Shape Memory Polymers and its Biomedical Applications

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ABSTRACT

The versatility of shape memory polymers (SMPs) and their potential applications are explored in this chapter, with a particular focus on their promising role within the biomedical field. SMPs, known for their ability to undergo shape changes under specific stimuli, are gaining traction due to their potential in creating advanced soft robots, facilitating repeatable actuation, and enabling multifunctional medical devices. In the biomedical realm, SMPs have garnered significant interest, finding applications in diverse areas such as self-retractable stents, drug delivery systems, self-tightening sutures, tissue engineering scaffolds, and more. These materials offer advantages of minimally invasive use, biodegradability, structural support, and controlled therapeutic agent release. While these developments hold great promise, the chapter emphasizes the importance of evaluating biocompatibility, degradation rates, and functional duration for safe implementation. Concluding on a forward-looking note, the chapter underscores the essential role SMPs play in minimally invasive procedures and their continuous evolution in shaping the future of biomedical applications.

Keywords— shape memory polymers; two-way shape memory effect; multiple-way shape memory effect; biomedical application

I. Introduction

The concept of smart materials refers to materials or combinations thereof that can undergo physical or chemical changes in response to specific environmental stimuli, such as heat, magnetism, electricity, moisture, etc., and revert to their original state once the stimulus is removed. Nature has served as a source of inspiration for the development of various responsive systems. Engineers have endeavoured to imitate and create materials and techniques that mimic natural responses to environmental conditions. Examples include the chameleon's ability to camouflage, the squid changing its body colour, and the Mimosa pudica (touch-me-not) plant's sensitivity to touch [1]–[3].

In the case of the chameleon, its skin has a transparent outer layer covering specialized cells called chromatophores. These chromatophores contain pigmented sacs that release specific colours based on factors like body temperature and mood. This allows the chameleon to change its colour (Figure 1a and b).

Similarly, squids possess colour-changing cells with a central sac containing pigment granules. Muscles encapsulate this sac, and muscle contraction spreads the pigment granules, effectively camouflaging the squid by altering its appearance (Figure 1c).

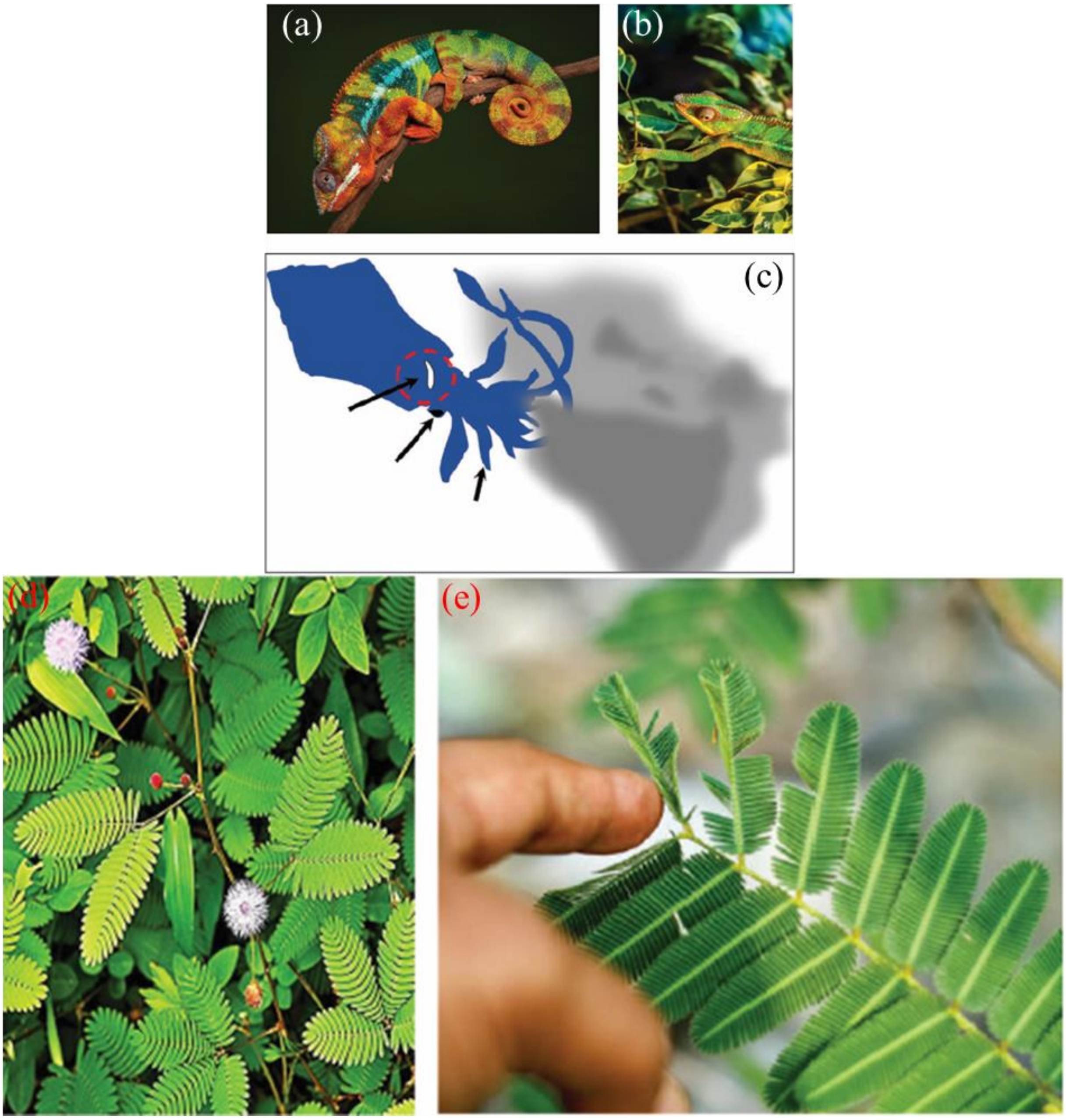

Figure 1 Clever responses from nature: (a and b) Chameleon colour change corresponding to the environment. (c) Squid ejecting ink to escape from its predators. (d) M. pudica plant leaf open. (e) Leaves close in response to touch; the receptors present in the plant's body are activated by an alteration or modification of the plant's shape.

