{-C_1^{pp}(T-T_g)}{C_2^{pp} + (T-T_g)} - \kappa(\lambda - \lambda_i)\right) + N_{np}(T_g) \exp\left(\frac{-C_1^{np}(T-T_g)}{C_2^{np} + (T-T_g)}\right) \right) \\ & \left(\lambda^2 + \frac{2}{\lambda} - 3 \right) + \xi N_{pp}(T_g) (1 - \exp(-\kappa(\lambda - \lambda_i))) \exp\left(-\frac{C_1^{pp}(T-T_g)}{C_2^{pp} + (T-T_g)}\right) \end{aligned} \quad (31)$$

In combination of equations (26) and (31), the relationship between recovery stress (σ) and stretch ratio (λ) can be expressed as,

$$\begin{aligned} \sigma = \frac{RT}{V_0} & \left(N_{pp}(T_g) \exp\left(\frac{-C_1^{pp}(T-T_g)}{C_2^{pp} + (T-T_g)} - \kappa(\lambda - \lambda_i)\right) + N_{np}(T_g) \exp\left(\frac{-C_1^{np}(T-T_g)}{C_2^{np} + (T-T_g)}\right) \right) \\ & \left(\lambda - \frac{1}{\lambda^2} \right) + \frac{\kappa N_{pp}(T_g)}{V_0} \exp\left(\frac{-C_1^{pp}(T-T_g)}{C_2^{pp} + (T-T_g)} - \kappa(\lambda - \lambda_i)\right) \left(\xi - \frac{RT}{2} \left(\lambda^2 + \frac{2}{\lambda} - 3 \right) \right) \end{aligned} \quad (32)$$

To verify equation (32), the analytical results of recovery stress as a function of

stretch ratio have been obtained and compared with the experimental results of TPI/GO (TPI: trans-1,4-polyisoprene, GO: graphene oxide) SMP nanocomposites reported in literature [30], where the temperature is above their T_g values. Values of the parameters used in equation (32) are presented in Table 4. As shown in Fig. 7(a), these analytical results values are in good agreements with the experimental ones. The recovery stress is increased from 0.9 MPa to 1.1 MPa with an increase in the weight concentration of nanoparticles (ϕ_n) from 0.6% to 0.9%, at a constant value of stretch ratio $\lambda=3.0$. Meanwhile, the effect of temperature on the recovery stress has been plotted in Fig. 7(b). The recovery stress is significantly increased from 1.1 MPa to 3.4 MPa with a decrease in temperature from 341 K to 321 K, at the weight concentration of nanoparticle $\phi_n=0.9\%$. On the other hand, the effect of number of topological entanglement ($N_{np}(T_g)$) on recovery stress has also been studies and the results are plotted in Fig. 7(b). The recovery stress is gradually increased from 0.26 MPa to 0.57 MPa with an increase in $N_{np}(T_g)$ from 3 mol/L to 7mol/L. These analytical results verify that the topological entanglement is helpful to enhance the recovery stress of SMP nanocomposites.

Fig. 7. (a) Comparison between analytical results from equation (32) and the experimental data [30] for the recovery stress with respect to stretch ratio above T_g . (b) Analytical results of recovery stress as functions of temperature and stretch ratio, at given number of topological entanglement of $N_{np}=3, 4, 5, 6$ and 7mol/L.

Table 4. Values of parameters used in equation (32) for the TPI/GO nanocomposites.

$T(K)$	$\phi_n(\%)$	λ_i	$N_{np}(T_g)$	C_1^{pp}	C_2^{pp}	$N_{pp}(T_g)$	C_1^{np}	C_2^{np}	$V_0(cm^3)$	κ
321K	0.6	1.09	3.47	1.3	78.6	0.039	3.1	73.9	444.8	-0.6
	0.9	1.13	3.91							
341K	0.6	1.19	3.47							
	0.9	1.21	3.91							

4.3. Modelling of shape recovery behavior

Based on the phase transition theory [46,47], the phase evolution function (ϕ_f) is generally used to characterize the recovery strain and can be written as,

$$\phi_f(T) = \frac{\varepsilon_s(T) - \varepsilon_r}{\varepsilon_{pre} - \varepsilon_r} = \left[1 - \exp\left(-\frac{\Delta H(T)}{RT}\right) \right]^{\frac{\Delta t}{\tau_{ref}}} \quad (33)$$

where ε_s is the stored strain at temperature T , ε_{pre} is the pre-stretched strain, ε_r is the residual strain, $\Delta H(T)$ is the activation energy per mole of macromolecule chain, τ_{ref} is the relaxation time and Δt is the observation time.

