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Insight in thermomechanical constitutive modeling of shape memory polymers

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Shape memory polymers (SMPs) are a new member of the smart materials family. SMPs have found wide applications or potential applications in almost all manmade structures and devices. In order to better design smart structures and devices using SMPs, thermomechanical constitutive modeling is essential. In this insight paper, we will focus on presenting several multi-length-scale and multi-physics modeling frameworks, including the thermodynamics consistent model, elasto-viscoplastic model, statistical mechanics model, and phase evaluation law model. The SMPs modeled will include amorphous one-way shape memory polymers, semicrystalline one-way shape memory polymers, semicrystalline two-way shape memory polymers, and functional and mechanical damage effects on SMPs. Finally, we will give some in-depth perspectives on future development in this area of study.

KEYWORDS

shape memory polymer, constitutive modeling, thermoset polymers, semicrystalline polymers, machine learning

Introduction

Shape memory polymers (SMPs) can store a prescribed shape for a long time and recover them by specific external trigger, for example, heat. SMPs have the potential to be deployed in various engineering structures and devices, including, but are not limited to, automotive (Lendlein and Kelch, 2002; Hu et al., 2012; Meng and Li, 2013; Zhao et al., 2015), aerospace (Leng et al., 2008; Liu et al., 2014), marine time (Ma et al., 2021), oil and gas (Taleghani et al., 2017; Santos et al., 2018; Mansour et al., 2019; Santos et al., 2021; Tabatabaei et al., 2021), geothermal (Elhag et al., 2021; Magzoub et al., 2021; Mohamed et al., 2022), civil engineering (Li and Xu, 2011a; Li et al., 2013b; Li et al., 2015; Ouyang and Li, 2009), and biomedical industries (Lendlein and Langer, 2002; Small et al., 2010). The same as any engineering materials, constitutive laws are essential to design and manufacture SMPs into engineering structures and devices because constitutive laws are a key component in forming the governing differential equations. For SMPs, the constitutive laws, or stress-strain relationships, are more complex than classical engineering materials because they depend on external loading and loading rate, time and temperature, damage status, and programming history. Particularly, programming is

a special step to make SMPs exhibit the shape memory effect (SME). Using thermally triggered SMPs as an example, a typical hot programming may consist of the following steps: 1) heating the SMP to above its transition temperature (the glass-transition temperature for amorphous SMPs or the melting temperature for semicrystalline SMPs), resting isothermally for a while (for instance 30 min) to make sure a uniform temperature within the SMP specimen; 2) loading the specimen by the desired type of loads to the designed pre-strain; 3) cooling down to below the transition temperature while holding the load or displacement constant; and 4) unloading at the end of cooling (Lendlein and Kelch, 2002). The programmed SMP specimens can be then heated up again to above the transition temperature to cause free shape recovery (if no constraint is applied) or fully constrained stress recovery (if zero recovery strain is allowed) or partially constrained stress recovery (if some strain is allowed to recover). While hot programming is popular for thermally triggered SMPs, it needs the heating and cooling steps and is energy-consuming. Therefore, cold programming, that is, programming isothermally at the glassy state, has also been proposed (Li and Xu, 2011b; Li and Shojai, 2012; Li, 2014; Li and Wang, 2016; Xiao and Tian, 2019). The requirement is that the load applied during cold programming must cause yielding and plastic deformation of the SMPs. Usually, the longer the time of loading the specimen, the more the structural relaxation and the better the shape fixity ratio.

In recent years, many efforts have been made to model the constitutive behavior of SMPs. Several representative approaches include the rheological model (Tobushi et al., 1997; Bhattacharyya, and Tobushi, 2000), elasto-viscoplastic model (Nguyen et al., 2008a; Chen and Nguyen, 2011; Balogun and Mo, 2016; Li et al., 2017a; Li and Liu, 2018), phase evolution law model (Liu et al., 2006; Li et al., 2017b), molecular dynamics model (Diani and Gall, 2007; Wick, et al., 2021), statistical mechanics model (Shojaei and Li, 2014b), and multibranch model (Gu et al., 2014; Yu et al., 2014). In 2013, Nguyen (2013) summarized the constitutive models for SMPs. A recent comprehensive review article was published by Yarali et al. (2020). Most recently, Yan and Li published a tutorial paper on modeling SMPs (Yan and Li, 2022).

Since 2010, our lab at Louisiana State University has developed several constitutive models for various SMPs. The focus of this insight paper is to use the models developed in our lab in tandem with models developed by other labs to shed some lights into the various ways of modeling SMPs. The paper will be arranged in the following sections. In *Thermomechanical constitutive modeling of amorphous SMPs*, we will present modeling on amorphous SMPs, including the elasto-viscoplastic model, phase evolution law model, and four-chain model. In *Thermomechanical constitutive modeling of semicrystalline SMPs*, our focus will be on modeling semicrystalline SMPs, including one-way shape memory polymers and two-way shape memory polymers. In *Modeling*

of SMPs including mechanical and functional damage effects, we will focus on modeling amorphous SMPs with mechanical and functional damage effects within the continuum damage mechanics framework. In *Challenges and future perspectives*, we will present our perspectives on future development in this research direction. In *Conclusion*, we will conclude this paper.

Thermomechanical constitutive modeling of amorphous SMPs

Elasto-viscoplastic model

To address the time dependence and complicated deformation response of SMPs that are largely overlooked in the early-stage one-dimensional small-strain models, the thermo-viscoelastic-plastic-based structure-function approach has since been intensively pursued in many of the subsequent computational efforts. Such studies, in lieu of representing the shape memory behaviors as a class of special but purely elastic problems, mathematically elucidated the experimentally observed hysteresis from a structural and stress relaxation perspective, which, in particular, propelled the model predictability into the three-dimensional large strain domain as well as intimately intertwined the shape memory phenomena and the glass-transition physics.

The initial attempt pioneered by Diani et al. (2006) in fact represented a conceptual extension of the standard linear solid model rheology. Later macroscopic intermediate models by Xu and Li (2010), Baghani et al. (2012), Baghani et al. (2014), and Li et al. (2014) provided further enhancement by resolving the rate-dependent shape memory responses through various forms of multi-phase viscoelastic mixture analogy. A schematic example of such rheological representation proposed in Xu and Li (2010) is illustrated in Figure 1 below.

Leveraging combinations of hyperelasticity and viscoplasticity into the constitutive formulation to capture both the molecular chain orientation at elevated temperatures and the sluggish mechanical response below T_g , Qi et al. (2008) presented an integrated experimental and computational study in the finite deformation region which was then implemented into finite element analysis. Despite still employing a similar phenomenological first-order three-phase transition method to describe the amorphous SMP through terms of phase fractions, the model introduced a concept that the deformation of the newly formed glassy phase (F_T) should originate from a redistribution of the total deformation (F) as elaborated in Eqs 1, 2 below for any incremental change during a monotonic thermal loading from step n to $n+1$, which effectively eliminates the need of purely nonphysical descriptions such as histories of “stored strain” (Qi et al., 2008).

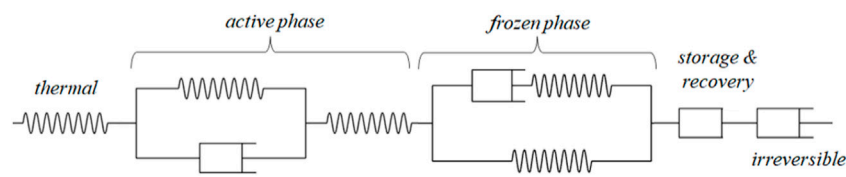


FIGURE 1
Linear rheological representation of multi-phase viscoelastic mixture analogy.

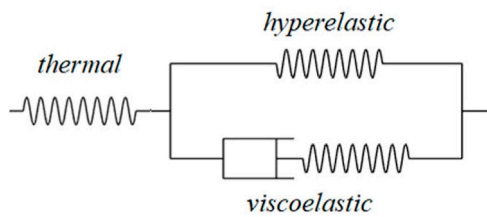


FIGURE 2
One-dimensional rheological representation of the thermoviscoelastic model.

$$\Delta \mathbf{F}_T^{n+1} = \begin{cases} \mathbf{F}^{n+1} (\mathbf{F}^n)^{-1} & \Delta T \neq 0 \\ \mathbf{I} & \Delta T = 0 \end{cases} \quad (1)$$

$$\mathbf{F}_T^{n+1} = \Delta \mathbf{F}_T^{n+1} \mathbf{F}_T^n \quad (2)$$

The representation of the underlying material morphology evolution that had frequently relied on the phase transition analogy was eventually favored for a structural and stress relaxation-based interpretation at the core of the physical glass-transition process as inspired by Nguyen and co-workers (Nguyen et al., 2008a; Nguyen et al., 2008b). The shape memory phenomena of the amorphous SMP were argued to be primarily driven by the drastic change of molecular chain mobility and the local rearrangement capability of macromolecular chain segments to restore the structural equilibrium. The structural relaxation occurs instantaneously at high temperatures above T_g but responds slowly below it and thus effectively locks the structure in a nonequilibrium configuration and a temporary shape macroscopically as well during cooling. Heating brings back the mobility which then allows for the shape recovery. A combined structural relaxation model of Tool's fictive temperature T_f (Tool, 1946) and Adam-Gibbs's description of the temperature-dependent retardation time τ_R (Adam and Gibbs, 1965) was then adopted, along with a modified Eyring model of viscous flow, into a thermoviscoelastic framework of which the one-dimensional linear rheology is illustrated below in Figure 2, where a volumetric thermal response spring is followed by a mechanical response component consisting of a hyperelastic spring that represents the mobile rubbery state in parallel with a Maxwell element corresponding to the viscoelastic stress relaxation.

The expression of the isobaric thermal deformation Ω_T responding to a temperature change from T_0 to T thus included a time-dependent nonequilibrium part δ^{neq} that was in turn evaluated following an evolution equation proposed by Tool (Tool, 1946) as follows (Qi et al., 2008):

$$\Omega_T = 1 + \alpha_r (T - T_0) + \left(-(\alpha_r - \alpha_g)(T - T_f) \right) = 1 + \alpha_r (T - T_0) + \delta^{neq} \quad (3)$$

$$\frac{d\delta^{neq}}{dt} = -\frac{1}{\tau_R} \delta^{neq} - \left(-(\alpha_r - \alpha_g) \frac{dT}{dt} \right) \quad (4)$$

where α_r and α_g are the rubbery and glassy volumetric thermal expansion coefficients, respectively; T_f is Tool's fictive temperature, and δ^{neq} measures the departure from the equilibrium.

Since such an integrated structural and stress relaxation approach has proven to be quite effective in interpreting and reproducing the amorphous SMP morphological evolution, researchers continue to make strides in this direction to improve the model sophistication for better representation of the complicated thermo-elasto-visco-plastic behaviors. For example, in view of the potential to capture both thermal and mechanical behaviors in a single thermodynamically consistent manner, Gu et al. (2017) adopted a more definite physics-based internal state variable description in the vicinity of the glass transition following the previous work by Lion and Peters (2010). Concerning that the assumption of the same temperature and structural dependence being shared between structural relaxation time and stress relaxation times may not be well inclusive, Zeng et al. (2018) introduced uncoupled structural and stress relaxation mechanisms which are linked only through an internal state variable that reflects the degree of volume departure from equilibrium. On the other hand, Westbrook et al. (2011) incorporated extra nonequilibrium rubbery Maxwell branches in a similar scheme of the generalized viscoelastic model or Prony series to capture the multitude of relaxation modes, while Xiao et al. (2013) further extended the formulation of the relaxation times for structure, stress, and viscous flow into multiple discrete relaxation processes and indicated that the recovery response can be potentially well engineered through designed shape fixity thermomechanical profiles that are not solely limited to deformation upon heating.

