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Shape-memory polymers and their composites: Stimulus methods and applications

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Abstract

Shape-memory polymers (SMPs) undergo significant macroscopic deformation upon the application of an external stimulus (e.g., heat, electricity, light, magnetism, moisture and even a change in pH value). They have been widely researched since the 1980s and are an example of a promising smart material. This paper aims to provide a comprehensive review of SMPs, encompassing a fundamental understanding of the shape-memory effect, fabrication, modeling and characterization of SMPs, various actuation methods and multifunctional properties of SMP composites, and potential applications for SMP structures. A definition of SMPs and their fundamentals are first presented. Next, a description of their fabrication, characterization and constitutive models of SMPs are introduced. SMP composites, which act to improve a certain function as functional materials or the general mechanical properties as structural materials, are briefly discussed. Specially, the SMP composites can be developed into multifunctional materials actuated by various methods, such as thermal-induced, electro-activated, light-induced, magnetic-actuated and solution-responsive SMPs. As smart materials, the applications of SMPs and their composites receive much interest, including deployable structures, morphing structures, biomaterials, smart textiles and fabrics, SMP foams, automobile actuators and self-healing composite systems.

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1. Introduction

Since the discovery of the shape-memory polymers (SMPs) in the 1980s, international research interest into the shape-memory effect in polymers has been rapidly growing [1–7]. The SMPs are stimuli-responsive smart materials with the ability to undergo a large recoverable deformation upon the application of an external stimulus [8]. While the reversible martensitic transformation is the mechanism behind the shape-memory phenomenon in shape-memory alloys (SMAs) [9–12], the shape-memory phenomenon in SMPs stems from a dual-segment system: cross-links to determine the permanent shape and switching segments with transition temperature ($T_{\text{trans}}$) to fix the temporary shape [13]. Below $T_{\text{trans}}$, SMPs are stiff, while they will be relatively soft upon heating above $T_{\text{trans}}$ and consequently they can be deformed into a desired temporary shape through applying an external force. When cooling and subsequently remove this external force, their temporary shape can be maintained for long. Upon re-heating, their temporary deformed shape will automatically recover the original permanent shape.

SMPs can be activated not only by heat [14,15] and magnetism [16,17] similar to SMAs, but also by electricity [18,19], light [20] moisture [21,22], even certain chemical stimulus (e.g., a change in pH value [13]), etc. [23–25] SMPs present many potential technical advantages that surpass those of SMAs and shape-memory ceramics such as good shape recoverability (up to 400% recoverable strain), low density, ease in processing and in tailoring of properties (e.g., transition temperature, stiffness, biodegradability, and ease of functionally grading), programmability and controllability of recovery behavior, and most importantly, low cost.

Based on the above advantages, SMP composites and some novel multi-functional SMPs have also been developed. Furthermore, there is an increased activity in integrating SMPs with nanotechnology to develop novel materials for the realistic applications. The latest developments in nanotechnology enable SMPs to be better accommodate the requirements of a particular application in biomaterials, sensors, actuators or textiles. SMPs, SMP composites or SMP structures have been applied in forms such as space deployable structures (e.g., hinges, trusses, mirrors and reflectors), morphing skins used for folding or variable camber wings in aircraft, biomedical and bioinspirational instruments (e.g., a polymer vascular stent with shape-memory as a drug delivery system, smart surgical sutures, and laser-activated SMP microactuator to remove a clot in a blood vessel), SMP textiles, automobile actuators and self-healing systems.

The present paper aims to provide a systematic and comprehensive analysis of SMPs, SMP composites and their potential applications. Section 1 presents a brief introduction of SMPs, and the fundamentals of SMPs are summarized in Section 2. Sections 3 review their synthesis, characterization and modeling. Subsequently, in Section 4, the particles and fiber filled SMP composites are discussed, followed by a presentation of the various multi-functional SMP composites. Finally, relevant potential applications of SMPs or their composites are provided in Section 5. We conclude with future directions in developing new SMPs and applications.

2. Fundamentals of shape-memory polymers

2.1. Background and definition

Shape-memory polymers (SMPs) are able to respond to a specific external stimulus by means of certain significantly macroscopic properties such as shape [26,27]. The basic molecular architecture of SMPs is a polymer network underlying active movement [28]. A SMP must consist of dual-segments,
one that is highly elastic and another that is able to reduce its stiffness upon a particular stimulus. The latter can be either molecular switches or stimulus sensitive domains. Upon exposure to a specific stimulus the switching/transition is triggered and strain energy stored in the temporary shape is released, which consequently results in the shape recovery [29,30].

SMPs and their composites can recover their original shapes after large deformation when subjected to an external stimulus, such as Joule heating, light, magnetism or moisture [31]. Among these SMPs, the thermo-responsive SMPs are the most common [32–34]. At a macroscopic level, as illustrated in Fig. 1, the typical thermomechanical cycle of a thermo-responsive SMP consists of the following steps [35,36]: (1) fabrication of the SMPs into an original shape; (2) heating the SMP above the thermal transition temperature (\(T_{trans}\)) (either a glass transition temperature, \(T_g\), or a melting temperature, \(T_m\)), and deformation of the SMP by applying an external force, cooling well below \(T_{trans}\), removal of the constraint to obtain a temporary pre-deformed shape; (3) when needed, heating of the pre-deformed SMP above \(T_{trans}\), and then recovery of the SMP towards its original shape (a recovered shape).

The first SMP was polynorbornene with a \(T_g\) range of 35–40 °C developed by the French CdF Chimie Company and commercialized by the Japan Nippon Zeon Company in 1984 [37,38]. However, the \(T_g\) of the polymer is very difficult to tailor due to its high molecular weight. Styrene butadiene based SMPs were developed by the Asahi Company. They presented a \(T_g\) of about 60–90 °C. However, their processability was also poor [37,39]. Recently, the Cornerstone Research Group (CRG), Inc. has developed some commercialized thermosetting SMPs [40], including a styrene-based SMP (Veriflex®) with a \(T_g\) ranging from 60 to 70 °C, a one part epoxy SMP with a \(T_g\) of about 90 °C, a two parts epoxy SMP with a \(T_g\) of about 104 °C, and a cyanate ester SMP with a high \(T_g\) range from 135 to 230 °C. Composite Technology Development (CTD), Inc. has developed a thermosetting epoxy SMP (CTD-101 K) with a \(T_g\) of about 113 °C [41]. Moreover, a series of thermoplastic polyurethane SMPs is commercially available from Mitsubishi Heavy Industry, with the \(T_g\) ranging from 40 to 55 °C.

As SMPs show a variety of novel properties, they have been widely researched since the 1980s. To date, research activities regarding SMPs have been widely conducted in more than 60 institutes or companies all over the world. In the recent years, a variety of polymers has been synthesised with shape-memory effects and certain unique performance ability has been developed. Based on the shape-memory effect, some novel multi-functional SMPs or nano SMP composites have also been proposed.

2.2. Comparison between shape-memory alloys and shape-memory polymers

Shape-memory alloys (SMAs) can deform at a low-temperature and then recover to their prior shape upon heating above a particular temperature-related to the properties of alloy. SMAs mainly include three types: nickel-titanium (NiTi) alloys, copper–zinc–aluminum–nickel and copper–aluminum–nickel. SMA changes from austenite to martensite upon cooling. The martensite phase exists at lower temperatures and is the relatively soft and easily deformed phase of SMAs. Austenite is a stronger phase of SMAs that occurs at higher temperatures. When the temperature of the SMA is cooled to below the transition temperature (\(T_s\)), the shape-memory effect can be observed and the alloy is entirely composed of martensite. Upon re-heating above the transition temperature, the deformed shape will recover to its initial shape. The deformed martensite transforms into the cubic austenite phase [42].

SMAs show both one-way and two-way shape-memory effect. For one-way shape-memory effect, upon heating a SMA at deformed martensite phase, the shape changes to its original. However, when the metal cools again it will remain in the hot shape. With the one-way effect, cooling from high temperatures does not cause a macroscopic shape change. An external deformation is necessary to create
the low-temperature shape. For two-way shape-memory effect, when a SMA is cooled at hot austenite phase it will automatically deform without any external deformation. That is to say, the cool deformed shape and hot original shape can automatically transfer in the heating–cooling cycle.

On the other hand, the shape-memory effect of SMPs depends on the existence of separated phases related to the coiled polymer structure and cross-links, etc. In the deformed shape below \( T_g \), molecular chains of the SMPs are constrained by chemical or physical cross-link. When reheated again, these molecular chains will go back to the random coiled configuration. The shape-memory transformation depends on the mechanism by which polymer molecules transpose between the constrained and random entangled conformations [42]. SMPs only show one-way shape-memory effect. That is, the SMP at “soft” stage can only deform with the help of external force rather than automatically deform by cooling.

The advantage of SMPs over SMAs relies mostly on their intrinsic properties such as lower cost, lower density, easier processing and larger attainable strains. SMPs exhibiting up to 200% strain have been reported compared to less than 10%, 1%, and 0.1% for SMA, shape-memory ceramics, and glasses, respectively [43]. Table 1 lists the main properties compared between NiTi SMA and polystyrene SMP. It reveals that \( T_g \) of NiTi SMA and polystyrene SMP are adjustable. As a polymer, polystyrene SMP shows a lower actuation force but a higher recoverable strain than those of NiTi SMAs. In addition, Fig. 2 shows some comparison of mechanical properties among some typical materials, where SMPs perform a large strain but a relatively low stress [44].

### Table 1

Main properties compared between typical SMA and SMP.

<table>
<thead>
<tr>
<th></th>
<th>NiTi SMA</th>
<th>Polystyrene SMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_g ), °C</td>
<td>Approx. 40–100</td>
<td>62</td>
</tr>
<tr>
<td>Transformation strain, %</td>
<td>Max 8</td>
<td>50–100</td>
</tr>
<tr>
<td>Actuation stress, MPa</td>
<td>Approx. 100</td>
<td>2–10</td>
</tr>
<tr>
<td>Young’s Modulus above ( T_g ), GPa</td>
<td>Approx. 83</td>
<td>1.24</td>
</tr>
<tr>
<td>Young’s Modulus below ( T_g ), MPa</td>
<td>Approx. 28–41</td>
<td>2–10</td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td>0.33</td>
<td>0.30</td>
</tr>
<tr>
<td>Density, gms/cc</td>
<td>6.45</td>
<td>0.92</td>
</tr>
</tbody>
</table>

**Fig. 2.** Comparison of mechanical properties among some typical materials [44].

2.3. Architecture of shape-memory polymers

SMPs are typically dual-shape in nature, being comprised of an original shape and a deformed shape. This shape-memory feature is resulted from a combination of the polymer’s molecular architecture
and a particular programming procedure that enables the formation of a temporary deformed shape [45]. The special chemical architecture consists of netpoints, and molecular switches that are sensitive to an external stimulus. In this sense, SMPs can be considered as copolymers with a hard segment acting as a fixed phase and a soft segment acting as a reversible phase [46]. The fixed phase prevents ‘free’ flow of the surrounding polymer chains upon the application of a stress. The reversible phase, on the other hand, undergoes deformation in a shape-memory cycle and is responsible for elasticity [47]. This phase acts as a ‘molecular switch’, freezing the deformed shape below the transition temperature while releasing them towards the original shape at or above the transition temperature.

2.4. Stimulus methods of shape-memory polymers

The actuation methods of SMPs can be generally divided into heat, electricity, light, magnetism, moisture, etc. The shape-memory effect of thermal-responsive SMPs is directly triggered by Joule heating from a source such as hot gas or hot water [48]. Fig. 3 shows an example of a thermally induced shape recovery process for a pure SMP (Fig. 3, top row) and a glass-fiber-reinforced SMP (Fig. 3, bottom row) in hot gas. Because it is not convenient to use hot water or gas to directly activate the SMPs in most applications, the corresponding studies have received little attention. Alternatively, special functional fillers can be incorporated into SMPs to trigger shape-memory effect through electricity, light, magnetism or moisture, etc. While the SMPs induced by these methods are still triggered by Joule heat intrinsically, this heat is produced by various indirect methods. For the water or solvent driven SMPs, solvent molecules are diffused into the polymer sample and act as plasticizers when immersed in water, leading to a reduction in the transition temperature and consequently resulting in shape recovery. This could also be classified as an indirectly thermal-induced actuation method. In particular, the intrinsically light-induced SMPs are produced by incorporating reversible photoactive molecular switches; the stimulation is not considered to be related to any temperature effects and should, therefore, be differentiated from the indirect actuation of the thermal-responsive shape-memory effect. The various actuation methods of SMPs will be discussed in Section 4.

2.5. Categorization of shape-memory polymers

SMPs are considered to consist of netpoints and molecular switches. Netpoints can be achieved formed by covalent bonds or intermolecular interactions. Hence, they can be either of a chemical or physical nature. Chemically cross-linked SMPs can be achieved through a suitable cross-linking chemistry, which are referred to as thermosets. Physically cross-linked ones require a polymer morphology consisting of at least two segregated domains, which are referred to as thermoplastics.

