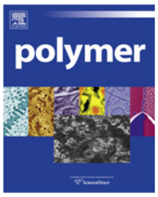
Polymer 52 (2011) 4985–5000

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



Feature Article

Recent advances in polymer shape memory

Tao Xie*

Chemical Sciences and Materials Systems Laboratory, General Motors Research and Development Center, Mail Code: 480-106-224, 30500 Mound Road, Warren, MI 48090-9055, USA

ARTICLE INFO

Article history:
Received 16 June 2011
Received in revised form
28 July 2011
Accepted 4 August 2011
Available online 10 August 2011

Keywords:
Shape memory polymer
Stimuli-responsive polymer
Polymer actuator

ABSTRACT

Traditional shape memory polymers (SMPs) are those capable of memorizing a temporary shape and recovering to the permanent shape upon heating. Although such a basic concept has been known for half a century, recent progresses have challenged the conventional understanding of the polymer shape memory effect and significantly expanded the practical potential of SMPs. In this article, notable recent advances in the field of SMPs are highlighted. Particular emphasis is placed on how the new developments have changed the conventional view of SMPs, what they mean for practical applications, and where the future opportunities are.

1. Introduction

Shape memory polymers (SMPs) represent a technologically important class of stimuli-responsive materials for which the response lies in the shape change. More specifically, the conventional definition of an SMP is a polymer can be deformed and subsequently fixed into a temporary shape, which would remain stable unless it is exposed to an appropriate external stimulus that triggers the polymer to recover to its original (or permanent) shape. Accordingly, the associated behavior of SMP is called polymer shape memory effect (SME). Although various forms of external stimuli may be utilized as the recovery trigger, the most typical one is direct heating that leads to a temperature increase.

The first recognition of polymer SME, as suggested by Mather et al., can be traced back to a patent in 1940s in which "elastic memory" was mentioned [1]. The well-known heat shrinkage tubing that appeared in 1960s, on the other hand, represents a commercial application of SMP even before the terminology became being used. It is thought that the first official use of the SMP term may have started in 1984, with the development of the polynorbornene based SMP by CDF Chimie Company (France) [2]. Despite the long history of SMP, however, the phenomenon of polymer SME had remained little known and the scientific paper in this area had been rather limited until 1990s. Along this time frame, the discovery of segmented polyurethane SMP by Mitsubishi Heavy Industries Ltd. stimulated significant interests in SMPs, presumably due to the versatility of urethane chemistry that allows easy structural tuning and the industrial significance of polyurethane. For the same reasons, research on shape memory polyurethanes has remained quite active even today, despite many different SMPs that have since been discovered.

Historically, the advancement of the SMP field has been closely associated with its practical potential. As such, the lack of excitement and research activities in the early days of SMPs can be attributed to the limited applications envisioned for such materials. In 2002, Lendlein et al. demonstrated that SMP could be used as self-tightening suture for minimum invasive surgery [3]. The SMP in the form of suture was first deformed into an elongated form. The SMP suture in this temporary shape was applied loosely to the wound (the left image in Fig. 1). The shape recovery of the suture was then triggered by human body heat, leading to the shrinkage of the suture and the tightening of the knot (the right images in Fig. 1) without external intervention. Here, the polymeric nature of the material can be conveniently utilized to incorporate additional functionalities such as biodegradability, which eliminates the need for an additional operation for suture removal. This prototype demonstration has raised significant interests in other biomedical uses of SMP. Today, tailoring SMP for various biomedical uses represents a significant portion of the SMP research [4,5]. This intense focus on biomedical applications of SMP is in part due to the associated high value that is unmatched by most non-biomedical applications. An additional driving force lies presumably in the relatively large funding allocated to biomedical research in general.

---

* Tel.: +1 586 947 2471; fax: +1 586 986 1207.
E-mail address: tao.xie@gm.com.

doi:10.1016/j.polymer.2011.08.003

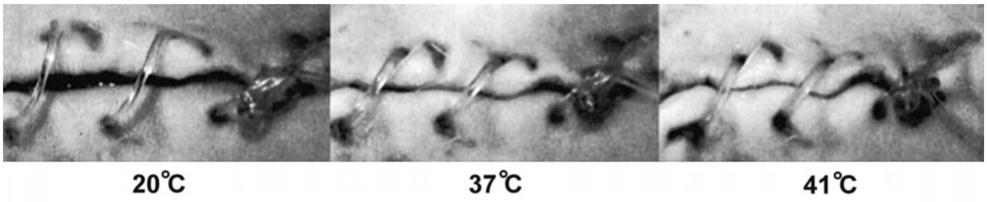


Fig. 1. SMP based self-tightening suture for wound closure. The photos from left to right show the shrinkage and tightening of the suture with temperature increase. Reproduced from Ref. [3] with permission.

Benefited in no small part to the potential for biomedical uses, the SMP field has undergone explosive growth within the last decade. Along the way, many SMP systems and innovative non-biomedical applications have emerged. Since 2000s, a number of excellent reviews have been published that cover the general aspects of SMPs [6–11], SMP composites [12,13], biomedical applications [4,5], and non-biomedical applications [14,15]. On the other hand, recent progresses in the last five years in the SMP field have significantly challenged the conventional view of polymer SME. As such, the intent of the current paper is not to provide an extensive review of the SMP research. Instead, the focus is on highlighting examples of recently emerged shape memory phenomena, their profound impact to the field of SMP on both scientific and practical fronts, and future outlook. The sub-topics in the main text are organized in the following order: dual-shape memory effect; molecular origin of polymer SME; unconventional molecular designs; recovery stress; reversible plasticity shape memory effect; small strain shape memory phenomena; surface shape memory effect; two-way shape memory effect; triple-shape memory effect; tunable multi-shape effect and temperature memory effect; alternative actuation mechanisms, and conclusions and outlook.

2. Dual-shape memory effect

The conventional and most basic form of the polymer SME is schematically illustrated in Fig. 2a. The SMP is first heated to a deformation temperature (T_d), which leads to the material softening (modulus drop). A deformation force is subsequently applied (i.e. loading). The SMP is then cooled down under the load. Upon load removal (unloading), the deformed temporary shape is fixed, which marks the completion of the shape fixing. When the SMP in its temporary shape is re-heated to a recovery temperature (T_r) under a stress free condition, the original (or permanent) shape is recovered. In typical cases, both T_d and T_r are above the reversible thermal transition temperature (glass transition temperature T_g or melting point T_m) of the SMP, which is thus called shape memory transition temperature (T_{trans}). The evolution of the strain, stress, and temperature with time in a cycle such as Fig. 2a can be fully captured in a quantitative thermomechanical analysis (TMA) cycle (Fig. 2b).

In both Fig. 2a and b, a total of two shapes (one temporary shape and one permanent shape) are involved in each shape memory cycle. Such an SME is thus referred to as the dual-shape memory effect (dual-SME), in distinction to the recently emerged triple-shape memory effect (triple-SME) and multi-shape memory effect (multi-SME) discussed later in this article. The strain evolution curve is Fig. 2b serves as the typical basis for quantifying the dual-SME. Specifically, the abilities of an SMP to fix and recover shapes are respectively defined as shape fixity (R_f) and shape recovery (R_r) according to Eqs. (1) and (2):

$$R_f = 100\% \times \varepsilon/\varepsilon_{load} \tag{1}$$

$$R_r = 100\% \times (\varepsilon - \varepsilon_{rec})/\varepsilon \tag{2}$$

where ε_{load} represents the maximum strain under load, ε is the fixed strain after cooling and load removal, and ε_{rec} is the strain after recovery. In a standard dual-shape memory cycle such as Fig. 2b, the stress and temperature curves may be omitted as they are not used in the evaluation of the shape fixity (R_f) and shape recovery (R_r) [16]. Similarly, the stress, strain, and temperature evolution in a shape memory cycle may be plotted in a three dimensional figure that is also sufficient for such evaluations [1,6]. Fig. 2b, on the other hand, provides complete information of the stress, strain, and temperature at any time during the cycle, which is essential for more sophisticated shape memory cycles. This point will become readily evident later in the context.

SMPs may also be evaluated by the recovery speed (or strain recovery rate). The instantaneous recovery speed V_r, for instance, is defined as the time (t) derivative of strain ε (Eq. (3)),

$$V_r = \frac{\partial \varepsilon}{\partial t} \cdot 100\% \tag{3}$$

Whereas the recovery speed is a practically important parameter, its evaluation has not been commonly practiced. This is at least in part due to the fact that the absolute value of the shape recovery speed is highly dependent on a variety of factors beyond the intrinsic properties of an SMP, which may include the thermal

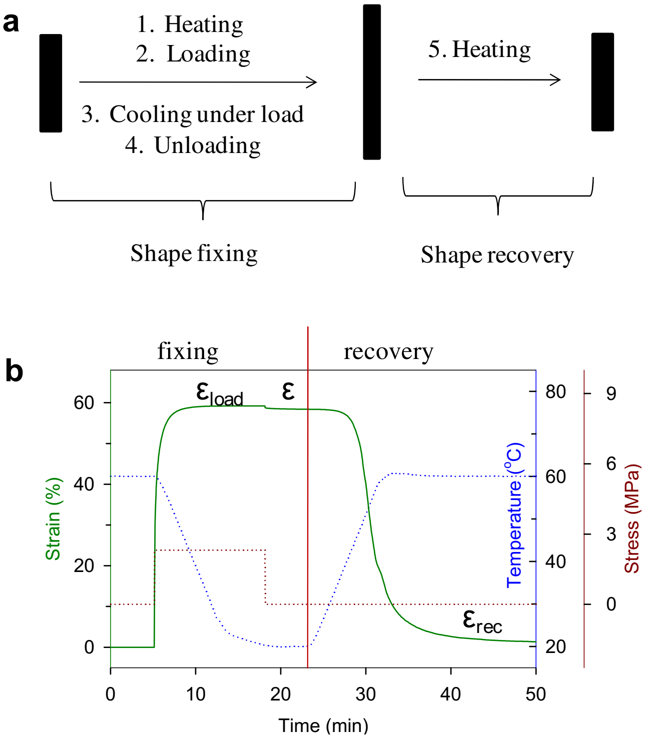


Fig. 2. Conventional dual-shape memory cycle. (a) Schematic illustration; and (b) quantitative TMA cycle.

environment, the thermal conductivity of the fillers for SMP composites, and even the heating method. It is therefore challenging to find a quantitative correlation between the recovery speed and the molecular structures of SMPs, particularly among experimental results from different groups. Interestingly, however, Lendlein's group has been using recovery speed to define the shape memory switch temperature (T_{sw}), which is the temperature corresponding to the peak recovery speed [17]. Presumably, the motivation for T_{sw} is to find a parameter that is more closely related to the shape recovery behavior than T_{trans}, which is usually determined using thermal analysis methods that are not directly linked to shape memory tests such as differential scanning calorimetry (DSC) or dynamic mechanical analysis (DMA). Whereas such a distinction between T_{sw} and T_{trans} may seem trivial in common cases of dual-SME, it does play a significant role for more sophisticated SME mentioned later.

3. Molecular origin of polymer SME

In the larger context of shape memory materials, SMP have been often compared to shape memory alloys (SMA) as these two classes of materials share similar names and, to certain extent, similar behaviors. Although SMA is beyond the scope of the current report, it is important to note that such a comparison should be made carefully to avoid confusion. The SME of alloys relies on the reversible thermal transition between two crystalline phases, i.e., the low temperature yieldable martensinic phase and the high temperature austentinic phase. Metallic alloys meeting such a requirement are quite limited in numbers. Thus, SME is not commonly expected for metallic alloys.

In contrast, polymer SME is predominantly an entropic phenomenon. The changes in temperature (thus molecular mobility) and macroscopic shape (thus chain conformation) in a typical dual-shape memory cycle are illustrated in Fig. 3. In its permanent macroscopic shape, the molecular chains of an SMP adopt conformations with the highest entropy, that is, the chains are in a thermodynamically stable state. Upon heating above the T_{trans}, the chain mobility is significantly activated. When an external deformation load is applied, the chain conformations are changed, leading to a lower entropy state and macroscopic shape change. When the SMP is cooled below T_{trans}, this lower entropy state (or the temporary shape) is kinetically trapped due to the freezing of the molecular chain segments, resulting in the macroscopic shape fixation. Upon reheating above T_{trans} under a stress free condition, the molecular mobility is re-activated, which allows the chains to return to their highest entropy state (i.e. recovery of the permanent shape). Here, the exact nature of chain conformation change during deformation has not been a major focus in the literature. One would, however, anticipate that this would depend on the molecular structure of the SMP and may have to be considered on a case-by-case basis.