Li and Xu (2011b) proposed a continuum finite-strain-based thermo-viscoelastic-viscoplastic model through an integrated experimental and theoretical effort with a focus on characterizing the shape fixity and recovery of amorphous SMPs programmed by cold compression, in which it was contended and demonstrated that it is the creation of a nonequilibrium configuration rather than a necessity of a temperature event that eventually underpins the acquiring of the shape memory capacity. In light of the fact that the postulation of a single exponential structural relaxation process would potentially lead to missing “memory effects” of the thermal deformation in response to successive temperature changes as described by Kovacs et al. (1979), a continuous structural relaxation spectrum as shown below was employed, where Tool's fictive temperature is defined and a response function following Moynihan et al. (1976) was adopted. Here, $0 < \beta \leq 1$ describes the nonexponential attribute of the relaxation process and τ_s measures the characteristic retardation time of the volume creep in the formulation of the dimensionless material time difference $\Delta\zeta$ (Li and Xu, 2011b)

$$T_f(t) = T(t) - \int_{t_0}^t \exp\left[-(\Delta\zeta)^\beta\right] dT(t) \quad (5)$$

$$\Delta\zeta = \zeta(t) - \zeta(t') = \int_{t'}^t \frac{dt}{\tau_s} \quad (6)$$

From a similar perspective, later advancement by Dai et al. (2020) further considered the rejuvenation-induced strain softening in the constitutive relations along with the incorporation of the relaxation mechanism into the strain hardening representation to account for the effects from the dissipative orientation process.

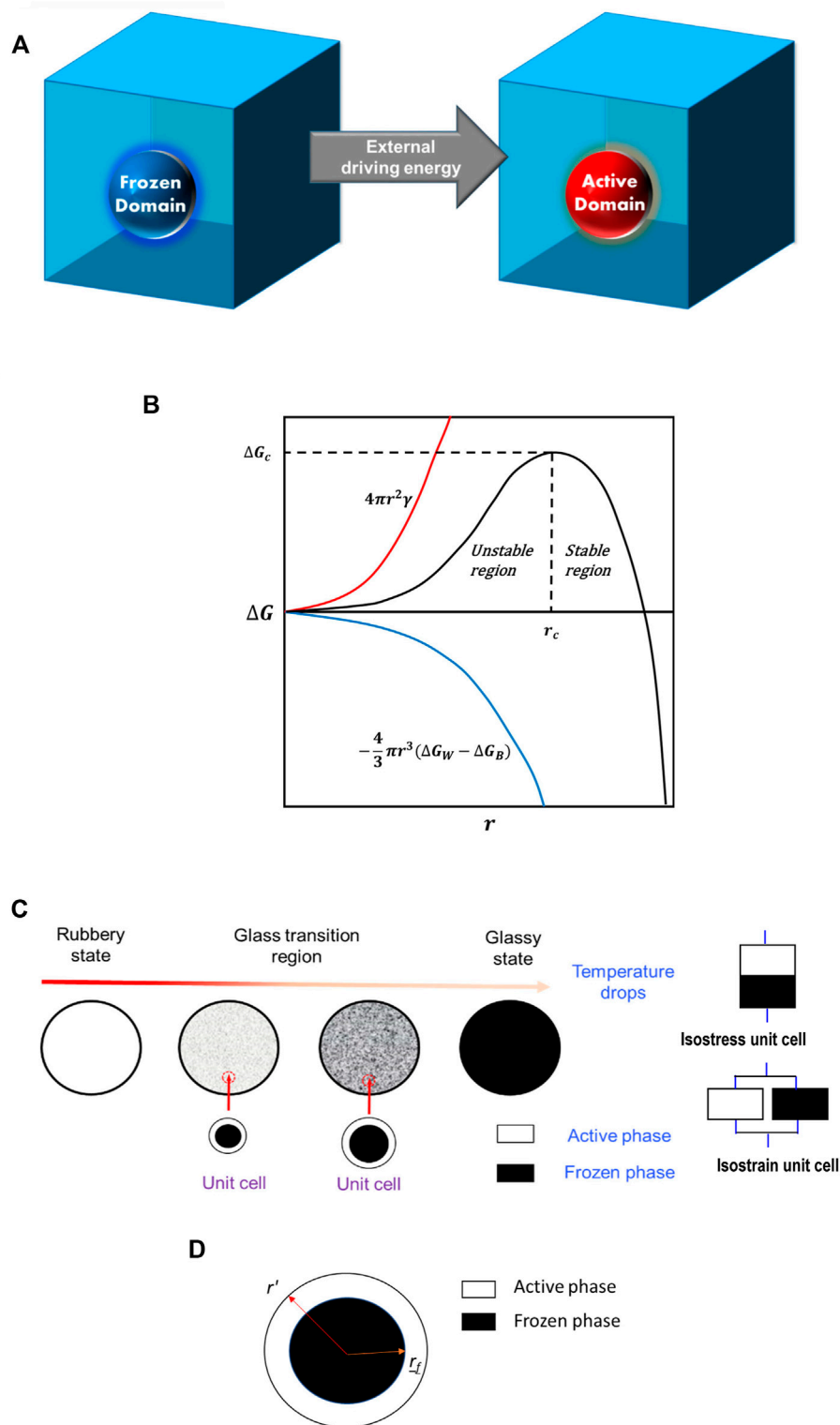
Most recently, aiming for a reconciliation between the need for modeling the physical significance and the complexities arising from the material parameter calibration, Su and Peng (2018) derived the constitutive equations through energy decomposition in accordance with the second law of thermodynamics and instituted a temperature-dependent weight function in formulating the material parameters through the shape memory cycle. Subsequent refinement pursued by Wang et al. (2021) then advocated that the parameter identification could be further simplified by adopting a modified Adam-Gibbs model and Arrhenius-type time-temperature superposition shift factor along with a physics-based viscosity expression.

Phase evolution law-based model

Of all the approaches on constitutive modeling of SMPs, the phase evolution law-based model has attracted much attention (Liu et al., 2006). The reason for this is that by treating the programming and shape recovery process as a phenomenon of

phase change or more accurately evolution from an active phase to a frozen phase in hot programming and evolution from a frozen phase to an active phase during shape recovery, the shape memory effect is fully controlled by the phase evolution law. Although this concept seems to have a clearer physical interpretation in semicrystalline shape memory polymers, because the shape memory effect can be understood as crystallization-melt transition (Long et al., 2009; Westbrook et al., 2010; Scalet et al., 2015), this approach has been more popular in modeling amorphous thermoset shape memory polymers (TSMPs). In 2006, Liu et al. (2006) proposed the phase evolution law model for constitutive modeling of TSMPs, which has been further refined by other researchers (Baghianiet al., 2012; Chen and Lagoudas, 2008a; Chen and Lagoudas, 2008b; Gilormini and Diani, 2012; Guo et al., 2016; Kafka, 2008; Kazakeviciute-Makovska et al., 2012; Kim et al., 2010; Li and Liu, 2018; Long et al., 2009; Pieczyska et al., 2015; Qi et al., 2008; Reese et al., 2010; Scalet et al., 2015; Volk et al., 2011; Wang et al., 2009; Xu and Li, 2010; Yan and Li, 2019). It is noted that this approach can only be applied to hot programming of TSMPs; for cold programming, which is a process of programming TSMPs isothermally in the glassy state until yielding (Xu and Li, 2011; Li and Shojaei, 2012; Li et al., 2013a; Li, 2014; Li and Wang, 2016; Li and Xu, 2011b), the phase evolution law approach cannot be used because there is no substantial phase transition during the cold programming process.

In a broader sense, the phase evolution law-based approach has a deeper root in constitutive modeling of materials, with the original model for shape memory alloys (SMAs). The pseudoelastic thermomechanical response, shape memory effect, and stress-induced phase transformation phenomena for SMAs were described by Dachkovski and Böhm, 2004; Müller and Bruhns, 2006; Auricchio et al., 2007; Popov and Lagoudas, 2007; Thamburaja and Ekambaram, 2007; Hassan et al., 2008; Moumni et al., 2008; Reese and Christ, 2008; Wang et al., 2008; Levitas and Ozsoy, 2009a; Levitas and Ozsoy, 2009b; Thamburaja and Nikabdullah, 2009. Unlike SMAs, which have a clear phase change from martensite to austenite during shape recovery, TSMPs may not see such a clear phase change, although there is some evidence that thermoset polymers are generally heterogeneous in the nanoscale, with highly crosslinked regions or domains dispersed in a lightly crosslinked matrix (Magonov and Reneker, 1997; Morsch et al., 2015). In other words, it seems that TSMPs may be treated as a two-phase composite for the convenience of mathematical modeling. With the treatment as a two-phase composite, several composite materials theories can be utilized to determine its effective elastic properties (Hill, 1965; Mori and Tanaka, 1973; Hori and Nemat-Nasser, 1993; Ju and Chen, 1994; Hu

**FIGURE 3**

(A) Schematic illustration of how a frozen domain (blue sphere) in the frozen phase matrix (blue cube) evolves into an active domain (red sphere). (B) Free-energy change caused by the appearance of the active domain as a function of domain radius r . ΔG_c is the energy change when the domain size reaches the critical value r_c . The domains with $r > r_c$ will be stabilized in the active phase (and may grow infinitely upon perturbation), while the domains with $r < r_c$ will revert to the frozen phase upon fluctuations. (Reproduced with permission from International Journal of Plasticity, 80:168-186, (2016). Copyright 2016 Elsevier.) (C) Schematic of transition from the active phase to frozen phase as the temperature drops (left) and isostress and isotrain unit cells (right), which are currently used in the literature. (D) Proposed two-phase unit cell, which is neither isostress nor isotrain (Reproduced with permission from Smart Materials and Structures, 28: 095030 (2019). Copyright 2019 IOP.)

and Weng, 2000; Li and Wang, 2005; Peng et al., 2009; Westbrook et al., 2010).

In the first paper published by Liu et al. (2006), the authors proposed a phenomenological concept, that is, TSMPs are made of two phases: active phase and frozen phase. During hot programming, the TSMPs are almost 100% active phase in the rubbery state, and with cooling, the active phase is gradually transferred to the frozen phase, and at the glassy state, the majority of the TSMPs is in the frozen phase. The pre-strain is fixed in the frozen phase due to the loss of mobility of the polymer chains. During shape recovery, the molecules gradually gain mobility with heating, and the frozen phase is gradually transferred to the active phase. As a result of the phase transition, the stored pre-strain is released, and the shape is recovered. Later, the concept proposed by Liu et al. (2006) was further developed. For example, Chen and Lagoudas (2008a; 2008b) established a three-dimensional framework, which was used by Volk et al. (2011) to determine the shape memory effect of shape memory polyurethane (SMPU). A three-phase phenomenological model [one hard segment phase and two (active and frozen) soft segment phases] was developed by Kim et al. (2010) to predict the deformation behavior of SMPUs. Wang et al. (2009) considered the heating rate and hysteresis. In 2008, Qi et al. (2008) developed a three-dimensional finite deformation model for the thermomechanical behavior of TSMPs, which was based on the evolution of the deformation energy from an entropy-based state to an enthalpy-based state. In the framework of both macromechanics and micromechanics, Reese et al. (2010) developed a new model. In the small strain regime, Baghani et al. (2012) presented a three-dimensional phenomenological model under time-dependent multiaxial thermomechanical loadings. Gilormini and Diani (2012) combined the model of Liu et al. (2006) with the homogenization approach, which got rid of the uniform stress assumption and may be more appropriate. Recently, researchers have been seeking more physical bases for the concept of the phase evolution law. For example, Guo et al. (2016) proposed a physics-based constitutive model for TSMPs. Yang and Li (2016) developed a new physics-based phase evolution law by treating the TSMP as a two-phase composite with frozen domains dispersed in the active phase matrix. They proposed that the shape fixity and shape recovery were governed by the free energy change during the programming and recovery process, see Figures 3A,B. Most recently, Yan and Li (2019) proposed another physical process of the phase evolution. For the case of hot programming, a TSMP is almost 100% in the active phase in the rubbery state. However, some frozen phase nuclei may form and disappear dynamically. As the temperature drops, the high-energy active phase may move to the frozen phase nuclei, dump the kinetic energy, and adhere to the surface of the frozen nuclei. As a result, the frozen phase grows and the active phase reduces with

further temperature dropping, until the majority of the TSMP becomes frozen in the glassy state, see the schematic in Figure 3C. Based on this understanding, the basic building block or unit cell of the two-phase model is a frozen phase coated by an active layer, see Figure 3D. As against the previous isostress or isostrain assumption, this new unit cell does not have isostress or isostrain in the active and frozen phases. Some typical phase evolution laws proposed by other groups are summarized in Table 1.