The network chains of SMPs can be either amorphous or crystalline, and therefore the transition temperature ($T_{trans}$) is either a glass transition temperature ($T_g$), or a melting temperature ($T_m$) [49]. If the thermal transition is a glass transition, the micro Brownian motion of the network chains is frozen at temperatures below $T_g$, and will be “switched” on at temperatures at or above $T_g$ upon
reheating. When the thermal transition is a melting point, the switching segments crystallize at temperatures below $T_m$, and then recover their original shape at an elevated temperature at or above $T_m$ [50]. Detailed discussions will be provided in Section 3.

3. Fabrication, characterization and modeling of shape-memory polymers

The shape-memory behavior has been observed in several polymers with significantly different chemical compositions. In this section, we discuss the structural requirements for the various chemical compositions of SMPs, structural categorization, and the synthesis of three typical SMPs (polyurethane, styrene-based and epoxy SMPs). Subsequently, we discuss the main characterization techniques and the corresponding chemical, thermal and mechanical parameters. In addition, wide engineering applications demand effective and simple theoretical models that can explain and predict the shape-memory effect of SMPs. Theoretical modeling of the mechanical constitutive behavior of an SMP proves difficult due to the large recoverable deformation capability of SMPs, and the heavy dependence of polymer properties on both time and temperature. Generally, there are two approaches to developing a constitutive model for SMPs, which we apply here. One is based on the linear or non-linear viscoelastic theory [32,33], while the other is based on the micromechanical theorem of phase transformation [51,52].

3.1. Chemical architecture requirements of shape-memory polymers

Like normal polymers, SMPs also possess three-dimensional molecular network-like architectures [53–58]. The network architectures are thought to be constructed through cross-linking net points, with polymer segments connecting adjacent net points. These strongly cross-linked architectures ensure that the polymer can maintain a stable shape on the macroscopic level for enabling both the original and recovered shapes [5]. The domain of the cross-linking netpoints can be either physically or chemically cross-linked structures. Physically cross-linked polymers (thermoplastics) exhibit a reversible nature (see Fig. 4a), meaning that they can be melted or dissolved in certain solutions. The interconnection of the individual polymer chains in a physically cross-linked network is achieved by the formation of crystalline or glassy phases. For the chemically cross-linked polymers (thermosets) (see Fig. 4b), the individual polymer chains are connected by covalent bonds, which are more stable than the physical cross-linking network and show an irreversible nature [53,54].

The other basic requirement of an SMP is the formation of strong reversible interactions (secondary cross-links) between the polymer segments so that a macroscopic shape deformation, namely temporary pre-deformed shape, can be fixed [29,53,59,60]. As shown in Fig. 5, when an SMP is heated above

![Fig. 4. Schematics of the typical structures of a polymer network that is (a) physically cross-linked network; (b) chemically cross-linked network (modified from [53]).](image-url)
$T_{\text{trans}}$, a polymer chain between two network points is randomly coiled without deformation of the SMP. Upon applying an external stretching stress on the material, the polymer segments are elongated. It results in an orientation of most of the polymer chains and a dislocation of the network points (physically or chemically cross-linked net points). Upon cooling and maintaining the macroscopic deformed shape, the secondary cross-links will form among the new orientational polymer segments. The fixation of this additional order in the network segments is the main principle underlying the shape-memory effect, and upon cooling, it can occur by effectively reducing the dynamics and flexibility of the segments. In suitable polymer architectures, these secondary cross-linked domains are formed by side chains or by chain segments linking two netpoints. The secondary cross-links can be glassy or crystalline domains. Consequently, the transition temperature $T_{\text{trans}}$ of SMPs is either a $T_g$ or a $T_m$ [29]. In both cases, the temporary stabilization is formed by the aggregation of the switching segments. Upon reheating, the shape-memory effect is realized by detaching the secondary cross-links, the strain energy will be released, and the macroscopic shape recovery of the SMPs will occur. The recovery shape of SMPs is determined by the primary cross-links and polymer segments when no secondary cross-links existed.

Based on the chemical architectures and corresponding evolution in the shape-memory programming process, the polymer segments can fulfill two types of structural tasks: the hard segments and the soft segments [47,53,61]. The hard segments form the ‘netpoints’ that link the soft segments, acting as a fixed phase. The hard segments may be of physical or chemical nature, such as crystals, glassy domains, chain entanglements or chemical cross-links. The soft segments work as a reversible molecular switch (reversible phase) and show a thermal transition at temperature $T_{\text{trans}}$. They fix (“freeze in”) the temporary pre-deformed shapes below $T_{\text{trans}}$, while freezing the pre-deformed shapes towards the original shapes at or above the transition temperature.
3.2. Structural categorization of shape-memory polymers

SMPs consist of netpoints and molecular switches. Netpoints are constructed with either physical cross-links through physical intermolecular interactions or chemical cross-links through covalent bonds [50]. Thermal-responsive SMPs can be classified according to the nature of their permanent netpoints and the thermal transition related to the switching domains into four different categories: (I) physically cross-linked thermoplastics with $T_{\text{trans}} = T_g$; (II) physically cross-linked thermoplastics with $T_{\text{trans}} = T_m$. (III) chemically cross-linked amorphous polymers ($T_{\text{trans}} = T_g$); (IV) chemically cross-linked semi-crystalline polymer networks ($T_{\text{trans}} = T_m$).

3.2.1. Thermoplastic shape-memory polymers

For the physically cross-linked SMPs, the formation of a phase-segregated morphology is the fundamental mechanism behind the thermally induced shape-memory effect of these materials. One phase provides the physical cross-links while another phase acts as a molecular switch [29]. They can be further classified into linear polymers [63,64], branched polymers [65] or a polymer complex. The linear SMPs consist of block copolymers and high molecular weight polymers [50].

Among thermoplastic SMPs, the polyurethane SMP performs many advantages when compared with other available SMPs, including higher shape recoverability (maximum recoverable strain >400%) [66], a wider range of shape recovery temperature (from −30 to 70 °C), better biocompatibility and better processing ability [67,5].

3.2.2. Thermosetting shape-memory polymers

For the chemically cross-linked SMPs, there are two methods to synthesize covalently cross-linked networks [29,53]. First of all, the polymer network can be synthesized by adding a multi-functional cross-linker during the polymerization. The chemical, thermal and mechanical properties of the network can be adjusted by the choice of monomers, their functionality, and the cross-linker content. The second method to obtain polymer networks is the subsequent cross-linking of a linear or branched polymer. The networks are formed based on many different polymer backbones, such as polystyrene, polyurethanes, and polyolines. Covalently cross-linked SMPs possess chemically interconnected structures that determine the original macroscopic shape of SMPs. The switching segments of the chemically cross-linked SMPs are generally the network chains between netpoints, and a thermal transition of the polymer segments is used as the shape-memory switch. The chemical, thermal, mechanical and shape-memory properties are determined by the reaction conditions, curing times, the type and length of network chains, and the cross-linking density.

Additionally, according to the thermal transition of the switching segment, SMPs can be divided into two categories. Either the transition temperature $T_{\text{trans}}$ is a melting temperature $T_m$ or a glass transition temperature $T_g$ [50]. If the thermal transition belongs to a glass transition, the micro Brownian motion of the network chains is frozen and the temporary shape is fixed at low-temperatures; correspondingly, the network chain segments are in the glassy state. The SMPs will remember the temporary shape and store the strain energy. When heating at or above $T_g$, the micro Brownian motion will be triggered and the ‘switch’ will be opened. In the case of glass transition, glass transitions usually extend over a broad temperature range. When the thermal transition is a melting point, the switching segments crystallize at low-temperature as a fixed segment to store the strain energy, and then recover the original shape at elevated temperatures at or above $T_m$. In the case of melting temperature, the transition presents a relatively sharp transition in most cases.

Compared with physically cross-linked SMPs, the chemically cross-linked SMPs often show less creep, thus the irreversible deformation during shape recovery is less. Chemically cross-linked SMPs usually show better chemical, thermal, mechanical and shape-memory properties than physically cross-linked SMPs. Additionally, these properties can be adjusted by controlling the cross-link density, curing conditions and curing times.

The shape recovery ratio of the thermoplastic polyurethane SMP is usually in the range of 90–95% within 20 shape recovery cycles. The elastic modulus of the SMP is between 0.5 and 2.5 GPa at room temperature. Additionally, when exposed to air, it is very sensitive to moisture and therefore shows unstable mechanical properties. In contrast, the epoxy SMP exhibits better overall performance. The
shape recovery ratio can approach 98–100%, and the elastic modulus approaches 2–4.5 GPa. In addition, it performs better stabilization against moisture and space radiation. Because of the relatively poor thermal and mechanical properties, the thermoplastic SMPs (e.g., polyurethane SMP) are mostly researched and used as functional materials at a small scale, such as for biomaterials and shape-memory polymer textiles. On the other hand, the thermosetting SMPs (e.g., styrene-based SMP and epoxy SMP) are generally used for structural materials, such as space deployable structures and automobile actuators.

3.3. Synthesis of typical shape-memory polymers

More than twenty types of SMPs have been synthesised and widely researched in the recent years. Fig. 6 presents the classification scheme for existing polymer networks that exhibit the shape-memory effect [50].

The physically cross-linked SMPs include linear polymers [50,63,68,69], branched polymers [65] or a polymer complex [70–72]. The shape-memory effect of linear polymer is due to the phase separation and the domain orientation. The typical physically cross-linked SMP is linear block copolymers, such as polyurethanes. In polyurethanes, oligourethane segments are the hard elastic segments, while polyester serves as the switching segment [73,74]. The phase separation and the domain orientation of poly(ɛ-caprolactone) based polyesterurethanes can be determined by Raman spectroscopy [75]. A similar effect is found for copolyester based ionomers obtained by the bulk polymerization of adipic acid and mixed monomers (bis(poly(oxyethylene)) sulfonated dimethyl fumarate and 1,4-butanediol) [76]. The polycarbonate segment is synthesised by the copolymerization of ethylene oxide in the presence of CO₂ catalyzed by a polymer supported bimetallic catalyst, which yields an aliphatic polycarbonate diol. This macrodiol is further processed by the prepolymer method into a polyurethane SMP [77].

Covalent netpoints can be obtained by cross-linking of linear or branched polymers as well as by (co)polymerization/poly(co)condensation of one or several monomers, whereby at least one has to be at least tri-functional [45]. Depending on the synthesis strategy, cross-links can be created during synthesis or by post-processing. The shape recovery is triggered by controlled by the trans-vinylene

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**Fig. 6.** Schematic of structural categorization of SMPs (modified from [50]).
content [78]. The other synthesis routes to obtain polymer networks involve the copolymerization of monofunctional monomers with low-molecular weight or oligomeric difunctional cross-linkers [79]. The copolymerization of monofunctional monomers of low molecular weight with oligomeric difunctional cross-linkers enables the creation of AB copolymer networks with increased toughness and elasticity at room temperature [80,81]. To date, many kinds of SMPs have been developed through chemical cross-linking, such as cross-linked polystyrene, epoxy, poly(vinyl chloride), polyethylene and PE/poly(vinyl acetate) copolymer [2,50].

It should be noted that, in this paper, the further studies in SMPs (e.g., various actuation methods of multi-functional SMPs or SMP composites (Section 4), and the corresponding potential applications (Section 5)) are generally concerned about three types of SMPs (polyurethane, styrene-based and epoxy SMPs). Consequently, the synthesis of these three types of SMPs is discussed emphatically in this paper. Readers could refer to relevant literatures that discuss the synthesis of other types of SMPs [82–84], such as polyolefines SMP [85], polyethylene-poly(vinyl acetate) copolymers [86], polysiloxanes SMP [87], poly((meth)acrylates) SMP [88], polyethylene SMP [89], poly(epsilon-caprolactone) SMP [90], polycyclooctene SMP [34,91], soybean oil-styrene–divinylbenzene SMP [92], stearyl acrylate SMP [93], poly(ethylene oxide-ethylene terephthalate) copolymers [94–96] and trans-poly(1,4-butadiene)-PS copolymer [97,98].

3.3.1. Thermoplastic polyurethane shape-memory polymer

Since the development of the shape-memory segmented polyurethane (PU) copolymer by Hayashi of Mitsubishi Heavy Industry, extensive studies on this materials have been carried out [99–108]. PU SMP consists of a two-phase structure: a hard segment and soft segment. The hard segments are formed either from a long chain macro diol with a higher thermal transition temperature, or from diisocyanates and chain extenders [53]. Typically, the linear polyurethane can be usually synthesised using the following process: through the reaction of difunctional, hydroxy-terminated oligoesters and -ethers with an excess of a low molecular weight diisocyanate, the isocyanate-terminated pre-polymers can be obtained [47,109]. The basic structure of the diisocyanate can be either aromatic or aliphatic; each type of diisocyanate has a different ability to form a semi-crystalline hard segment. Then low molecular weight diols or diamines are incorporated as chain extenders to further couple these pre-polymers. In this way, the linear, phase-segregated polyurethane or polyurethane–urea block copolymers are formed. As shown in Fig. 7, the phase separation morphology of the molecular structure of such polyurethanes is obtained.