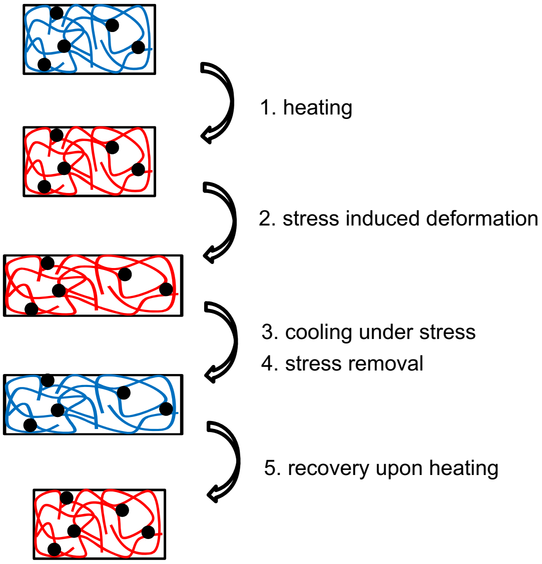


Fig. 3. Molecular mechanism of dual-SME. Black dots: netpoints; blue lines: molecular chains of low mobility below T_{trans}; red lines: molecular chains of high mobility above T_{trans}.

For a polymer to display dual-SME, it has to meet two structural requirements: (1) a reversible thermal transition (or shape memory transition) for temporary shape fixing and recovery; (2) a crosslinking network that sets the permanent shape. The first requirement allows suppression and activation of the molecular mobility for entropy trapping (shape fixing) and releasing (recovery), respectively. Polymers are in general intrinsically viscoelastic materials with at least one thermal reversible phase transition (glass transition or melting point), with few exceptions for which the polymer may decompose before it reaches the thermal transition temperature (i.e. the thermal transition is practically non-existent). Thus, most (if not all) polymers meet the first requirement.

The network that sets the permanent shape (i.e. the second requirement) can be chemical and physical crosslinking. Without the crosslinking, the deformation force imposed onto a polymer above its thermal transition (step 2 in Fig. 3) would lead to long-range chain slippage that is reflected as macroscopic material flow. Under such a scenario, the polymer does change macroscopic shape, yet with little or no change in polymer chain conformation (i.e. entropy). The entropic energy, which is the driving force for the shape recovery, is thus absent. As a consequence, the polymer would not possess the SME. By prohibiting the long-range chain slippage, the crosslinking network ensures that the macroscopic shape change arises from entropy, which is recoverable. Complete prohibition of the long-range chain slippage is thus necessary for ideal shape recovery performance, as is often the case for chemically crosslinked SMP systems. By comparison, incomplete suppression of the long-range chain slippage would lead to compromised shape memory behaviors.

Based on the nature of the thermo-reversible transition and the crosslinking, traditional SMP can be classified into four categories: (1) chemically crosslinked glassy polymers, (2) chemically crosslinked semicrystalline polymers, (3) physically crosslinked glassy polymers, and (4) physically crosslinked semicrystalline polymers [1]. Majority of known SMPs would handily fall into one of the four categories.

The commonly known physically crosslinked SMP comprises of two phases, with the high and low temperature transition phases serving as the physical crosslinks and the shape memory transition, respectively. Extensive chain entanglements for ultrahigh molecular weight polymers may also function as the physical crosslinking. Regardless of the nature of the physical crosslinks, however, they do not exist universally in polymers. Chemical crosslinking, by contrast, can be generally introduced into any polymers utilizing generically applied methods such as e-beam radiation. As such, most (if not all) polymers can be converted into dual-shape memory polymers by chemical crosslinking.

The two molecular structural requirements for SMP can be further illustrated in a simple experiment with a capped rubber tube filled with water. The rubber tube is bended and put into a refrigerator while the bending force is maintained. Upon freezing of water, the force is removed but the bended shape (a temporary shape) is fixed. Upon melting of the ice inside the tube, the original tube shape can be recovered. Here, water and the surrounding rubber wall provide the reversible thermal transition and the mechanism to set the permanent shape, respectively. If there is any leak in the rubber tube, water will flow outside and the experiment would fail. The physical confinement of rubber tube is thus similar to the crosslinks and any leak in the rubber is analogous to the long-range chain slippage that is detrimental to polymer SME.

The above water tube experiment, while can be envisioned by anybody without much scientific knowledge, bears striking similarity to an SMP design approach by Mather et al. In the Mather's work [18], a non-woven fiber mat of a non-crosslinked polycaprolactone was first fabricated using electrospinning. The fiber mat was subsequently incorporated into a continuous matrix of crosslinked silicone rubber. This resulting elastomer composite shows excellent shape memory properties with the polycaprolactone and silicon rubber serving the respective roles of water and rubber tube. In subsequent work, the same group demonstrated that this approach can even be expanded to fabricate triple-shape polymer composite (details provided later).

In a less obvious way, the water tube experiment is also helpful in understanding the physically crosslinked polyurethane SMP. As a result of the typical multi-block structures, such polyurethanes often time possess two phases corresponding to two thermal reversible transitions. The molecular segments responsible for the low and high temperature transitions are called soft and hard segments, respectively. The soft segment is typically used as the shape memory transition, whereas the hard segment serves as the physical crosslink. The distinctive functions of the soft and hard segments thus resemble the water and rubber tube combination. Perhaps because of the popularity of polyurethane SMPs, especially in the early days, this notion of soft and hard segments has sometimes been generalized in explaining the two molecular requirements for SMP. This generalization may cause great confusion for the scientific community since it implies that a polymer should possess two distinctive phases (or segments) to have shape memory characteristics. In reality, most chemically crosslinked SMPs exhibiting superior shape memory properties do not possess two distinct phases or segments [16,19–21]. A classic example lies in polystyrene crosslinked by divinyl benzene. Whereas it meets both requirements for SMP and is fully expected to possess shape memory characteristics, there is only one type of molecular segment (the structural units from styrene and divinyl benzene) in the polymer structure. In light of this, the more appropriate terms for the two structural requirements are switch segments and netpoints. Applying this terminology to the example of crosslinked polystyrene, all molecular chain segments would belong to switch segments and the netpoints are indeed the crosslinking points aroused from divinyl benzene.

Regardless of the molecular structures, the judgment on whether or not a polymer is an SMP can be made from its DMA curve. Ideally, an SMP upon heating should have a 2–3 orders of magnitude drop in the elastic modulus but reaches a plateau modulus value after such a drop [1]. These two DMA features are and will continue to be the most important guidelines in designing SMPs. From the molecular dynamics standpoint, the modulus drop is indicative of the significant activation of molecular mobility at the multi-segmental scales. The rubbery plateau, on the other hand, arises from the prohibition of chain slippage at a longer length scale (e.g. the entire polymer chains slip pass one another). Herein, a glass transition or melting transition offers the mechanism for controlling the molecular mobility, whereas the crosslinking is responsible for the prohibition of the long-range chain slippage (thus the rubbery plateau). To emphasize the relative nature of molecular dynamics involved in polymer SME, we propose that a polymer can exhibit shape memory characteristics as long as thermomechanical conditions can be identified under which the molecular mobility is at least partially activated, yet long-range molecular chain slippages are largely suppressed within the time scale of the shape memory experiment (i.e. the polymer does not necessarily have a rubbery plateau). Absence of quantitative DMA data, the empirical indication of the polymer SME is that a polymer becomes softened upon heating, yet the material remains resistance to flow. Whereas thermoset polymers cannot flow, the difficulty in thermal processing of certain thermoplastic polymers (high flow resistance) is also a good indication that the polymers may exhibit shape memory characteristics. Such a view, while qualitative, is more inclusive in nature. Indeed, some examples that would be discussed in the context deviate from the traditional SMP classification, but can be better understood with the broadened viewpoint.

Regardless of a polymer structure, its SME is only reflected in thermomechanical shape memory cycles such as the one in Fig. 2. The shape-fixing (also called programming) step is necessary for shape changing in the recovery step. Therefore, polymer SME can be interpreted as a thermomechanically programmed effect (an external factor) originated from the viscoelasticity (time and temperature dependent material property) intrinsic to polymers. This is in sharp contrast to SMAs, which can only be expected for limited numbers of metallic alloys with certain compositions. Despite the fact that typical SMP exhibits much low recovery stress and slow actuation compared to SMAs, SMPs do hold a number of advantages over SMAs in processability, maximum recoverable strain, and easy tunability in shape memory characteristics.

Given the somewhat universal nature of the SME for polymers, a key aspect of the SMP research lies in the search of innovative ways to take advantages of the not so uncommon shape memory properties to achieve practical benefits. On the other hand, any given application may require SMPs with specific characteristics such as the shape memory transition temperature, maximum recoverable strain, and recovery stress. This can be conveniently achieved via chemical composition tuning for SMPs that fall within the traditional classification [16,19–21]. Although this aspect has been and will continue to be an essential part of SMP research, we consider it traditional and thus outside the scope of the current report. Despite the importance of potential applications for SMPs, we have blended this aspect into the following sections on various polymer SMEs to emphasize their intertwined nature.

4. Unconventional molecular designs

The molecular origins of the polymer SME suggest that the polymer SME is largely about activation of molecular mobility while suppressing long-range chain slippage within the time scale of the relevant shape memory experiment(s). This broad view of the SME is supported by a number of examples of SMP that do not readily fall into the traditional classifications.

Whereas a glassy or crystalline transition has been the typical mechanism to activate or deactivate molecular mobility, thermoreversible non-covalent molecular interactions have also been found effective for such a purpose. By introducing a small percentage of ureidopyrimidinone (UPy) structural units onto the side chains of a chemically crosslinked butylacrylate elastomers, Li et al. showed that the self-complementary hydrogen bonding (SCHB) interactions aroused from the UPy units can be utilized to design SMP [22]. In this example, the temperature dependent association constant of the SCHB serves as a mechanism to activate and deactivate the molecular mobility, while the permanent chemical crosslinking prohibits long-range chain slippage. Along the same line, Guan's group demonstrated that a thermoplastic polymer with cyclic UPy dimmers (molecular modules) on the main chain also exhibited shape memory behavior [23]. Although the above two examples bear some similarity in terms of the role of UPy, the latter is particularly intriguing since it is not chemically crosslinked. The non-crosslinked nature ensures that the polymer is reprocessable, yet the deformation induced molecular conformation change is restricted to changes within the molecular modules due to the cyclic linkage. When the complementary UPy pairs are pulled apart under stress, the cyclic linkages ensure that the original pairs are within the close vicinity to recombine with each other upon heating. In the absence of the cyclic linkages, it is highly likely that the recombination of UPy units would occur between the non-original pairs, leading to non-recoverable strain. In such a sense, the cyclic linkages serve as localized chemical crosslinking that is essential for shape memory but does not compromising the reprocessability.

Although it is well known that non-covalent interactions could affect characteristics of SMP [24], the two examples above stand out since the SCHB interactions serve as the dominant mechanism responsible for the shape memory properties. The characteristics of the SCHB interactions that make them suitable for such a task are (1) at low temperatures they are sufficiently strong for entropy trapping; and (2) their shift towards the dissociated states upon heating allows the release of the stored entropic energy (i.e. molecular chains returning to the highest entropic state). Although hydrogen bonding in general dissociates upon heating, typical hydrogen bonding is much weaker than SCHB and does not possess sufficient strength for strain locking (i.e. shape fixing).