The Mimosa pudica plant exhibits a remarkable touch-response property, which has been extensively studied to understand traits like habituation and memory within the Plantae kingdom. Habituation involves adapting to the environment and ceasing responses to irrelevant biological events. Memory, on the other hand, involves responding to specific stimuli. When physically touched, the Mimosa pudica releases various chemicals such as potassium ions in specific parts of its body. These chemicals induce the flow or diffusion of water or electrolytes into or out of cells, resulting in a loss of cell pressure. This causes the touched cells to collapse, leading to the closing of the plant's leaves. This response propagates to neighbouring leaves, creating the characteristic "touch me not" effect (Figure 1d and e). This behaviour serves as a defence mechanism against predators or insects that feed on the leaves. Despite the energy cost associated with this response, the leaves demonstrate smart behaviour by reacting effectively to external stimuli, illustrating a natural example of the smart material concept. Closed leaves of the Mimosa pudica plant can regain their original open configuration when the stimulus is removed, demonstrating both the plant's responsiveness to stimuli and its shape-memory capability.

Nature offers numerous examples of stimuli-responsive systems that can inspire the development of materials, structures, and methods for everyday use. An example of this is seen in spacecraft antennas, which experience extreme temperature fluctuations causing dimensional changes (expansion or contraction) and associated issues. To ensure optimal performance, these materials should exhibit minimal dimensional variations. Smart materials are well suited for such applications. In this context, a smart antenna would detect dimension changes, assess the required corrections, and autonomously optimize its performance. Unlike conventional materials that behave inertly, smart materials intelligently address problems, often defying established principles of physics and mechanics. These unconventional yet functional materials possess inherent sensing, actuating, and controlling capabilities embedded within their microstructure, enabling them to respond to changes in their environment. Such changes can include temperature fluctuations, electric/magnetic fields, moisture, light, gas adsorption, and pH levels.

In today's context, the push towards technologically advanced "smart" systems with adaptive and intelligent functions has led to a growing reliance on sensors, actuators, and microcontrollers. However, this trend also brings with it the challenge of increased weight and volume of the associated machine components. The pursuit of high "functional density" and the integration of smart functionalities need to address both technical and commercial constraints. These constraints include considerations of available space, operating environment, response time, and cost limitations. As a result, the development of such advanced applications must find ways to navigate these challenges to create efficient and effective solutions [4]–[7].

A. Discovery of Shape Memory Effect

These intelligent materials, known as Shape Memory Materials (SMMs), possess the remarkable ability to respond to various external stimuli such as heat, light, electric or magnetic fields, by modifying specific properties like stiffness, colour, and shape. The most remarkable aspect of the SME is the capacity of SMMs to "remember" their original configuration and revert to it from a temporary deformed state under appropriate stimuli. This behaviour relies on two essential features: fixability and recoverability. Fixability enables SMMs to shift from their original shape to a temporarily deformed shape through a programming process, while recoverability allows them to return to their original shape upon being triggered.

The shape memory effect (SME) was discovered by Arne Olander [8], a Swedish physicist, in 1932, as the shape-remembering behaviour of gold–cadmium alloys. However, the discovery of a nickel–titanium shape memory alloy (SMA) by William J. Buehler (1962) [9] of the US Naval Ordinance Laboratory became the turning point in making use of the shape memory property of materials. Vernon coined the phrase "shape memory" to characterize his polymeric dental material in 1941. It wasn't until 1962, when William Buehler and Frederick Wang discovered the SME in a nickel-titanium (NiTi) alloy, that the significance of shape memory materials (SMMs) was realized [9], It is also known as Nitinol (a combination of NiTi and Naval Ordnance Laboratory), which refers to the material's composition and the location of discovery.

Indeed, over the past few decades, Shape Memory Materials (SMMs) have undergone rapid advancements, leading to a diverse range of materials within this category. This includes shape-memory alloys, shape-memory ceramics (SMC) [10], shape-memory polymers (SMP) [11], shape-memory hybrids (SMH) [12], and shape-memory gels (SMG) [13]. Among these, Shape Memory Polymers (SMPs) have garnered significant attention due to their notable scientific and technological implications [16]. SMMs can be categorized based on various criteria, one of which is outlined in Figure 2.

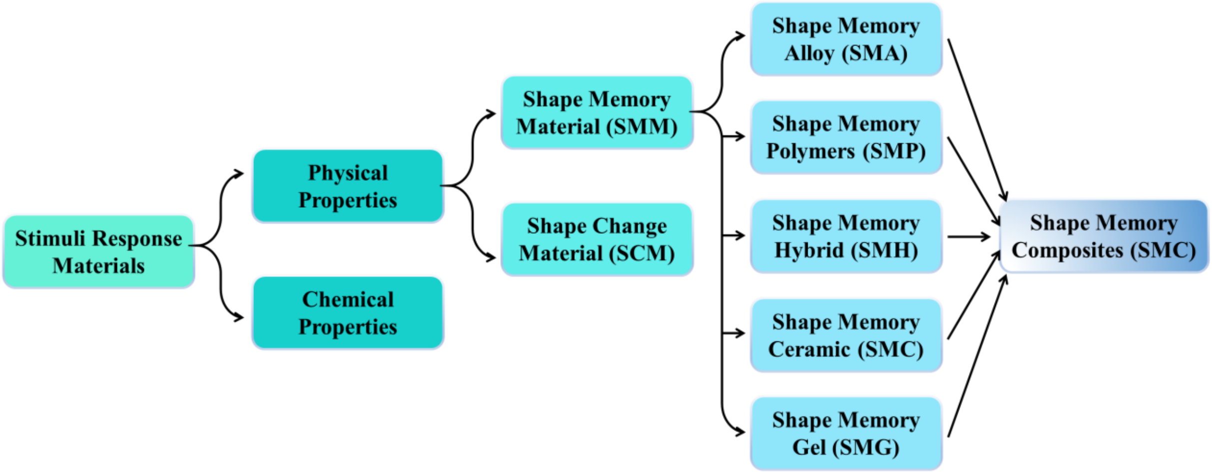

Figure 2 Brief classification of shape memory materials.