3.3.2. Thermosetting styrene-based shape-memory polymer

Styrene-based SMP must have two-phases or exhibit a cross-linked structure to exhibit the shape-memory effect. The variety of methods to polymerize styrene and the wide availability of possible comonomers enable these necessary features. Styrene can be polymerized by anionic, cationic, or free radical polymerization methods. In this way, a huge variety of network architectures may be designed by the proper choice of mechanism, initiator and comonomers [53]. Through cationic polymerization, random copolymer networks formed from renewable natural oils with a high degree of unsaturation, like soy bean oils, copolymerized with styrene and divinylbenzene are obtained [110]. Styrene-based SMPs have been prepared through the cationic copolymerization of the following candidate materials: regular soybean oil, low saturation soybean oil (LoSatSoy) and conjugated LoSatSoy oil with various alkene comonomers including styrene and divinylbenzene, norbornadiene, or dicyclopentadiene (comonomers used as cross-linking agents) initiated by boron trifluoride diethyl etherate

\[
\text{R’—NHCOO—R’—OOCHN—R’—NHCOO} \quad \text{R—O—\left[—CO—(CH₂)ₙ—O\right]ₙ—H}
\]

(Hard segment, Diisocyanate + extender) (Soft segment, Polyol)

Fig. 7. Polyurethane with micro-phase separation structure (modified from [50]).
or related modified initiators [111,112]. By controlling the cross-link densities and the rigidity of the polymer backbones, the SMP shows a tunable $T_g$, mechanical properties, and a good shape-memory effect. In addition, the materials show good reprogramming properties upon numerous shape recovery cycles, and excellent shape fixity and recovery ratios. The advantage of the soybean oil polymers lies in the high degree of chemical control over the shape-memory characteristics. This makes these shape-memory materials particularly promising in applications.

A new shape-memory styrene copolymer has been developed for some particular applications, such as the contact lenses [113]. This new SMP is prepared from the reaction product of styrene, a vinyl compound other than styrene, a multi-functional cross-linking agent and an initiator. The SMP can employ norbornene homopolymers and copolymers of norbornene and alkylated, cyano, alkoxylated, mono- or di-esterified imides, or carboxylic acid derivatives. In addition, the copolymer may also include, as a comonomer, dimethaneoctahydronaphthalene (DMON).

Leng et al. [78,114] have synthesised SMP based on styrene copolymer networks with different degrees of cross-linking. The monomers of copolymer included styrene, a vinyl compound and a cross-linking agent (a difunctional monomer). During the process of synthesis, the inhibitor was removed by passing the liquid monomers through an initiator removal column. Benzoyl peroxide (BPO) was used as thermal initiator. The purified monomers (styrene and the vinyl compound) and the cross-linking agent (difunctional monomer) were mixed in varying proportions with BPO at the room temperature by stirring. The mixture was then polymerized between two casting glass plates, placed into an oven and kept at 75 °C for 36 h. This prolonged curing time minimized shrinkage and the temperature was kept at 75 °C for 48 h in order to complete the reaction. The SMP, with $T_g$ in the range from 35 to 55 °C, experienced good shape recovery performance. Moreover, the $T_g$ can be adjusted through the alternation of the gel content of the copolymer; the $T_g$ increased with increasing gel content. The largest reversible strain of the SMP reached as high as 100% and the reversible strain of the copolymer decreased with increasing gel content.

3.3.3. Thermosetting epoxy shape-memory polymer

Shape-memory behaviors can be observed in several polymers, including polyurethane-based polymers [115,116], styrene-based polymers, epoxy polymer [117,118] and others. Controlling macroscopic properties through variation of network parameters is suggested to play an important role in the investigation of SMPs. For example, Kim [119] studied the effect of soft/hard segment phase separation and soft segment crystallization on shape-memory property in polyurethane SMP. Hu and her coworkers [116] reported that the molecule weight of polymer network influences the shape-memory effect in PU shape-memory films. Studies have also been performed on the relation of network structure and shape recovery in copolymers of methyl methacrylate and poly(ethyleneglycol)-dimethacrylate [120]. However, few works have been preformed to investigate the systematic tailoring of thermomechanical properties in addition to the shape-memory response for polymers [121].

In particular, epoxy SMP is a high-performance thermosetting resin possessing a unique thermomechanical property together with excellent shape-memory effect. Leng et al. [121] have synthesised the epoxy SMP, from an epoxy resin, a hardener and another linear epoxy monomer. The epoxy resin was mixed with the hardener at a 1:1 weight ratio. An active linear epoxy monomer was copolymerized with the polymer matrix to tailor the network. The monomer is composed of a long linear chain of $\text{C-O}$ bonds and two epoxy groups at the chain ends. With an increase in the linear monomer content, the $T_g$ ranges from 37 to 96 °C, and a decrease in the rubber modulus is obtained from dynamic mechanical analysis.

3.3.4. Some novel shape-memory polymers

Several researchers have reported the intrinsically light-induced deformation of polymers [122] or gels [123,124], including bending [125], contraction [126] or volume changes [20]. Lendlein et al. [1,20,127] have described the light-induced SMPs that have no relation with thermal effect during the shape recovery, despite most of the SMPs are considered as directly or indirectly thermal-responsive polymers. A grafted polymer has been used to design the light sensitive SMPs at a molecular scale [1,20]. Cinnamic acid (CA) molecules are grafted onto a permanent polymer network. The polymer architecture is formed by the copolymerization of $n$-butylacrylate, hydroxyethyl methacrylate,
ethyleneglycol-1-acrylate-2-CA, and poly (propylene glycol)-dimethacrylate) working as the cross-linker.

To construct a permanent polymer network, it is made from BA with 3.0 wt.% poly(propylene glycol)-dimethacrylate as the cross-linker, with 20 wt.% star-poly(ethylene glycol) end capped with (cinnamylidene acetic acid (CAA) terminal groups (SCAA). This SCAA molecule yields a photo-sensitive interpenetrating network that will change shape in response to light of a special wavelength light. In this case, cross-links of the amorphous polymer network determine the permanent shape [20].

Biodegradable SMPs are a promising field during the development of SMPs [2,13,55,128]. They can be synthesised from a few monomers which have been already used in synthesis of exiting biodegradable materials [129–131]. A poly(ε-caprolactone) (PCL)-based biodegradable SMP has been demonstrated its potential in medical applications [2,77,132]. The biodegradable SMP, is mainly based on polyglycolide (PGA), poly(ε-lactide) (PLLA) and PCL [133–138]. By selecting molecular weight of PCL, hard phase component and soft phase/hard phase compositions, the transition temperature of the biodegradable SMP with PCL soft phase can be adjusted to meet the requirement for the biomedical or other applications [5].

Some other types of SMPs with novel functions also attract extensive interest. Mather et al. [139] developed a two-way reversible SMP in a semicrystalline network. In this polymer, the cooling-induced crystallization of cross-linked poly(cyclooctene) films under a tensile load results in a significant elongation and subsequent heating to melt the network reverses this elongation (contraction). In this way, the crystallization-induced elongation on cooling and melting-induced shrinkage on heating yield a two-way shape-memory effect. Peng et al. [140] demonstrated a novel SMP with two transition temperatures. For this SMP, a PMMA-PEG (poly(ethylene oxide)-poly(methyl methacrylate) (PMMA)) semi-interpenetrating network (semi-IPN) exhibits excellent shape-memory behaviors at two transition temperatures, namely the $T_m$ of the poly(ethylene glycol) (PEG) crystal and the $T_g$ of the semi-IPN. In addition, Lendlein et al. [141–144] have demonstrated the triple-shape effect of polymer network with crystallizable network segments and grafted side chains. In this SMP, the multi-phased networks are synthesised by photopolymerization from PEG monomethyl ether monomethacrylate and PCL dimethacrylate as cross-linker. The triple-shape effect is a general concept that requires the application of a two-step programming process for suitable polymers. As shown in Fig. 8, the SMP is able to change from a first shape (A) to a second shape (B) and finally deform into a third shape (C). The triple-shape SMP has great potential for various applications.

3.4. Characterization for shape-memory polymers

3.4.1. Chemical, thermal and mechanical properties

The main characterization techniques and the corresponding chemical, thermal and mechanical parameters are discussed here. These include Fourier transform infrared spectroscopy, optical microscopy, scanning electron microscopy, transmission electron microscopy, electrical conductivity measurements, and temperature distribution measurements detected by infrared camera, thermogravimetric analysis, differential scanning calorimetry, dynamic mechanical analysis, and mechanical properties testing.

3.4.1.1. Fourier transform infrared spectroscopy (FTIR). Fourier transform infrared spectroscopy (FTIR) is a measurement technique for collecting infrared spectra and is a powerful tool for identifying types of chemical bonds (i.e., functional groups). The wavelength of light absorbed is characteristic of the chemical bond, which can be distinguished in this annotated spectrum. By interpreting the infrared absorption spectrum, the chemical bonds can be determined. FTIR spectrometry is often used to investigate the difference in structure of the networks in a molecule during the synthesis of an SMP [34,121]. In addition, Raman spectroscopy and X-ray diffraction (XRD) are generally used to determine the corresponding chemical structures of SMPs [145].

3.4.1.2. Morphology detection. Optical microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) can be used to observe the surface morphology of SMPs or SMPs composites [26,46]. An optical microscope is a type of microscope that uses visible light and a system of lenses to magnify images of small samples; the resulting resolution is often at the micron level. SEM is
used for inspecting topographies of specimens at high magnifications [76]. The scattered electrons produce an image with a depth of field that is typically 300–600 times better than that of an optical microscope. Most SEMs have magnification ranges from 20× to 100,000×. TEM is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through, which is analogous to optical microscopy. Under favorable conditions, TEM can resolve detail at the magnitude of about 1 nm [146].

3.4.1.3. Electrical conductivity measurement. Some types of electrically conductive fillers may be incorporated into SMPs to fabricate conductive SMP composites. In order to evaluate the electro-active performance, many researchers have used a variety of methods to measure the electrical conductivity [18,19,46]. If the electrical resistance ranges from $10^8$ to $10^{11}$ Ohms, a digital high resistivity determiner should be employed. The Four-Point-Probes measurement, which eliminates the lead resistance, may also be used to determine the conductivity. During resistive heating, an infrared camera
can be employed to investigate the temperature distribution of the SMPs during the shape recovery process.

3.4.1.4. Thermogravimetric analysis (TGA). Thermogravimetric analysis (TGA) is employed to investigate thermal stability by evaluating the change in mass as a function of temperature. During the shape recovery process, the highest temperature should be lower than the onset temperature point of decomposition of SMPs. TGA or differential gravimetric analysis (DTG) is used to determine the critical temperature during the decomposition process of SMPs or SMP composites. TGA is a very useful tool for a first, simple and fast evaluation of the thermal stability properties before planning their shape-memory effect [21].

3.4.1.5. Differential scanning calorimetry (DSC). Since differential scanning calorimetry (DSC) is used in many different industries, its application in the plastics industry is widely accepted. It is used to characterize materials for their glass transition temperature, melting points and other material-reaction characteristics such as specific heat, percent crystallinity, and reaction kinetics [147]. For SMPs, in most cases, DSC is used to determine the critical glass transition temperature, $T_g$, during the transition process, which is often defined as the median point of the glass transition range in the heating ramp [46].

3.4.1.6. Dynamic mechanical analysis (DMA). Dynamic mechanical analysis (DMA) is used to monitor the thermal and dynamic mechanical properties of the SMPs and their composites. In this technique, a strain or stress is applied to a sample at a set frequency and the response analyzed to obtain phase angle and deformation data. These data allow the calculation of the complex modulus in Eq. (1) (e.g., storage modulus and loss modulus), damping or tan delta ($\delta$) as well as viscosity data. The dynamic mechanical properties of a polymer are described in terms of a complex dynamic modulus [146]:

$$E^* = E' + iE''$$

where $E'$ is the storage modulus and is a measurement of the recoverable strain energy; when deformation is small, it is approximately equal to the Young's modulus. $E''$ denotes the loss modulus and is related to the hysteresial energy dissipation. The phase angle ($\delta$) is given by:

$$\tan \delta = \frac{E''}{E'}$$

DMA allows the rapid scanning of the modulus and viscosity of an SMP as a function of temperature or frequency [148]. In addition, DMA is very sensitive to the motions of polymer chains and, therefore, they are powerful tools for measuring the glass transitions in SMPs.