Ionic hydrogen bonding represents another type of hydrogen bonding with very high bond strength [25]. Ionomers, in their acid states, possess ionic hydrogen bonding in their structures. Even in the solid state, some free ions do exist due to the partial dissociation of protons, particularly for ionomers containing strong acidic groups. A prime example lies in Nafion, a perfluorinated sulfonic acid material best known for its use as proton exchange membrane. Of relevance here is that Nafion has a broad thermo-reversible transition between 55 and 135 °C. Although the nature of this transition had been hotly debated historically [26], this transition is now called an α transition and believed to originate from the molecular dynamics of the ionic phase [27]. Between 55 and 100 °C, the dominant molecular dynamics is the short range segmental motions within a static electrostatic network. At temperatures above 100 °C, the ionic network becomes dynamic due to the destabilization of electrostatic network. Due to the high temperature crystalline phase, however, Nafion is highly resistant to flow even at temperatures much higher than 135 °C. This flow resistance, while undesirable for polymer thermal process, is essential for the shape memory. Indeed, Nafion shows near perfect shape fixity and recovery when deformed and recovered at 140 °C (above its α transition) [28]. Intriguingly, when Nafion is deformed and recovered at 55 °C (around the onset of its α transition), the shape fixity and recovery remain excellent [28]. This is rather surprising given that a typical SMP is expected to exhibit compromised shape fixity if deformed below the thermo-reversible transition (i.e. spring back). One plausible explanation for this unusual shape memory behavior for Nafion lies in its unique morphology. The ionic phase is believed to exhibit a micro-fibrillar morphology or high aspect ratio cyclinders with diameters around 4 nm [29]. A recent SANS study suggested that the orientation of the microfibers is responsible for the shape memory behavior of Nafion [30]. This orientation occurs at a length scale much longer than conformation changes occurred in typical SMPs. Consequently, the instantaneous relaxation of the orientation, which is detrimental to shape fixity, is much more difficult. Another likely cause for the absence of spring back at the onset of the α transition is the strength of the ionic hydrogen bonding. Here, the ionic hydrogen bonding refers to the molecular interaction between a hydrogen and an oxyanion, which is a hydrogen bonding acceptor with an excess of electron density compared to a non-charged oxygen atom [25]. Despite its non-covalent and dynamic nature, ionic hydrogen bonding possesses high bond energy comparable to even some covalent bonds [25]. Such unusually high bond energy implies that it is more effective in trapping conformation changes compared to a typical glassy or crystalline phase. Besides the unusual dual-shape memory properties, the versatility of Nafion as an SMP is further highlighted by its multi-shape and temperature memory effects (vide infra). Given the synthetic accessibility of ionomers in general, the popularity of ionomeric SMPs could significantly grow in the future.

Unlike the dynamic ionic hydrogen bonding, traditional ionic interactions existing in neutralized ionomers are highly temperature resistant. Such a feature was also proven useful in designing SMPs. Weiss et al. reported that, through the introduction of a fatty acid salt (crystallizable small molecule) into sulfonated EPDM (an elastomeric thermoplastic ionomer), the resulting composite exhibited shape memory properties [31]. The principle of this SMP system is analogous to the water–rubber tube system with the respective roles of the elastomer matrix and fatty acid resembling those of the rubber tube and water. The temperature resistant ionic interactions between the fatty acid salt and the ionic phase serve as the robust molecular confinement similar to the wall of the rubber tubing. On the practical front, the T_{trans} of Weiss' SMP system is determined by the melting point of the fatty acid salt. As such, it can be altered through the physical doping of various fatty acid salts, providing thus a highly flexible way to tailor the T_{trans} of the SMP without resorting to covalent chemistry.

Similarly to Weiss' approach, Guan et al. showed that, an SMP can be obtained by introducing cetyltrimethylammonium bromide (C_{16}TAB) (a surfactant molecule with a melting point of 98 °C) into a matrix of poly(acrylic acid-co-methyl methacrylate) (PAA-co-MMA) (T_g around 116 °C) [32]. In this system, the glassy phase in the matrix polymer serves as the physical crosslinking and the surfactant molecules provide the thermo-reversible phase securely linked to the matrix through the ionic interactions.

In typical thermoplastic polyurethane SMPs, the hard and soft segments are contained in one macromolecule. That is, the two segments contributing to shape memory are covalently linked. Tuning the shape memory characteristics for such a system normally requires the compositional changes via synthesis of new polymers. In contrast, Behl et al. accomplished such through physical blending of two miscible polyurethanes [17]. The two polyurethanes contain crystalline phases with T_m of 90 and 40 °C, respectively. Although they do not possess the soft and hard segment combination individually (thus no shape memory capability), blending combines the two crystalline transitions and leads to an SMP blend. The resulting material is macroscopically homogeneous, yet remains microscopically phase separated. Presumably, the miscibility arises from the multiple intermolecular hydrogen bonding associated with the polyurethane structures. By varying the ratio between the two individual polyurethanes in the blend, the elasticity of the SMP can be conveniently tuned without affecting the transition temperatures of the soft segment.

Cyclodextrins (CDs) are known to form strong hydrogen bonding based complex with polymer chains, leading to thermally more stable crystalline structures. This feature has been explored as a physical way to introduce hard segments into an SMP. Polyethylene glycol (PEG), for instance, has only one thermo-reversible transition and does not meet the SMP requirement. Partial inclusion of α-CD, however, resulted in an SMP system with CD–PEG inclusion crystallites as the hard segment and the non-complexed PEG as the soft segments [33]. This physical approach is in contrast to the conventional approach of introducing the hard segment via chemical synthesis.

Utilizing a coagulation spinning process, Miaudet et al. fabricated nanocomposite fibers consisting of a large fraction of carbon nanotubes (CNTs, 20 wt%) in a non-crosslinked polyvinyl alcohol (PVA) matrix [34]. The resulting fibers exhibit shape memory behavior despite the fact that they do not fit the typical profile of an SMP. That is, they are neither chemically crosslinked nor physically crosslinked via a distinct high temperature phase. The inclusion of the CNT, however, drastically changed the thermomechanical behavior of PVA, leading to significant broadening of the glass transition. The large surface area of the nanofiller as well as its high weight fraction plays a critical role. Together, they ensure a high fraction of interfacial zone within which the molecular mobility is hindered by the strong binding between the CNT and PVA. Although not specified by the authors, the non-covalent binding may arise presumably from the non-conventional hydrogen bonding interactions (OH–pi interaction [35]) between the abundant pi electrons on CNTs surface and the numerous hydroxyl groups in PVA. Although the resulting PVA-CNT fibers exhibit an intriguing temperature memory effect and extremely large recovery stress (vide infra), their R_rs are lower than 60%. The low R_r implies that the long-range molecular movements are only partially suppressed by the corporative OH–pi interactions.

It is important to note that some of the examples presented in this section do not necessarily possess robust shape memory performance (e.g. R_f or R_r) comparable to conventional chemically crosslinked SMP. At minimum, however, their significance resides in the enrichment in scientific understanding of polymer shape memory phenomena.

5. Recovery stress

The terminology of "shape memory" emphasizes the shape fixing and shape recovery and indeed reflects how SMPs had been exclusively used in the earlier days of development. Recently, increasing attention has been paid to utilize the strain energy stored in a temporary shape to perform work. That is, after the completion of shape fixing in Fig. 2, instead of allowing shape recovery under a free stress condition in the next step, the SMP is constrained such that the fixed shape is not allowed to change (i.e. an isostrain condition). Under such a condition, heating does not lead to shape change due to the external mechanical constraint, but the tendency of shape recovery generates a recovery stress (or force). In a typical stress recovery experiment, the recovery stress is monitored with respect to temperature and a maximum recovery stress at a certain temperature is typically observed. Often time the maximum recovery stress, which is simply referred to as the recovery stress, is reported for a given SMP.

It is important to recognize that, in a stress recovery event, the total strain energy (and stress) is released in the form of both recovery stress and viscous stress. To a first approximation, however, the ratio between recovery stress and total stress may be constant for the same material [36]. The stored strain energy, on the other hand, should be dependent on the energy required in the deformation, although the exact correlation is not known (i.e. the amount of energy loss during the shape-fixing step is not known). Thus, there should be at least a qualitative correlation between recovery stress and deformation energy (or input energy).

The deformation energy, which can be calculated from the total area underneath the deformation stress strain curve, is dependent on the material modulus at T_d and strain. The former is a function of T_d if the deformation occurs outside the rubbery plateau, or that the SMP does not possess a rubbery plateau at all. As such, the same material deformed to the same strain at different T_ds could exhibit variation of recovery stress by a factor of 4–5 [28]. Similarly, deforming the same SMP at a given T_d to different strains would require varied amounts of deformation energy, resulting in a similar magnitude difference in recovery stress. Intriguingly, even the deformation rate (or strain rate) could affect recovery stress [36]. A higher strain rate was found to result in a higher recovery stress, and vice versa.

Given its strong dependence on the applied thermomechanical conditions, recovery stress should not be considered as an intrinsic SMP property. Whereas the concern on the shape recovery of SMP under partially constrained conditions may have been originally the reason recovery stress drew attention [37], more recent focus has shifted towards utilizing SMP as linear actuators to take advantage of the recovery force. To this end, the low recovery stress (around several to tens of MPa) for typical SMP becomes a significant barrier. Various strategies have thus been explored to enhance the recovery stress, including increasing the rubbery modulus by nanofillers reinforcement, raising the rubbery modulus through a higher crosslinking density, and deforming SMP at a relatively high modulus state instead of the rubbery region. Dispersion of carbon nanotubes (1–5 vol.%) in a thermoplastic elastomer, for instance, could increase the recovery stress by as much as 50% [38]. By incorporating a very high fraction of carbon nanotube (~20wt%) into a polyvinyl alcohol matrix and deforming the resulting material at a low T_d, Miaudet et al. [34] achieved recovery stress as high as 130 MPa. This recovery stress, while still lower than that for the best SMA, is about 1–2 orders of magnitude higher than typical SMP.

Despite the experimental explorations of SMP exhibiting high recovery stress, the fundamental understanding of recovery stress remains at an early stage. In particular, recovery stress in itself is not a thermodynamic energy term. In an isostrain stress recovery experiment, the SMP does not really perform any work since the displacement is zero. Theoretical understanding of the energy balance throughout the shape fixing and stress recovery cycle may be critical. The correlation between energy terms (deformation and stored strain energies) and recovery stress is highly desirable since such knowledge could be very helpful in predicting the ability of SMP to perform work under partially constrained conditions. In any attempt, the energy loss due to the thermal transition could be quite significant and should not be ignored.

6. Reversible plasticity shape memory effect

Referring back to the traditional shape memory cycle in Fig. 2, the shape fixing involves applying the deformation force when the SMP is in a heated state and cooling under the deformation force to lock in the temporary deformed shape. The deformation force may also be applied to a non-heated SMP and at least part of deformation may remain (or be fixed) after the load removal (i.e. plastic deformation). Importantly, the deformation introduced this way can still be recovered at an elevated temperature under a stress free condition. This non-conventional shape memory cycle is different from the conventional cycle in Fig. 2 in that steps 1 and 3 in the shape-fixing step are omitted. The fact that polymers in general may experience "irreversible" plastic deformation has been long known, but the recognition that such "irreversible" deformation can be reverted upon heating is uniquely important for polymer shape memory phenomenon. Mather et al. suggested the use of "reversible plasticity shape memory effect (RP-SME)" to emphasize its significance and its distinction with a conventional SME [39].

This terminology is helpful in raising the awareness and potentially promoting its usefulness. Notably, the deformation step in RP-SME is also commonly referred to as cold drawing if the deformation is in a linear elongation mode.

Under an RP-SME condition, R_f values are typically compromised compared to the R_f approaching 100% for many typical examples of conventional SME. The importance of RP-SME, however, does not lie in shape fixing. In addition to a simplified shape fixing process, its benefits are reflected in potentially higher recovery stress; enhanced material deformability; and self-healing.

For RP-SME, an SMP is deformed at its glassy (or crystalline) state. Glassy moduli of SMPs are typically 2–3 orders of magnitude higher than their rubbery moduli. Under the assumption that an SMP does not yield in the deformation process, the deformation force can be considered somewhat proportional to its modulus at the deformation temperature. As such, the deformation force required for RP-SME is 2–3 orders of magnitude higher than that for conventional SME. This point, while may be viewed unfavorable in terms of ease of deformation, is exactly why RP-SME could be useful. A larger deformation force would correspond to higher stored energy, which could lead to higher recovery stress upon heating. In fact, several recent studies reported 3–5 folds of increase in recovery stress when the SMPs were deformed at temperatures within (not above) the thermal transition [28,34,40]. Gall et al.'s work, on the other hand, suggests that the extent of increase in recovery stress would be much less than the increase in the deformation force for SMP deformed completely at its glassy state [41].