Figures 4A–C show the performance of the new model by Yang and Li (2016). It is seen that this model can reasonably reproduce the test results by Liu et al. (2006). On the other hand, Yan and Li used their model in finite element analysis of a dogbone specimen under uniaxial loading. Figure 4D shows the comparison between the finite element modeling results and experimental results. Again, it is seen that the model can reasonably capture the experimental results.

Four-chain model

In solid mechanics modeling, a macroscopically homogeneous body can be characterized by a representative volume element (RVE). In doing so, both the material points in the heterogeneous body or isotropic body can be effectively modeled and the connection between macroscopic deformation and microscopic deformation can be bridged. In the past, most studies on SMPs utilized the Arruda-Boyce eight-chain diagonal model (Arruda and Boyce, 1993). This model has found its wide applications in a variety of SMP modeling (Qi et al., 2008; Li and Xu, 2011b; Ge et al., 2014; Xiao and Tian, 2019). However, by observing the unit cell in the SMP network, Yan and Li, (2020a) argued that the conventional Arruda-Boyce eight-chain diagonal model is not suitable for describing the microscopic RVE or unit cell for a recently discovered SMP made of EPON-IPD (Fan and Li, 2018). Therefore, they introduced a tetrahedron unit cell to replace the commonly used Arruda-Boyce RVE model, see Figure 5. Furthermore, in order to reasonably describe the dramatic stress recovery for EPON-IPD, they borrowed an idea from an early developed fiber-forming polymer model (Lyons, 1958), that is, a novel modulus transition mechanism. That is, with increasing deformation, the energy source gradually transits from bond rotation in the low-energy state to bond stretch in the high-energy state. The Cauchy stress is divided into three parts, that is, rubbery stress σ_r , the switchable hyperelastic stress σ_g^r , and viscoplastic stress σ_g^p , which reads (Yan and Li, 2020a)

$$\sigma = f_r \sigma_r + f_g (\sigma_g^p + \sigma_g^r) \quad (7)$$

where f_g and f_r are the volume fractions of the glassy phase and rubbery phase, respectively. The three stress components can be written as

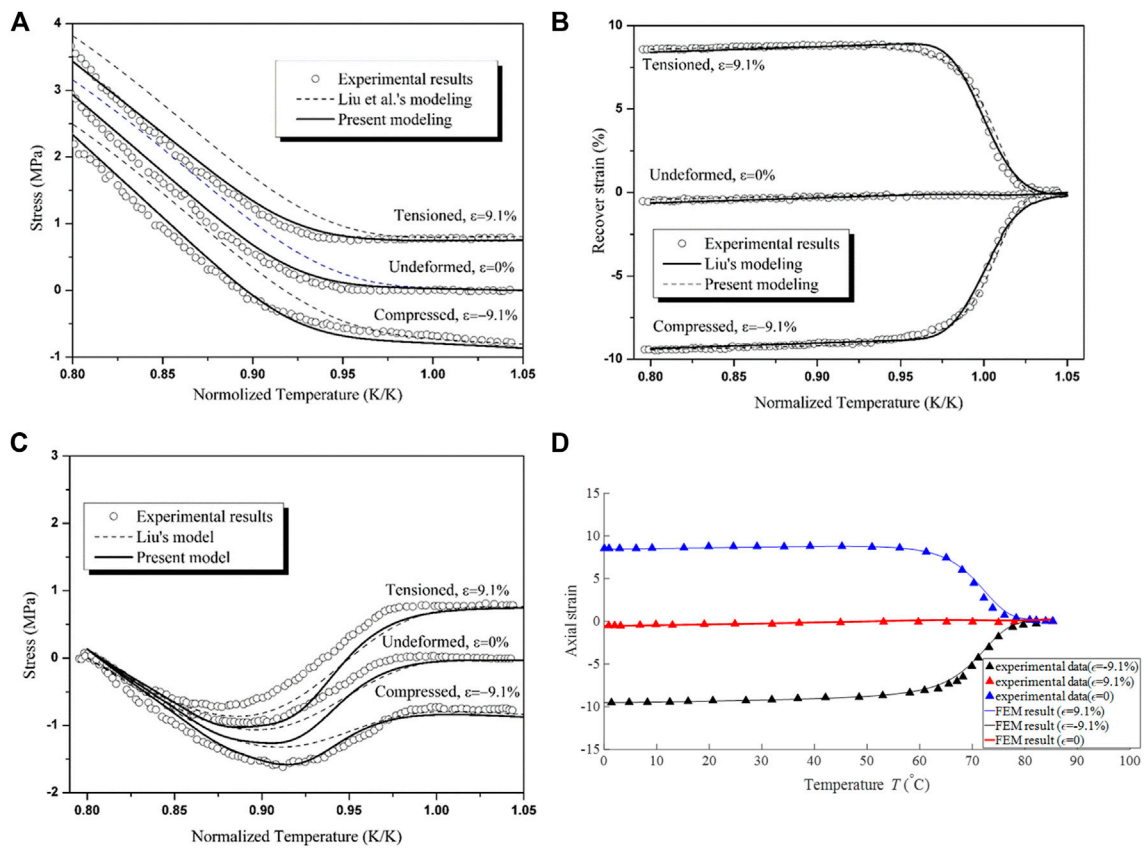


FIGURE 4

Modeling results for (A) stress responses of SMPs during cooling under different pre-strain conditions; (B) free strain recovery tests of SMPs programmed by different pre-strains [Reproduced with permission from International Journal of Plasticity, 80:168-186, (2016). Copyright 2016 Elsevier]. (C) constraint stress recovery tests of SMPs programmed by different pre-strains; (D) comparison between experimental results and finite element analysis results of a dogbone specimen under uniaxial loading [Reproduced with permission from Smart Materials and Structures, 28: 095030, (2019). Copyright 2019 IOP].

TABLE 1 Frozen phase volume fraction functions proposed in existing literature studies.

Frozen phase volume fraction $\phi(T)$	References
$\phi(T) = 1 - \frac{1}{1 + c_f (T_h - T)^n}$	Liu et al. (2006)
$\phi(T) = \frac{1}{1 + \exp(-\frac{(T - T_s)}{A})}$	Qi et al. (2008)
$\phi(T) = \alpha \exp(-(\frac{T - T_s}{\beta})^m)$	Wang et al. (2009)
$\phi(T) = \frac{1}{1 + \exp(\frac{2w}{T - T_g})}$	Reese et al. (2010)
$\phi(T) = \frac{b - \tanh((T - A)/B)}{b - a}$	Volk et al. (2011)
$\phi(T) = (1 - (\frac{T - T_{min}}{T_{max} - T_{min}})^m)^n$	Gilormini and Diani, (2012)
$\phi(T) = \int_{T_s}^T \frac{1}{s\sqrt{2\pi}} \exp(-\frac{(T - T_s)^2}{2s^2}) dT$	Guo et al. (2016)

In all the formulae in this table, T is the temperature, T_r is the reference temperature that is close to the glass-transition temperature T_g . T_{max} and T_{min} are the highest temperature and lowest temperature in the programming and recovery process, and T_s is the start temperature of the phase transition. Other parameters (such as $m, n, c_f, a, b, w, A, B, s, \beta$, etc.) are curve-fitting parameters in different formulae and have no explicit physical meaning.

$$\sigma_r = 2 \left[M_r \left(I - \frac{1}{3} I_1 F^{-1} F^{-T} \right) \right] F F^T - \frac{1}{J} \left(\sigma_r \frac{\partial E}{\partial F} + E \frac{\partial \sigma_r}{\partial F} \right) F^T - \left(\frac{\partial \hat{p}_r}{\partial F} \right) F^T - 3 \kappa_r \alpha_r (\theta - \theta_0) I \quad (8)$$

$$\sigma_g^r = H(E_{eq} - E_c) \left(2 \left[M_g \left(I - \frac{1}{3} I_1 F_g^{r-1} F_g^{r-T} \right) \right] F_g^r F_g^{r-T} - \left(\sigma_g^r \frac{\partial E_g^r}{\partial F_g^r} + E_g^r \frac{\partial \sigma_g^r}{\partial F_g^r} \right) F_g^{r-T} - \left(\frac{\partial \hat{p}_g^r}{\partial F_g^r} \right) F_g^{r-T} - 3 \kappa_g \alpha_g (\theta - \theta_0) I \right) \quad (9)$$

$$\sigma_g^p = \frac{1}{J^e} \left[C^e : E^e - 3 \alpha_g \kappa_g (\theta - \theta_0) I \right] \quad (10)$$

in which J^e , C^e , and κ_g are the *Jacobian* for the elastic part, the isotropic elasticity tensor, and the bulk modulus for the glassy phase, respectively. M_r and M_g are two functions with respect to

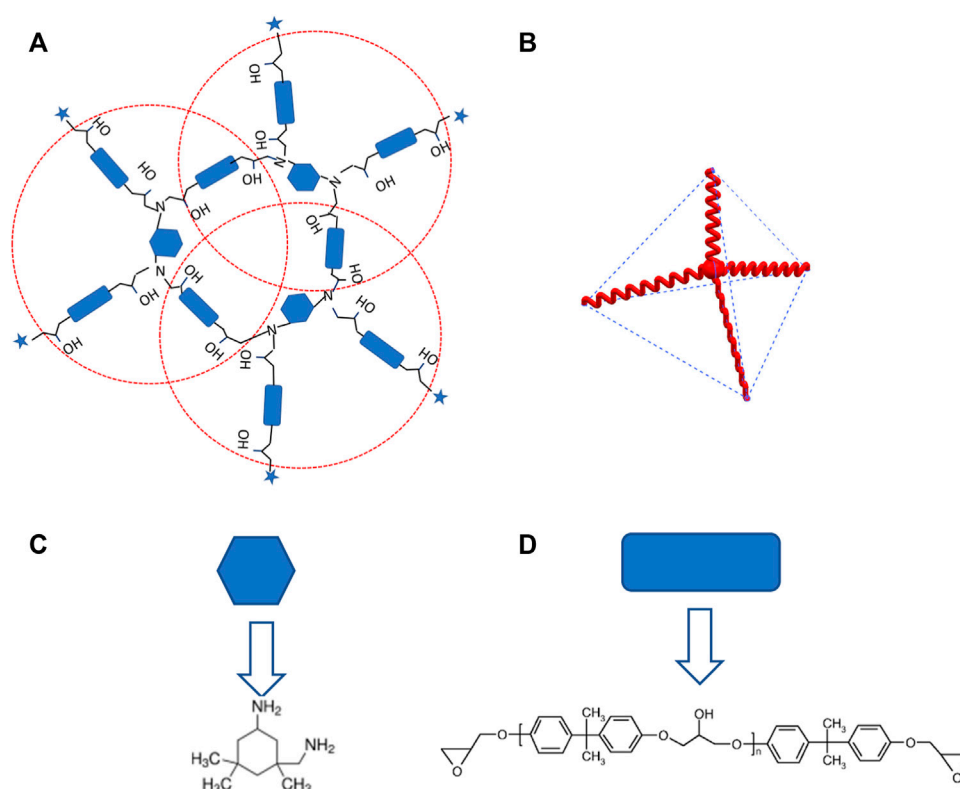


FIGURE 5

(A) Planar schematic for the molecular configuration of the EPON-IPD network; (B) unit cell in the EPON-IPD network; (C) monomer of isophorone diamine (IPD); (D) partial structure of the epoxy resin (EPON 826); ★represents the extended structure. For each dotted red circle in (A), it consists of one IPD at the center, connected by four epoxy arms, which are the EPON epoxy monomers. In three dimensions, this planar schematic is represented by the tetrahedron unit cell in (B). From (A), it is seen that every epoxy monomer arm is shared by two-unit cells, growing into the three-dimensional space network. [Reproduced with permission from Journal of Applied mechanics, 87(6): 061007, (2020a). Copyright 2020 American Society of Mechanical Engineers].

microscopic deformation quantities. \mathbf{E} is the Biot strain tensor. θ and θ_0 are the current temperature and initial temperature, respectively. The subscripts “r” and “g” represent the rubbery state and glassy state, respectively. Meanwhile, Yan and Li (2020a) believe that this energy transition corresponds to a change from entropy-driven deformation to enthalpy-driven deformation. The model was validated in three scenarios, that is, uniaxial deformation in the glassy state, the step-relaxation loading in the rubbery state, and the recovery stress under different programming strains, and all of them can well capture the experiment trends.