3.4.1.7. Mechanical properties evaluation. The mechanical properties of SMPs under varying temperature conditions are important parameters to evaluate the thermal, mechanical and shape-memory performance. The relevant tests include uniaxial tension tests, compression tests, three point bending tests, relaxation tests, creep tests, and nanoscale indentations by atomic force microscopy (AFM). Ni et al. [149] investigated an SMP filled with carbon nanotubes. The results indicate that CNT/SMP nanocomposites exhibit a good shape-memory effect and their recovery stress with only 3.3% weight fraction of carbon nanotubes will reach almost twice of that bulk SMP. Yang et al. [150] studied nanoscale indentation on polymer surfaces using AFM. With increasing molecular weight of cross-linker and decreasing cross-linker concentration, the contact pressures decreased at a fixed maximum load. The results provide insight into the nanoscale response of these novel materials. Yang [151] have demonstrated that the polyurethane SMPs filled with carbon powders exhibited better mechanical and thermomechanical properties than pure SMP. In addition, many other researchers have conducted the relevant mechanical tests to investigate the basic mechanical and thermomechanical performance of these materials [15,31,32,36,152–154].
3.4.2. Shape memory performance

The typical programming of shape recovery process of thermo-responsive SMPs is introduced here [151,154]. A cyclical thermomechanical test is the standard approach to characterize the mechanical and shape-memory properties of SMPs. As shown in Fig. 9, a three-dimensional stress–strain–temperature relationship of thermo-responsive SMPs is illustrated in the following steps [32,155]: (a) at an elevated temperature $T_h$ ($T_h > T_{\text{trans}}$), the SMP specimen is deformed to a pre-determined maximum strain ($\varepsilon_m$) at a constant strain rate ($\dot{\varepsilon}$) under the external loading; (b) the sample is held at the strain $\varepsilon_m$ and then cooled well below $T_g$ to a new temperature $T_l$ ($T_l < T_{\text{trans}}$); (c) after the constraint is released at $T_l$, the stress is reduced to zero, and a very small elastic strain is recovered (shape fixity) where $\varepsilon_f$ is defined as the pre-deformed remaining strain after the applied stress is fully removed; and (d) the sample is reheated from $T_l$ to $T_h$ at a constant heating rate $\dot{T}$ without applying any external loading ($\sigma = 0$). The pre-deformed strain $\varepsilon_f$ is recovered with only a very small irreversible strain $\varepsilon_i$ left at $T_h$ (shape recovery).

As shown in Fig. 9, the cyclical thermomechanical tests mainly consist of two processes, namely shape fixity and shape recovery [156]. Tobushi et al. [37,157] systematically investigated the mechanical properties of a polyurethane SMP, including the cyclic deformation properties at high temperatures, thermomechanical cycling properties, creep and stress relaxation. The results showed that the shape fixity with loading above $T_g$ did not change under thermomechanical cycling, and the residual strain recovered in the vicinity of $T_g$ during the heating process. Gall et al. [155,158] demonstrated that the SiC/SMP nanocomposite can generate higher recovery forces than those of a pure SMP specimen. Hu et al. [50,15] have also systematically reviewed and conducted an analysis of the shape-memory test.

For the practical application of SMPs, their shape recovery performance is extremely important and is generally evaluated using a bending test. During these tests, the main parameter is the angle of the SMP upon bending. The following descriptions illustrate the measurement of this angle and shape recovery ratio during the bending program.

As shown in Fig. 10, the typical thermomechanical bending cycling for an SMP includes the following steps [36,159]: (1) the specimen in its original shape is kept in a water bath at $T_h$; (2) the SMP is bent to a storage angle $\theta_0$ around a mandrel with a radius of $r$ in the soft rubbery state, and then the SMP is kept in cool water with the external constraint to “freeze” the elastic deformation energy (Storage); and (3) the SMP specimen fixed on the apparatus is immersed into another water bath at a elevated temperature, and then it recovers to an angle $\theta_N$ (Recovery). The method used to quantify the precision of deployment is illustrated in Fig. 10, where, $r$ denotes the radius of mandrel, $t$ represents the thickness of the SMP specimen, $\theta_0$ is the original storage angle of the specimen in storage state.

![Fig. 9. Stress–strain–temperature relationship showing the loading path in the thermomechanical test.](image-url)
during the first bending cycle, \( S(x_0, y_0) \) is a point selected to determine \( \theta_0 \). \( \theta_N \) is the residual angle in recovery state during the \( N \)th thermomechanical bending cycle \((N = 1, 2, 3 \ldots)\). \( R(x_N, y_N) \) is a testing point in order to calculate \( \theta_N \):

\[
\theta_N = \text{ArcCot} \left( \frac{x_N}{y_N} \right), \quad (N = 1, 2, 3 \ldots, 0 \leq \theta_N \leq 180^\circ),
\]

The value of the shape recovery ratio is calculated by:

\[
R_N = \frac{\theta_0 - \theta_N}{\theta_0} \times 100\% \quad (N = 1, 2, 3 \ldots),
\]

where \( R_N \) denotes the shape recovery ratio of the \( N \)th thermomechanical bending cycle. \( S(x_0, y_0) \) and \( R(x_N, y_N) \) can be measured by a vernier caliper. Finally, \( \theta_N \) and \( R_N \) are obtained through Eqs. (3) and (4). In the following tests, the radius \( r \) of mandrel and thickness \( t \) of the SMP specimen are 2 mm and 3 mm, respectively.

3.5. Constitutive models for shape-memory polymers

In many practical applications, SMPs often undergo large three-dimensional deformations [160,161,162]. To date, an understanding of the thermomechanical behavior of SMPs is still limited to the special cases of small one-dimensional deformation [51,52,163,164]. A constitutive model that describes three-dimensional finite deformation, is useful for the development of SMP components. The finite element method based on the three-dimensional constitutive model is also important for engineering analysis and design of SMP components. In our brief review, we introduce two thermomechanical constitutive models for SMPs based on viscoelasticity [32,33,165] and based on phase transition, respectively [35,166,167].

3.5.1. Models based on viscoelasticity

Models based on linear viscoelasticity are usually used to describe rate-dependent behavior of polymer on macroscopic level [51]. In these models, materials are assumed as the combinations of elements, including springs, dashpots or frictional elements. Some constitutive models of the SMPs can be viewed as an extension of viscoelastic models to describe the thermomechanical behaviors, such as Chen model [168,169], Li model [170], Tobushi model [32,33], Abrahamsen model [171] and Nguyen model [172].

As a typical constitutive model based on viscoelasticity, Tobushi et al. [32] established a linear one-dimensional constitutive equation for SMP on the basis of a standard linear viscoelastic model. In this equation the stress–strain–temperature relationship of an SMP is expressed as
\[
\begin{align*}
\dot{\varepsilon} &= \frac{\sigma}{E} + \frac{\varepsilon - \varepsilon_s}{\varepsilon} + xT \\
\dot{\varepsilon}_S &= C(\varepsilon_c - \varepsilon_f)
\end{align*}
\] (5)

where \(\sigma, \varepsilon\) and \(T\) denote stress, strain, and temperature, respectively. The dot denotes a time derivative. \(\varepsilon_s\) is irrecoverable strain. The temperature-related parameters \(E, \mu, \lambda\) represent elastic modulus, viscosity, and retardation time, respectively. The temperature-related \(C\) and \(\varepsilon_f\) are related to the process of shape fixity. They are expressed by the same function of temperature, expressed as

\[
x = x_g \exp \left[ a \frac{(T - T_g)}{T - T_l} \right] (T \leq T \leq T_h)
\] (6)

where \(x_g\) is the value of \(x\) at \(T = T_g\). \(T_l, T_h\) are the temperatures at the starting and finishing points of the glass transition from the glassy to rubbery state in SMP.

The shape-memory thermomechanical cycle of polyurethane-based SMP can be predicted by the constitutive equation, Eq. (5), coupled with the material parameter function, Eq. (6).

In 2001, Tobushi et al. [33] developed a nonlinear constitutive equation based on the linear constitutive equation mentioned above. In this equation the stress–strain–temperature relationship of an SMP is expressed as

\[
\begin{align*}
\dot{\varepsilon} &= \frac{\sigma}{E} + m(\frac{\sigma - \sigma_f}{\sigma})^{m-1} \frac{\sigma}{\mu} + \frac{1}{b}(\frac{\sigma}{\mu_f} - 1)^n - \frac{\varepsilon - \varepsilon_s}{\varepsilon} + xT \\
\dot{\varepsilon}_S &= S(\varepsilon_c - \varepsilon_f)
\end{align*}
\] (7)

where \(\sigma\) and \(\sigma_f\) denote the elastic and viscous proportional limits of SMP. The shape-memory thermomechanical cycle of an SMP was simulated by using the nonlinear constitutive equation, Eq. (3), and the material parameter function, Eq. (6).

### 3.5.2. Models based on phase transition

In 2006, Liu et al. [35,166] developed a constitutive model under uniaxial loading conditions of SMP. The model uses internal state variables based on experimental results and the molecular mechanism of the shape-memory effect of SMP. According to this model there are two kinds of extreme phases, frozen and active phases, in SMP at an arbitrary temperature. The fractions of frozen and active phases are defined as follows:

\[
\phi_f = \frac{V_{frz}}{V}, \quad \phi_a = \frac{V_{act}}{V}, \quad \phi_f + \phi_a = 1
\] (8)

where \(\phi_f\) and \(\phi_a\) denote the fractions of frozen and active phases in SMP, respectively. \(V, V_{frz}, V_{act}\) stand for the total volume, the volume of the frozen phase and active phase, respectively.

The strain of the SMP is composed of three parts: the stored strain, mechanical elastic strain, and thermal expansion strain, expressed as

\[
\varepsilon = \varepsilon_s + \varepsilon_m + \varepsilon_T
\] (9)

where \(\varepsilon\) denotes a second order total strain tensor. \(\varepsilon_s, \varepsilon_m, \varepsilon_T\) present second order stored strain, mechanical elastic strain, and thermal expansion strain, respectively. The stored strain of an SMP is expressed as

\[
\varepsilon_s = \int_0^1 \varepsilon_f(x) d\phi
\] (10)

where \(\varepsilon_f\) denotes the entropic frozen strain. The mechanical elastic strain of an SMP is expressed as

\[
\varepsilon_m = [\phi_f S_i + (1 - \phi_f) S_e] : \sigma
\] (11)

where \(\sigma\) denotes a second order stress tensor. \(S_i\) is the elastic compliance fourth order tensor corresponding to the internal energetic deformation, while \(S_e\) is the elastic compliance fourth order tensor corresponding to the entropic deformation. The thermal expansion strain is expressed as
\[
\varepsilon_T = \left\{ \int_{T_0}^{T} \left[ \phi_T \varepsilon_f(\theta) + (1 - \phi_T) \varepsilon_a(\theta) \right] d\theta \right\} I
\]  
(12)

where \( \varepsilon_f \) and \( \varepsilon_a \) are the thermal expansion coefficients of the frozen phase and the active phase, and \( I \) is the identity tensor.

In addition, Qi et al. [167] also conducted a comprehensive study of the thermomechanical behavior of the SMPs. In the 3D finite deformation constitutive model, it assumes that the glassy phase formed during cooling has a different stress free configuration compared to the initial glassy phase. In this sense, the deformation storage process can be captured. Therefore, the SMPs can be assumed to consist of three phases: rubbery phase, initial glassy phase and frozen glassy phase. Recently, Chen and Lagoudas [51,52] developed a nonlinear constitutive model for SMPs to describe the thermomechanical properties under large deformation. The model is based on the idea that developed in the work of Liu et al. [35] Due to the coexisting active and frozen phases of SMP and the transition between them, they provide the underlying mechanisms for strain storage and recovery during a shape-memory cycle. Their model presents excellent agreement with the experimental results of Liu et al. [35]. In addition, the similar models based on phase transition have been comprehensively developed by Barot and Rao [173–175].

4. Stimulus methods of multi-functional shape-memory polymer composites

The actuation of SMPs and their corresponding composites have been carried out controllably and with programmability. They exhibit the shape-memory effect and have various responses to stimuli. In addition to thermal actuation, SMP composites filled with functional fillers can also be triggered by other external stimuli, such as electrical resistive heating, light or magnetic field. Moreover, the traditional thermo-responsive SMPs can be driven by a solvent. SMP response to water or solution is due to the plasticizing effect of the solution molecule on polymer materials.

These novel actuation approaches play a critical role in the development of multi-functional materials that not only exhibit the shape-memory effect but also perform particular functions [78]. In this way, the triggering and subsequent actions of SMPs are sensitive to a particular stimulus and SMPs may be used as a particular sensor or actuator [176–179]. For instance, the electrically conductive SMP composites filled with carbon particles could be used as a strain sensor, which is based on the relation between electrical conductivity and strain. This SMP composites could monitor its own real-time deformation by testing the evolution of conductivity when it recovered to its original shape. In addition, if light-induced SMPs are exposed to light of a particular wavelength, an instant reaction, or deformation, could result that would enable their use as both sensors and actuators. The applications of these multi-functional SMPs and SMP composites may cover a broad range of fields from biomedicine to micro-sensors and actuators, to MEMS/NEMS. They are proposed to provide cheaper, accurate and faster alternatives to devices already on the market.

As discussed in Section 2.4, most of the stimulus forms for SMPs (e.g., electricity, light, magnetism and moisture) intrinsically belong to thermal response. Actually, except for the intrinsically light-induced SMPs, all of the other SMPs and SMP composites belong to directly or indirectly thermal-responsive polymers. Consequently, the thermal-responsive SMPs and their composites will not be discussed particularly in this section. The contents of this section discuss the stimulus methods, including electricity, light, solution and magnetism. The multi-function of SMPs or their composites will be introduced respectively in each part. When considering the composites, the mechanical properties of particle-filled or fiber-reinforced SMPs will be briefly introduced.