In contrast to the reversible martensitic transformation that underlies the SME in SMAs [4], [14], [15], SMPs operate based on a distinctive dual-segment system. These materials are characterized by the presence of cross-links that determine the permanent shape, and switching segments equipped with a transition temperature (T_{trans}) that defines the temporary shape [16]. When below T_{trans}, SMPs exhibit stiffness, but heating them above this threshold renders them flexible. As a result, they can be deformed into a desired temporary shape by applying external force. Upon cooling and removal of the force, the temporary shape remains preserved. Subsequent reheating triggers an automatic recovery of the temporary deformed shape to the original permanent shape.

Interestingly, the true significance of SMPs was not fully recognized until the 1960s [17]–[21]. It was during this period that the use of cross-linked polyethylene (PE) to produce heat-shrinkable tubes and films marked a pivotal milestone in the development of SMPs [22], [23]. Following this discovery, dedicated efforts to advance SMP technology commenced in the late 1980s, gained momentum in the 1990s, and have continued to make remarkable progress over the past 5 to 10 years. This journey from initial recognition to contemporary prominence highlights the evolution of SMPs as impactful smart materials that have found applications across various scientific and technological domains.

Due to their unique multi-field coupling qualities and numerous applications in the fields of aircraft, vehicles, civil constructions, medical devices, information storage, energy harvesting, and other fields, intelligent or smart materials and structures have recently drawn increasing amounts of attention. Understanding the complicated multi-field coupling behaviours of different smart materials and structures is a difficult academic task, and improving the performance and dependability of these materials and structures in industrial applications is important from an engineering perspective.

II. Fundamentals of shape memory polymers (SMPs)

A. History and Definition

Shape memory polymers are materials that exhibit the ability to actively switch between multiple shapes in response to external stimuli. In comparison to other materials, SMPs offer several advantages that contribute to their prominence. They possess high stress tolerance [15] and can undergo significant deformations [2]. Additionally, SMPs provide a diverse range of triggering methods, including heat [24], [25], light [26], electricity [27], [28], magnetism [29], [30], wetting [31], and pH variations [32]–[34]. These materials exhibit remarkable radiation resistance and excellent biocompatibility [17], rendering them a focal point of research in the domain of dynamic materials.

Among Shape Memory Polymers (SMPs), those responsive to temperature changes, known as thermo-responsive SMPs, are the most prevalent [35]–[37]. On a macroscopic scale, as depicted in Figure, the typical thermomechanical cycle of a thermo-responsive SMP involves the following stages [38], [39],

- Shaping the SMPs into an initial form
- Subjecting the SMP to temperatures surpassing the thermal transition temperature (T_{trans}), which could be a glass transition temperature (T_g) or a melting temperature (T_m), and applying an external force to

induce deformation. Following this, the SMP is cooled well below T_{trans}, and the constraint is removed to attain a temporary pre-deformed shape (programming shape)

- When necessary, the pre-deformed SMP is heated above T_{trans}, leading to the recovery of the SMP toward its original shape (recovered shape).

The advent of SMPs began with polynorborene, the first known SMP, which exhibited a T_g range of 35–40°C. This material was developed by the French Company CdF Chimie and commercialized by Japan's Nippon Zeon Company in 1984 [40]. However, the polymer's large molecular weight made it difficult to alter the T_g. Styrene butadiene-based SMPs with a Tg range of around 60–90°C were introduced by the Asahi Company. Their processing abilities was constrained, though. Thermosetting SMPs have recently been commercialized by Cornerstone Research Group (CRG), Inc. These SMPs include a cyanate ester SMP with a high T_g range of 135 to 230°C and a styrene-based SMP with a T_g ranging from 60 to 70°C. Additionally, Composite Technology Development (CTD), Inc. created the CTD-101 K thermosetting epoxy SMP, which has a T_g of about 113°C. Additionally, Mitsubishi Heavy Industry provides a variety of thermoplastic polyurethane SMPs with T_g values ranging from 40 to 55°C that are commercially available.

Given the diverse novel properties exhibited by SMPs, they have been the subject of extensive research since the 1980s. Research endeavours related to SMPs have been carried out across more than 60 institutions and companies worldwide. In recent years, a wide array of polymers has been synthesized to incorporate shape-memory effects, leading to the development of unique performance capabilities. Building upon the principles of the shape-memory effect, novel multifunctional SMPs and nano SMP composites have also been proposed.

Currently, shape memory polymers find numerous applications in various fields such as aerospace [41], medicine [42], smart textiles with self-finishing capabilities [43], [44], electronic devices [45], and self-assembling structures [46]–[48]. Notable instances of these applications encompass low-impact release mechanisms within aerospace, the creation of large spatial deployable structures, shape memory polymer sutures, minimally invasive surgical tools characterized by biocompatibility, active deformation or self-finishing textiles, electronic devices, and adaptable mandrels. These applications effectively address challenging issues in their respective domains, demonstrating the substantial potential of shape memory polymers.

B. Shape memory polymer mechanism and features

The conventional process for programming the shape recovery behaviour of thermo-responsive SMPs is outlined in this discussion [49], [50]. A cyclical thermomechanical test stands as the established method to characterize both the mechanical properties and shape memory attributes of SMPs. The illustrative depiction in Figure 3 captures the multidimensional interplay of stress, strain, and temperature in the context of thermo-responsive SMPs, following these stages [35], [51]:

- At an elevated temperature T_h (where $T_h > T_{trans}$), the SMP specimen is subjected to deformation, achieving a predetermined maximum strain (ε_{max}) through constant strain rate ($\dot{\varepsilon}$) under external loading.
- The specimen is then maintained at the strain ε_{max} and subsequently cooled well below T_g, arriving at a new temperature T_c (where $T_c <$ Ttrans).
- Upon releasing the constraint at T_c, the stress decreases to zero, and a minute elastic strain is recovered (shape fixity). This recovered strain, denoted as ε_r, represents the residual deformation remaining after the applied stress is fully relieved.
- The sample is once again heated from T_c to T_h, this time with a constant heating rate, and without the application of any external loading. The pre-deformed strain ε_r is restored, accompanied by a minor irreversible strain ε_i, which remains at T_h (shape recovery).