Thermomechanical constitutive modeling of semicrystalline SMPs

Modeling of semicrystalline one-way shape memory polymers

Amorphous and crystalline polymers are both constituted from randomly disordered molecular chains. During the

polymerization process, if the randomness of molecular chains is preserved, a specific structure could be developed during the crystallization process in which the disordered polymeric network is oriented in predefined directions. Polymer crystallization may include 1) temperature gradient-induced crystallization, in which the crystalline lamellae are oriented with respect to the largest temperature gradients (Shojaei et al., 2013), 2) stress-induced crystallization in which external thermomechanical loadings are utilized to align the molecular chains (Shojaei et al., 2013; Lu et al., 2018), and 3) chemical processes. Due to the statistical nature of the crystallization processes, the resulting microstructure contains 10 wt% up to 80 wt% crystalline segments, while the remaining molecular chains retain their amorphous structure. The composite structure made of amorphous and crystalline phases is called the semicrystalline polymer, and their properties are dominated by both crystalline and amorphous segments (Seefried et al., 1975; Brunette et al., 1982; Tobushi et al., 1997; Shojaei et al., 2013).

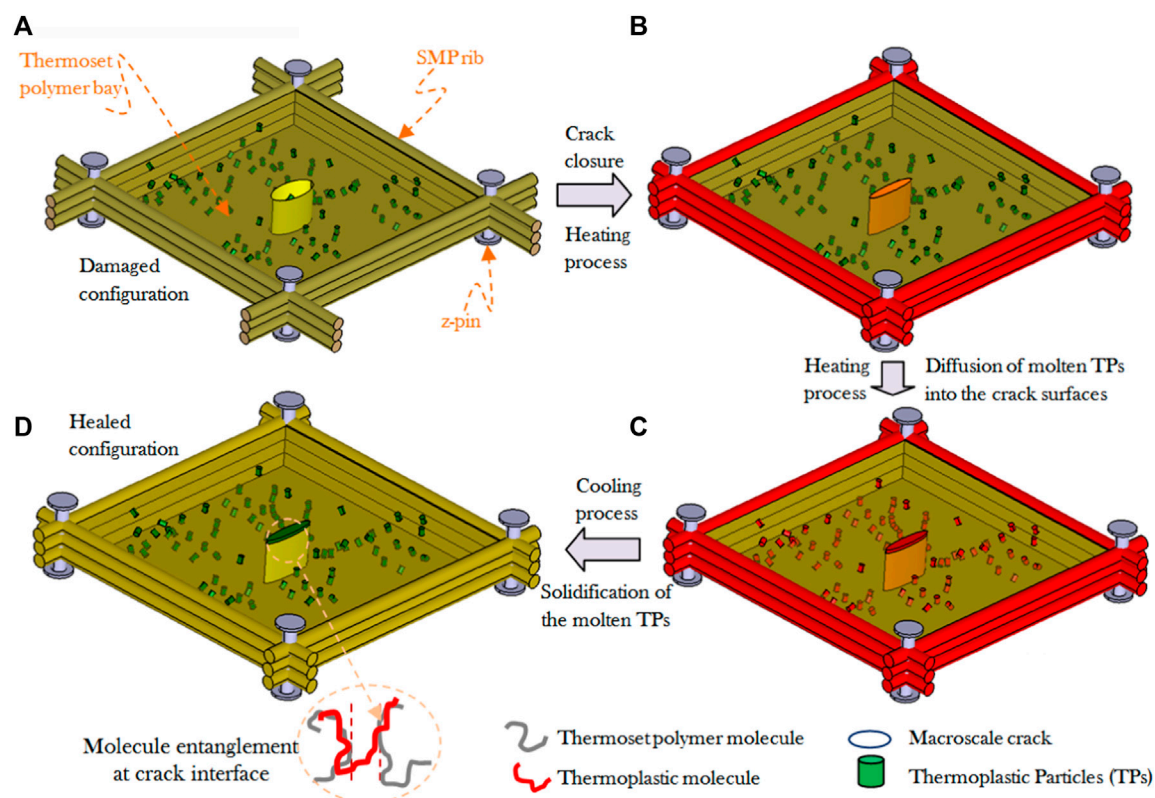


FIGURE 6

Bio-inspired healing composite structure consists of the SMP fiber grid. (A) Unit cell of the SMP grid (ribs and z-pins) with a macroscopic crack ($T < T_g$), (B) crack closure process ($T > T_g$), (C) thermoplastic particle melting process ($T > T_m$), and (D) cooling down process ($T < T_g$). For more details, refer to Li and Shojaei, 2012 [Reproduced with permission from Proceedings of the Royal Society A: Mathematical, Physical and Engineering Science 468, 2319–2346, (2012). Copyright 2012 Royal Society].

Phase separation and stress-induced crystallization processes may alter the microstructure of the semicrystalline SMPs in which crystalline and amorphous phase separation may occur. The phase separation, induced during severe thermomechanical loading, may alter the amorphous, crystalline, and morphological textures of the semicrystalline polymers. Since the thermomechanical properties of crystalline and amorphous polymers have been well studied in the literature, one could utilize the established properties to predict the performance of semicrystalline polymers using the multiscale analysis methodology. These methods, which have been used for reinforced composites, can effectively correlate the micro-constituent properties to the macroscale mechanical behavior. Li and Shojaei (2012) developed a physically consistent micromechanics framework to correlate the macroscopic mechanical responses to the microscale constitutive behaviors. The developed constitutive models are further expanded to capture SMP polymer performance in self-healing structures.

One of the major challenges in structural damage healing is the need for an external stimulus to bring the fractured surfaces in contact, that is, sealing the crack, before the actual healing can

occur (Li and Uppu, 2010). Li and Shojaei (2012) developed a novel self-healing scheme that utilizes SMP fibers to stitch the crack faces. In this process, the crack surfaces are forced in contact through constrained shape recovery of tension-programmed SMP fibers which are embedded in the body (Zhang et al., 2016a; Zhang and Li, 2016; Zhang et al., 2016b). For example, an SMP fiber-reinforced grid skeleton, as shown in Figure 6, could act like stitch a cut in the human skin by suture. The scheme illustrated in Figure 6 is a practical bio-mimetic solution, and it is feasible to manufacture using existing SMP fibers (Li et al., 2012; Li and Zhang, 2013; Shojaei and Li, 2013).

Because manufacturing of the systems shown in Figure 6 is costly and time-consuming, a modeling tool is required to study the performance of different configurations. Li and Shojaei (2012) and Shojaei and Li (2013) developed a multiscale viscoplastic model to predict the thermomechanical behaviors of the SMP fibers. Particularly, they considered the cyclic hardening and stress recovery responses in their model. The physics-based models consider the stress-induced crystallization as well as the evolution of the morphological texture. Thermomechanical cycling test data of the SMP fibers are

utilized to evaluate the performance of the proposed constitutive laws. In the case of viscoplastic laws, each individual microconstituent is modeled to establish microstress and microstrain states within each of these phases. Averaging techniques is then incorporated, within the micromechanics framework, to correlate the microstates to macroscale constitutive behavior. The main goal in this multiscale modeling approach is to incorporate experimentally characterizable material inputs versus numerical curve fitting parameters when compared to the phenomenological models.

In the case of amorphous microconstituents, the well-established Boyce model is used for modeling the inelastic deformation. For details of the constitutive modeling and material parameters, the interested reader may refer to Boyce et al., 1989; Li and Shojaei, 2012; Nemat-Nasser and Hori, 1993; Shojaei and Li, 2013; Shojaei et al., 2014a. The plastic multiplier for the amorphous microconstituent is defined as follows:

$$|\dot{\gamma}^p| = \dot{\gamma}_0^a \exp \left[-A \frac{s + ap}{\theta} \left(1 - \left(\frac{|\tau|}{s + ap} \right)^{5/6} \right) \right] \quad (11)$$

where the plastic strain is driven by both the pressure and shear stress. The material parameters and the evolution laws are defined in Boyce et al., 1989.

In the case of the crystalline phase, three different inelastic deformation mechanisms were considered by Shojaei and Li, 2013: (a) crystallographic slip, (b) twining, and (c) martensite transformations. The inelastic crystalline stretch rate tensor, \dot{D}_{ij}^{cp} , is defined by (Lee et al., 1993; Shojaei and Li, 2013)

$$\dot{D}_{ij}^{cp} = \sum_{\alpha=1}^K \dot{\gamma}^{(\alpha)} R_{ij}^{(\alpha)} \quad (12)$$

where $R_{ij}^{(\alpha)}$ is the symmetric part of the Schmid tensor and α denotes the crystalline slip plane in which the shear rate, $\dot{\gamma}^{(\alpha)}$, is defined. Please refer to Lee et al., 1993; Shojaei and Li, 2013 for the details.

To link microconstituents' thermomechanical response to macroscale constitutive behavior, a multiscale micromechanics modeling framework was developed by Li and Shojaei (2012) and Shojaei and Li (2013). Viscoelastic-viscoplastic behavior in amorphous and crystalline phases and the morphological texture updates are incorporated in this framework (Li and Shojaei, 2012). In the case of the amorphous microstate, the texture is updated using the stress-induced crystallization process. In the case of the crystalline microstate, the texture is updated via evolution of the crystallographic axes under applied stresses (Li and Shojaei, 2012; Shojaei and Li, 2013).

Shojaei and Li (2013) generalized the two-phase transformation field analysis (TFA); micromechanics was originally developed by Dvorak et al. (Dvorak, 1990; Dvorak 1992; Dvorak and Benveniste 1992). The modification allowed to utilize TFA for capturing large deformations in semicrystalline polymers. Interested readers may refer to Shojaei and Li, 2013 for

the details. In the modified TFA framework, a representative volume element (RVE), as shown in Figure 7, is utilized to develop the micromechanics correlations. The crystalline microconstituents in the semicrystalline polymer are modeled as inclusions embedded in the amorphous phase, see Figure 7 (Shojaei and Li, 2013). The fibrous and penny shape inclusions are respectively depicted in Figures 7A,B, where the interfacial unit vector configurations are shown in Figure 7C.

The stress/strain concentration tensors and micromechanics averaging techniques are then incorporated to link the microscale and macroscale thermomechanical behaviors in semicrystalline SMPs. The details of micromechanics formulation can be found in Shojaei and Li, 2013, in which macroscopic RVEs are divided into subvolumes.

The test data from Szymczyk et al. (2011) are shown in Figures 8A,B together with the simulation results. As discussed by Shojaei and Li (2013), the experimental test results are utilized to model the soft segment (Figure 8A) and to calculate the material parameters for the amorphous subphase. The crystalline subphase constitutive model is calibrated using hard segment test data (Figure 8B). The calibrated model is then utilized to model a 20 wt% soft segment copolymer, as shown in Figure 8C (Shojaei and Li, 2013).