4.1. Shape-memory polymer composites

4.1.1. Particle-filled shape-memory polymers

The thermomechanical behavior of SMPs can be designed either through modification of the molecular structure of the polymer or through the addition of functional fillers into the polymer as a matrix for multi-phase composites. The SMP composites can be classified as particle- or fiber-reinforced depending on the type of filler they employ. SMP composites filled with particles (e.g., carbon black,
carbon nanotubes [180], carbon nanofibers, SiC, Ni, Fe$_3$O$_4$, clay [181,182], and short or continuous fibers may meet various requirements in practical applications [182,183]. In general, the SMP composites filled with particles or short fiber develop some particular function, such as high electrical conductivity, magnetic-responsive performance, or high stiffness on the micro scale. Hence, this type of SMP composites is studied as a multi-functional material.

Yang [151] investigated the thermomechanical properties of polyurethane SMP filled with carbon powders. Their results demonstrate that the incorporation of carbon powders is an efficient means of increasing the recovery stress. In addition, Gall et al. [184,185] comprehensively investigated the thermomechanics of SMPs and their composites, including a SiC reinforced epoxy SMP [155,158]. The SiC/SMP nanocomposites were found to have a higher elastic modulus and were capable of generating higher recovery forces in comparison with a pure SMP specimen.

Carbon nanofibers have the potential to be used in nano-electronic devices, such as artificial muscles, as well as in electrochemical energy storage matrices. Carbon nanofibers usually vary from 5 to 1000 μm in length and are between 50 and 300 nm in diameter. The Young’s modulus of these nanofibers can reach as high as 1.2 TPa and some samples have been reported to have tensile strengths up to 64 GPa, compared to conventional carbon-fibers that have strengths equal to about 4.0–5.0 GPa. Thus, it is expected that composites filled with carbon nanofibers may present better performances when compared to the conventional carbon-fiber-reinforced materials [186]. Consequently, carbon nanofibers with diameters of 24 nm and lengths 300 nm were used for reinforcement of SMPs by Manpreet [186]. They demonstrated that the presence of nanofibers in SMP leaded to significant reinforcement for SMPs.

Pure SMPs or particle-reinforced SMPs are not suitable for use as structural materials; however, they are generally used as functional materials through the addition of some particular particle fillers. For instance, electrically conductive carbon black, carbon nanotubes, nickel powders and chopped carbon-fibers are incorporated into SMPs to develop electro-active SMPs. Ferromagnetic Fe$_3$O$_4$-filled SMPs can lead to magnetism induced SMPs. Moreover, infrared optical fiber could be embedded into SMPs to develop light-induced SMPs by transmitting the infrared light through the fiber to heat the SMP.

4.1.2. Fiber-reinforced shape-memory polymers

In general, since the improvement in their mechanical properties is quite limited and their strength and stiffness remain low, SMP composite’s reinforced with particles or short fibers cannot be used as structural materials [38]. In contrast, continuous fiber-reinforced SMPs offer a significant improved in strength, stiffness and resistance against relaxation and creep, thereby providing better mechanical properties. As both a functional and structural material, these SMPs show good potential for many advanced applications. When used as actuator materials, they require no moving parts. Substantial interest has therefore been generated for the use of fiber-reinforced SMPs in deployable structures including antennas, trusses and solar arrays.

In addition, most studies regarding SMP composites are focused on thermoplastic SMP resins such as polyurethane SMP. However, the relatively poor thermal and mechanical properties (e.g., temperature, moisture and chemical resistance) of thermoplastic SMPs cannot fully meet practical requirements. Thermosetting SMPs, however, show an improvement in the aforementioned properties and can be widely used as functional or structural materials.

A carbon-fiber fabric reinforced polyurethane SMP was developed for industrial applications [152,187]. The bending recovery ratio of this SMP based laminates was larger than that of pure SMP sheet for any given recovery time. Epoxy SMP composites (Elastic Memory Composite, EMC) show great potential for light weight deployable spacecraft structures applications. Composite Technology Development (CTD), Inc. firstly started to comprehensively researched the EMC and the relevant applications in deployable structures since the 1990s [188–191]. A study of the micro-mechanisms of deformation in EMC materials has been conducted by CTD and Gall et al. [192]. Their studies have investigated several interaction phenomena between the reinforcement fibers and the SMP resin in an epoxy EMC laminate. Due to the effects of microbuckling and the shift in the neutral-strain surface, the fiber-reinforced SMP composites laminate can achieve much larger compressive strains than traditional hard-resin composite. In addition, Leng et al. [36,171] developed a
fiber-reinforced thermosetting styrene-based SMP composite. Based on the high-strain capability and relatively good mechanical properties, the fiber-reinforced SMP composites show potential for deployable structures applications [36,171,192,193].

The aforementioned carbon-fiber-reinforced SMP composites exhibit better mechanical and thermomechanical properties than pure SMPs, and they can also be activated by loading a voltage on the carbon-fibers embedded in the SMP matrix [36,171]. Hence, they could be somewhat described as a multi-functional materials. In addition to carbon-fiber-reinforced SMPS, glass-fiber or Kevlar-fiber-reinforced SMPs are also an important type of shape-memory composite. Liang et al. [38] previously investigated glass and Kevlar-fiber-reinforced thermoplastic SMP composites. They found an improvement in stiffness but a decrease in recoverable strain as a result of the incorporation of the reinforcement. Ohki et al. [194] investigated the mechanical and shape recovery properties of thermoplastic SMP composites reinforced by chopped strand glass-fiber, especially for the relationship between fiber weight fraction and recoverability. With the incorporation of 50 wt.% of glass-fiber, they found that the failure stress increased by 140% while the recovery rate decreased by 62%.

4.2. Electro-activated shape-memory polymer composites

In the past decade, much research has explored on the mechanism, shape recovery and electrical properties of SMPs filled with conductive filler and their corresponding applications [195,196]. This review discusses the most recent developments in undergoing electro-induced shape recovery and summarizes the growth of electro-activate shape-memory polymer. Electricity as a stimulus enables resistive actuation of SMPs filled with conductive fillers. In this way, external heating, which is unfavorable for many applications and is used to stimulate conventional shape-memory polymers, can be avoided. The electric triggering of SMP composites enlarges their technological potential [197,198,199].

4.2.1. Shape-memory polymer filled with carbon nanotubes

SMPs are characterized by their remarkable recoverability and shape-memory effect; however their mechanical properties such as strength and elastic modulus are low. Carbon nanotubes (CNT) based composites (e.g., CNT/PP [200,201], CNT/PVDF [202], CNT/nylon [203], CNT/polystyrene [204,205], CNT/epoxy [206,207], and CNT/PVA [208]) on the other hand, have remarkable mechanical properties with very high elastic modulus and electrical conductivity [209,210,155]. Based on the above consideration, Goo et al. [18] reinforced shape-memory polyurethane (PU) with multi-walled carbon nanotubes (MWNTs) of 10–20 nm diameter and 20 mm length. Surface-modification of the MWNTs in mixed solvents of nitric acid and sulfuric acid was found to further improve the mechanical properties of the composites. The mechanical properties of shape-memory composites were improved by using acid treatment and sonication of the nanotubes at optimum conditions. In addition, the surface modified MWNT content increased the conductivity increased. Electro-active shape recovery was observed for the surface-modified MWNT composites with an energy conversion efficiency of 10.4% (Fig. 11). Hence, PU-MWNT composites may prove promising candidates for use as smart actuators [18].

4.2.2. Shape-memory polymer filled with carbon particles

Leng et al. [211,212] demonstrated that the thermosetting styrene-based SMP exhibited better mechanical properties and moisture resistance than the thermoplastic polyurethane SMP. A new

![Fig. 11.](image_url)

Fig. 11. Electro-active shape recovery behavior of PU-MWNT composites. The pictured transition occurs within 10 s when a constant voltage of 40 V is applied [18].
A thermosetting styrene-based shape-memory polymer (SMP) filled with nanocarbon powders has been presented [46, 213]. Thermosetting polystyrene was reinforced with electrically conductive carbon black particles (30 nm). It was found that thermal conductivity and storage modulus were significantly improved, while the glass transition temperature is slightly decreased. This SMP composite has good electrical conductivity with a percolation threshold from approximately 3.0–5.0% in volume fraction (see Fig. 12), which is associated with the high-structure of carbon black and its agglomerations at nanoscale. The electrical resistivity was reduced slightly during resistive heating, and then increased after the applied voltage was removed. This is opposite to the conventional PTC effect. The room temperature resistivity increases slightly after repeated heating.

Yang [151] investigated the effect of tensile strain on electrical resistivity. In practical applications, the conductive SMPs may be used as strain sensors based on the relation between electrical conductivity and strain. As shown in Fig. 13, the electrical resistivity increases with an increase in strain. The increase of electrical resistivity is remarkable at the lower strain range below 10%. Based on the effect of strain on conductivity, the SMP can be used as a multi-functional material to fabricate strain sensors.
4.2.3. Shape-memory polymer filled with electromagnetic fillers

(1) Electro-active thermoplastic SMP composites filled with Ni powder chains

Electrically conductive powders, fibers and even nanowires/tubes have been utilized as fillers to improve the electrical conductivity of polymers [214]. Although conductive fiber and nanowires/tubes can significantly enhance the stiffness and strength of polymers, their deformable strain is limited to within a few percent. Since the recoverable strain in SMPs is normally on an order of one hundred percent, there is a potential problem of deformation compatibility [215,183]. As such, electrically conductive powders, such as Ni powder, would be a better choice.

The electrical resistivity of a thermo-responsive polyurethane shape-memory polymer (SMP) filled with micron-sized Ni powders is investigated [214]. By forming conductive Ni chains under a weak static magnetic field (0.03 T), the electrical conductivity of the SMP composite in the chain direction can be significantly improved, which makes it more suitable for Joule heat induced shape recovery. In addition, Ni chains reinforce the SMP significantly but their influence on the glass transition temperature is about the same as that of the randomly distributed Ni powders. SEM images reveal that single chains start to form at 1% volume fraction of Ni. With an increase in Ni content, multi-chains (bundles) result, and eventually no clear Ni chain can be recognized (Fig. 14, left column). In addition, after five stretching-shape recovery cycles, the Ni chains still exist (Fig. 14, right column), which indicates the possibility of using chained SMPs for cyclic actuation.

The results show that the electrical resistivity \( \rho \) of the chained samples in the chain direction is always the lowest. For example, at 10% volume fraction of Ni powder, \( \rho \) of the random sample is

Fig. 14. Typical SEM images before (left column) and after (right column) five stretching (at 50% strain)-shape recovery cycles [214].
2.36 × 10^4 Ω cm while that of the chained sample is 2.93 × 10^6 Ω cm in the transverse direction and only 12.18 Ω cm in the chain direction. However, at a high Ni content, ρ of all of the samples is close. This is due to the fact that the Ni chains become unrecognizable at a high Ni content, as revealed in Fig. 14. At 10% volume fraction of Ni, the chained sample (with dimensions of 16 × 0.6 × 5mm^3) can be heated from room temperature (20 °C) to 55 °C by applying a voltage of 6 V (refer to infrared image in Fig. 15, bottom-left insert), which is enough to trigger shape recovery.

(2) Electro-active thermoplastic SMP/CB composite filled with Ni powder chains

An approach to significantly reduce the electrical resistivity in a polyurethane SMP filled with randomly distributed carbon black (CB) is presented [184]. With an additional small amount of randomly distributed Ni micro particles (0.5 vol.%) in the SMP/CB composite, its electrical resistivity is reduced only slightly. However, if these Ni particles are aligned into chains (by applying a low magnetic field on the SMP/CB/Ni solution before curing), the drop in electrical resistivity becomes significant. Three types of thin films were fabricated using the same method as for the SMP/Ni composite, namely, SMP/CB/Ni (chained) (Fig. 16), SMP/CB/Ni (random), and SMP/CB (i.e., without Ni).

In order to demonstrate the shape recovery by Joule heating, three samples [SMP/CB/Ni (chained), SMP/CB/Ni (random) and SMP/CB], were bent by about 150°. A 30 V of power was applied.
right) presents four snapshots of each sample. It is clearly revealed that Sample (c) [SMP/CB/Ni (chained)] reaches the highest temperature, while the temperature of Sample (a) [SMP/CB] is the lowest. Hence, the shape recovery is small. Sample (b) [SMP/CB/Ni (random)] reaches around 65 °C, and the shape recovery is not completed after 120 s.

4.2.4. Shape-memory polymer filled with hybrid fibers
The electrical and thermomechanical properties of styrene-based SMP composites containing CB nanoparticle and short carbon-fiber (SCF) of 0.5–3 mm length and 7 μm diameter were investigated. Fig. 18 shows the typical relation between the resistivity of composites versus filler content. The data obtained for the SMP filled with micro carbon powder and the SMP filled with micro carbon powder and SCF were compared to the results found in [216,217]. Through comparison, the composites containing nanoparticles have a higher conductivity than those blended with micro-dimension conductive filler.