Based on the Adam-Gibbs theory [22], the activation energy ($\Delta H(T)$) of macromolecule chain can be obtained using domain size ($z(T, \phi_n)$) and chemical potential ($\Delta\mu$),

$$\Delta H(T, \phi_n) = z(T, \phi_n) \Delta\mu \quad (34)$$

By substituting equation (34) into (33), the phase evolution factor ($\phi_f(T)$) as functions of temperature and weight concentration of nanoparticles can be obtained,

$$\phi_f(T) = \left\{ 1 - \exp \left\{ - \left[\frac{T^* - T_0}{T^*} \frac{T}{T - T_0} - \frac{s^*}{R} \frac{r_n}{\phi_n} \left[\ln \phi_n + \tanh \left(\frac{\sigma_n}{\sigma_p} - 1 \right) \frac{4\phi_n - 3\phi_n^2}{\phi_p^2} \right] \right] \Delta\mu / (RT) \right\} \right\}^{\frac{\Delta t}{\tau_{ref}}} \quad (35)$$

To verify the equation (35), we compared the analytical results of stored strains with those of the experimental data obtained from the PU/GNPs SMP nanocomposites

[31]. Values of parameters used in equation (35) have been listed in Table 5. As revealed from Fig. 8(a), the analytical results fit well with the experimental ones for the stored strains as a function of relaxation time, for the PU/GNPs nanocomposites with a variety of weight concentrations of $\phi_n=0\%$, 0.1%, 0.25% and 0.5%. With an increase in temperature from 263 K to 343 K, the stored strain is gradually decreased until 0%. Furthermore, the effect of diameter ratio of nanoparticle to macromolecule chain on the stored strain has been characterized and the results are plotted in Fig. 8(b). With an increase in diameter ratio from 0.5 to 0.9, the release rate of the stored strain becomes slow. These analytical results reveal that the smaller size of nanoparticle and lower value of diameter ratio both result in a faster release of stored strain of SMP nanocomposite. Therefore, the size effect of nanoparticle on the SME of SMP nanocomposite can be explained using our newly proposed model.

Table 5. Value of parameters used in equation (35).

Nanocomposite	$T_g(K)$	$\varepsilon_{pre}(\%)$	$\varepsilon_r(\%)$	$\tau_{ref}(\text{min})$	s^*	$T_0(K)$	$\Delta\mu(KJ / mol)$
PU0	294.2	45.4	6.6	7.2	9.9	262.6	533.07
PU0.1	306.6	82.4	10.8	10.1			
PU0.25	308.5	32	3.7	6.8			
PU0.5	312.2	58.19	8.3	9.3

Fig. 8. (a) Comparisons between analytical results from equation (35) and the experimental data [31] for the stored strains (ε_s) with respect to the relaxation time, at a given weight concentration of nanoparticle of $\phi_n=0\%$, 0.1%, 0.25% and 0.5%. (b) Analytical results of the stored strains with respect to relaxation time at a given

diameter ratios of $\sigma_n / \sigma_p = 0.5, 0.6, 0.7, 0.8$ and 0.9 .

4.4 Modelling of shape fixity behavior

Shape fixity ratio (R_f) is also a critical factor in modelling the shape memory behavior of SMP nanocomposites. In the programming progress, SMP nanocomposite is initially heated above the T_g and deformed under the external force (σ). It is then cooled back to the temperature (T_l) below the T_g , enabling it with a maximum value of programming strain of ($\varepsilon_{\max}$) while the external force is removed, where it has a stored strain (ε_s). As discussed by Yu et.al [48], the shape fixity ratio (R_f) is calculated by the following expression,

$$R_f = \frac{\varepsilon_s}{\varepsilon_{\max}} = 1 - \frac{\sigma(t)}{E|_{T=T_l} \varepsilon_{\max}} \quad (36)$$

where $E|_{T=T_l}$ is the storage modulus of SMP nanocomposite at the T_l .