The cyclical thermomechanical tests, as depicted in Figure 3, are primarily comprised of two key processes, namely shape fixity and shape recovery [52]. Tobushi et al. [35] conducted an exhaustive study into the mechanical properties of a polyurethane SMP, including properties like cyclic deformation at elevated temperatures, thermomechanical cycling, creep, and stress relaxation. Their findings indicated that shape fixity, when loaded above T_g, exhibited stability under thermomechanical cycling, with the residual strain recovering in proximity to T_g during the heating stage. Gall et al. [51] displayed that the SiC/SMP nanocomposite can generate superior recovery forces compared to pure SMP specimens. Additionally, Hu et al. [25], [53] systematically reviewed and conducted an in-depth analysis of shape memory testing.

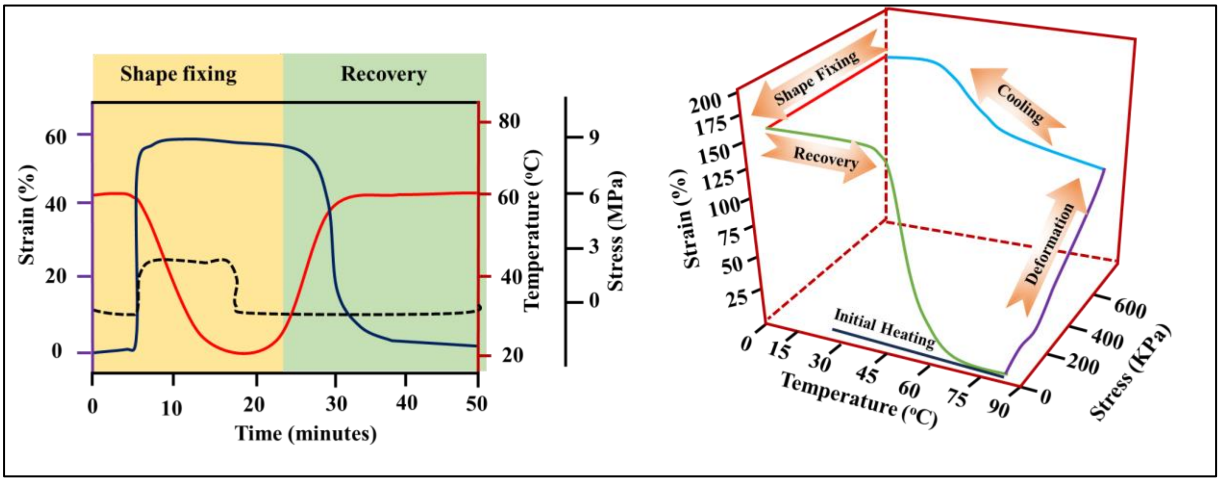

Figure 3

In the practical utilization of SMPs, their capacity for shape fixity and shape recovery takes on paramount importance, frequently evaluated through bending tests. These tests centre around a key parameter – the angle that the SMP forms upon bending. The ensuing descriptions elucidate the angle measurement process and the calculation of the shape recovery ratio within the bending regimen. Figure 3 outlines the customary thermomechanical bending cycle for an SMP, encompassing the following steps [39], [54],

- The specimen, in its original form, is immersed in a water bath at a temperature T_h.
- The SMP undergoes bending, adopting a storage angle θ_S around a mandrel with radius r, while existing in its rubbery state. Subsequently, the SMP is placed in cool water at a temperature T_c with an external restraint, effectively "freezing" the elastic deformation energy.
- The SMP specimen affixed to the apparatus is immersed in another water bath at an elevated temperature T_h, prompting recovery to an angle θ_R.

The following formula is used for computation of shape fixity ratio (SFR) and shape recovery ratio (SRR):

SFR = (Permanent deformation / Total deformation) * 100%

$$SFR = \frac{\theta_S - \theta_f}{\theta_S} \tag{1}$$

SRR = (Deformation recovered within heating process / Fixed deformation) * 100%

$$SRR = \frac{\theta_f - \theta_R}{\theta_f} \tag{2}$$

Where,

θ_S = Storage angle or maximum bending angle or programming angle

θ_f = Fixity angle

θ_R = Recovery angle

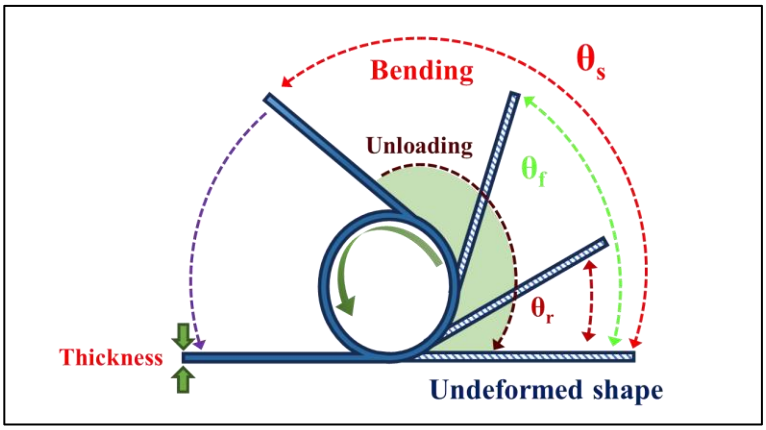

Figure 4 Schematic of bending test as thermomechanical cycle test.

III. Classification of shape memory polymers

With the emergence of new types of shape-memory polymers, a fundamental framework for their classification has been established. The most commonly employed classification of shape-memory polymers (SMPs), revolves around three key criteria: the composition and structure of the polymers, the specific type of stimulus that triggers the return to their permanent shape, and the nature of their shape-memory functionality. This comprehensive approach to SMP classification was proposed by Hu et al. [55]. Additionally, another categorization based on the nature of their net points divides SMPs into physically and chemically cross-linked variants, as introduced by Liu and colleagues [56]. A diverse range of polymers, including polyacrylate copolymers [57], polynorbornene [11], segmented polyurethanes [58], segmented polyurethane ionomers [59], epoxy-based polymers [23], thio-ene-based polymers [60], cross-linked polycyclooctene, cross-linked ethylene-vinyl acetate copolymer [61], and styrene-based polymers [62], exhibit Shape Memory Effect (SME). The majority of these polymers fall under the category of thermally induced Shape Memory Polymers (SMPs), which utilize heat as the triggering stimulus. Figure 1.3 provides an illustration of various thermally induced SMPs.