As shown in Fig. 19, the short fibers disperse randomly. There are many interconnections between the fibers, which form the conductive networks that explain the excellent electrical conductivity of the composites filled with SCF. The two microstructural images in Fig. 19 show the formation of co-supporting conductive networks. Such conductive networks could improve the electrical properties of SMP composites. It demonstrates that a distinct difference in the influence on conductivity of the composites results from the use of fibrous and particulate fillers.

4.3. Light-induced shape-memory polymers and their composites

4.3.1. Intrinsically light-induced shape-memory polymers
Intrinsically light-induced SMPs have been produced by incorporating reversible photoreactive molecular switches when light of a special wavenumber light is applied [20,177,179,218]. The stimulation is considered to have no relation with any temperature effects [127,219]. Therefore, it should be differentiated from the indirect actuation of the thermal-responsive shape-memory effect. As shown
in Fig. 20, Lendlein and Langer et al. [1,20] reported a light-induced SMP. In the programming cycle, the polymer is firstly stretched, resulting in strained, coiled polymer segments. Subsequently, the network is irradiated with ultraviolet light with a wavelength $>260$ nm and new covalent netpoints are created to fix the strains, leading to the temporary shape. The permanent shape can be recovered upon irradiation with UV light of $\lambda < 260$ nm through cleavage of the cross-links.

4.3.2. Shape-memory polymers induced by radiant thermal energy of light

Indirect actuation of the shape-memory effect has been realized by two typical strategies. One method involves indirect heating, that is, magnetically induced SMPs filled with magnetic particles with the inductive Joule heating achieved through an alternating magnetic field [17,220]. The other possibility is irradiation, that is, the thermally induced SMPs can be heated by illumination with radiant thermal energy of infrared light. As shown in Fig. 21, the laser-induced SMP has been demonstrated and subsequently considered for use as a medical device [221,222]. In such devices, heat transfer can be enhanced by incorporation of conductive fillers (e.g., carbon black and carbon nanotubes) [223]. The irradiation by infrared light possesses a wide emission spectra and a unique heating effect, and the infrared light actuation method can be non-contact and non-medium and may, therefore, dramatically expand the applications in smart structures [1,164].

Leng et al. [224] systematically investigated the relative performance of infrared light-induced SMPs filled with carbon black. For the capability of absorbing infrared light, it is apparent that the absorption spectrum of the SMP/CB composite not only covers a wider range but also exhibits higher
The presence of CB particles remarkably increases the capability to absorb infrared light. When a SMP and SMP/CB nanocomposite are exposed to infrared light, most of the emitted energy is transmitted by the SMP, which is semitransparent, while most of the emitted infrared light is absorbed by the nanocomposite since it is black and opaque. In addition, the SMP and the nanocomposite have approximately equal reflection since their surfaces are of similar smoothness. Therefore, the black CB absorbs infrared radiation much more notably than the pure SMP. Infrared light is unique in that it exhibits a notable heating effect. It demonstrated that CB can absorb infrared radiation remarkably and produce a notable heating effect for wavenumbers between 500 and 3000 cm\(^{-1}\). In addition, the high capability to absorb infrared light in the nanocomposite will result in more generated heat. In addition, Fig. 22 shows the curves of the shape recovery angle as a function of time for the SMP and SMP/CB composite at 90 °C. Results show that the CB additive not only increased the recovery force but also enhanced the capability to absorb infrared light for
the SMP/CB composite; as a result, the shape recovery ability and shape recovery speed for the composite are much quicker than for the SMP.

4.3.3. Light-induced shape-memory polymer embedded with an optical fiber

Thermally activated SMPs make it possible to initiate an original shape using a non-contact and highly selective infrared laser stimulus. For light-induced SMPs, the infrared laser stimulation of the SMP is interesting for sensor and actuator systems as well as for medical applications. An infrared light-induced SMP embedded with an optical fiber was proposed by Leng et al. [225,226]. Fig. 23 is the schematic illustration, which shows the treated optical fiber that embedded into the SMP. The optical fiber was treated by an aqueous solution of sodium-hydroxide and the cladding was removed. In this way, the light may transmit from the side of the fiber, which provides a better method of heating a large region. Furthermore, an optical fiber network may be embedded into the SMP for actuation as a fast response.

The results of IR spectra reveal a strong absorption peak about the value of 3000 cm\(^{-1}\), characteristic of the C–H bond of the benzene ring. Hence, the working length of the infrared laser is chosen at 3–4 µm. Therefore, an optical fiber was embedded into the SMP for delivery of the laser light at a wavelength of 3–4 µm for actuation. The free strain recovery investigation of a SMP thread embedded with an optical fiber was performed and the results are shown in Fig. 24.
4.4. Solution-responsive shape-memory polymers

4.4.1. Water-driven shape-memory effect

The shape-memory effect for shape-memory polyurethanes and their composites with carbon nanotubes reinforcement has been triggered by inductively lowering $T_{\text{trans}}$ [227,21,228]. When immersed in water, solvent molecules diffuse into the polymer sample and act as plasticizers, leading to a reduction in the transition temperature and resulting in shape recovery (Fig. 25). In the polyurethane polymers and their composites, $T_g$ is lowered from the transition temperature to ambient

Fig. 24. Shape recovery process of SMP [226].

Fig. 25. Water-driven actuation of a shape-memory effect. A shape-memory polyurethane with a circular temporary shape is immersed into water. After 30 min, the recovery of the linear permanent shape begins [22].
temperatures or below. The experimental results reveal that the lowering of $T_g$ depends on the moisture uptake, namely it indirectly depends on the immersion time. In time-dependent immersion tests, the water uptake can be adjusted between 0 and 4.5 wt.%, which coincides with a decrease in the $T_g$ of between 0 and 35 K. As the maximum moisture uptake is around 4.5 wt.% after 240 h, this SMP is still considered to be a polymer and not a hydrogel. Another strategy for water-actuated SMPs has been carried out in polyetherurethane polysilesquisiloxane block copolymers [22,229]. Here low molecular weight poly(ethylene glycol), or PEG, has been used as the polyether segment. Upon immersion in water, the PEG segment is dissolved, leading to the disappearance of $T_m$, resulting in recovery of the permanent shape.

4.4.2. Solution driven shape-memory effect

The mechanism behind the response of SMPs to solution (namely solvent or mixture) is that the solution molecule has a plasticizing effect on polymeric materials and thus increases the flexibility of the macromolecular chains. These two effects reduce the transition temperature of materials until shape recovery occurs. This study of Leng et al. [230–233] is made in the context of and in reference to the many reported theories explaining the mechanism of water-driven polyurethane SMP and aims to enlarge its extension.

(1) Solution driven shape-memory effect by chemical interaction

It is well known that phase transition often accompanies great changes in physical properties of polymeric materials, such as a large decrease in modulus on which the solution-responsive SMP is based. The mechanism involves the interaction between polymeric macromolecules and micro-molecules of the absorbed solution [230,231]. There are three major explanations. First, the hydrogen bonding enlarges the flexibility of the polymeric chains. Secondly, the interaction resulting in a volume change of the polymer destroys the modulus of the polymer as explained by continuum theories of rubber elasticity, the Mooney–Rivlin equation and volume change refinement theory [232,233]. And, finally, when the temperature of the solution (or the ambient temperature) is lower than the glass transition temperature ($T_g$) of the polymer, the solution first intenates the polymer until the $T_g$ is lowered to the temperature of the solution and following this, the solution has other effects on the polymer. Thus, the actuation of SMPs can be triggered by their solutions. The styrene-based thermosetting SMP can recover from the pre-deformed ‘n’ shape sequentially after being immersed in N, N-Dimethyl formamide (DMF) by forming the hydrogen bonding shown in Fig. 26.

Solution-driven SMPs provide an alternative approach, making stimulation by heating unnecessary. The actuation can be triggered upon immersion of the material into solution. Instead of heating the material to above its $T_g$, shape recovery can be achieved by means of reducing the $T_g$ of the material itself upon immersion of the SMP into a solution that is, in principle, similar to the process used for water-driven PU SMPs.

(2) Solution driven shape-memory effect by physical swelling effect

Work has been carried out by Leng et al. [232,233] to activate SMPs through the physical swelling effect. Based on the free-volume theory, rubber elasticity theory and Mooney–Rivlin equation, the feasibility of SMP activated through physical swelling is theoretically predicted. The swelling effect

![Fig. 26. Shape recovery of a 2.88 mm diameter SMP wire in DMF. The wire was bent into an “n” like shape [230].](image-url)
occurs due to the interaction between macromolecules and solvent molecules, leading to an increase in the free-volume of polymeric chains (namely, the flexibility of the polymer chains is increasing) and resulting a decrease in $T_g$. Toluene solvent was selected for a styrene-based SMP driven by the physical swelling effect. It is found that this solvent had an intensive swelling effect on the polymer. The flexibility of the macromolecular chains increased after being swollen. The increase in flexibility subsequently led to a decrease in the transition temperature and resulted in the shape recovery occurring at a lower temperature. These phenomena all obey continuum theories of rubber elasticity, the Mooney–Rivlin equation and volume change refinement theory [234,235].

In summary, the response of polyurethane SMP to water or to solution (namely, a solvent or mixture) is due to the plasticizing effect of the solution molecule on the polymeric materials, which then increases the flexibility of the macromolecular chains. These two effects reduce the transition temperature of the materials until shape recovery occurs. This approach makes tremendous progress in the actuation of SMPs, and many results and achievements are based on it.

4.5. Magnetic-responsive shape-memory polymer composites

The magnetically induced shape recovery of SMP composites could be realized by incorporating magnetic nanoparticles (e.g., Fe$_2$O$_3$ and Fe$_3$O$_4$) in SMPs [16,17,236–240]. The shape-memory effect of the composites can be triggered by inductive Joule heating in an alternating magnetic field, i.e., transforming electromagnetic energy from an external high frequency field to heat [241]. The magnetically induced SMPs can be remotely controlled to induce heating energy locally and selectively. They show potential to be used in biomaterials, such as in tumor therapy (magnetic fluid hyperthermia) and as contactless magnetically actuated SMP microactuators for the removal of a clot in a blood vessel.
Mohr et al. [16] investigated magnetically induced thermoplastic SMP composites filled with Fe$_2$O$_3$ nanoparticles. Iron oxide particles with average diameters at the nanoscale (20–30 nm) support a preferably homogeneous distribution within the SMP matrix. The shape recovery of SMP composites could be induced by inductive heating in an alternating magnetic field ($f = 258$ kHz; $H = 3.0$ kA m$^{-1}$). The maximum temperatures achieved by inductive heating in a specific magnetic field depend on sample geometry and nanoparticle content. As shown in Fig. 27, the magnetically induced shape-memory effect is exemplarily demonstrated.

In addition, Schmidt [17] incorporated surface-modified super-paramagnetic nanoparticles (Fe$_3$O$_4$, diameter: 11 nm) into a SMP matrix. The thermosetting SMP composite of oligo(e-caprolactone)dimethacrylate/butyl acrylate contains between 2 and 12 wt.% magnetite nanoparticles serving as nano-antennas for magnetic heating. The specific power loss of the particles is determined to be $30 \text{ W g}^{-1}$ at 300 kHz and 5.0 W. As shown in Fig. 28, a photo series presents the electromagnetically induced shape-memory effect of the sample. The rectangular strip (about 15 mm $\times$ 2 mm $\times$ 0.5 mm) was deformed to a helix temporary shape at 70 °C. It recovers to the original straight shape in about 20 s with the application of an AC field of 300 kHz.

5. Applications of shape-memory polymers and their composites

As a novel kind of smart materials, SMPs currently cover a broad range of application areas ranging from outer space to automobiles. Recently, they are being developed and qualified especially for deployable components and structures in aerospace [242]. The applications include hinges, trusses, booms, antennas, optical reflectors and morphing skins [24,243,244]. In addition, SMPs also present additional potential in the areas of biomedicine, smart textiles, self-healing composite systems and automobile actuators. Additionally, there are many patents in relation to SMPs applications, such as gripper [245], intravascular delivery system [246], hood/seat assembly and tunable automotive brackets in vehicles [247–249].

5.1. Deployable structures

For the traditional aerospace deployable devices, the change of structural configuration in-orbit is accomplished through the use of a mechanical hinge, stored energy devices or motor driven tools. There are some intrinsic drawbacks for the traditional deployment devices, such as complex assembling process, massive mechanisms, large volumes and undesired effects during deployment. In contrast, the deployment devices fabricated using SMPs and their composites may overcome certain inherent disadvantages [250].

5.1.1. Hinge

Leng et al. [36] investigated a carbon-fiber-reinforced SMP composite that can be used in actively deformable structures. In these structures [251], the flexural deformation is the main mode of the

![Fig. 29. Shape-memory polymer composite hinge: (a) Illustration of the hinge (1: curved SMP-composite shell; 2, 3: fixture of the hinge) and (b) real scale hinge.](image-url)
deformation in the structures with thin shells where the bending angle is almost larger than $90^\circ$ but the strain is often smaller than 10%. In this way, the shape recovery process of the structure concerns structural deployment dynamics.