Figure 9 shows the simulation and test data for an amorphous SMP under compression loading (Shojaei and Li, 2013).

Modeling of semicrystalline two-way shape memory polymers

The two-way shape memory effect (2W-SME) was first reported for liquid crystalline elastomers by (Thomson et al., 2002). To date, it has been found in a number of polymers (Chung et al., 2008; Lee et al., 2008; Qin and Mather, 2009; Hong et al., 2010; Xie, 2010; Li et al., 2011; Raquez et al., 2011; Brömmel et al., 2012; Meng et al., 2013; Zhou et al., 2014; Lu and Li, 2016; Pandini et al., 2016; Lu et al., 2017; Lu et al., 2018; Sarrafan et al., 2022). Among them, the semicrystalline two-way shape memory polymer (2W-SMP) was discovered by Chung et al. (Chung et al., 2008) and will be the focus of this section.

The modeling works for the shape memory polymer (SMP) dated from Tobushi et al.'s model in 1997 (Tobushi et al., 1997), and later on, plenty of constitutive models were developed (Liu et al., 2006; Qi et al., 2008; Xu and Li, 2011; Shojaei and Li, 2014b; Yang and Li, 2016; Yan and Li, 2019; Yan et al., 2020b). However, these works mainly focus on amorphous one-way shape memory polymers (1W-SMPs), and only a few theoretical studies were conducted on semi-crystalline 2W-SMPs (Westbrook et al., 2010; Dolynchuk et al., 2014; Scalet et al., 2018; Yan et al., 2020b; Zeng et al., 2021). Basically, the detailed model frameworks accord with the modeling approach proposed by Yan and Li (2022). To be specific, these models were constructed by depending on Newton's law of motion and three basic physical laws

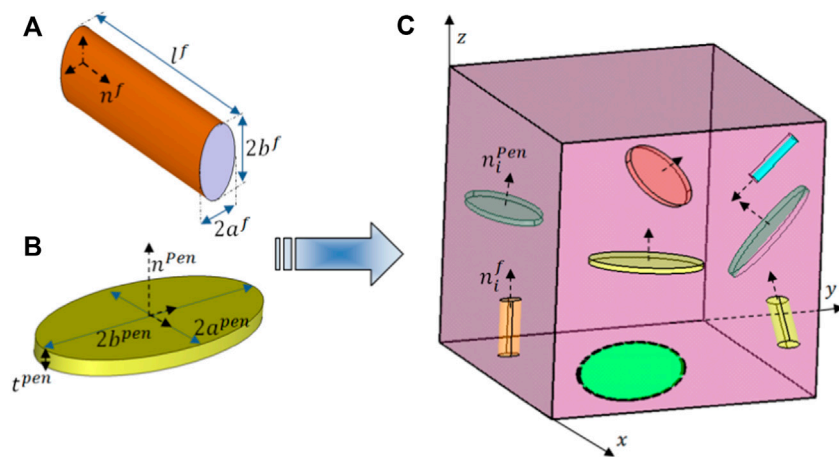


FIGURE 7

Schematic representations of (A) fibrous inclusion, (B) Penny-shape inclusion, and (C) assembled RVE in a micro length scale (Shojaei and Li, 2013) [Reproduced with permission from International Journal of Plasticity, 42: 31-49., (2013). Copyright 2013 Elsevier].

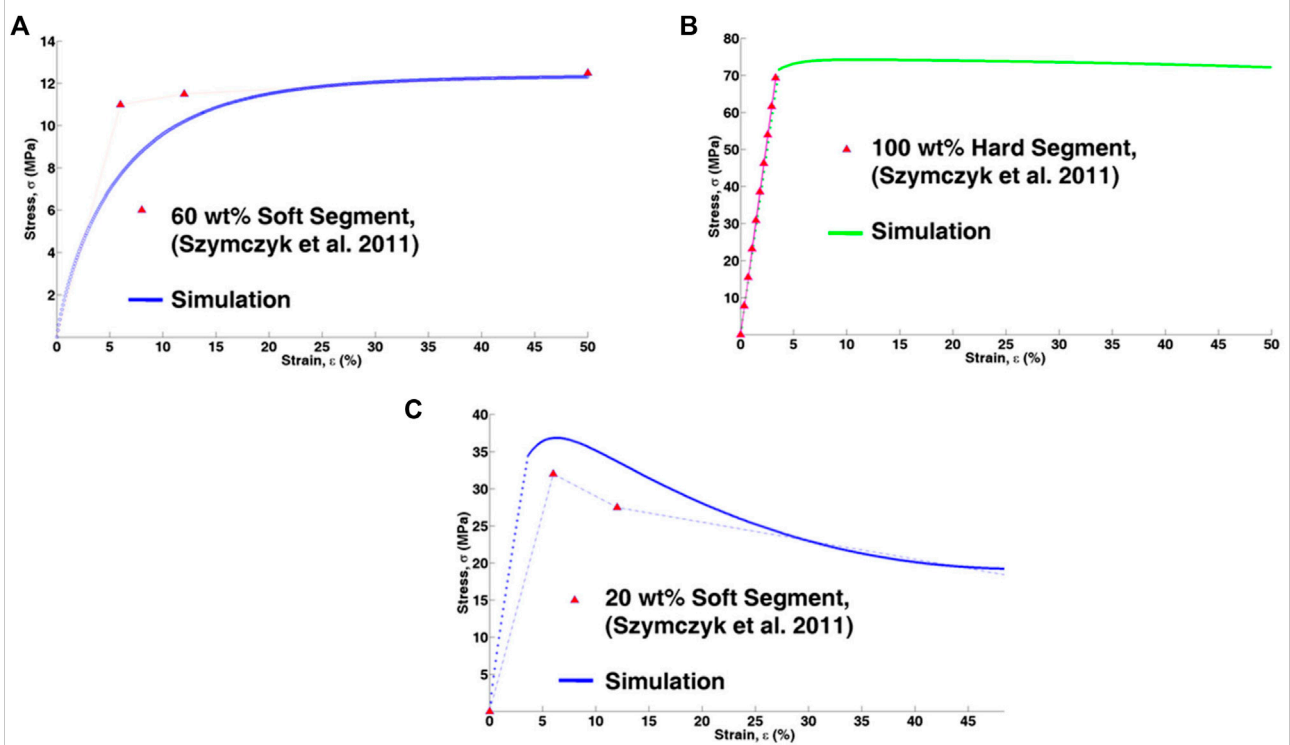


FIGURE 8

(A) Amorphous computation module calibration, (B) crystalline computation module calibration, (C) performance of the model in capturing 20 wt% soft segment tensile test experiment (Szymczyk et al., 2011; Shojaei and Li 2013). [Reproduced with permission from International Journal of Plasticity, 42: 31-49., (2013). Copyright 2013 Elsevier].

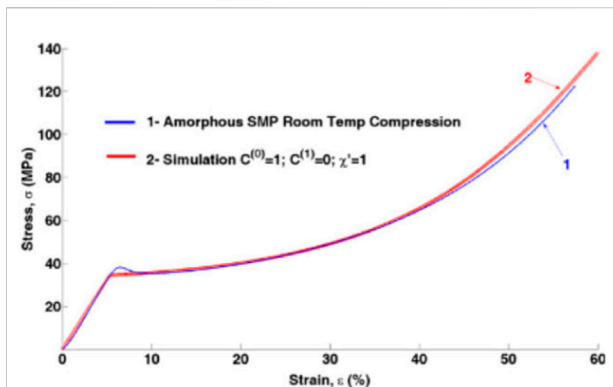


FIGURE 9

Compression test of an amorphous SMP matrix versus simulation data (Shojaei and Li, 2013). [Reproduced with permission from International Journal of Plasticity, 42: 31-49., (2013). Copyright 2013 Elsevier].

(i.e., thermodynamics laws, conservation of mass, and conservation of momentum) and some auxiliary equations (see Figure 10). In fact, 2W-SME still inherits the most classical physical characteristics of 1W-SME, such as temperature-dependent moduli, phase transition, heating rate sensitivity, and so on. However, as shown in Figure 11, 2W-SME bears two unique characteristics that 1W-SME lacks. First, 2W-SME can only be realized by applying pre-tension programming. Second, the phase transition for 2W-SME possesses a first-order phase transformation (between the

amorphous phase to crystalline phase), while 1W-SME possesses a second-order phase transformation that completely occurs in the amorphous phase (between the glassy state to rubbery state). Because of the pre-tension, crystallites are mainly generated along the loading direction and the tensile stress is stored in the material. In the next work step, further crystallization will mainly occur along the direction of pre-tension; hence, the 2W-SMP cannot be viewed as an isotropic material anymore. This crystallization further induces an abnormal cooling-induced elongation (CIE) and a heating-induced contraction (HIC), which are the keys for the simulation.

In the proposed models, every model possesses some unique characteristics. For example, Dolynchuk et al.'s model (Dolynchuk et al., 2014) is built based on the microscopic level, which is different from other phenomenological models. This model considers the conformation change and establishes the relation between the affine microscopic deformation of the crystalline chain and amorphous chain and the macroscopic deformation. The other models are phenomenological models and were established based on the framework of continuum mechanics. Among them, Westbrook et al.'s model (Westbrook et al., 2010) is a pioneer work, wherein they established an implementable one-dimensional model and simply assumed that both the amorphous phase and crystalline phase are linear elastic materials. Also, a simple phase evolution law was proposed, which is connected to the stresses in two phases to illustrate the CIE and HIC. Later,

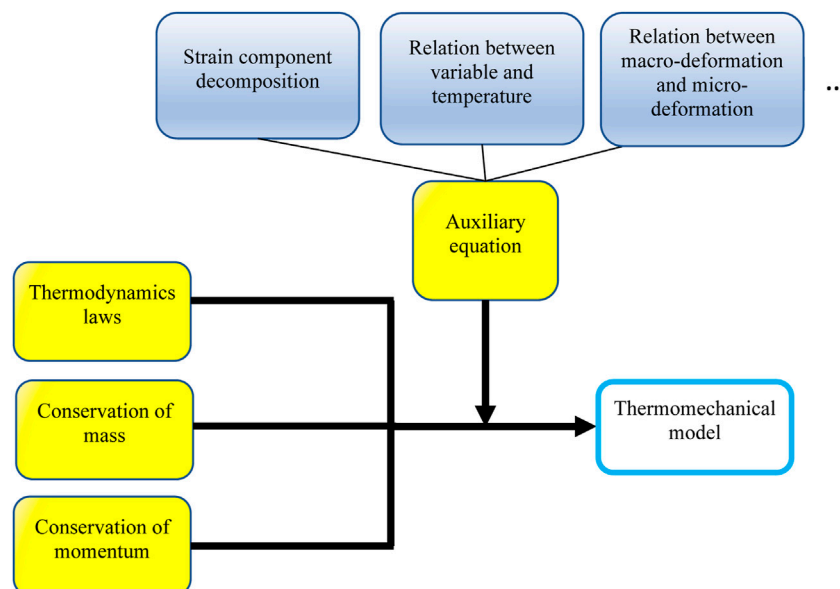


FIGURE 10

Flowchart of the general thermomechanical model for SMPs [Reproduced with permission from Journal of Applied Physics, 131: 111101, (2022). Copyright 2022 American Institute of Physics].