Deformability in the context of SMP is related to its strain-at-break (or maximum recoverable strain) [42]. For a given amorphous SMP, Gall et al. observed that its strain-at-break increased notably when the deformation was conducted near the onset of (instead of above) its glass transition [42]. Similar conclusion was reached by Rousseau et al. for a different glassy SMP system [43]. Accordingly, the deformation temperature corresponding to the maximum recoverable strain was defined as the deformability peak. Zotzmann et al. showed that the deformability of crosslinked semicrystalline polyurethanes could also be significantly enhanced when they were subjected to a cold-drawing process (deformation at room temperature instead of the onset of the thermal transition) [44]. Deformation under an RP-SME condition represents thus an effective approach to improve SMP deformability without changing its composition.

The significance of RP-SME is also reflected in the so-called self-healing effect. For instance, typical plastic goods may experience surface damages (e.g. indents or scratches) under the conditions of practical usage. Such damages correspond to plastic deformation in a scientific term. By the mechanism of RP-SME, such plastic deformation would recover or damages be healed via heating. Although this healing mechanism does not require physical contact, it only occurs when an external stimulus (heating in this case) is applied. This healing mechanism thus falls into the category of non-autonomous self-healing. This is in contrast to the autonomous self-healing mechanism in which the force that causes the damage also triggers the healing, thus no additional external stimulus is needed [45]. It is important to note that the RP-SME based self-healing mechanism heals only non-permanent damages such as surface scratches [46]. If during a scratching situation, permanent damages such as cracking occur, heating would reduce the crack width but the cracks would not heal. This was precisely what happened to the neat epoxy SMP illustrated in Fig. 4 [46]. Such a limitation is somewhat inherent to SMP. Deformation related to a scratch corresponds to more condensed packing of molecular chains (i.e. entropy change), whereas cracking means macroscopic material separation. To heal macroscopic material separation would require material flow (or long-range molecular movements), which is contrary to the molecular origin of polymer SME. One solution to this problem is to improve the cracking resistance of the SMP so that cracks do not form during scratching, as we have successfully demonstrated by adding a trace amount of nanolayered graphene into an SMP matrix (Fig. 4) [46]. Another approach is to disperse a flowable polymer component into an SMP matrix to form a semi-interpenetration network [39]. This flowable component would not contribute to the shape memory function or the crack narrowing, but would help heal the cracks. In contrast, the SMP component does not directly heal the crack, but assists in bringing closer the fractured interface for the diffusion based cracking healing.

In contrast, typical autonomous self-healing mechanisms through embedded reactive microcapsules are particularly effective in healing cracks [45]. The forces that cause the cracking break the capsules. The liquid healing agents are released, flow to the cracking sites, and react to repair the damage. This mechanism, however, cannot repair non-permanent damages such as plastic bending. In fact, unintended releasing and curing of the healing agents in a plastic bending situation could lead to permanent part distortion. Given their somewhat complementary nature, it

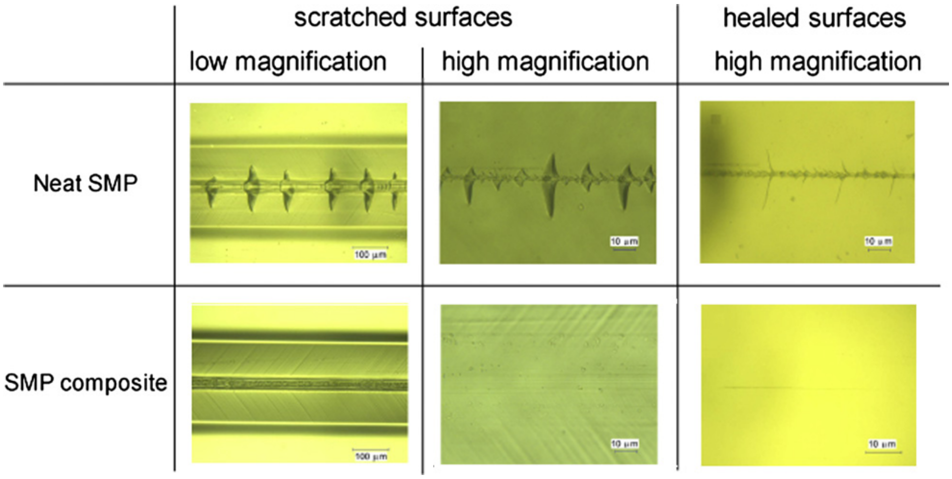


Fig. 4. Heat triggered non-autonomous self-healing of SMP surfaces. Adapted from Ref. [46] with modification.

remains interesting if the RP-SME based self-healing mechanism can be combined with autonomous self-healing mechanisms to repair both structural and appearance functions of polymers.

In the context of RP-SME, strain-induced crystallization for elastomers should also be mentioned. The simplest and commonly known example of strain-induced crystallization involves uniaxial rubber stretching [38]. Rubbers can be stretched and the stretching strain would normally be recovered as soon as the stretching force is released. If, however, the rubber is stretched to a sufficiently large strain, crystallization may occur. This strain-induced crystallization would serve as the physical crosslinking mechanism that inhibits the instantaneous strain recovery. That is, at least part of the strain is retained (or fixed) upon removal of the stretching force. Subsequent heating, on the other hand, would melt the crystals and lead to recovery. In this case, the shape fixing is conducted when the material is in its rubbery state. Strictly speaking, the term "RP-SME" is thus inappropriate here. Phenomenologically, however, if RP-SME is interpreted more broadly to emphasize no heating and cooling in shape fixing, the term becomes applicable. Although strain-induced crystallization of elastomers does not lead to ideal shape fixing (e.g. $R_f \approx 80\%$), the phenomenon and underlying mechanism represent drastic departure from typical SME. In addition, the shape fixity can be significantly improved by the addition of nanofillers, through promoted crystallization via non-covalent molecular interactions at the filler and matrix interface [38].

7. Small strain shape memory phenomena

It is commonly believed that SMP holds a big advantage over SMA in that the former can be tailored to exhibit very large maximum recoverable strains (as large as 1000%) compared to the highest recoverable strain around 14% for SMA [47]. Although some SMP applications may indeed require large recoverable strains, that an SMP has to have a large recoverable strain to be useful is a misconception. Many real world applications of shape memory materials involve geometric changes, while drastic, are actually associated with small strains. Despite their low recoverable strains, SMAs have found more success in commercial applications than SMPs owing to their fast actuation and high recovery stress. The more important advantage of SMP thus lies in its processability (i.e. they can be easily processed into complex bulk devices), not necessarily recoverable strain.

An extreme case of an SMP application that does not require a large strain is our reversible dry adhesive system [48]. The adhesive comprises of two layers: a rigid SMP backing layer and a sticky elastomer layer (Fig. 5a). Both layers are thermoset, thus qualifying the system as a dry adhesive. The as fabricated (or original) bilayer adhesive has a slight curvature (Fig. 5a) originating from the thermal mismatch between the two layers. Due to the curvature, the adhesive does not form intimate contact when placed on a flat substrate. As a result, the adhesion is low. Owing to the SMP backing layer, the bilayer adhesive can be deformed to achieve conformal contact with the substrate (Fig. 5a), leading to adhesion as high as 200 N/cm^2. Upon heating, the shape recovery of SMP layer creates a peeling force that detaches the adhesive (Fig. 5a). In the bonding and debonding process, only a very small strain change was involved. Instead of a large recoverable strain, excellent shape fixing and large recovery stress are important in this instance.

Representing an extension of the concept above, we have developed solid based SMP adhesive systems with extremely strong adhesion (>600 N/cm^2) comparable to even conventional liquid curable adhesives [49,50]. The idea originated from the hypothesis that strong direct bonding between two solid surfaces is possible if intimate molecular contact and favorable molecular interactions can be designed at the interface. The issue lies in that the surface profiles of two rigid solid polymers do not typically match unless the surfaces are atomically flat. If the rigid polymers have shape memory characteristics, however, they can be pressed together upon heating to achieve conformal contact. When specific functional moieties are introduced onto two polymer surfaces, strong non-covalent interactions (corporative hydrogen bonding or cation–pi interactions) can be realized at the interface. The result is extremely strong direct bonding between two rigid polymer surfaces (i.e. no traditional glue is used). Here again, the strain that is needed for the two surfaces to match can be extremely small.

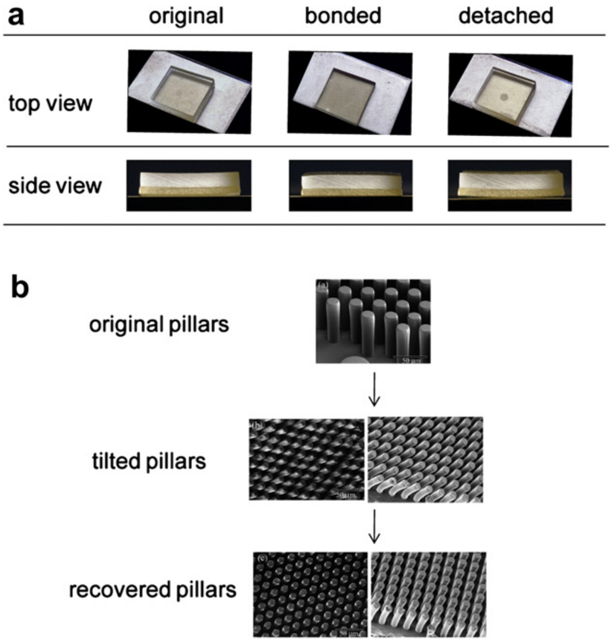


Fig. 5. Low strain applications of SMP. (a) Self-peeling reversible dry adhesive; (b) SMP pillar based switchable dry adhesive. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced from Refs. [48,51] with permission.

Another example is the switchable structured dry adhesives (gecko adhesives) [51]. The dry adhesive contains SMP micropillars perpendicular to the surface (Fig. 5b). The pillars can be deformed and fixed into tilted shapes (Fig. 5b). Despite the small strain related to such a deformation, the adhesion exhibited by the original surface (~3 N/cm^2) was transitioned to a non-detectable level for the tilted pillar surface. In addition, the adhesive and non-adhesive states can be repeatedly switched owing to the shape memory characteristics of the pillar material.

Upon heating, SMP typically becomes soft or melts microscopically without running into the risk of losing the material integrity due to macroscopic flow. This particular feature by itself has also been proven useful without necessarily any shape changing. Kim et al., for instance, fabricated an SMP pillar surface covered by a continuous film of a thermoset adhesive rubber [52]. Whereas the top rubber layer provides the high intrinsic adhesion, the temperature dependent compliance of the underlying SMP pillars offers a mechanism to thermally control adhesion. As such, the same adhesive exhibited drastically different levels of adhesion depending on the temperatures during the loading and unloading events in the adhesion test. Also falling into this category is a color changing SMP by Kunzelman et al. [53]. The SMP system consists of a fluorescent dye in a crosslinked semicrystalline SMP matrix. At temperatures below the melting point of the SMP matrix, the dye molecules exist as aggregates. Heating the SMP above its melting point leads to dissolution of the dye molecules. The dissolution and aggregation of dye molecules are reversible and the dye molecules at these two states exhibit different fluorescence colors. As a result, the SMP is capable of reversible color change. Of relevance in the current context is that, whereas the same crystalline transition is responsible for both the color change and the shape memory function, the change in color does not require any strain or shape change. On the other hand, the chemical crosslinking necessary for the shape memory function ensures material integrity during the color changing events.

8. Surface shape memory effect

In the early days, the SMP applications have been focused primarily on bulk structural devices. Increasingly, more and more attention has been paid to shape memory phenomena that occur on surfaces. The underlying molecular principle for surface SME is identical to bulk SME. They differ only in the type of deformation, i.e., surface versus bulk. Notably, however, some of the main drawbacks for bulk SMP applications (e.g. low recovery speed and recovery stress) become irrelevant for most applications based on surface SME.