As shown in Fig. 29, an SMP-composite hinge was designed, which consists of two curved circular SMP-composite shells in the opposite directions. Fig. 30 shows the deployment process for the SMP-composite hinge. A voltage of 20 V is applied on the resistor heater embedded in each circular laminate. The temperature of the hinge remains at about 80°C after heating for 30 s. The whole deployment process takes about 100 s. In addition, a deployment of a solar array prototype which is actuated by a SMP-composite hinge is demonstrated (see Fig. 31).

During the launching of a spacecraft, the room inside the spacecraft is quite limited. Hence, the spacecraft needs lightweight, reliable and cost effective mechanisms for the deployment of radiators, solar arrays or other devices. Composite Technology Development (CTD), Inc. has developed epoxy SMP composites reinforced by carbon-fiber (Elastic Memory Composite, EMC) material. The EMC materials show very high recoverable strains and high deployed stiffness- and strength-to-weight ratios. CTD has developed a deployable hinge fabricated with EMC materials (see Fig. 32). Recently, CTD performed an extensive ground testing on an EMC deployable hinge that may be used for deployable spacecraft components [252].

5.1.2. Truss and boom

An EMC boom has also been designed by CTD used on a micro-satellite. This extendable boom is lightweight and can support a variety of tip payloads (see Fig. 33). It has been identified to support
a micro-propulsion attitude control system. The EMC is the central element of the boom. To stow the boom, the longerons are in a z shape and, thus, the EMC are flattened and bent in both the equal- and opposite-sense in a pre-deformed shape [253].

A new generation of deployable structures experiment was proposed to deploy large and lightweight solar arrays. This type of structure has very little deployed structural depth over a very large...
deployed area. To minimize the impacts to the spacecraft system, the structural mass and complexity should be minimized. Based on the above considerations, the structure fabricated by EMC is proposed for the deployed solar array and the actuation to deploy the solar array from its packaged configuration. As shown in Fig. 34, the longeron booms fabricated by the thin film foldable EMC tubular are currently being fabricated by CTD to meet the needs for the deployable structure [253,254]. Based on the experimental demonstration, a detailed theoretical study is being put forward. Geometric nonlinearity should be considered because of the large deformation of the longeron. In addition, the presence of microbuckling of the composite leading to material nonlinearity should also be considered.

5.1.3. Ground-based deployable mirror

With their unique properties, SMPs are suitable for the fabrication of thin, lightweight deployable ground-based mirrors [255]. The mirror consists of a SMP composite substrate and the coated reflective side of the composite-reflector (see Fig. 35). The reflective surfaces are mainly composed of electroplated nickel to provide high quality reflectance. The electroplated nickel metal surface, which is less than 30 μm thick, is adhered on the surface of the SMP-composite mirror. The substrate has the ability to be deformed for packaging and then achieve shape recovery upon Joule heating from an external power supply. Similarly, Cornerstone Research Group (CRG), Inc. has proposed a deployable mirror fabricated by SMP composites, as shown in Fig. 36. The support structure of the mirror consists of a honeycomb support structure fabricated by SMPs and a mirror surface, including carbon nanofibers, a reflective coating, fabrics, and microspheres.

5.1.4. Reflector

(1) Stiffeners for a flexible reflector

A new kind of solid surface deployable reflector was developed by Harris Corporation, which is similar to a springback reflector. By enabling large-aperture antennas to be stowed within an existing launch vehicle, the reflector is envisioned to significantly promote the ability of satellite
communication systems. In addition, Harris Corporation is now considering the use of EMC materials for the system (see Fig. 37) to realize the full potential of the FPR design [256]. The stiffener around the edge of the antenna can be made by EMC materials. The antenna can be stowed in the spacecraft and then its deployment can be triggered by the shape-memory effect to finally hold the surface of the antenna in a precision micro-system.

(2) Parabolic dish antenna reflector

The large-aperture inflatable antenna is one important kind of deployment reflector. However, the deformation of the central part of inflatable antenna is mostly very large, which often makes it very difficult to realize inflatable deployment. Recently, SMP composite materials have been envisioned for the fabrication of the central part of the antenna to enable a large deformation (see Fig. 38 and Fig. 39) [257]. In the design, both the dish and the supporting structure are made of the SMP composite. Further research and development work are on-going to improve the properties of the SMP composite for this application.

5.2. Morphing structures

Flight vehicles are envisioned to be multi-functional so that they can perform more missions during a single flight, such as an efficient cruising and a high maneuverability mode [258,259]. When the airplane moves towards other portions of the flight envelope, its performance and efficiency may deteriorate rapidly. To solve this problem, researchers have proposed to radically change the shape of the aircraft during flight [260]. By applying this kind of technology, both the efficiency and flight envelope can be improved. This is because different shapes correspond to different trade-offs between
beneficial characteristics, such as speed, low energy consumption and maneuverability. For instance, the Defense Advanced Research Projects Agency (DARPA) is also developing morphing technology to demonstrate such radical shape changes. As illustrated in Fig. 40, Lockheed Martin is addressing technologies to achieve a z-shaped morphing change under the DARPA’s program fund [261].

During the development of morphing aircraft, finding a proper skin under certain criteria is crucial. Generally, a wing skin is necessary, especially for the wing of a morphing aircraft. Researchers focus their works on investigating proper types of materials that are currently available to be used as a skin material for a morphing wing. In this case, the SMPs show more advantages for this application. It becomes flexible when heated to a certain degree, and then returns to a solid state when the stimulus is terminated. Since SMPs holds the ability to change its elastic modulus, they could potentially be used in the mentioned concept designs.

5.2.1. Folding wing

Cornerstone Research Group (CRG) developed an improved SMP, which appears to be a prime candidate for seamless skin at the wing fold (see Fig. 41) [262]. As shown in Fig. 42, the feasibility of morphing SMP skin concepts in a 2-dimensional test jig has been demonstrated.

5.2.2. Variable camber wing

A morphing concept of a variable camber wing was developed by Leng et al. [263,264], as shown in Fig. 43. It comprises a flexible SMP skin, a metal sheet and a honeycomb structure. Metal sheet is used to replace the traditional hinges to keep the surface smooth during the camber changing. Honeycomb, which is high-strain capable in one direction without dimensional change in the perpendicular

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Fig. 39. SMP reflector (0.5-m diameter) in both deployed and packed configurations [257].

Fig. 40. z-shaped morphing wing produced by Lockheed Martin [261].
in-plane axis, provides distributed support to the flexible skin. The flexible SMP skin is covered to create the smooth aerodynamic surface. The baseline airfoil is assumed to have an NACA 0020 profile and a chord of 150 mm.

5.3. Biomedicine and bioinspiration

SMPs show extensive interest in used for biomaterials and bioinspiration [265,266,243]. For instance, polyurethane SMP performs excellent biocompatibility, and it can be used for the deployment of different clinical devices when contacted or implanted in the human body [267,268]. Recently,
Fig. 44. Schematic of the shape-memory effect prior to application (left) and right after reset (right) [269].

Fig. 45. Through increasing the temperature from 20 °C (A) to 40 °C (B) an initial shape change was induced followed by a second shape change through increasing the temperature to 60 °C (C) [143].
Wache et al. [269] have conducted a feasibility study and preliminary development on a polymer vascular stent with an SMP as the drug delivery system (see Fig. 44). The field of applications of this polymer stent was demonstrated in pre-trials. The use of the SMP stent as a drug delivery system leads to significant reduction of restenosis and thrombosis. An improved biological tolerance in general is expected when using biocompatible SMP materials.

The exciting SMPs can move from one shape to another in response to a stimulus. Thus, SMPs are dual-shape materials. A triple-shape polymer was recently reported in [141,143,144]. As shown in Fig. 45, the SMP is able to change from an initial shape (A) to a second shape (B) and finally deform to a third shape (C). It may be inserted into the body, expanded at a target site, and be removed at a later point in time which may be necessary even with degradable materials.

The thermo/moisture-responsive polyurethane SMP sheds light for the possibility to fabricate micro/nano devices for surgery/operation at the cellular level. Ikuta and Hayato [270,271] have developed many polymer micro-machines, which are similar to the size of cells or even smaller and can be triggered for operation by a laser beam outside the cell. However, there are tremendous difficulties to deliver such machines into cells. The thermo/moisture-responsive polyurethane SMP offers a possible solution. As illustrated in Fig. 46, a piece of original curved SMP is straightened and then inserted into a living cell. Upon absorbing moisture inside the cell, the SMP recovers its original shape. As the recovery strain in solid or porous SMPs is on an order of hundred percent, it becomes possible to make cell or sub-cell sized machines using the thermo/moisture-responsive SMP and then deliver the machines into living cells for operation controlled by an outside laser beam.

Biodegradable SMPs may be used in medical devices. The usefulness of SMPs in wound closure has been recently investigated and a design of smart surgical sutures has been examined, where a temporary shape is obtained by elongating the fiber under controlled stress (see Figs. 47 and 48). This suture can be applied loosely in its temporary shape under elongated stress. When the temperature is raised above $T_g$, the suture will shrink and then tighten the knot, in which case it will apply an optimal force [13,29]. The biocompatibility and degradation products should be considered.

These sutures should be degradable and show gradual mass loss during degradation. The hydrolyzable ester bonds are introduced into the polymers so that they would cleave under physiological conditions. In this way, the degradation kinetics could be controlled through the composition and relative mass content of the precursor macrodiols. The multi-block copolymers show linear mass loss in vitro (Fig. 49), resulting in a continuous release of degradation products [272].

A blood clot may cause an ischemic stroke, depriving the brain of oxygen and often resulting in permanent disability. As an alternative to conventional clot-dissolving drug treatment, a laser-activated device for the mechanical removal of blood clots is also proposed (Fig. 50) [1,272]. The
SMP microactuator, in its secondary straight rod form, could be inserted minimally by invasive surgery into the vascular occlusion. The microactuator, which is mounted on the end of an optical fiber, is then transformed into its pre-deformed straight shape by laser heating. Once deployed into the corkscrew

![Fig. 47. A fiber of a thermoplastic SMP is programmed by stretching about 200%. The knot tightened in 20 s when heated to 40 °C [13].](image)

![Fig. 48. Degradable shape-memory suture for wound closure [13].](image)

![Fig. 49. Hydrolytic degradation of thermoplastic shape-memory elastomers in aqueous buffer solution (pH = 7) at 37 °C [272].](image)

SMP microactuator, in its secondary straight rod form, could be inserted minimally by invasive surgery into the vascular occlusion. The microactuator, which is mounted on the end of an optical fiber, is then transformed into its pre-deformed straight shape by laser heating. Once deployed into the corkscrew
shape, the microactuator is retracted and captures the thrombus, enabling the mechanical removal of the thrombus.

Leng et al. [225, 226] have also investigated the infrared light-induced SMP actuator. An infrared light with a working wave band of 2–4 \( \mu \text{m} \) is coupled to the fiber in an SMP to study the realistic actuating effect of infrared laser (see Fig. 51). In Fig. 110a \((t = 2\text{s})\), the bright position is located at the end of the fiber, which indicates that the infrared laser is mainly refracted at that position. In the subsequent snapshots, the actuator gets brighter globally. The temperature of the SMP around the treated optical fiber rises to 21.4 °C, with an increase in temperature of 2.4 °C compared to the ambient temperature. In contrast, the temperature of the SMP at the end of the optical fiber increases to 48 °C, with an increase in temperature of 29 °C. It indicates that more light is refracted from the end of the optical fiber than from the side of the optical fiber. This experimental phenomenon can be explained by the fact that the optical fiber is treated by chemical corrosion. Therefore, after removing the cladding, the surface of the core is uneven. Laser energy absorbed at the treated position of the optical fiber is in a relatively small amount so the increase of temperature is slow. However, no laser is refracted back at the end of the fiber and a high temperature is engendered for more laser-energy absorption. The temperature at the treated position of the fiber is shown in Fig. 51. It exhibits that the SMP actuator deploys promptly in about 12 s.
5.4. MEMS and NEMS applications

In recent years, it has been reported that the shape-memory effect in SMPs is not only a macroscopic phenomenon, but also occurs even on the 10s of nm scale in bulk SMPs [273]. As such, SMPs have great potential for micron and even submicron scale actuation for MEMS and NEMS applications, micro/nano patterning [274,275], biomedical device [276,277], etc.

Micron-sized thermo/moisture-responsive PU SMP/Ni powder chains were fabricated and their shape recovery was investigated as an indirect way to demonstrate the SME in micron/submicron-sized SMPs. Vertical protrusive SMP/Ni chains were fabricated by applying a vertical magnetic field during curing of SMP/Ni mixture. Fig. 52 presents the morphology of the array of flattened chains atop the 2 vol.% Ni sample and the morphology after subsequent heating for shape recovery. The zoomed-in view of a small chain reveals that in the flattened shape, the initially vertical chain was bent around 90°. However, after heating, the bending angle was largely recovered, which reveals the shape recovery phenomenon in the chain and indirectly demonstrates the SME in micron/submicron-sized SMP. The shape-memory effect in an array of such chains (like a micro brush) may provide a simple mechanism and convenient approach to achieve reversible surface morphology for a significant change in many surface related properties such as friction and wetting ability.