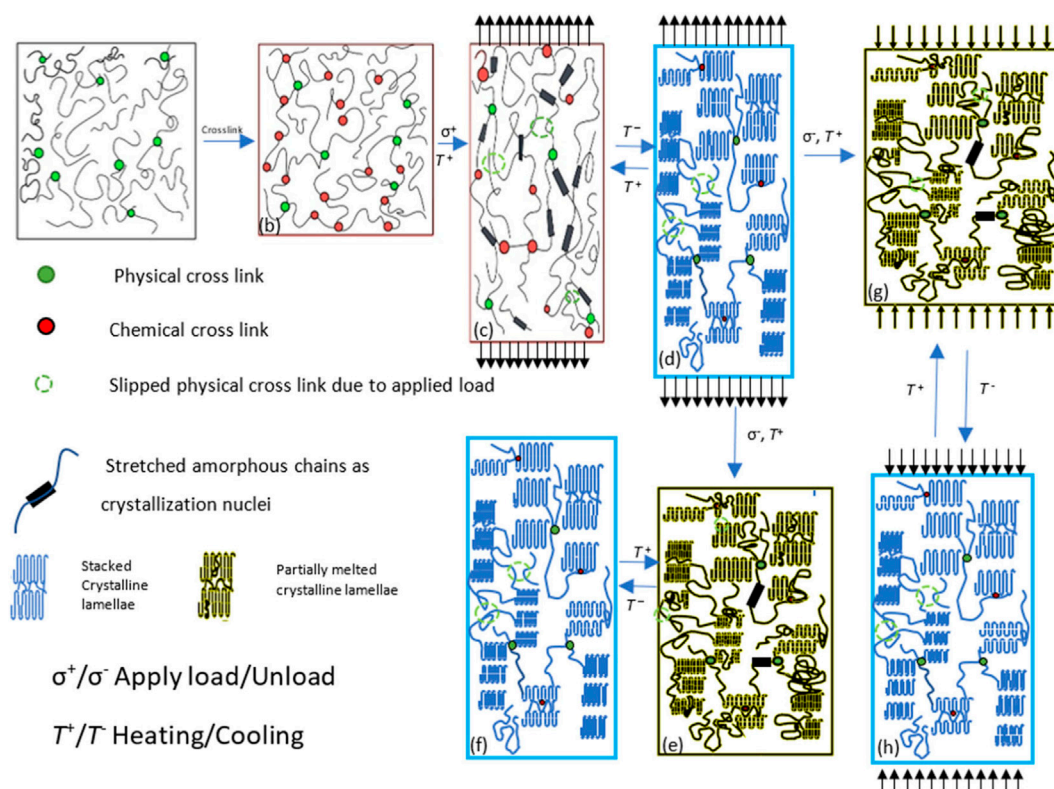


FIGURE 11

Schematic of how the chemically crosslinked two-way shape memory polymer works at a molecular level [redrawn from Figure 1 in ref (Yan et al., 2020b); T : temperature; σ : stress] [Reproduced with permission from Int. J. Mech. Sci., 177 (2020). Copyright 2020 from Elsevier].

Scalet et al. also (Scalet et al., 2018) presented a simple isostress one-dimensional rheological model and comprehensively investigated the multiple applicabilities. In this model, they presented a new exponential function for the phase evolution law. It is shown that this model can well describe the 2W-SMP with a high crosslinked density and the 2W-SME under higher pre-tension. In 2020, Yan et al. (2020b) proposed a three-dimensional model based on Barot et al.'s model (Rao and Rajagopal, 2002; Barot et al., 2008). This model comprehensively studied three types of 2W-SMEs, that is, quasi 2W-SME, true 2W-SME, and advanced 2W-SME. Additionally, in order to model the stretch under multiple thermomechanical loading, they first introduced Mullins effects into 2W-SME modeling and enabled it well to simulate the gradually softened effects for some advanced 2W-SMEs. A most recent three-dimensional model was developed by Zeng et al. (2021), wherein they introduced a new switch to quantify the strain generated by CIH and HIC. In a nutshell, from the standpoint of view for engineering applications, the present models are able to well capture the variety of 2W-SME responses under different experimental loadings; hence, they are well behaved. However, from the

aspect of physics, these models are not perfect and still bear three disadvantages. First, most of them simulated crystallinity by assuming that crystallinity only relates to temperature, which actually does not capture the underlying physics. As indicated above, crystallites are produced along the loading direction, which means that the crystallization and stress are interactively coupled, and this is not reflected by the models. Second, although a few three-dimensional models were developed, they resorted to one-dimensional experiments for validation, which could be less convincing. Third, there are still too many parameters in the models. To be specific, these parameters mainly come from two aspects, that is, establishment of the free-energy function and construction of the phase-transition function. In the future, it is expected that the three disadvantages can be resolved with a further understanding of physics. Additionally, it should be mentioned that recent machine learning models (Yan et al., 2021a; Yan et al., 2021b) indicate that the behaviors for SMP (such as recovery stress, moduli, etc.) can be completely determined once we know the chemical structures of the SMP monomers. It provides another thought for researchers to develop

constitutive models or at least determine key parameters for 2W-SMPs.

Modeling of SMPs including mechanical and functional damage effects

Similar to all other mechanical engineering materials, SMPs also experience various types of damages during production, transportation, installation, and service. An additional damage mechanism in SMP composites happens when they undergo programming and shape recovery processes. [Shojaei and Li \(2014b\)](#) proposed a unified modeling scheme within the continuum damage mechanics (CDM) framework to capture these two different categories of damages in SMPs: 1) physical damage or mechanical damage (MD), which are associated with the duty and life cycle of the SMP composites, and 2) nonmechanical damage or functional damage (FD), which is associated with their thermomechanical (TM) programming and shape recovery cycles. In other words, MD damage captures structural damages that may result in a weaker composite structure, and FD damage give rise to the loss of SMP shape recovery functionality ([Shojaei and Li, 2014](#)). It is experimentally demonstrated that SMPs under cyclic TM programming and recovery may gradually lose their functionality, such as reduction in their shape recovery ratio and stress recovery ratio ([Shojaei and Li, 2014](#)). The FD damage contributes to degradation of the functionality in SMPs, but this FD damage may not necessarily deteriorate the structural properties such as elastic properties.

[Shojaei and Li \(2014\)](#) proposed a modeling framework and addressed the need for a physically consistent CDM theoretical framework for capturing MD and FD damages in SMPs. The statistical mechanics provides a powerful simulation tool for modeling the deformation mechanisms in SMPs. Due to the nature of deformation mechanisms in polymeric materials, developing physically consistent statistical models that can capture polymer chain deformation mechanisms could be very valuable. A successful statistical model could capture various data sources including manufacturing data, loading history, and TM history. Also, statistical approaches could be used to drive confidence level information about the predicted results that is currently not available for non-statistical-based constitutive models. To capture thermomechanical behavior of SMP polymers, [Shojaei and Li \(2014\)](#) proposed a physically consistent model within the statistical mechanics framework that is formulated within the finite deformation

kinematics framework. The developed constitutive models were utilized to study the behavior of SMPs during both the programming and in-service duty cycles. Then, the MD and FD damage mechanisms are coupled with the statistical constitutive behavior to provide a full modeling scheme for SMP composites. The main advantages of the proposed physics-based statistical constitutive laws, as compared to the existing ones, include 1) reducing the effort needed for curve fitting to determine model parameters and 2) modeling flexibility in simulating the nonlinear response of amorphous, semicrystalline, and crystalline SMPs. The proposed constitutive laws consider several deformation mechanisms, including temperature-dependent material properties, glass-transition loss events, shape recovery transient events, stress relaxation, and damage effects. Interested readers may refer to [Shojaei and Li, 2014](#) for the details of the constitutive laws.

As discussed in [Shojaei and Li, 2014](#), the finite deformation kinematics is utilized, in which the deformation gradient, F_{ij} , is utilized to link the Lagrangian $x_i(X_i, t)$ and Eulerian $X_i(x_i, t)$ material coordinates,

$$F_{ij} = \partial x_i / \partial X_j \quad (13)$$

The multiplicative decomposition of the total deformation gradient, F_{ij} , into the elastic F_{ij}^e , plastic F_{ij}^p , and damage F_{ij}^d gradients is then used to facilitate the numerical solution of coupled plasticity damage via return mapping algorithms ([Shojaei and Li, 2014](#))

$$F_{ij} = F_{ik}^e F_{kl}^p F_{lj}^d \quad (14)$$

[Shojaei and Li \(2014\)](#) utilized two sets of constitutive models, namely, “Background” and “Shape memory affected” properties, to model the thermomechanical behavior of SMPs. A nonprogrammed SMP is modeled similar to conventional polymers. The *background* constitutive laws capture the properties of a nonprogrammed SMP. In the case of a programmed SMP, *shape memory affected* constitutive laws are utilized to capture the thermomechanical behavior. It is noted that both the “Background” and “Shape memory affected” properties are coupled, which are interrelated via constitutive relations.

Shape recovery and glass-transition events

[Shojaei and Li \(2014\)](#) utilized statistical mechanics to model shape recovery and glass-transition events. Gaussian distribution and its cumulative norm can effectively capture the recovery transition, that is, T_r for a programmed SMP, and the glass

transition, that is, T_g , as discussed in (Shojaei and Li, 2014). Gaussian distributions are assumed for the shape recovery and the glass-transition events. The normal distribution is defined through ' $dnorm_r$ ' and ' $dnorm_g$ ' terms, respectively, and their respective cumulative values, that is, ' $pnorm_r$ ' and ' $dnorm_g$ ', are defined as follows (Shojaei and Li, 2014):

$$\begin{aligned} dnorm_{\#}(T, T_{\#}, \sigma_{\#}) &= \frac{1}{\sigma\sqrt{2\pi}} \times \exp\left(-\left(\frac{(T - T_{\#})^2}{2\sigma_{\#}^2}\right)\right) \\ pnorm_{\#}(T, T_{\#}, \sigma_{\#}) &= \int_{T_1}^{T_2} dnorm_{\#}(T, T_{\#}, \sigma_{\#})dT \end{aligned} \quad (15)$$

where the subscript “#” will accordingly be replaced with “g” or “r” to indicate the “glass transition” or the “recovery transition” processes, respectively. The dynamic mechanical analysis (DMA) test data can be used to obtain the material parameters in Eq. 15, see (Shojaei and Li, 2014).

Background storage elastic moduli

Statistical terms for the elastic tensile modulus E , decomposed into elastic storage modulus, that is, E' , and loss modulus, that is, E'' , were proposed in (Shojaei and Li, 2014). The elastic tensile, E' , and bulk, B' , storage moduli are constitutively prescribed as follows (Shojaei and Li, 2014):

$$\begin{aligned} E' &= E'_0 \times \frac{(1 - pnorm_g)}{(1 - pnorm_g^{max})} \\ B' &= B'_0 \times \frac{(1 - pnorm_g)}{(1 - pnorm_g^{max})} \end{aligned} \quad (16)$$

where E'_0 and B'_0 are reference elastic and bulk moduli, respectively. Also, $pnorm_g^{max}$ is the max value of $pnorm_g$. Interested readers may refer to (Shojaei and Li, 2014) for a full description of the mathematical model.

Shojaei and Li (2014) studied the SMP shape memory modeling and functional damage (FD) phenomena within the context of statistical mechanics. In a thermomechanical cycle, three main factors dominate the shape recovery in SMPs, which include 1) pre-strain, 2) stress relaxation effect during programming, that is, loading time, and 3) the rate of heating (Shojaei and Li, 2014). A thermomechanical cycle of SMPs includes several mechanisms, which are experimentally observed, including the following: 1) higher recovery strain can be achieved with higher holding times at elevated temperatures, 2) the effect of heating rate during shape recovery can increase the transition temperature but not the recovery strain, and 3) the FD leads to reduction or total loss of shape memory functionality, which is larger with higher programming strain and high thermomechanical cycles.

Shojaei and Li (2014) proposed that the damage mechanics of SMPs should be classified into two distinct classes (Figure 12): 1) mechanical damage (MD): damage induced during operational conditions and under their service loads, and 2) FD: induced during thermomechanical cycles. The MD definition helps to identify lifetime- and reliability-related issues, while FD can be used to characterize SMP programming and shape recovery performance.