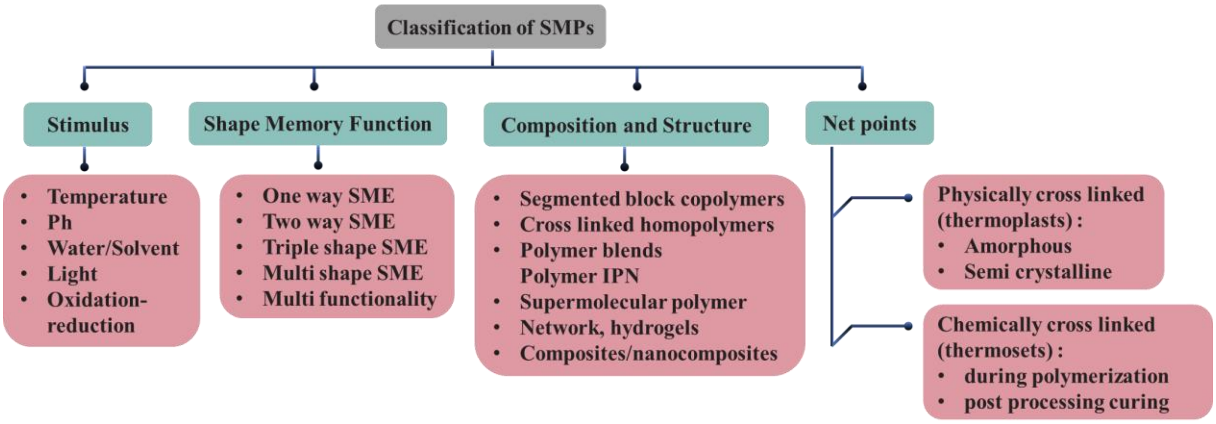

Figure 5 Schematic view of classification criteria of shape memory polymers.

The classification of SMPs has been thoroughly discussed and encompasses various categories. SMPs can be classified based on their responsiveness to different external stimuli: thermally induced, light-induced, electro-active, water/moisture/solvent-induced, pH-sensitive, and magnetic-sensitive. Additionally, classifications introduced by Ratna and Karger-Kocsis [21] and Liu and co-workers [56] categorize SMPs into physically cross-linked and chemically cross-linked variants, primarily based on the nature of their net points. Another dimension of classification includes biodegradable SMPs as a distinct category. Another categorization approach differentiates SMPs based on their switch type: glass transition temperature-type SMPs with an amorphous phase, and Tm-type SMPs with a crystalline phase, as proposed by Ratna and Karger-Kocsis [21]. Furthermore, Behl and Lendlein introduced a classification based on active movement, dividing SMPs into shape-memory and shape-changing polymers [63]. It is worth noting that these classifications may not uniformly capture the entire spectrum of SMP principles.

In addition to that, SMPs exhibit a diverse array of SMEs, encompassing one-way and two-way shape-memory, multi-shape capabilities, and multi-functionality. Achieving various shape-memory functions, as well as other functionalities, is possible by carefully controlling the composition, chemistry, and polymerization processes of SMPs. There are three main categories of SMPs based on their shape memory behaviour: one-way SMPs (possessing a single permanent shape and one temporary shape), two-way SMPs (capable of reversible transitions between two temporary shapes), and multiple-way SMPs (featuring one permanent shape and (n - 1) temporary shapes.). Here's a breakdown of each type:

A. One-Way Shape Memory Polymers (SMPs)

The concept of the one-way shape memory effect (SME) in thermo-responsive shape memory polymers (SMPs) revolves around their capacity to revert from a "temporary" shape, programmed into them, to their original "permanent". This phenomenon is intimately tied to the polymer's transition temperature (T_{trans}) and emerges from the interplay between the material's thermo-mechanical history and its macromolecular architecture. This process encompasses two distinct phases: programming and recovery (as shown in first row of Figure 6). In the programming phase, the SMP undergoes the following stages:

I. The programming phase involves a sequence of actions:
    - Heating ($T_1 > T_{trans}$): Elevation of the temperature beyond T_{trans} augments the mobility of the polymer chains.
    - Deformation: The material experiences deformation, prompting alignment of molecular chains and inducing alterations in macromolecular conformation. This introduces an unstable, high-energy state.
    - Cooling ($T_2 < T_{trans}$): Through cooling below T_{trans}, molecular mobility is constrained, effectively locking in the temporary shape.
    - Unload: Any applied force is released.

II. The recovery phase, aimed at reinstating the permanent shape from the temporary one, unfolds as follows:
    - Heating (T_1): The material is subjected to heating, surpassing T_{trans} and thereby restoring the mobility of chain segments.
    - Shape Recovery: A phase transition follows suit, culminating in the revival of the original, permanent shape.

As depicted in the figure 4, it is evident that both the establishment of the temporary shape and the restoration of the permanent shape are dictated by the transition temperature (T_{trans}). Notably, the one-way SME is irreversible; once the permanent shape is regained, the SMP cannot revert to its temporary configuration via cooling. Instead, a fresh programming phase is requisite to reimpose the temporary shape. Remarkably, the cycle of shape memory can be iterated without limit, constrained solely by potential material degradation [64], [65].