Other micro-sized protrusion arrays can be realized by laser heating [278]. During the fabrication process, a pre-compressed SMP is heated by a local laser beam. The working principle of forming a protrusive bump atop the SMP by laser heating is illustrated in Fig. 53. First, a polished SMP sample is pre-compressed. A laser beam is then shone atop its surface, and the protrusive SMP arrays are produced. Fig. 54 reveals a typical bump atop an SMP sample, which is pre-compressed to a maximum

Fig. 52. Typical shape-memory effect in protrusive chains (2 vol.% Ni).

Fig. 53. Illustration of forming a protrusive bump atop an SMP using a laser: (a) original sample, (b) pre-compressed sample, and (c) sample after laser heating; a bump is formed [278].
strain of 50%, while Fig. 55 presents an array of protrusive bumps atop a 20% pre-compressed sample. It is significant that an array of bumps is formed [275].

5.5. Shape-memory polymer textiles and applications

Shape-memory fibers based on SMPs can be implemented to develop smart textiles that respond to thermal stimulus [14]. SMPs can be used for textiles, clothing and related products in the form of shape-memory fibers, shape-memory yarns and shape-memory fabrics [279,280]. Hu et al. [14,37,99,101,102,109,281] at Hong Kong Polytechnic University have comprehensively investigated shape-memory finishing chemicals and technologies for cotton fabrics, wool fabrics and garment finishing. Fig. 56 shows a morphology of a shape-memory fiber detected by SEM. On the surface of a single filament of this shape-memory fiber, the grooves can be observed which are due to the traces after
the solution is extruded from the pinholes of the spinneret. The diameter of the single filament is measured as about 16 μm. Furthermore, shape-memory finishing fabrics can be produced with coating shape-memory emulsion or combining shape-memory films. When washed in hot water or dried at temperatures higher than $T_g$, their wrinkles will disappear and they can recover the original flat shape. It is also expected that the smart fibers may be used for novel fiber sensors or advanced medical usage [14].

5.6. Shape-memory polymer foams and applications

A technology called “cold hibernated elastic memory” (CHEM) based on SMPs received much attention in recent years. This CHEM materials utilizes SMPs foam structure or sandwich structures made of SMP foam cores and polymeric composite skins [282]. This SMP foam was proposed for space-bound structural applications by Sokolowski of Jet Propulsion Laboratory, California [276,283–286]. This SMP foam exhibits micron-size cells that are uniformly and evenly distributed within the cellular structure and, therefore, it is suitable for ultra-lightweight porous membrane or thin film space applications [287–289]. A study on the influence of long-term storage in cold hibernation on the recovery strain–stress of a polyurethane SMP foam revealed its excellent stability [276,290]. As one of these applications, a spring-lock truss-element concept for large boom structures was proposed [289]. It involved a unique hybrid design of SMP foams and normal polymer composites. As shown in Fig. 57, the truss-element consists of two carbon-fiber-reinforced polymer laminates separated by the SMP foams.

![Fig. 56. Scanning electron microscopy of shape-memory fibers. (a) View of multi-filament (500×); (b) view of an isolated single filament (4000×)](image)

![Fig. 57. Truss element based on SMP foam][289]
In this way, the two material systems allow the truss-element to be stowed in a small volume and then deployed without the use of complex mechanisms.

5.7. Automobile

SMPs have been used in automobile engineering, and many interesting products have been developed. Some interesting applications of SMPs include seat assemblies, reconfigurable storage bins, energy absorbing assemblies, tunable vehicle structures, hood assemblies, releasable fastener systems, airflow control devices, adaptive lens assemblies and morphable automotive body molding [247,291–297]. The reasons for using SMPs are due to their excellent advantages such as shape-memory behavior, easy manufacturing, high deformed strain and low cost. That is why they have attracted a lot of attention in automobile engineering and have even been used to replace the traditional structural materials, actuators or sensors.

As a typical example, SMPs are proposed to be used for the reversible attachments, as shown in Fig. 58 [298]. In this embodiment (see Fig. 58a), one of the two surfaces to be engaged contains smart hooks, at least one portion of which is made from SMP materials. By actuating the hook and/or the loop, the on-demand remote engagement and disengagement of joints/attachments can be realized (see Fig. 58b). With a “memorized” hook shape, the release is effective and the pull-off force can be
dramatically reduced by heating above the $T_g$. It can be used for a reversible lockdown system in the lockdown regions between the vehicle body and closure [295,299].

SMPs can also be used in an airflow control system to solve a long-time problem for automobiles. As we know, airflow over, under, around, and/or through a vehicle can affect many aspects of vehicle performance, including vehicle drag, vehicle lift and down force, and cooling/heating exchange. Reduction to vehicle drag reduces the consumption of fuel. A vehicle airflow control system, which comprises an activation device made of SMP material, actively responds to the external activation signal and alters the deflection angle accordingly [300–303]. Thus, the airflow is under control based on the environmental changes.

5.8. Self-healing composite system

A healable composite system for use as primary load-bearing aircraft components has been developed by Cornerstone Research Group (CRG), Inc. [304,305]. The composite system consists of piezoelectric structural health monitoring system and thermal activation systems based on SMPs (see Fig. 59). Upon damaging, the monitoring system will sense the location and magnitude of damage, send the corresponding signals to the controlling system, resistively heat the SMPs at the location of damage, and finally the induced shape recovery of SMPs will heal the damage. As shown in Fig. 60, the SMP composite system can recover 75–85% of flexural strength upon bending test.

![Fig. 59. Self-healing system based on SMP [304].](image)

![Fig. 60. Flexural strength of epoxy composites before damage and after healing [304].](image)
5.9. Other applications

Referenced from [306], there is a list of potential applications for SMPs:

(I) SMPs packaging: packaging of thermal sensitive products; sensors/drug/food air delivery systems.

(II) Deployable structures: thermally insulated deployable shelters, hubs; prefabricated walls/slabs; access denial barriers/walls; automatic disassembly of electronic products [307–310]; reusable shape-memory polymer mandrel [311].

(III) Recreation/sport products: tents and camping equipment; life jacket, floating wheels; water and snow skis; surf and snow boards.

(IV) SMPs food equipment: dishes and meal containers; plates and coffee cups; hot/cold storage for food.

(V) SMPs toys: toys that take the advantage of simple reversible compaction, deployment and rigidization cycle: decoys with high fidelity features.

6. Concluding remarks and outlook

6.1. Concluding remarks

The present paper has systematically discussed various aspects of SMPs, including the fundamentals, fabrication, modeling and characterization of SMPs, SMP composites, stimulus methods of multi-functional SMPs, and the corresponding potential applications across a wide variety of fields. The following points can be concluded:

(I) The chemical architecture of SMPs consists of hard and soft segments. The hard segments determine the original macroscopic shape and may be of physical (thermoplastic) or chemical (thermosetting) nature. The soft segments work as a reversible molecular switch and show a thermal transition at temperature $T_{\text{trans}}$. The temporary pre-deformed shapes are fixed below $T_{\text{trans}}$, while they are freed towards the original shapes at or above $T_{\text{trans}}$.

(II) The constitutive models to describe the thermomechanical properties of SMPs are mainly based on viscoelasticity and the two-phase assumption based on phase transition. Exact models, especially 2D and 3D models, need to be developed to describe and predict the shape-memory behavior of pure SMPs, particle-filled SMP composites, and fiber-reinforced SMP composites. The following parameters are proposed to be included in the future models: stress, strain, time, external stimulus parameters (e.g., temperature, electrical current intensity, strength of magnetic field, some special chemical parameters, or even light intensity), and filler or reinforcement content.

(III) Particle-filled and fiber-reinforced SMP composites have been studied comprehensively to develop some special functions or enhance the general mechanical properties for SMPs. Due to the relatively poor mechanical properties and simple functions, fundamental research into SMPs composites is highly demanded in order to meet the requirements of SMPs in various practical applications. Some novel fillers (e.g., carbon nanofibers, carbon nanotubes, nano clay, graphite selenium, graphene, or some other micro or nano materials) can result in high-performance SMPs with tailored properties for a particular application. In addition, orthotropic SMPs filled with particles may be proposed. SMPs with fillers (e.g., nickel particles or carbon nanotubes), if formed in special pattern inside a polymer matrix, can result in better performance along certain directions than those with randomly distributed fillers.

(IV) SMPs can experience a large recoverable deformation upon various types of stimulus including heat, electricity, magnetism, light, moisture, or even some kind of chemical stimuli. However, the thermal-responsive SMPs are the most common ones, and most of the forms, like electricity, magnetism or even moisture, still intrinsically belong to thermal-responsive methods. In addition to these actuation methods, hybrid actuations of SMPs may be developed in the future.
SMPs and their composites receive much attention due to their potential applications in many fields. It should be noted that the relatively poor mechanical properties are still the obstacle to the broad application of SMPs. Thus, the fabrication of SMP composites may be the main approach to overcoming this difficulty. In addition, insight into structural performance of SMPs, including structural fatigue, relaxation, creep and duration, need to be obtained.

6.2. Key challenges and possible future directions

The advantages of SMPs include lower density, lower cost, easier processing, larger recoverable strains, etc. However, some of the major drawbacks of SMPs are their relatively low modulus that results in their lower recovery stress/forces, their long response time, their lower cycle life, and their weak material stability. SMPs show only one-way shape-memory effect, which is different from that of SMAs. This is because most SMPs become much softer upon applying the corresponding stimuli. In order to obtain cyclic operation for SMPs, an automatic resetting system may be developed [43].

Reliable thermomechanical properties of a SMP are required in the early design stage for engineers. Due to different processing techniques and procedures, the variation in properties (e.g., the shape fixity, shape recovery, switching and response temperature), recovery speed, and fill factor) provides us a convenient way for tailoring a material for better performance, but in the mean time, brings the challenge and/or uncertainty in design [312]. As such, first-hand experiments are most likely required to get reliable data for applications.

Considering the comparison between chemically cross-linked thermosets and physically cross-linked thermoplastics, it shows that the former SMPs are better candidate for realistic applications. The advantages of chemically cross-linked thermostet SMPs include excellent shape fixity and recovery ratio, higher transition temperature, better chemical and thermal stability.

Recently SMPs shows interest in making medical devices (see Section 5.3). One of the key challenges in realizing SMP medical devices is the implementation of a safe and effective method of thermally actuating various SMP devices in vivo. One of the possible way is to load ferromagnetic particles into SMP to realize remote stimuli, namely by applying an alternating magnetic field to induce heating [313]. The drawback is that the required power is quite high but the efficiency is quite low.

Based on the previous results, the potential directions and applications of SMPs are proposed to be developed in future research:

(I) Novel SMPs. Prospective SMPs may include: energy harvesting from solar energy (light-responsive SMP), chemical energy (chemical-responsive SMP) or waste heat, SMPs with functionally graded $T_g$ at different locations, two-way SMPs, and SMPs controlled in multi-step manners. For instance, the deformation of an SMP may be better controlled in a step-by-step manner than current ones, which is achieved by having either two $T_g$s for different transitions (two-step) or functionally graded $T_g$s at different locations. Additionally, two-way SMPs may be developed to achieve cyclical deformation as is the case for shape-memory alloys.

(II) Stimulus of SMPs. Wireless and remote-controllable SMPs are proposed (magnetic-field actuated SMP composites filled with ferroelectrics, electric-field actuated SMP composites filled with piezoelectrics, intrinsically light-induced SMPs). High actuation force and fast actuation speed in the new SMPs are necessary. In thermo-responsive SMPs, a narrow transition temperature range, down to only a few degrees, could dramatically increase the actuation speed. Alternative stimuli, e.g., light (in particular, visible light), sound, chemicals or molecular stimuli, for actuation may be developed. Chemical-responsive SMPs can be designed to detect the change in environmental conditions and even make reactions automatically.

(III) Multi-functional SMPs. The following directions are proposed: self-healing or self-repairing composite systems, automatic chemical sensing and water cleaning after harmful chemicals based SMPs. In addition to the shape-memory effect, built-in temperature sensors have been integrated into SMPs for temperature monitoring. SMPs with other types of sensing capabilities should be very useful.
Applications of SMPs in biomedicine. Potential research interests may include: polymer vascular stents with shape-memory polymers as the drug delivery system, smart surgical suture, synthesis of protein-polymer conjugates for therapeutic, laser-activated SMP microactuators to remove clots in a blood vessel, implants for minimally invasive surgery, SMPs with excellent biocompatibility and/or bio-degradability with adjustable degradation rates for intelligent medical devices.

Other applications of SMPs. The following applications are prospective: space deployable structures, such as for hinges, trusses, mirrors and reflectors, SMP skins used for morphing aircraft wings, automobile actuators such as hood/seat assemblies and tunable automotive brackets, smart textiles and fabrics, self-disassembling mobile phones, and shape-memory toys.

As a relatively new type of shape-memory material, the current development and application of SMPs seemingly lag behind other smart materials. However, given their advantages and multi-functional nature, SMPs and their composites are expected to become one of the leading roles in the field of smart materials in near future.

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