Constitutive models for MD and FD of SMPs were developed based upon continuum damage mechanics (CDM), please refer to (Shojaei and Li, 2014) for details. Figures 13–19 highlight the performance of the developed statistical model in capturing different aspects of SMP thermomechanical behavior under service loads as well as during the programming cycles. Figure 13 illustrates the performance of the proposed framework in capturing glass-transition events. Figures 14A,B show respectively the model performance in capturing strain rate-dependent and temperature-dependent yield behavior of SMPs. The elasto-viscoplastic behavior of SMPs is studied in Figures 15A,B, in which the strain rate effect and temperature effects have been modeled. Figure 16 shows the effect of programming strain levels on the final shape recovery process. In Figure 17, the heating rate effect on the shape recovery process is demonstrated. The effect of the holding (relaxation) time on the recovered strain level is studied in Figure 18. Experimental data as well as simulation results for the FD of SMPs are depicted in Figure 19.

Challenges and future perspectives

Since the first SMP was discovered in 1985, considerable advancements have been made in designing, synthesizing, and manufacturing SMP-based devices and structures. Discovery of new SMPs is accelerated by the understanding of the mechanisms controlling the shape memory effect. Our understanding of the mechanisms controlling the shape memory effect for various types of SMPs has been progressing quickly, which in turn helps designing new SMPs. For example, our initial understanding of the driving force for the shape memory effect of thermoset SMPs is primarily through entropy change, that is, entropy reduction during programming and entropy increase during shape recovery (Behl and Lendlein, 2007; Meng and Li, 2013), which leads to many thermoset SMPs with very low recovery stress in the rubbery state. Our new understanding indicates that energy input during programming can also be stored through enthalpy increases by bond length change and bond angle change, which is stable at the glassy state due to steric hindrance (Fan and Li, 2018; Yan and Li, 2020a; Wick et al., 2021). Upon heating, the stored energy will be released, leading to shape and/or stress recovery. Based on this understanding,

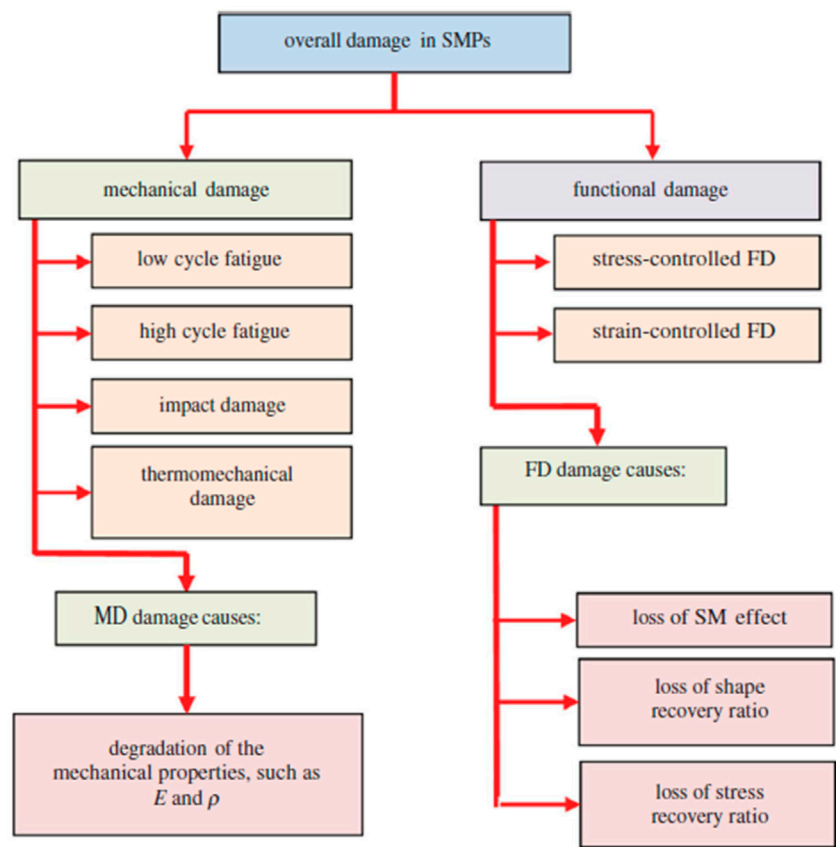


FIGURE 12
Flowchart for the damage categories in an SMP system (Shojaei and Li, 2014). [Reproduced with permission from Proceedings of the Royal Society A, 470: 20140199., (2014). Copyright 2014 Royal Society].

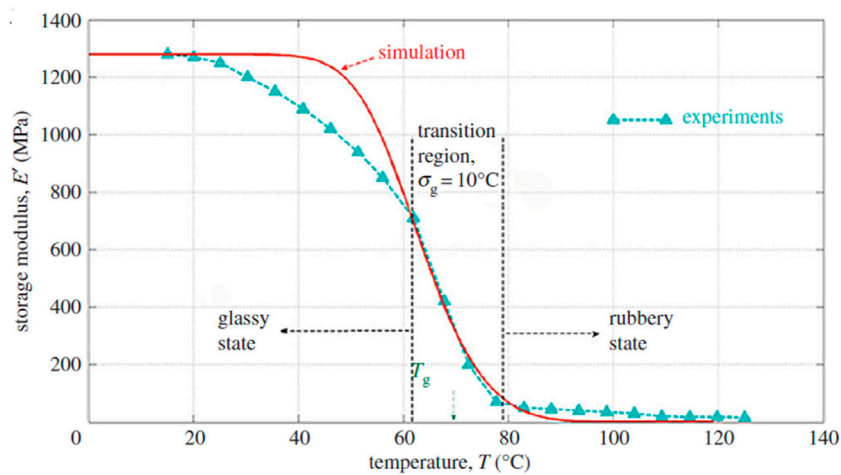


FIGURE 13
Experimental and simulation results for the storage tensile modulus, E' , with storage modulus $E'_0 = 1,290$ MPa (Shojaei and Li, 2014). [Reproduced with permission from Proceedings of the Royal Society A, 470: 20140199., (2014). Copyright 2014 Royal Society].

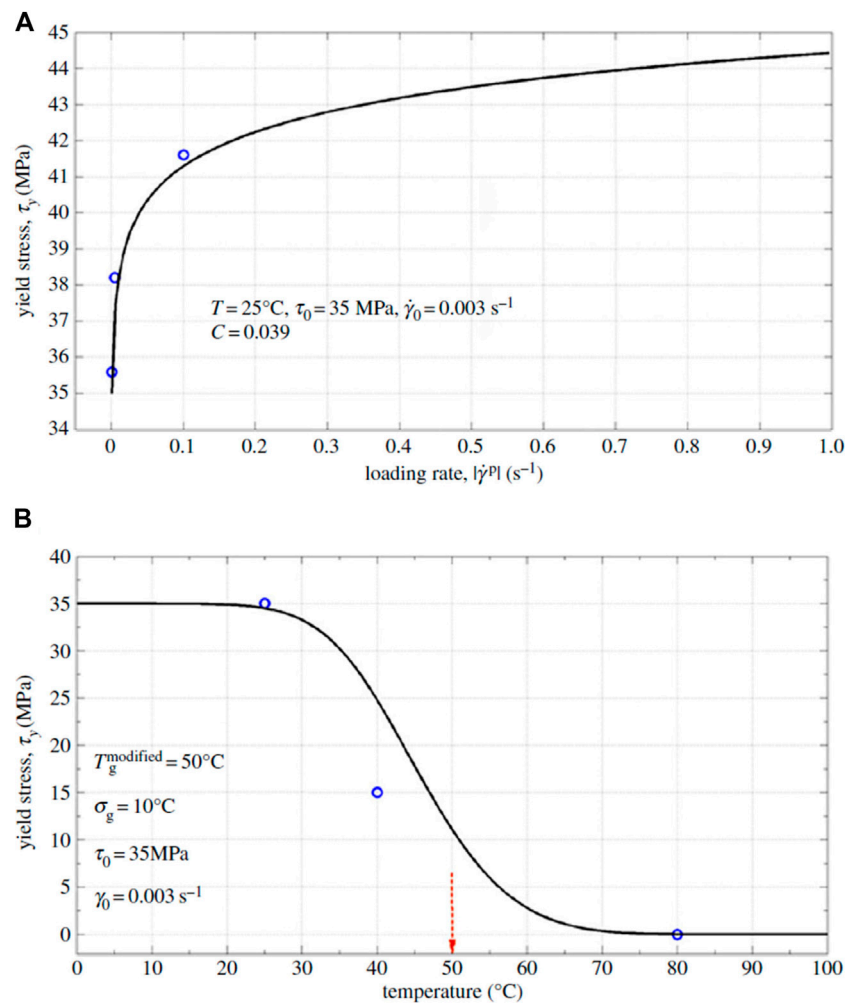


FIGURE 14

Comparison of experimental and simulation results for (A) strain rate-dependent and (B) temperature-dependent yield stresses. Circles denote experimental results, and the solid line denotes simulation results (Shojaei and Li, 2014). [Reproduced with permission from Proceedings of the Royal Society A, 470: 20140199., (2014). Copyright 2014 Royal Society].

polymers with high recovery stress in the rubbery state have been designed, synthesized, and characterized (Fan and Li, 2018; Li et al., 2018; Feng and Li, 2021b). It is envisioned that with the ever-increasing discovery of new SMPs, constitutive modeling will continuously be an essential player in the design and manufacturing of new SMP-based structures and devices. For example, Yan and Li (2020a) developed a four-chain model to describe the constitutive behavior of enthalpy-driven SMPs, which was also validated by molecular dynamics simulation (Wick et al., 2021).

A recent development in amorphous SMPs is the combination of the shape memory effect and other functionalities, such as self-healing and recycling capabilities within the framework of vitrimers (Montarnal et al., 2011; Lu et al., 2012; Gandini, 2013; Denissen et al., 2015; Obadia et al., 2015; Chao et al., 2016; de Luzuriaga et al.,

2016; Lu et al., 2016; Zhang et al., 2016; Lu et al., 2017; Nishimura et al., 2017; Rottger et al., 2017; Li et al., 2018; Feng et al., 2019; Yuan et al., 2019; Feng et al., 2020a; Feng and Li, 2020b; Konlan et al., 2020; Suslu et al., 2020; Feng and Li, 2021a; Feng and Li, 2021b; Feng and Li, 2021c; Feng and Li, 2022; Konlan et al., 2022), which seamlessly utilized the shape memory effect to close the wide-opened crack first and heal the closed crack by the adaptable covalent network (CAN), per the close-then-heal (CTH) strategy initiated in Li's lab (John and Li, 2010; Li and John, 2008; Li and Nettles, 2010; Li and Uppu, 2010; Nji and Li, 2010a; Nji and Li, 2010b; Nji and Li, 2012). The combination of the shape memory effect with flame retardancy is another new development (Feng et al., 2019; Feng et al., 2020a; Feng et al., 2020b; Feng and Li, 2021a; Feng and Li, 2021b; Feng and Li, 2022; Zhang et al., 2022). SMPs for four-dimensional printing are also a new development (Ge et al., 2016; Tibbits, 2014; Kuang et al.,