Among the first to investigate surface SME were Nelson et al. [54]. Utilizing AFM tips, they created surface nanoscale indents with depth from 3 to 16 nm and lateral dimensions around 200–300 nm onto an SMP surface. Despite the expected heterogeneity of the crosslinked network structures at the molecular level, the indents can fully recover upon sufficient heating. The erasable nature of the nanoscale deformation (nanoindents or nanoimprints), when combined with a massively parallel operation of scanning probes, makes it attractive for use as rewritable high density data storage media [55]. On a more general basis, surface SME could become more and more attractive options for soft lithography (e.g. microcontact printing and microfluidics [56,57]), given the erasable and reprogrammable nature.

Another notable use of surface SME lies in the creation of localized surface wrinkles based structural colors [58]. In general, surface wrinkling occurs when a rigid thin film supported on a soft substrate is compressed laterally beyond a critical strain. Typically, surface wrinkling are created uniformly on a rubber substrate. The use of an SMP as the wrinkle substrate presents a unique opportunity to create localized wrinkle structures. The process of forming localized wrinkles is illustrated in Fig. 6a. Localized indents are first created on an SMP surface (steps 1 and 2), followed by the deposition of a metallic thin film (step 3). Heat triggered recovery of the indent (step 4) induced a lateral compressive strain at the edge of the indent (zone II), resulting in localized wrinkle formation. The wavelength of resulting surface wrinkles falls within the vicinity of the visible wavelength. As such, the wrinkled surface showed angle dependent structural colors. Reflecting the flexible and controllable nature of the wrinkling process, the method can be utilized to capture any macroscopic object when the object itself is used as the indenter. The images in Fig. 5b, for instance, represent a wrinkled surface created using a commercial logo as the indenter and viewed from different angles. The optical micro-images in Fig. 5c and d, on the other hand, confirmed that the colors indeed stem from the localized wrinkles. It should also be noted that strains as low as 2.6% is sufficient to generate wrinkles, representing yet another example of a small strain shape memory phenomenon.

9. Two-way shape memory effect

All the polymer shape memory effects described so far belong to the so-called one-way shape memory effect (1W-SMW). That is, the shape changing only follows the arrow direction in Fig. 2a and is not reversible. It is important to note, however, that any one-way shape memory cycles can be repeatedly run, but going from the original (or a recovered) shape to the previous temporary shape always requires the application of an external mechanical manipulation (i.e. programming). In contrast, two-way (or reversible) shape memory effect (2W-SME) refers to the phenomenon that a polymer can reversibly switching shapes without the need for external mechanical manipulation. Polymers with 2W-SME are sometimes called shape-changing polymers, in distinction to 1W-SMP. The term shape-changing polymers, however, may apply broadly to any polymer systems that can undergo reversible shape changing. In the current context, 2W-SME refers to reversible shape changing phenomena that stem from phase transitions in the polymer (i.e. similar to 1W-SMP). This notably excludes other shape-changing polymers such as electroactive polymers. The above distinction is non-trivial as the phase transition in 2W-SMP offers a unique mechanism in tuning the shape-changing event that is absent in other shape-changing polymers.

SMA and liquid crystalline elastomers (LCEs) have been long known to exhibit the 2W-SME. 2W-SME for SMA can be realized under a stress free condition but the strain is limited to 8%, although recent development reported 14% [47]. The range of

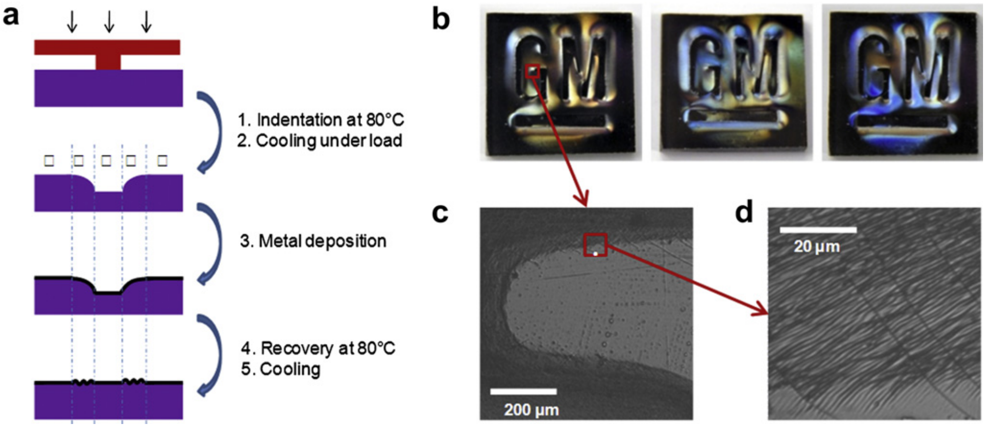


Fig. 6. Formation of localized wrinkle structures on an SMP. (a) Cross-sectional illustration of the wrinkle formation process (red, blue, and black represent indenter, SMP, and thin film, respectively); (b) photos of a logo with diffraction-colored letter edges, taken under regular fluorescent light with the only change in the viewing angle; (c and d) optical microscopic images of localized wrinkles. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced from Ref. [58] with permission.

reversible strain for LCEs, on the other hand, can be very high (e.g. 300%), but it can only be realized under a constant non-zero stress condition [2,59,60]. The constant stress required for 2W-SME should be distinguished against the deformation force required for the programming of 1W-SME. This distinction is of practical importance in that a constant stress can be more easily built into a device. As such, no physical access for applying deformation force is needed for the reversible shape changing.

A notable drawback for LCEs is that their synthesis typically involves sophisticated chemistry and that the transition temperature cannot be easily tuned as transitional SMPs. On this front, 2W-SME demonstrated by Mather's group for a chemically crosslinked semicrystalline polymer network represents an important advance [61]. Under a constant tensile load, the crosslinked semicrystalline network was found to elongate upon cooling across its crystallization temperature range (i.e. crystallization induced elongation or CIE). Under the same tensile load, the elongation was reversed upon heating across the melting temperature (i.e. melting induced contraction or MIC). The level of reversible strain change in the process was found to depend on the tensile load and up to ∼200% was demonstrated. Mechanistically, the CIE and MIC arise, respectively, from the formation and melting of the tension induced anisotropic crystalline orientation. Both the phenomenon and the underlying mechanism are similar to the 2W-SME for LCEs except the nature of the phase transition (liquid crystalline versus crystalline). Practically, however, the extension of 2W-SME to semicrystalline polymers opens up the door in structural tuning and material selections. Benefiting from the wider material accessibility, Lendlein's group demonstrated an interesting example of a 2W-triple-shape memory polymer system [62]. This system is a crosslinked network containing two crystalline phases corresponding to two discrete transition temperatures. As such, the system exhibits two CIE events upon cooling and two MIC events upon heating (Fig. 7a). Essentially, the multi-phase polymer, under a constant stress, can reversibly switch among three shapes with temperature changes (Fig. 7b). In theory, 2W-triple-shape effect can also be realized for LCE but the synthesis of an LCE with two discrete liquid crystalline transitions would be significantly more complicated.

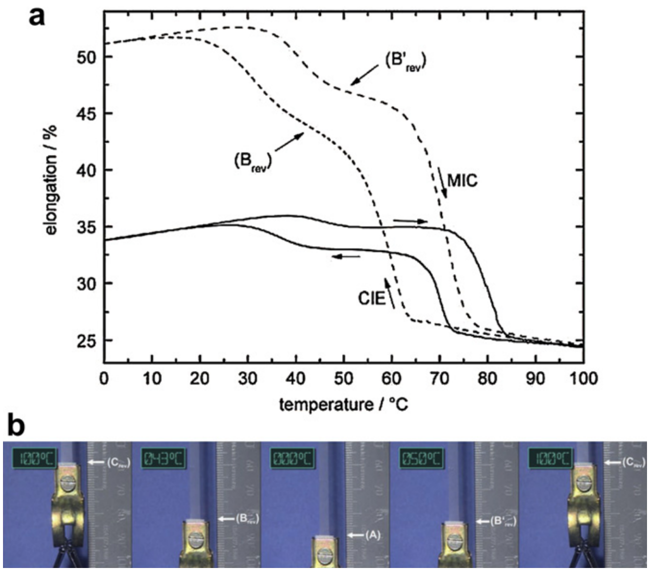


Fig. 7. 2W-triple-shape memory cycle. (a) Quantitative themo-mechanical cycle; and (b) visual demonstration. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced from Ref. [62] with permission.

The requirement for maintaining a constant non-zero stress represents a practical limitation for the 2W-SME. Unless further innovative engineering is involved, it would limit potential applications to simple elongation and contraction (e.g. linear actuators). Chen et al. reported a bilayer system capable of temperature driven reversible bending actions under zero stress [63]. This was realized by bonding a pre-elongated crystalline polyurethane SMP (active layer) to a non-elongated elastic polyurethane. Upon heating above the thermal transition temperature of the active layer (thus its shape recovery), the laminate bends towards the direction of the active layer, creating a first shape. Upon cooling to 25 °C, the bending angle was significantly reduced, resulting in a second shape. The transition between the two shapes is reversible without the need for an external stress. Although the authors did not offer a mechanistic explanation, the reversible bending phenomenon most likely shares the same root as the 2W-SME described above. The intriguing point, however, is that the non-active elastic layer may have provided an internal stress (or a mechanical bias) that is somewhat similar to the role of the constant non-zero stress required for 2W-SME. Although the reversible bending still represents simple geometric changes, it does imply that more complicated reversible shape changing can be potentially realized under a zero stress condition.

We should note that abrupt volume (or strain) change is typical when a polymer goes through a phase transition. Such a strain change is completely reversible without requiring any stress. However, the strain involved is typically very small (less than 1%) and thus does not typically carry practical benefits. More importantly, such a strain change is not programmable and should thus be distinguished from 2W-SME. On the other hand, if such a small strain change can be somehow amplified to a practically relevant level, it could potentially be interpreted as 2W-SME. Interestingly, recent work by Sellinger et al. explored such a feasibility [64]. Their material system is a carbon nanotube polyimide composite beam. The two ends of the initially straight beam were fixed. Upon resistive heating below its T_g (220 °C), the beam bended upward due to thermal expansion. Above its glass transition, the polymer became significantly softened and the gravity drove the beam to bend downward. Importantly, the shape changing is reversible, from straight beam to upward bending to downward bending. Although the strain involved in the process may be small, the reversible bending was macroscopically quite noticeable.

10. Triple-shape memory effect

In 2006, Bellin et al. discovered that two distinct thermal transitions in a crosslinked network can be independently utilized to fix and recover two temporary shapes, all in one shape memory cycle [65]. This is called the triple-shape memory effect (triple-SME), indicative of a total of three shapes involved (including the permanent shape). The triple-SME represents more or less an extension of the traditional dual-SME, which relies on one thermal transition for one temporary shape. In retrospect, the timing of the discovery is thus somewhat surprising given the long history of SMP. The significance of the triple-SME, however, cannot be overemphasized since it has the potential to drastically impact the technological development.