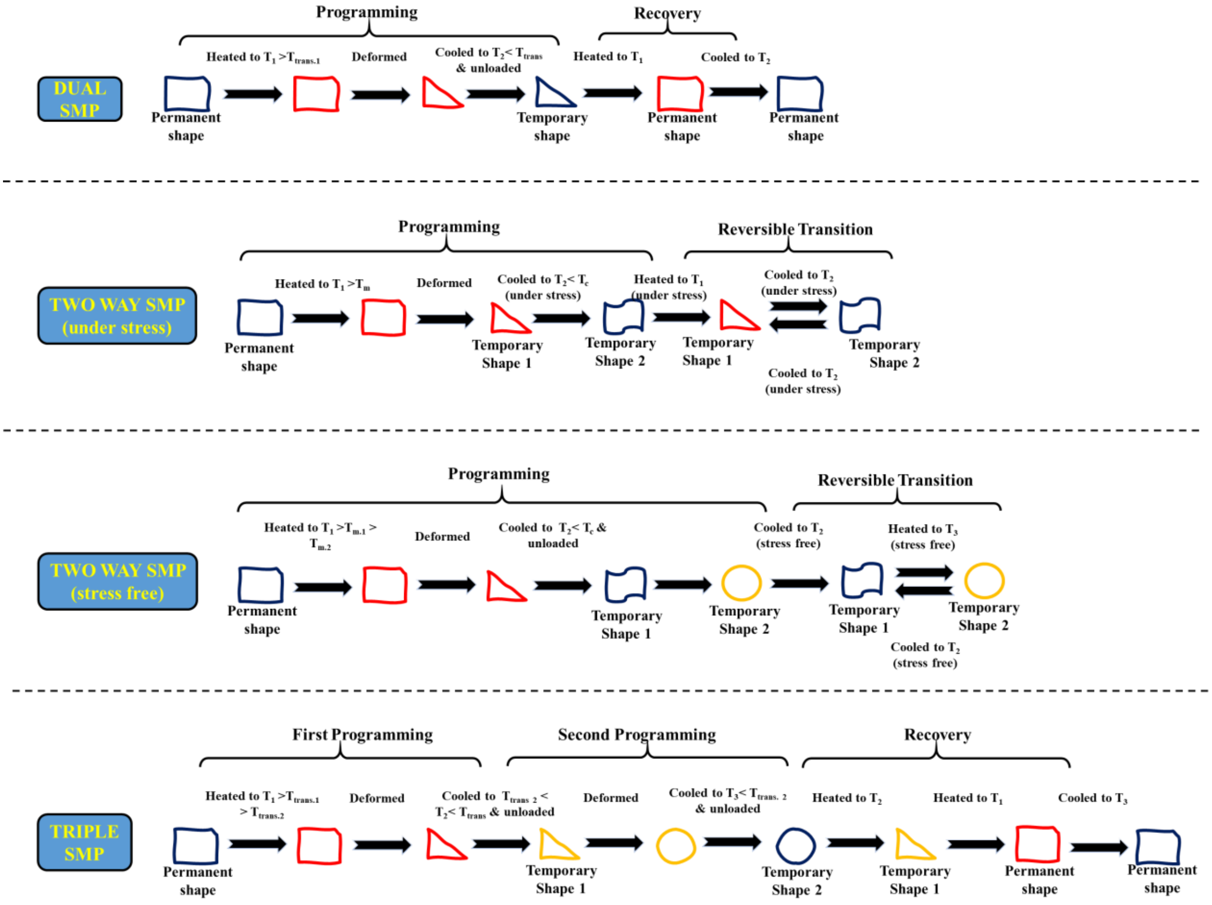

Figure 6 Shape memory cycle in dual, two-way (under stress and stress free) and, triple SMPs.

B. Two-Way Shape Memory Polymers (SMPs):

The ability to undergo reversible shape changes between two different configurations is demonstrated by two-way thermo-responsive SMPs when an on-off stimulus is applied, typically a cooling-heating cycle. Alternatively, depending on the kind of polymer, other stimuli, such as various light wavelengths or combinations of stimuli, such as light cooling or electric current cooling, may also be used. This skill, known as the two-way SME, can appear both under situations of constant applied stress and in the absence of stress. The two-way SME develops from an appropriate interaction between the polymer's macromolecular architecture and its thermo-mechanical history, much like the one-way and multiple-way SMEs.

B.1 Two-way SMEs under constant applied stress are primarily observed in two classes of SMPs: (a) semi-crystalline networks (cross-linked polymers with crystallisable phases) and (b) liquid crystalline elastomers (LCEs).

B.1.1 The two-way shape memory effect (SME) in semi-crystalline networks is observed when there is a combination of a crystallisable phase and chemical crosslinks. This method is based on the rubbery region's entropy elasticity effect, coupled with crystallization upon cooling below the crystallization temperature (crystallization-induced elongation, CIE), and melting of the temporarily oriented crystalline domain upon heating above the melting temperature (melting-induced contraction, MIC). The second row of Figure 6 shows the shape memory cycle for a two-way SMP with temperatures for crystallization and melting, indicated as Tc and Tm, respectively. The substance is initially processed using customary methods to create a permanent form. The material is next heated to a temperature T_1 higher than Tm and deformed under external force, which causes the chain segments to preorient and causes the material to acquire the first reversible temporary shape. The material is then cooled down to a temperature T_2 below T_c while keeping the applied stress constant. The second reversible temporary shape is produced by this cooling process, which crystallization also causes [66]. Due to the rubbery behaviour of the material, the chain reorientation-related first elongation adheres to entropic elasticity constraints. The second elongation is caused by crystallite formation under stress and may be accompanied by the alignment of newly formed crystallites. This second lengthening is a result of a structural evolution process where the growth of crystallites, intended to reduce stress, results in additional stretching to maintain constant stress conditions [67]. Temperatures T_1 and T_2 are typically 15 to 40 °C above and below, respectively, T_m and T_c. Reheating to T_1 causes crystallite melting, which causes the material to MIC back to the initial reversible temporary shape. Material characteristics and testing conditions, among other things, have an impact on how much the first reversible temporary form recovers [68]. The reversible transition between the first and second temporary shapes is enabled by thermal cycling under constant applied stress. Much like the one-way SME, the two-way SME is determined by the transition temperatures (T_c and T_m) and is connected to changes in the material's entropy. Contributions related to semi-crystalline networks and their behaviour can be found in relevant literature references [68]–[72]. The two-way SME's basic ideas have even been adapted to triple SMPs, where reversible SMEs happen at two transition temperatures and allow for the rapid switching between three forms while under stress [73]–[76]. Semi-crystalline networks can generally be made easily, and their transition temperatures can be adjusted to meet particular needs.