The experimental data obtained from the PU/GNPs SMP nanocomposites [31] are employed to verify the equation (36). The equations (27) and (32) are used to determine the maximum value of programming strain ($\varepsilon_{\max}$), fitting parameters are presented in Table 6. As shown in Fig. 9(a), the temperature is kept at 343 K which is higher than the T_g s of PU/GNPs SMP nanocomposites, where the $\phi_n = 0\%$, $\phi_n = 0.1\%$, $\phi_n = 0.25\%$ and $\phi_n = 0.5\%$, respectively. Analytical results reveal that the programming strains are $0.49, 0.87, 0.34$ and 0.62 , respectively.

As shown in Fig. 9(b), the analytical results of equation (36) are well in agreement with the experimental data of PU/GNPs nanocomposites with respect to the concentration of GNPs. The shape fixity ratio of nanocomposite is significantly increased from 92.2% to 96.3% with an increase in the weight concentration of nanoparticle from 0% to 0.68% . Due to the increase in the weight concentration of nanoparticle, the topological entanglement between PU matrix and GNPs nanofillers is helpful to enhance the storage modulus. However, with a further increase in the

weight concentration of GNPs from 0.68% into 1%, the shape fixity ratio is then decreased from 96.3% to 95.4%. As discussed in Ref. [31], the slippage effect of nanoparticle, rather than the coupled confinement, plays an important role in determining the shape fixity ratio of nanocomposites with a high weight concentration of nanoparticle. Therefore, the slippage effect of GNPs is able to depress the shape fixity ratio of SMP nanocomposites, when there is a high concentration of GNPs used.

Table 6. Value of parameters used in equations (27) and (32).

Nanocomposite	λ_i	$N_{np}(T_g)$	$N_{pp}(T_g)$	C_1^{pp}	C_2^{pp}	C_1^{np}	C_2^{np}	$V_0(cm^3)$	d	κ
PU0	1.05	0	4.5	5.4	71.9	7.2	66.3	238.9	11.2	-0.4
PU0.1	1.07	0.2	3.9							
PU0.25	1.12	0.6	3.7							
PU0.5	1.17	0.9	2.2

Figure 9. (a) Comparisons between the analytical results of equations (27) and (32) with the experimental data [31] for the programming strain (ϵ) with respect to the holding time, at a given weight concentration of nanoparticle of $\phi_n=0\%$, 0.1%, 0.25% and 0.5%. (b) Comparisons between analytical results of equation (36) and the experimental data [31] for the shape fixity ratio (R_f) with respect to the weight concentration of nanoparticle.

5. Conclusions

In this study, we propose a thermodynamic coupling model to investigate the selective entanglement effects, i.e. sub-entanglement and topological entanglement, on thermomechanical behaviors of SMP nanocomposites. A constitutive relationship among the weight concentration of nanoparticle, temperature, recovery stress and

stored strain is constructed to identify the toughening mechanisms of SMP nanocomposites below and above glass transition temperature. It is found that the recovery stress can be significantly improved by the topological entanglement of macromolecule chain, of which the thermodynamic relaxation and motion are determined by the entanglement effect of nanoparticle. However, there is a cooperative effect of sub-entanglement and topological entanglement on the mechanical properties of SMP nanocomposite below the glass transition temperature. This is because the thermodynamic relaxation is determined by both polymer-to-polymer and polymer-to-nanoparticle interactions. The enhancement of recovery stress can be as high as 242%. The glass transition temperature, relaxation time and release rate of stored strain can all be designed by the selective entanglement coupling of these two entanglement effects. Finally, the accuracy of analytical results is verified using a series of experimental data, including recovery stress, thermomechanical modulus and shape fixity ratio. This newly proposed model is expected to provide an essential tool to understand the toughening mechanism and provide an effective strategy to design new types of SMP nanocomposites with high recovery stresses.

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