The triple-SME and the quantitative triple-shape cycle are illustrated in Fig. 8 for a crosslinked polymer with two distinctive T_gs (38 °C and 75 °C) [66]. Relative to the dual-shape cycle which has one shape fixing and one shape recovery step (Fig. 2), a triple-shape cycle comprises of two shape-fixing steps and two shape recovery steps. In the two-step shape fixing process, the permanent shape **A** was first heated to T_{high} (90 °C, above both T_gs) and deformed by imposing a first stress. Cooling under this stress to T_{mid}

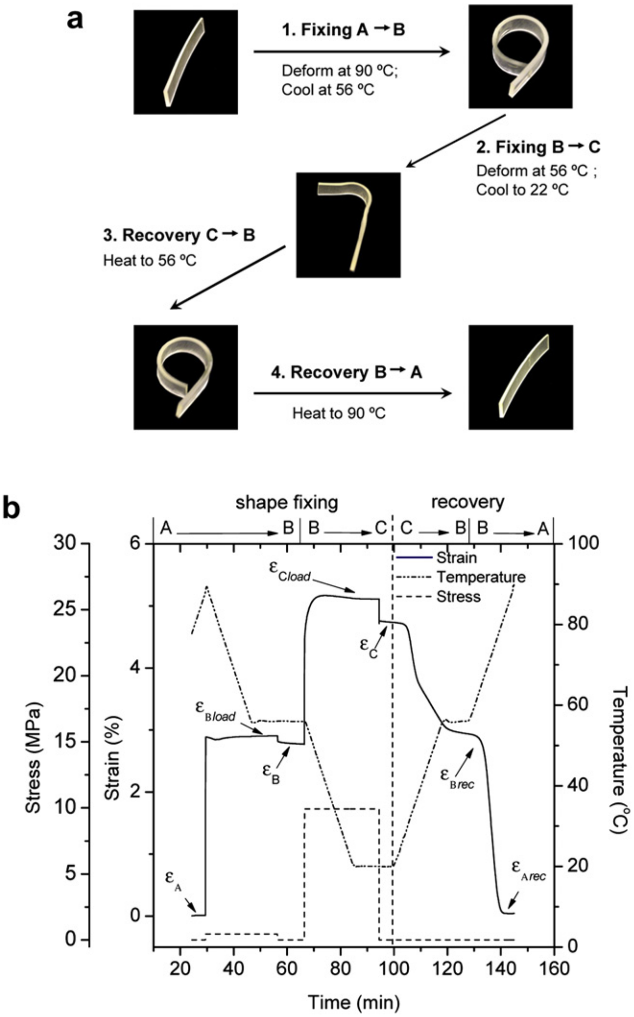


Fig. 8. Triple-shape cycles. (a) Visual demonstration; and (b) quantitative thermomechanical cycle. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced from Ref. [66] with permission.

(56 °C, between the two T_gs) and releasing the stress fixed temporary shape **B**, corresponding to ε_B. In the second fixing step, shape **B** was further deformed by imposing a second stress that is different from the first stress. This stress is maintained while the sample is cooled to T_{low} (20 °C, below both T_gs). Removal of the second stress after cooling led to temporary shape **C** (ε_C). Here, the vitrification of the high T_g component at T_{mid} and low T_g component at T_{low} was responsible for fixing **B** and **C**, respectively. Shape recovery, on the other hand, is conducted under a stress free condition. Heating of shape **C** to T_{mid} yields the recovered shape **B** (ε_{Brec}). Further heating of the recovered shape **B** to T_{high} leads to the recovered shape **A** (ε_{Arec}). With X and Y denote two different shapes, the respective shape fixity (R_f) and shape recovery (R_r) can be calculated based on the following equations using the thermomechanical data from Fig. 8b:

$$R_f(X \rightarrow Y) = (\varepsilon_y - \varepsilon_x)/(\varepsilon_{y\ load} - \varepsilon_x) \quad (4)$$

$$R_r(Y \rightarrow X) = (\varepsilon_y - \varepsilon_{x\ rec})/(\varepsilon_y - \varepsilon_x) \quad (5)$$

where ε_{yload} represents maximum strain under load, ε_y and ε_x are fixed strains after cooling and load removal, and ε_{xrec} is the strain after recovery.

Alternative triple-shape protocols have been reported in the literature. Instead of following the standard two-step shape fixing at T_{high} and T_{mid}, a one-step shape fixing at T_{high} has also been explored [67]. The one-step shape fixing may also be conducted at T_{low} (i.e. cold drawing one-step shape fixing). Regardless of the difference in the shape fixing process, the triple-SME is qualified if two distinct steps are present in the later recovery event. The one-step shape fixing protocols represent simpler ways for realization of triple-SME and enrich the scientific understanding of the phenomenon. However, they cannot be used when two independent strains are to be programmed into the SMP. In additional, one-step shape fixing protocols yield only an overall shape fixity and are unsuitable for independent evaluation of shape fixing capabilities of the two transition phases. As for shape recovery, the main variation lies in the heating method. Fig. 8 represents a staged heating method in which the two recovery events occurs iso-thermally at T_{mid} and T_{high}, respectively. The two-step recovery may also be triggered by continuous heating to T_{high}, typically at a low linear ramping rate. The distinction in the heating method is non-trivial and the advantages and disadvantages of the two different heating methods have been discussed in detail in our recent publication [68].

It is important to note that the coexistence of two thermal transitions in a single polymer is not uncommon. For instance, semicrystalline polymers typically possess an amorphous phase (thus a glass transition) in addition to their crystalline phase. If crosslinked, they are expected to possess triple-shape behaviors. Indeed, Pretsch [69] demonstrated that a physically crosslinked segmented polyurethane with a crystallizable soft segment (T_m of 34 °C) possesses also a glass transition (T_g of −49 °C). These two transitions can be utilized to achieve triple-shape function. The glass transition that is tied to the amorphous phase of a semicrystalline polymer may occur at temperatures below room temperature (e.g. polyethylene or poly(ethylene-vinyl acetate)). Polymers falling into this category may not be practically significant, but they do qualify as triple-SMP on a theoretical basis. By contrast, Qin and Mather [70] reported a triple-shape behavior for a liquid crystalline homopolymer based on two transitions that are both above room temperature (an isotropic-nematic transition of 150 °C and a glass transition of 80 °C). While interesting, it is difficult to tune the two transitions independently in this homopolymer.

Of technological importance are triple-SMP systems for which the triple-shape functions can be custom tuned by varying the relative fractions of the transition phases and transition temperatures. To this end, various strategies have also been reported in recent literature.

The triple-SMP systems by Bellin et al. were obtained by photopolymerizing a mono-methacrylate and a poly(ε-caprolactone) dimethacrylate (PCLDMA) macro-crosslinker [71]. In such systems, the PCLDMA macro-crosslinker provides a melting transition of 50 °C while a second transition is determined by the choice of the mono-methacrylate. When a poly(ethylene glycol) (PEG) containing mono-methacrylate was used as the monomer, the second transition was the melting transition associated with the PEG chain ($T_m = 34$ °C). When cyclohexyl methacrylate was employed instead, the second transition aroused from the glass transition of the poly(cyclohexyl methacrylate), which is 140 °C. Such an approach is highly versatile. The choice of the monomers and crosslinkers allows adjusting the two transition temperatures independently, whereas the variation in monomer ratio changes the relative fractions of the two phases.

Via ring-opening methathesis polymerization (ROMP) followed by radical initiated thermal crosslinking, Ahn et al., synthesized a crosslinked glassy network containing liquid crystalline side chains [72]. The authors demonstrated that the combination of the glass transition and the liquid crystalline transition can also be utilized to realize the triple-shape function. This liquid crystalline system shares in principle similar versatility to Bellin et al.'s system in terms of tunability. The limitation lies in the synthetic access to various liquid crystalline monomers of different liquid crystalline transition temperatures.

Polyurethane chemistry has also been explored in the synthesis of triple-SMP. Star-shaped hydroxy-telechelic poly(pentadecalactone) (PPD) and poly(ε-caprolactone) (PCL) precursors were crosslinked with a low-molecular weight diisocyanate, yielding a thermoset polymer network with two crystalline phases from the PPD ($T_m = 63-79$ °C) and PCL ($T_m = 27-55$ °C), respectively [44]. The resulting polymers exhibit triple-SME following various shape fixing protocols, including standard two-step shape fixing, one-step shape fixing, and cold drawing one-step shape fixing. Similarly, thermoplastic polyurethane triple-SMPs have also been synthesized [73]. The reaction components include a diisocyanate and three diols (1,4-butanenediol, poly(ε-caprolactone)diol ($T_m = 49$ °C), and poly(tetramethylene glycol) ($T_m = 23$ °C)). The resulting multi-block polyurethane contains one hard segment and two crystalline soft segments. The shape recovery behaviors of the resulting polymers were found to highly depend on the ratio between the two soft segments. Although detailed investigation of the triple-SME was not conducted, two-step shape recovery was illustrated for one of the polymer, indicative of the triple-SME.

The melting temperature of polyethylene is highly dependent on the degree of branching. This feature has also been explored for triple-SMP [74]. Via chemical crosslinking of a physical blend of linear and branched polyethylene, Kolesov and Radusch showed that the multiple melting transitions in the resulting network can indeed be explored for triple-shape functions.

The above triple-SMP systems represent macroscopically homogenous polymer systems with the two thermal transitions originating from two micro-separated phases. A different approach to achieve triple-SME was adopted by us by combining two epoxy based dual-SMP of two well-separated transition temperatures in a macroscopic bilayer [66]. In such a system, the two individual contributing layers are completely decoupled, allowing them to be independently tuned both in terms of their ratio and thermal transition temperatures. Fabrication of such a triple-SMP requires very little chemistry knowledge and skills due to the simplicity of the epoxy chemistry, which could be beneficial for non-chemists interested in building triple-SMP based devices. The interfacial strength between the two layers is crucial for triple-SME as large interfacial stresses are expected in the triple-shape cycle. Were the interface not sufficiently strong, delamination would have occurred and triple-shape behavior would not have been achieved. Interestingly, this learning on the macroscopic bilayer triple-SMP revealed an unobvious yet important requirement for the micro-phase separated triple-SMP systems: the strong interface. For such systems, if the interface between the micro-phases is weak, the significant stresses encountered in the triple-shape cycle would lead to interfacial chain slippage that could compromise the triple-SME, in analogous to the delamination for the bilayer triple-SMP.

Luo et al. [75] fabricated triple-SMP composites by physical embedment of a non-woven thermoplastic nanofibers of poly(ε-caprolactone) ($T_m \approx 55$ °C) into a continuous crosslinked SMP matrix ($20\,°C < T_g < 45\,°C$). Despite the lack of strong interactions (covalent or non-covalent) at the interface between the two contributing components, the triple-SME was also observed for the composite materials. Presumably, this suggests that robust physical confinement represents an alternative stress transfer mechanism effective for triple-SME. This composite approach is quite attractive in that the two contributing components in the composite material are decoupled. In principle, the concept could be expanded to a variety of material combinations with little chemistry constraint.

11. Tunable multi-shape effect and temperature memory effect

The emergence of the triple-SME invites a natural question: can multi-shape memory effect beyond triple be realized in a similar fashion by introducing additional discrete transition(s)? The answer is clearly yes. In fact, indication of the quadruple-SME had already been reported in the literature for a multi-phase polyolefin system [74]. On the other hand, the discussion on triple-SME highlights the ultimate importance of the tunability in various material concepts. In particular, tailoring T_{trans}'s has always been a major focus throughout the history of SMP. Traditionally, this has been achieved through material chemistry, i.e., alternation in the material chemical composition leads to different transition temperatures. Obviously, this task becomes more and more challenging as more discrete transitions are needed for multi-SME.

We have mentioned in a previous section that the shape recovery behaviors of the same Nafion polymer in dual-SMCs can be adjusted without performance compromises, via the selection of the deformation temperature alone [28]. That is, its dual-SME can be tuned without changes in its chemical composition. Such a phenomenon can be called tunable SME. We deduced that the tunable SME, which is associated with a single broad thermal transition, could be explored for multi-SMEs. Indeed, we showed that, despite having a single (albeit broad) transition, Nafion can exhibit multi-SME (triple-, quadruple-, or beyond) [28]. Of more importance than the multi-SME itself is the fact that the triple-SME, for instance, can be realized at any two arbitrary temperatures provided that they are sufficiently apart [28]. This is in sharp contrast to more typical triple-SMPs, for which the fixing and recovery of the two temporary shapes only occur in the temperature windows defined by the two transition temperatures (see Fig. 8 and related description). In essence, the tunable multi-SME allows a single material (Nafion in this case) to perform triple-shape memory functions that would normally be expected only for multiple triple-SMPs of different transition temperatures.