B.1.2 Liquid Crystalline Elastomers (LCEs) [76], [77], classified as class (ii), indicate shape-changing materials often looked at in the group of two-way SMPs owing to their interest to exhibit the two-way SME. The interaction between the placement of mesogenic units inside the polymer network and the network's inherent elastic characteristics results in the two-way SME observed by LCEs. Poly-domains, which are liquid crystalline domains found in LCEs, are typically chaotic in their orientation with respect to one another. In addition, mono-domains, which are liquid crystalline domains, can be aligned in a certain direction. One physical method that can be used to encourage the creation of mono-domains is the application of external stress. Elongation happens when anisotropic mono-domains aligned in the direction of stress form after cooling below the clearing temperature, which is similar to how semi-crystalline networks do. On the other hand, when heated above the clearing temperature, these domains compress. The repositioning of molecular groups across the material during phase transitions in LCEs is what causes shape changes. In contrast, phase transitions in SMPs result in the fixing or recovery of a predetermined shape. References like [78]–[84] can be used to locate literature contributions relating to LCEs. Furthermore, the concept of the two-way triple SME has been extended to achieve shape memory effects in LCEs [85].

B.2 A stress-free two-way SME is observed in different classes of SMPs [86], including (a) chemically cross-linked semi-crystalline polymer networks with broad melting temperatures or two distinct melting temperatures; (b) semi-crystalline polymer networks synthesised via a two-stage cross-linking method; (c) thermoplastic semi-crystalline polymers with broad or dual melting temperatures.

B.2.1 Similar programming is needed for two-way SMPs under stress for chemically cross-linked semi-crystalline polymer networks with two separate melting temperatures or a range of melting temperatures. The shape memory cycle for this class can be seen in the third row of Figure 6, which shows a two-way SMP with two different melting temperatures, indicated as $T_{m,1}$ and $T_{m,2}$, where $T_{m,1} > T_{m,2}$. The procedure starts with the material being initially processed conventionally into a permanent shape. Then, a stage in the programming process similar to those used for one-way and two-way SMPs is used.

- The temperature of the material is raised to $T_1 > T_{m,1} > T_{m,2}$.
- The material is subjected to deformation via external stress, which preorientates the chain segments.
- The network then receives a skeleton of geometry-determining domains when the material is cooled to a temperature of $T_2 < T_c$. This process corrects the first transitory, reversible shape that crystallite production produced [64].
- The applied load is removed.
- Under no stress, the material is heated to $T_{m,2} > T_3 > T_{m,1}$ once more. Due to partial melting, the material can take on a second reversible transient shape or a partially regained shape.
- Due to the polymer chains crystallising in the direction of the internal tensile force produced by the unmelted crystalline phase, further cooling back to T_2 enables recovery of the first reversible temporary shape [77], [87]–[90].

B.2.2 Stress-free two-way SMPs have been made using semi-crystalline polymer networks synthesised using a two-stage cross-linking technique, as shown in references like [136–138]. This method results in molecular interlacing within the matrix by joining at least two polymeric networks to produce an interpenetrating network. Incorporating a crystalline phase, which causes reversible shape shrinkage at high temperatures, as well as an elastomeric component, which provides a stretching force for shape extension upon cooling, is how this approach works. The procedure goes like this,

- The system is heated to the crystalline network's transition temperature. Thus, the system contracts due to the crystalline phase, while the elastomeric component is squeezed.
- The system is then cooled to the crystalline network's switching temperature. Because of the elastic recovery of the elastomeric component, crystallisation happens in the direction of the applied force.

Even at high temperatures, these SMPs maintain their two-way shape memory effect and have low transition temperatures. Practically speaking, the two-stage cross-linking approach has benefits since it avoids the programming process and does not require constant tensile stress application. The transitory shapes that the material exhibited during the process, however, are fixed and cannot be changed by heating. This class of SMPs has so far been able to produce very simple reversible shape changes, such elongation and contraction. This approach has also been raised to the world of LCEs and their composites, shown in references [91], [92]. The development of two-way SMPs with dynamic covalent connections using a technique similar to the two-stage cross-linking method is another recent development [93]. SMPs with dynamic covalent bonds cross-linked to them provide advantages such reprocessibility, favourable mechanical characteristics, and efficient recoverability [94].

Thermoplastic polymers that exhibit two-way SMEs under stress-free conditions are thermoplastic semi-crystalline polymers with broad or dual melting temperatures. The reversible shape changing capabilities of these polymers are typically not as strong as those of chemically cross-linked networks, but they do allow for reprocessing and reuse. An alternative strategy for creating two-way shape memory polymers (SMPs) or shape-changing materials involves the use of composites, hybrids, or laminates. This approach often employs two-layered polymeric networks, where each layer may consist of either SMPs or non-SMPs or a combination of the two. This concept is explored in studies such as [95]–[101].

Due to the different thermal or mechanical properties of the layers or, if SMPs are used, the shape memory effect itself, the material in this method experiences imbalanced mechanical forces when heated. In reaction to the applied stimuli, this results in form changes. This strategy has even enabled the discovery of laminated polymers with dual SMP layers that exhibit a two-way SME, regardless of stress-free conditions, as shown in references [102]–[104].

However, there are certain drawbacks associated with this approach. The preparation of such composite, hybrid or laminated materials can be complex and require careful design and fabrication. Additionally, the reversible strain change achievable using this approach is often limited, typically being lower than 10%.