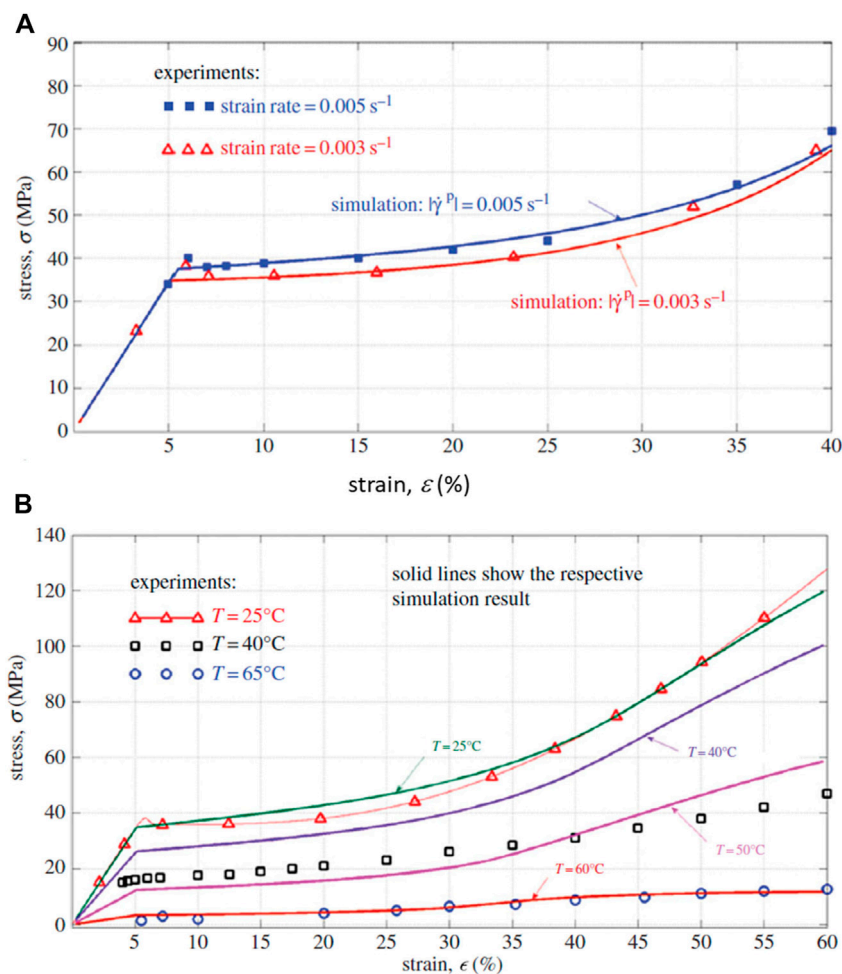


FIGURE 15

Comparison of experimental and simulation results for the viscoplastic stress–strain responses to (A) rate and (B) temperature (Shojaei and Li, 2014). [Reproduced with permission from Proceedings of the Royal Society A, 470: 20140199., (2014). Copyright 2014 Royal Society].

2018; Li et al., 2018; Li et al., 2019; Feng et al., 2021a). Clearly, these new types of multifunctional SMPs involve multi-length scale and multi-time scale as well as multi-physics, including coupling between CANs and the shape memory effect and phase change and compositional change during fire hazard. Efforts are thus needed to provide new constitutive models to describe these new types of multifunctional SMPs.

However, one grand challenge facing this community is that the existing constitutive modeling frameworks either lack generality or consist of too many curve fitting parameters or are impractical for engineering design or lack an understanding of molecular length scale mechanisms. For example, elastoviscoplastic models and phase evolution law models consist of a large number of parameters, and some of them must be determined by curve fitting, which make the models work only for a limited number of SMPs and cannot be generalized for other SMPs. Some models such as rheological models are

simple to use but clearly lack molecular scale insights. Some models such as molecular dynamics simulation are limited to a short time scale and very small strain and are also very time-consuming for computation, which is not proper for engineering design. Therefore, there is a clear need for more in-depth understanding of the mechanisms controlling the shape memory effect. The more the use of physical parameters such as gas constant, Boltzmann constant, and Avogadro number, the simpler and more general the model and the more applicable the model in practice.

One possible solution is through machine learning. With enough training data, machine learning algorithms can learn the hidden features, for example, the correlation between the molecular structures and material properties. Because of this, machine learning has been widely used in discovering new materials, including metals and alloys (Wen et al., 2019), ceramics (Yuan et al., 2018), drugs (Guyon et al., 2002), and

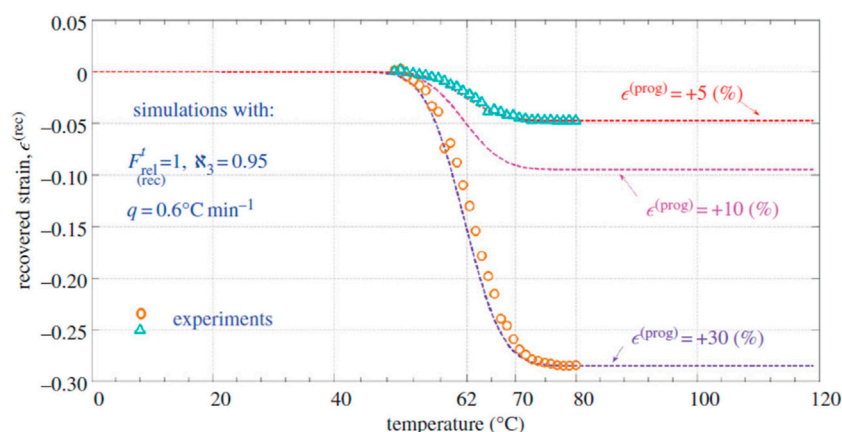


FIGURE 16

Comparison of experimental and simulation results for the effect of pre-strain levels on the final shape recovery process (Shojaei and Li, 2014). [Reproduced with permission from Proceedings of the Royal Society A, 470: 20140199., (2014). Copyright 2014 Royal Society].

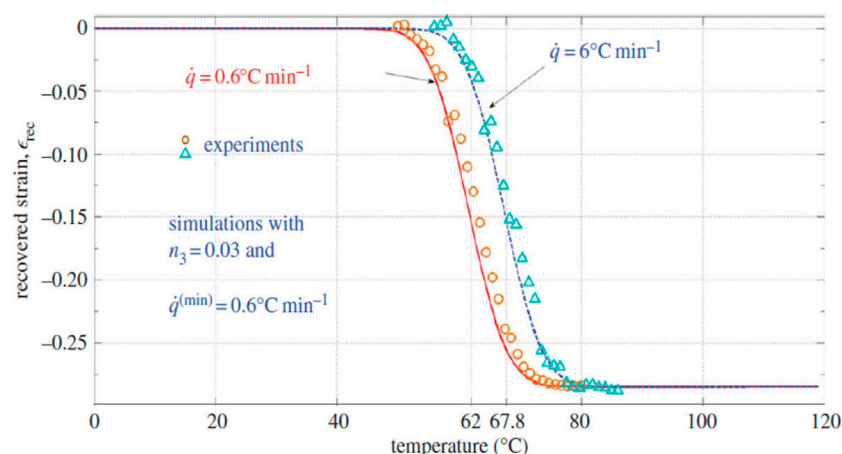
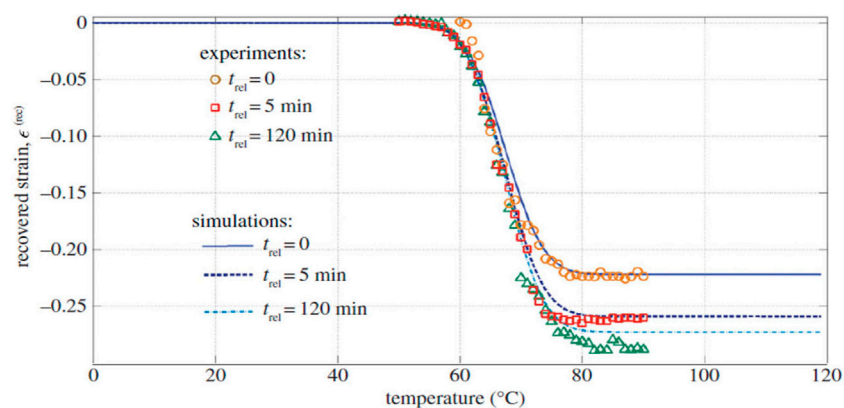


FIGURE 17

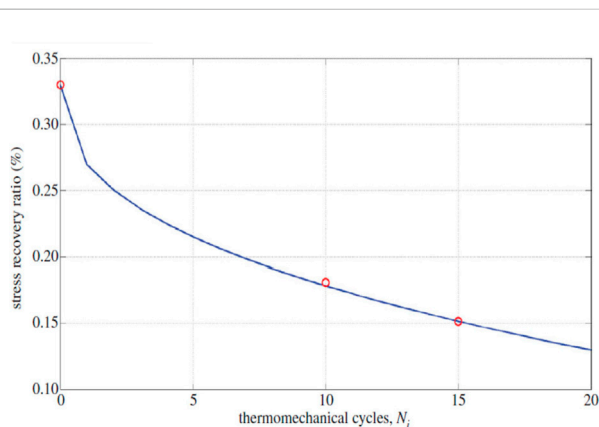
Dependence of the shape recovery process on the heating rate (Shojaei and Li, 2014). [Reproduced with permission from Proceedings of the Royal Society A, 470: 20140199., (2014). Copyright 2014 Royal Society].

polymers (Wu et al., 2019). Yan et al. (2021a, 2021b) also used machine learning and discovered new thermoset SMPs, which have been validated either by molecular dynamics simulation or by experimental testing (Wick et al., 2021). Shafe et al. (2022) studied the effect of atomistic fingerprints on thermomechanical properties of epoxy-diamine thermoset shape memory polymers, which facilitates machine learning discovery of TSMPs. Recently, we also established both forward and inverse machine learning frameworks and discovered quite a few columns, lattice unit cells, and thin-walled structures with much improved structural capacities, including structures three-dimensional-printed by SMPs (Challapalli and Li,

2020; Challapalli et al., 2021a; Challapalli et al., 2021b; Challapalli and Li, 2021). Following the same line, it is expected that machine learning may also be used to establish the constitutive laws for SMPs. Actually, machine learning has been used to establish constitutive laws for rocks (Wang and Sun, 2018), liquids (Tartakovsky et al., 2020), and other solids (Masi et al., 2021). In the field of computational mechanics, the majority of applications of machine learning were related to supervised learning, which trains feed-forward neural networks to replace rate- and path-dependent constitutive laws for solid mechanics problems (Ghaboussi et al., 1991; Furukawa and Yagawa, 1998). A different approach has recently been

**FIGURE 18**

Dependence of recovered strain [$(\text{prog}) = +0.3$] on the holding or relaxation time t_{rel} (Shojaei and Li, 2014). [Reproduced with permission from Proceedings of the Royal Society A, 470: 20140199., (2014). Copyright 2014 Royal Society].

**FIGURE 19**

Effect of FD on the stress recovery ratio for a one-dimensional constrained stress recovery. Circles denote experimental results for confined shape recovery, and the solid line denotes simulation results (Shojaei and Li, 2014). [Reproduced with permission from Proceedings of the Royal Society A, 470: 20140199., (2014). Copyright 2014 Royal Society].

proposed (Kirchdoerfer and Ortiz, 2016), where the supervised learning process was implemented without using the artificial neural network. Instead, a new constrained optimization approach that minimized the discrepancy between measured and predicted responses was proposed. In this approach, the universally accepted knowledge, such as the conservation of mass, conservation of energy, conservation of momentum, thermodynamics laws, and so on, was used as a constraint of the minimization problems. Consequently, by finding the saddle point of a constrained optimization problem, local data sets that were closest to the satisfaction of constraints were located and used to provide incremental updates of

elasticity problems. This method has been extended to plasticity problems in Ibanez et al., 2018 by reintroducing the yield surface and enforcing perfect plasticity. It is expected that machine learning, informed by physics and bounded by physical laws such as conservation laws and thermodynamics laws, will be one of the useful tools in developing constitutive models for SMPs.

Conclusion

In this work, multiple modeling frameworks, developed in Li's research lab within the past few years, have been reviewed and elucidated. The frameworks discussed include thermodynamics, phase evolution laws, unit cells, statistical mechanics, and continuum damage mechanics. When possible, physical insights were discussed. A large number of relevant references from other research labs were cited. Perspectives on future development were discussed in the context of challenges facing the existing model frameworks, fast growth in new multifunctional SMPs, and the potential use of the emerging machine learning technology in establishing thermomechanical constitutive models for SMPs. We hope that this insight paper will provide some fundamental knowledge on the common constitutive modeling frameworks of SMPs and shed some lights on future development in this amazing research direction.

Author contributions

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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Conflict of interest

WX was employed by the company Vitro Architectural Glass.

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