The basis of the tunable multi-SME is that a single broad thermal transition can be viewed as the continuous distribution of an infinite number of infinitely sharp transitions. Each of these sharp transitions can be further regarded as an elemental memory unit (EMU) with a corresponding T_{trans}. As such, only the EMUs with T_{trans} below T_d are activated for the memory function. The continuously distributed nature of the EMUs ensures that any change in T_d within the broad transition would always correspond to a variable group of activated EMUs. The selection of the two deformation temperatures (T_{d1} and T_{d2}) in a triple-SMC would activate two groups of EMUs that are variable depending on T_{d1} and T_{d2}. The triple-SME is thus tunable via the selection of the deformation temperatures. In contrast, the two distinct transitions for more typical triple-SMPs may be viewed as non-continuous distribution of two groups of EMUs within the two relatively narrow temperature windows. Accordingly, T_{d1} and T_{d2} have to be either above or in between the two transition temperatures to activate two different groups of EMUs to enable the triple-SME. The two groups of EMUs are non-variable unless the chemical composition of the polymer is changed, i.e., the triple-SME is thus non-tunable with the same polymer.

Bearing some similarity to the tunable multi-SMP is the functionally graded SMP [76]. A single piece of such an SMP possesses a linear spatial gradient in glass transition temperature, achieved by post-curing a pre-cured SMP in a linear temperature gradient. When a deformed functionally graded SMP is exposed to a continuous heating condition, the spatial gradient in T_{trans} enables spatially sequential recoveries. Such a behavior is quite unique and represents a conceptually different approach to the multi-SME. On the other hand, the graded SMP can be similarly viewed as the continuous distribution of EMUs of different T_{trans}, albeit in a spatial manner.

The broad thermal transition key to the tunable multi-SME has also been found responsible for the so-called temperature memory effect, which refers to the capability of an SMP system to memorize a temperature. Specifically, when an SMP is deformed at a T_d within its broad thermal transition and subsequently subjected to isostrain stress recovery experiments, the maximum recovery stress would appear at a temperature identical to the T_d [28,34,40]. Essentially, the T_d can be recorded in the SMP. The associated phenomenon represents a drastic departure from the concept of SMP, which emphasizes solely the memory of shapes (or strains). The temperature memory effect observed in the stress recovery experiments can be called the stress based temperature memory effect. Whereas multiple examples of the stress based temperature memory effect have emerged in the literature [28,34,40], we have recently demonstrated that this effect can also be established in stress free strain recovery experiments, i.e., strain based temperature memory effect [30]. To demonstrate the strain based temperature memory effect, three samples of the same polymer, Nafion, were first deformed at three different T_ds (58, 70, and 100 °C), respectively. Fig. 9a shows their strain recovery behaviors when they were heated at a constant temperature ramping rate under a stress free condition. Notably, these strain recovery curves represent parallel shifts to each other (Fig. 9a). Regardless of the T_d, the instantaneous strain recovery rate (Fig. 9b) always exhibits a maximum at a temperature roughly equal to the corresponding T_d. As mentioned earlier, the temperature corresponding to the maximum strain recovery rate is sometimes referred to as T_{sw}. Thus, $T_{\text{sw}} = T_d$ for a single polymer represents a simple definition of the strain based temperature memory effect.

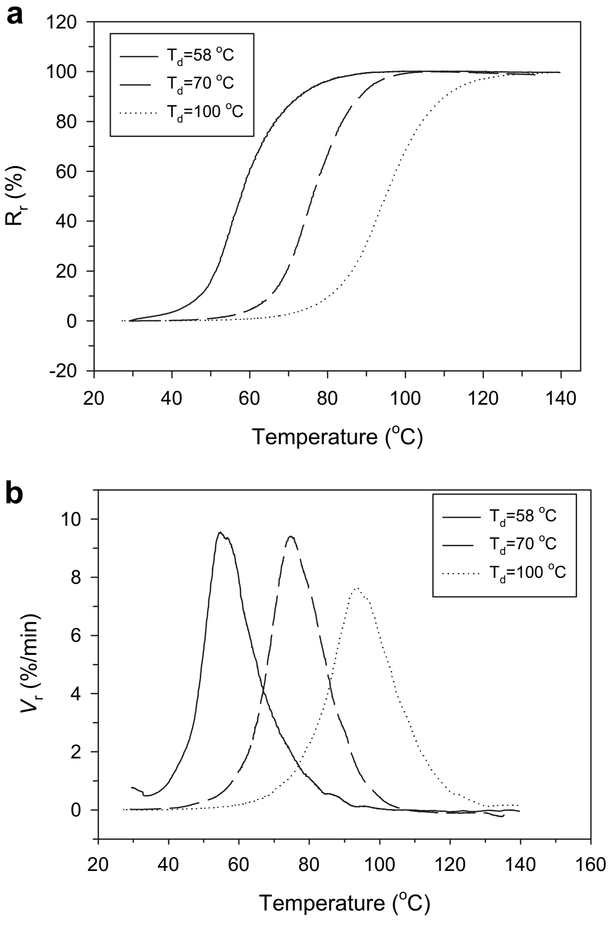


Fig. 9. Strain based temperature memory effect. (a) Evolution of strain recovery. (b) Evolution of instantaneous strain recovery rate. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced from Ref. [30] with permission.

The practical benefit of the temperature memory effect lies in that, with the same polymer, it allows the tuning of stress or strain recovery in a wide range and quantitatively predictive fashion. The strain based temperature memory effect also highlights the difference between T_{trans} and T_{sw}. The T_{trans} is typically determined from the DMA or DSC experiments, thus independent of a particular thermomechanical shape memory condition. Fig. 9 suggests that the same polymer (thus with a fixed T_{trans}) could exhibit drastically different T_{sw}s. On the other hand, without referring to the strain based temperature memory effect, the three strain recovery curves in Fig. 9a are very likely mistakenly regarded for three SMPs with different T_{trans}s.

The fact that the tunable multi-shape and temperature memory effect rely both on the broad transition is not a coincidence. In fact, the concept of EMUs used to interpret the tunable multi-SME can be readily applied to explain the temperature memory effect. According to the concept, only the EMUs with T_{trans}'s below the T_d are activated for the strain fixing function. In the corresponding recovery event, 100% of EMUs are re-activated for recovery only when the temperature reaches T_d. Consequently, a peak recovery rate or peak recovery stress is observed. Such a mechanistic interpretation is consistent with a theoretical mechanical framework proposed by Sun et al. [77], which also links the continuous broad thermal transition to both the tunable multi-SME and temperature memory effect.

12. Alternative actuation mechanisms

Quantitative evaluations of SMP are typically conducted through direct heating in highly controllable temperature environments such as an oven or a DMA machine. Access to direct heating may not be realistic for technological implementations of SMP devices, in particular for in vivo applications. As such, alternative recovery triggering methods have been one of the major focus areas of SMP research. Notably, infrared radiation [38] and magnetic induction heating [78] have emerged as attractive methods owing to their remote heating nature. Non-remote but indirect heating method such as resistive heating [79,80] has also been proven attractive due to its high speed.

Non-heating based light activated SMP systems have also been explored. Lendlein et al. demonstrated an SMP for which the shape fixing and recovery were enabled by actively changing the crosslinking density via photo-reversible cinnamate chemistry [81]. Practical issues for the cinnamate based light activated SMP range from limited shape fixity (30–50%), slow activation (~1 h), to limited light penetration into the SMP bulk. Nevertheless, light activation of SMP has drawn attention due to its mechanistic uniqueness. Very recently, Lee et al. [82] reported an intriguing light activated SMP system based on the photoisomerization of azo-functionalities in a glassy liquid crystalline network. A short exposure (<5 min) to eye-safe linearly polarized 442 nm light allowed a deformed shape to be fixed and the recovery was triggered by exposure to circularly polarized light of the same wavelength. Importantly, both the shape fixity and recovery were

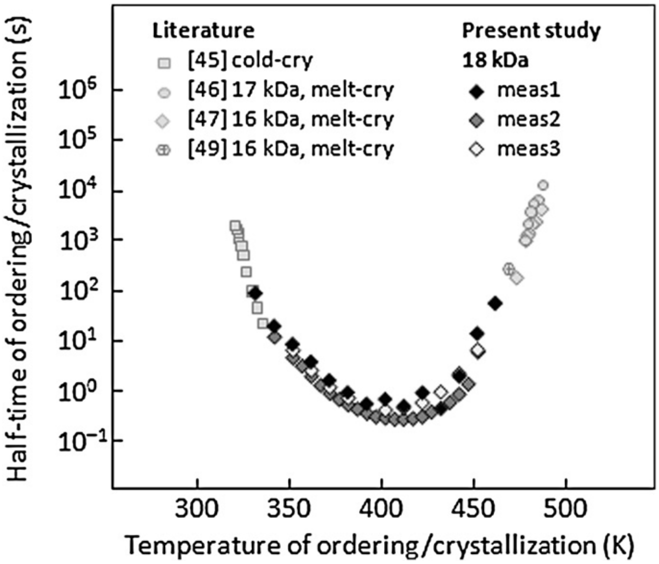


Fig. 10. Various shape recovery routes from Temp Shape #1 to the permanent shape. Five recovery routes are possible depending on the actuation sequences. RF1 and RF2 represent low and high radiofrequencies, respectively. In all the five recovery routes, the last recovery step to the permanent shape is always achieved by direct heating since the central neat SMP region does not contain any filler. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced from Ref. [85] with permission.

excellent for this system. Besides the mechanistic difference between heat and light activations, the latter offers a unique benefit in that light can be controlled spatially (e.g. with masks), which could lead to future innovation opportunities not offered by the former.

Another mode of triggering mechanism lies in water immersion, which induces recovery by reducing the transition temperature through the plastization by water instead of heating [83]. This last mode of recovery triggering cannot be universally applied, but it is quite relevant for SMP applications in which water is present in the environment, as is the case for biomedical-implanted devices.

Although much progress has been made in terms of alternative recovery triggering mechanisms, the emergence of the multi-SME presents a new challenge. The two distinct recovery steps for the triple-SME, for instance, can only be realized through slow and finely controlled continuous temperature ramping or more practically two-stage heating [68]. The profound impact of heating methods in achieving the triple-SME [68] highlights the challenge of controlling heating in a practical setting encountered in potential applications. This issue is particularly complicated for in vivo device applications, in which access to direct heating may be impossible. To overcome this issue, Kumar et al. introduced iron oxide (Fe_3O_4) nanoparticles into a triple-SMP [84]. Utilizing two different magnetic strengths at the same radiofrequency (RF), the material can be sequentially heated to two equilibrium temperatures. Consequently, a two-step recovery was realized in a remote fashion.

We have explored a different approach that relies on selective RF actuations for controlling the recovery of multiple shapes [85]. This approach is based on the principle that (Fe_3O_4) nanoparticles and carbon nanotubes (CNTs) can selectively induce heat at two very different radiofrequency (RF) ranges (296 kHz and of 13.56 MHz frequency, respectively). To fully take advantage of this, a multi-composite consisting of three spatially distinct regions (a CNT-SMP composite, a neat SMP, and a Fe_3O_4 composite) was fabricated (see the legend in Fig. 10). The multi-composite sample in a permanent straight strip form was deformed into the temporary shape #1, in which strains were introduced into all the three distinct regions (Fig. 10). For this multi-composite, an individual composite region can be selectively triggered for recovery by exposure to a particular RF frequency. Direct heating, on the other hand, would always trigger the recovery of all the three regions. As such, the recovery of the temporary shape #1 to the permanent shape could follow five different recovery routes (color coded) with a total of five different shapes involved. This is notably different from the multi-SMP discussed in the context for which the recovery sequence is fixed, that is, the lower temperature temporary shape is always recovered before the higher temperature temporary shape regardless of the actuation mechanism.

13. Conclusions and outlook

Although it may be debatable whether SME is an intrinsic polymer property, its molecular origin clearly suggests that polymer SMEs should not be regarded as "magic" properties reserved to a small number of specially designed polymers. To highlight this point, Nafion, a well-known commercial material that is not designed as an SMP, exhibits extremely versatile shape memory behaviors including tunable multi-SME and temperature memory effect. This invites the revisit of an old question: how should polymer SME be viewed phenomenologically? We suggest an analogy to the functions of computers. Whereas computer hardware provides the basis, what a computer can do is actually determined by the installed software. To certain extent, the combination and respective roles of material chemistry (e.g. two distinct transitions or a broad transition) and thermomechanical shape fixing conditions are similar to those of computer hardware and software. The word "programming" often used for shape fixing resonates with such an analogy. In the case of Nafion, the broad thermal transition simply offers a highly flexible platform (or powerful hardware), yet the type of shape memory behaviors depends largely how one programs the material in the shape fixing event, much like computer software installation. The design of the programming conditions, on the other hand, relies on fundamental physics of polymers. With the above analogy, the relative importance of polymer chemistry and physics becomes obvious.