C. Multiple-Way Shape Memory Polymers (SMPs):

Multiple-way (or multi(n)) SME in the context of thermo-responsive SMPs refers to the exceptional capacity to return from two or more separate "temporary" shapes encoded into the material to a "permanent" shape (the original form achieved by normal processing). Similar to the one-way SME, the multiple-way SME depends on an intelligent interaction between the macromolecular structure of the polymer and a particular thermo-mechanical history, including the shape memory cycle. Two strategies emerge for designing multiple-way thermo-responsive SMPs:

C.1 Taking Different Transition Temperatures Into Account: In this method, two or more transition temperatures that are well apart are introduced into the system, such as glass, melting, or clearing transitions. After a lengthy programming effort, a multiple-way SME can be achieved by using this approach. At temperatures below the corresponding transition temperatures, several transient forms are fixed throughout this process. Consider a triple SMP with two separate transition temperatures ($T_{trans,1}$ and $T_{trans,2}$), where $T_{trans,1} > T_{trans,2}$. This will help to clarify the idea. The fourth row of Figure 6 shows the form memory cycle for such a triple SMP. The material is initially processed conventionally to give it a permanent form. In order to "fix" the material into a first temporary shape and then a second temporary shape, two distinct and successive programming cycles are employed. The material is heated ($T_1 > T_{trans,1} > T_{trans,2}$), deformed ($T_{trans,2} < T_2 < T_{trans,1}$), unloaded, and then further deformed ($T_3 < T_{trans,2} < T_{trans,1}$), cooled ($T_{trans,2} < T_{trans,1}$), and unloaded again. The material is ultimately heated to T_1 in order to recover the permanent shape. The transition temperatures $T_{trans,1}$ and $T_{trans,2}$ control the fixing of transient shapes and the recovery of the permanent shape. The multiple-way SME is not reversible, just as the one-way SME. Cooling by itself will not return the SMP to temporary shapes once the permanent shape has been regained; a fresh programming step is necessary. Notably, using this method, multiple-way SMPs may progressively recall various shapes. Approach (I) has been extensively utilized, employing mechanisms such as glass or melting transitions [105]–[117], and nematic-isotropic transformations within nematic networks [118]–[125].

C.2 Utilizing Broad Transition Temperature Ranges: An alternative approach involves employing a broad glass or melting transition temperature range. In this case, the broad transition can be perceived as a sequence of distinct transitions, and the recovery of the permanent shape from various temporary shapes takes place at different temperatures aligned with the material's deformation temperatures [64], [126]. This particular variation of SME is also termed the temperature-memory effect (TME). By adopting this approach, SMPs with broad glass [127]–[137] or melting transitions [138]–[140] can achieve multiple-way SMEs. Programming parameters, including strain rate and temperature holding time, can be finely adjusted to control the TME. Strategies incorporating SMP-based composites or fillers have been explored to tailor polymer behaviour. Additionally, spatially distributing transition temperatures within a material, known as "macroscale spatio-design," has garnered attention as a method to achieve broad SME [127], [141].

IV. Biomedical application

Biodegradable SMPs that have been reported so far are primarily based on well-known biodegradable polymers used in the medical field, including polyglycolide (PGA), poly(L-lactide) (PLLA), and polycaprolactone (PCL) [21]. The selection of a shape-memory material depends on the specific application at hand.

Recent investigations have explored the efficacy of biodegradable SMPs in wound closure [21], [142]. Temporary shapes are achieved by elongating the fiber under controlled stress. These sutures can be applied in their temporary shapes, and when the temperature surpasses the glass transition temperature (T_g), the sutures shrink and tighten knots. Biodegradable sutures are designed to exhibit gradual mass loss during degradation.

Biodegradable SMPs could find utility in self-expandable stents [16]. Beyond biocompatibility and biodegradability, surface texture is a key consideration for medical devices. Surface modification techniques have been proposed for next-generation SMP stent devices, enhancing compatibility depending on the application. Hemocompatibility can particularly benefit from these modifications, achieved through roughening, patterning, chemical modification, and surface treatment for biomolecule and drug delivery.

Further intriguing biomedical applications of SMPs/SMPCs include:

- Orthodontic applications using shape-memory polyurethane [143], where shape-memory PU wire demonstrates potential for correcting misaligned teeth aesthetically.
- Cardiovascular stent interventions [21], [144], which could reduce catheter size for delivery and enable controlled deployment. The stents can be preprogramed to activate at body temperature, deploying without auxiliary devices.
- Fully polymeric self-expandable stents with drug delivery capabilities for constricted coronary blood vessels, potentially reducing restenosis and thrombosis [145].
- The integration of computer-aided design, computer-aided engineering, and additive manufacturing to develop shape-memory polymer-based actuators [146].
- "Smart" annuloplasty rings based on shape-memory polymers for treating mitral valve insufficiency [146].
- Utilization in minimally invasive procedures, such as diagnostic devices, sensors, tissue scaffolds for cell growth, artificial skin, and 3D printing of biomedical devices.

The ongoing development of new SMPs is expected to have an increasing impact on the field of biomedicine, providing innovative solutions to a wide array of challenges and applications. Aside from the applications already mentioned, shape-memory polymers have also been utilized in various other fields.

- Active Disassembly of Mobile Phones: The use of SMPs for active disassembly of modern mobile phones is a notable application. Polyurethane (PU) SMPs, particularly SMP screws, have been employed for this purpose. These screws facilitate the self-disassembly of mobile phones at end of life by utilizing specific triggering temperatures. This technique, known as Active Disassembly using Smart Materials (ADSM), has successfully demonstrated rapid disassembly of different mobile phone models [147], [148].
- Electro phosphorescent OLEDs on SMP Substrates: SMP substrates have been employed in green electro phosphorescent organic light-emitting diodes (OLEDs) with inverted top-emitting structures. These OLEDs, tested on biocompatible SMP substrates, hold potential for wearable electronic applications. This combination leverages the unique properties of SMP substrates and the light-emitting properties of OLEDs, making them suitable for smart skin devices, minimally invasive biomedical devices, and flexible lighting/display technologies [149].
- Automobile Engineering: SMPs have also found utility in automobile engineering with various applications, including 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 moulding. SMPs' shape-memory behaviour, ease of manufacturing, high deformed strain capacity, and cost-effectiveness contribute to their success in this field [150].

V. Conclusion

In conclusion, the integration of shape-memory polymers (SMPs) into biomedicine holds immense promise. Overcoming challenges such as safe thermal actuation and enhancing mechanical properties is essential. SMPs' adaptability across aerospace, biomedicine, automotive, and more underscores their potential. Their diverse stimuli responsiveness, including hybrid approaches, further fuels innovation. As SMPs and their composites gain traction, addressing mechanical limitations and understanding structural performance will be vital. The synergy between SMPs and biomedicine is poised to reshape medical technology, with transformative applications on the horizon.

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