As the history of SMP has clearly indicated, the future prospect of SMP would hinge heavily on how best to take advantages of such not so uncommon properties in innovative ways. On the positive front, the application potential for SMPs appears almost unlimited as manifested in the highly diverse application concepts that have appeared in both peer-reviewed journals and patent literature. This is, however, in sharp contrast to the very few real world applications such as low value-added toys. The real key thus lies in the discovery of high value-added applications for which SMP are enablers or at minimum highly attractive alternatives. Whereas biomedical applications of SMP represent a major focus for the SMP research today, stringent requirements and lengthy regulatory approval process present obstacles for commercial implementations. Under this scenario, whether or not any “silver bullets” beyond biomedical applications may emerge is an important issue. In fact, this is part of the reason why biomedical applications have been intentionally left out in this article.

Tailoring the characteristics of SMPs to meet the specific requirements of targeted applications will continue to be an essential aspect of SMP research. The discovery of novel SMEs will play a significant role as it pushes the material capability into new territories and has the potential to impact the field in a more drastic fashion. Although it is impossible to predict what new polymer shape memory behaviors will be discovered in the future, several notable challenges and opportunities are presented below.

Recovery stress. Can an SMP be developed that exhibits recovery stress comparable to shape memory alloys, without compromising shape fixing and recovery behavior?

2W-SME. Can the phenomenon be extended beyond crosslinked semi-crystalline polymers? Besides reversible bending, can a 2W-SME be realized that allows reversible shape switching in a non-linear fashion under zero external stress? Shape memory alloys can be trained to exhibit two-way reversible surface topographic changes [86]. Can this be realized with polymers?

Triple-SME (or multi-SME). Although the triple-SMPs based smart fastener demonstrated by Bellin et al. offers a useful hint [65], the discovery of various triple-SMPs has outpaced the exploration of potential applications. What makes most sense to fully utilize such a material capability at the device level has remained largely unexplored. Scientifically, a common feature for all known triple-SMPs is that at least one of the two shape fixities is notably compromised (i.e. R_{f1} or R_{f2} <80%). This issue originates from the partial freezing of the polymer chains during the shape-fixing steps. Is this unavoidable or can triple-SMPs with an entirely different operating mechanism (thus no compromise in shape fixing) be developed?

Acknowledgements

The author thanks Drs. William Rogers, Ingrid Rousseau, and Nilesh Mankame for general discussions on the subject of shape memory polymers.

References

[1] Liu C, Qin H, Mather P. J Mater Chem 2007;17:1543.
[2] Ratna D, Karger-Kocsis J. J Mater Sci 2008;43:254.
[3] Lendlein A, Langer R. Science 2002;296:1673.
[4] Lendlein A, Behl M, Hiebl B, Wischke C. Expert Rev Med Devices 2010;7:357.
[5] Small W, Singhal P, Wilson T, Maitland D. J Mater Chem 2010;20:3356.
[6] Lendlein A, Kelch S. Angew Chem Int Ed 2002;41:2034.
[7] Behl M, Lendlein A. Mater Today 2007;10:20.
[8] Behl M, Razzaq M, Lendlein A. Adv Mater 2010;22:3388.
[9] Mather P, Luo X, Rousseau I. Annu Rev Mater Res; 2009:445.
[10] Huang W, Ding Z, Wang C, Wei J, Zhao Y, Purnawali H. Mater Today 2010;13:44.
[11] Rousseau I. Polym Eng Sci 2008;48:2075.
[12] Gunes I, Jana SJ. Nanosci Nanotech 2008;8:1616.
[13] Liu Y, Lv H, Lan X, Leng J, Du S. Compos Sci Technol 2009;69:2064.
[14] Hu J, Chen S. J Mater Chem; 2010:3346–55.
[15] Dietsch B, Tong TJ. Adv Mater 2007;39:3.
[16] Xie T, Rousseau I. Polymer 2009;50:1852.
[17] Behl M, Ridder U, Feng Y, Kelch S, Lendlein A. Soft Matter 2009;5:676.
[18] Luo X, Mather P. Macromolecules 2009;42:7251.
[19] Liu C, Chun S, Mather P, Zheng L, Haley E, Coughlin E. Macromolecules 2002;35:9868.
[20] Yakacki C, Shandas R, Safranski D, Ortega A, Sassaman K, Gall K. Adv Funct Mater 2008;18:2428.
[21] Nair D, Cramer N, Scott T, Bowman C, Shandas R. Polymer 2010;51:4383.
[22] Li J, Viveros J, Wrue M, Anthamatten M. Adv Mater 2007;19:2851.
[23] Kushner A, Vossler J, Williams G, Guan ZJ. Am Chem Soc 2009;131:8766.
[24] Gunes I, Perez-Bolivar C, Cao F, Jimenez G, Anzenbacher P, Jana SJ. Mater Chem 2010;20:3467.
[25] Jeffrey G. An introduction to hydrogen bonding. New York: Oxford University Press, Inc.; 1997.
[26] Mauritz K, Moore R. Chem Rev 2004;104:4535.
[27] Page K, Cable K, Moore R. Macromolecules 2005;38:6472.
[28] Xie T. Nature 2010;464:267.
[29] Rubatat L, Diat O. Macromolecules 2007;40:9455.
[30] Xie T, Page K, Eastman R. Adv Func Mater 2011;21:2057.
[31] Weiss R, Izzo E, Mandelbaum S. Macromolecules 2008;41:2978.
[32] Guan Y, Cao Y, Peng Y, Xu J, Chen A. Chem Commun 2001;37:1694.
[33] Zhang S, Yu Z, Govender T, Luo H, Li B. Polymer 2008;49:3205.
[34] Miaudet P, Derre A, Maugey M, Zakri C, Piccione P, Inoubli R, et al. Science 2007;318:1294.
[35] Wang R, Xiao X, Xie T. Macromol Rapid Commun 2010;31:295.
[36] Bonner M, de Oca H, Brown M, Ward I. Polymer 2010;51:1432.
[37] Gall K, Dunn M, Liu Y, Finch D, Lake M, Munshi N. Acta Mater 2002;50:5115.
[38] Koerner H, Price G, Pearce N, Alexander M, Vaia R. Nat Mater 2004;3:115.
[39] Rodriguez E, Luo X, Mather P. ACS Appl Mater Interfaces 2011;3:152.
[40] Cui J, Kratz K, Lendlein A. Smart Mater Struct 2010;19:065019.
[41] Gall K, Dunn M, Liu Y, Stefanic G, Balzar D. Appl. Phys. Lett. 2004;85:290.
[42] Yakacki C, Willis S, Luders C, Gall K. Adv Eng Mater 2008;10:112.
[43] Feldkamp D, Rousseau I. Macromol Mater Eng 2010;8:726.
[44] Zotzmann J, Behl M, Feng Y, Lendlein A. Adv Funct Mater 2010;20:3583.
[45] White S, Sottos N, Geubelle P, Moore J, Kessler M, Sriram S, et al. Nature 2001;409:794.
[46] Xiao X, Xie T, Cheng YJ. Mater Chem 2010;20:3508.
[47] Tanaka Y, Himuro Y, Kainuma R, Sutou Y, Omori T, Ishida K. Science 2010;327:1488.
[48] Xie T, Xiao X. Chem Mater 2008;20:2866.
[49] Wang R. and Xie T. Langmuir 2010;26:2999.
[50] Wang R, Xie T. Chem Commun 2010;46:1341.
[51] Reddy S, Arzt E, del Campo A. Adv Mater 2007;19:3833.
[52] Kim S, Sitti M, Xie T, Xiao X. Soft Matter 2009;5(19):3689.
[53] Kunzelman J, Chung T, Mather P, Weder CJ. Mater Chem 2008;18(10):1082.
[54] Nelson B, King W, Gall K. Appl Phys Lett 2005;86:103108.
[55] Altebaeumer T, Gotsmann B, Pozidis H, Knoll A, Duerig U. Nano Lett 2008;8:4398.
[56] Gall K, Kreiner P, Turner D, Hulse M. J Microelectromech Syst 2004;13:472.
[57] Burke K, Mather P. J Mater Chem 2010;20:3449.
[58] Xie T, Xiao X, Li J, Wang R. Adv Mater 2010;22:4390.
[59] Tajbakhsh AR, Terentjev EM. Eur Phys J Ser E 2001;6:181.
[60] Thomsen D, Keller P, Naciri J, Pink R, Jeon H, Shenoy D, et al. Macromolecules 2001;34:5868.
[61] Chung T, Rorno-Uribe A, Mather P. Macromolecules 2008;41:184.
[62] Zotzmann J, Behl M, Hofmann D, Lendlein A. Adv Mater 2010;22:3424.
[63] Chen S, Hu J, Zhuo H. Compos Sci Technol 2010;70:1437.
[64] Sellinger A, Wang D, Tan L, Vaia R. Adv. Mater 2010;22:3430.
[65] Bellin I, Kelch S, Langer R, Lendlein A. Proc Natl Acad Sci U S A 2006;103:18043.
[66] Xie T, Xiao X, Cheng Y. Macromol Rapid Commun 2009;30:1823.
[67] Behl M, Bellin I, Kelch S, Wagermaier W, Lendlein A. Adv Funct Mater 2009;19:102.
[68] Li J, Xie T. Macromolecules 2011;44:175.
[69] Pretsch T. Smart Mater Struc 2010;19:015006.
[70] Qin H, Mather P. Macromolecules; 2009:273–80.
[71] Behl M, Lendlein A. J Mater Chem 2010;20:3335.
[72] Ahn S, Deshmukh P, Kasi R. Macromolecules 2010;43:7330.
[73] Chen S, Hu J, Yuen C, Chan L, Zhuo H. Polym Adv Technol 2010;3:377.
[74] Kolesov I, Radusch H. eXPRESS Polym Lett 2008;7:461.
[75] Luo X, Mather P. Adv Funct Mater; 2010:2649–56.
[76] DiOrio A, Luo X, Lee K, Mather P. Soft Matter 2011;7:68.
[77] Sun L, Huang W. Soft Matter 2010;6:4403.
[78] Mohr R, Kratz K, Weigel T, Lucka-Gabor M, Moneke M, Lendlein A. Proc Natl Acad Sci U S A 2006;103:3540.
[79] Gunes I, Jimenez G, Jana S. Carbon 2009;47:981.
[80] Luo X, Mather P. Soft Matter 2010;6:2146.
[81] Lendlein A, Jiang H, Junger O, Langer R. Nature 2005;434:879.
[82] Lee KM, Koerner H, Vaia RA, Bunning TJ, White TJ. Soft Matter 2011;7:4318.
[83] Huang W, Yang B, An L, Li C, Chan Y. Appl Phys Lett 2005;86:114105.
[84] Kumar U, Kratz K, Wagermaier W, Behl M, Lendlein A. J Mater Chem 2010;20:3404.
[85] He Z, Satarkar N, Xie T, Cheng YT, Hilt JZ. Adv Mater 2011;23:3192.
[86] Zhang Y, Cheng Y, Grummon D. Appl Phys Lett 2006;89:041912.

Tao Xie obtained his BS and MS degrees in Polymer Chemistry from Zhejiang University in China in 1993 and 1996, respectively. From University of Massachusetts at Amherst, he received his Ph.D. in Polymer Science and Engineering in 2001 and was the recipient of the Omnova Solution award for his research work there. He is currently staff research scientist at the Chemical Sciences and Materials Systems Lab of General Motors Global Research & Development Center in Warren, Michigan. At GM, he leads two research projects with focuses on both fundamental and applied aspects of bioinspired material systems and smart and/or functional polymers. His scientific contribution has led to a Campbell award (2011) and 14 peer-reviewed papers since 2009. He is also the inventor of over 40 patents (and applications) and the reversible adhesive technology he developed is selected as "2011 Innovations that could change the way you manufacture" by Society of Manufacturing Engineers.