Chapter 1

STIMULI-RESPONSIVE POLYMERIC MATERIALS WITH SHAPE MEMORY ABILITY

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ABSTRACT

Shape memory materials are able to change their shape upon application of an external stimulus such as temperature, humidity, light, electric or magnetic fields, etc. Due to their scientific and technological relevance, this book chapter reviews the main shape memory materials, briefly introducing metals, ceramics and polymers. In particular, shape memory polymers are discussed following the nature of the stimulus that allows their shape memory response, including their characterization methods. Polymeric materials show a wide range of relevant properties such as processability, versatility and biocompatibility, among others, characteristics that are responsible for the increased interest in recent years in the shape memory field.

Keywords: stimuli-responsive, shape memory polymers, humidity, temperature

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INTRODUCTION

Nature is a vast source of inspiration for engineering functional materials. Indeed, chemists and material scientists often follow the principles of nature for the design of new synthetic materials ("bio-inspired materials") [1]. In this context, one of the most inspiring features is the ability to change a specific property upon the application of an external trigger. The variety of the properties that can be changed upon application of an external stimulus is enormous, as well as the nature of the applied stimulus. Variation of mechanical properties is one feature, which for example can be found in sea cucumbers as reported from Bellamkonda et al. [2]. These animals are able to change their skin stiffness by several orders of magnitude in case of danger (i.e., an attack by a predator) [2]. In addition to these macroscopic changes, natural materials show a stimuli-responsiveness on the level of single molecules. For instance, proteins adopt different shapes depending on the conditions used (e.g., temperature, pH-value, salt concentration, etc.) [3]. Simplifying nature's inspiring examples, many stimuli-responsive polymeric systems have been developed by researchers over the last decades [4-5].

Among stimuli-responsive materials, shape-memory materials (SMMs) can respond by changing their shape toward the application of a specific stimulus. SMMs are characterized by the shape memory effect (SME), which is defined as the ability to recover their original shape at the presence of the right stimulus, after being severely and quasi-plastically distorted [6]. The growing interest on SMMs production is well-highlighted by the number of publications during the last seventeen years (Figure 1).

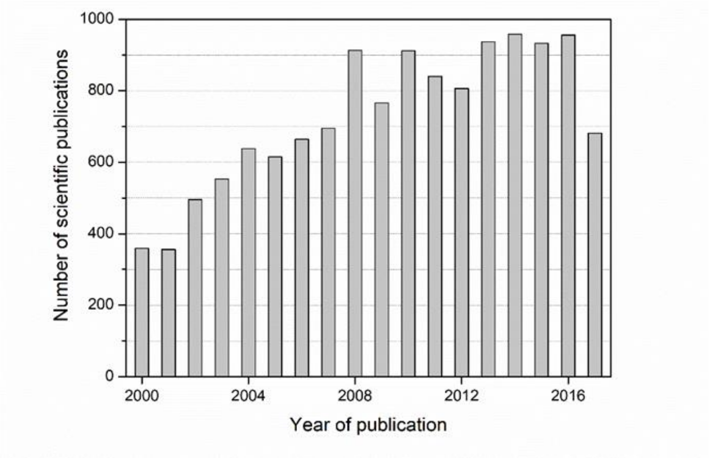

Figure 1. Number of scientific publications per year on the SMMs. Data Source: Scopus®; data research made on August, 2017.

SME has been observed in different kinds of materials like metal alloys [7-9], ceramic materials [10-12], hybrids [13-14] and gels [15-16] as well as polymeric materials [17-19]. A briefly state of the art of these materials is presented in the next pages.

METAL ALLOYS

Shape memory alloys (SMAs) or ‘‘smart alloys’’ was firstly discovered by Arne Ölander in 1932 [20], but the importance of SMMs was not recognized until William Buehler and Frederick Wang whom revealed the SME in a nickel-titanium (NiTi) alloy in 1962 [21], also known as Nitinol [22]. SMAs are a group of metallic alloys that can return to their original form (shape or size) when subjected to a memorization process between two transformation phases, which are temperature or magnetic field dependent [23]. In brief, SMAs can exist in two different phases with three different crystal structures, i.e., twinned martensite, detwinned martensite and austenite. The austenite structure is stable at high temperature, while the martensite structure is stable at lower temperatures. When a SMA is heated, it begins to transform from martensite into the austenite structure, i.e., to recover its original form. This transformation is possible even under high applied loads, and therefore, results in high actuation energy densities [23]. The SME in SMAs is a diffusionless solid phase transition between martensitic and austenitic crystal structures [24-25]. While at low temperatures, SMAs present the SME, at high temperatures, recovery can be achieved instantly and simultaneously upon releasing the applied load, just like rubber band. This is called “superelasticity” [26]. The SME and the superelasticity (or pseudoelasticity) on metallic materials, can be categorised into three shape memory characteristics as follows:

- One-way shape memory effect. The one-way SMAs retain a deformed state after the removal of an external force, and then they are able to recover their original shape upon heating.
- Two-way shape memory effect or reversible SME. In addition to the one-way SMAs, two-way SMAs can remember their shape at both high and low temperatures. However, two-way SMAs are less applied commercially due to the ‘training’ requirements and to the fact that they usually produce about half of the recovery strain provided by the one-way SMAs for the same material [27-28]. Furthermore, their strain tends to deteriorate quickly, especially at high temperatures [29]. Therefore, the first one provides more reliable and economical solution [23].
- Pseudoelasticity (PE) or Superelasticity (SE): The SMAs revert to their original shape after applying mechanical loading at temperatures between the temperature where the transformation in austenite structure is complete and the highest

temperature at which martensite can no longer be stress induced, without the need for any thermal activation [30].

Other forms or types of SMMs have been explored due to some obvious limitations or disadvantages of SMAs, such as high manufacturing cost, limited recoverable deformation, limited operating temperature and low bandwidth [17].

CERAMIC MATERIALS

Shape memory ceramics (SMCs) are inorganic or ceramic compounds that undergo martensitic or displacive transformations can be either stress or thermally-activated. Anyway, most of ceramics are very brittle and the transformations needed to active the SME, i.e., martensitic transformation, can cause cracking, most often because shape distortions in adjacent crystal grains are incommensurate with one to another, inducing large mismatch stresses and triggering fracture [10]. As a matter of fact, unlike SMAs such as Ni-Ti that can withstand low strains up to ~ 8% and at lower strain levels they can be reversibly transformed up to millions of cycles [31], in SMCs such as zirconia, at strains of only about ~ 2%, cracking is observed after only a few transformation cycles [32]. Using ceramics, some new shape memory device can be designed for high temperature application where ordinary SMAs are not applicable. However, the technological application of the shape-memory capacity is limited by the small magnitudes of recoverable strains and the tendency of the ceramics to microcracking. It is possible to classify these materials in terms of their shape memory mechanisms [13]:

- Martensitic SMCs are the most known and widespread one. The mechanism is analogous to the metallic alloys: a transition between two crystalline phases is able to produce shape changes. For these materials, the maximum strain achieved is not more than 4%. More displacive or martensitic-like transformations and potential shape-memory materials can be found in a variety of structural ceramics such as zirconia based ceramics [11, 33] or partially stabilized zirconia [34].
- Viscoelastic SMCs are sintered ceramics that contain very little glass phase including mica ($KMg_3AlSi_3O_{10}F_2$), silicon nitride (Si_3N_4), carbon nitride (SiC), zirconia (ZrO_2) and alumina (Al_2O_3) [35]. Some mica glass-ceramics typically have a heterostructure characterized by a volume fraction in between 0.4 and 0.6 of mica, as the principal crystalline phase, dispersed in a continuous glassy phase. These materials exhibit clear shape-memory phenomenon: after high-temperature plastic deformation, cooling under load to room temperature in order to fix the temporary shape thanks to mica phase, and then reheating to recover the original shape [36]. Because the sliding through dislocations in mica is not possible at low

temperature, the deformation of the material at elevated temperatures will be retained even if the load is removed, after cooling under load to ambient temperatures. The elastic strain energy stored in the glassy phase will thus provide a driving force for recovering the original shape. If the deformed mica is reheated to a high temperature at which the stored elastic strain energy is sufficient to activate the dislocation slide, the phase mixture will reverse the original plastic deformation. In these materials, the shape-recovery percentage shows a strong dependence on the deformation temperature, deformation rate, reheating temperature and heating time [36].

- Ferroelectric SMCs are pervoskite-type oxides where the crystallite domains may exist in a variety of states such as cubic, tetragonal, rhombohedral or orthorhombic, which may be either paraelectric, ferroelectric or antiferroelectric, depending on the exact composition, as well as external conditions such as temperature, stress and electric field. The phase transitions between the different structures, such as the paraelectric-ferroelectric transition and the antiferroelectric-ferroelectric transition may be accompanied by a considerable strain in the ceramics. When the electric field is removed, conventional electroceramics will return to their original state [37]. This is a typical ferroelectric behaviour. Although the shape-memory ceramics have lower strain levels than shape-memory alloys, they have some clear advantages and may be more suitable for certain applications. For instance, because an electric field can be readily changed at much higher rates than temperature, the shape-memory ceramics may be actuated at higher bandwidths, with the maximum response speed of only a microsecond.
- Ferromagnetic SMCs are transition metal oxides that undergo paramagnetic-ferromagnetic, paramagnetic-antiferromagnetic transformation, or orbital order-disorder transitions and the reversible transformations are also accompanied by recoverable lattice distortions. Because of spontaneous magnetization of these compounds is only achievable at very low temperatures, the effects of the magnetic field on the transformation and ferromagnetic shape-memory effect in these compounds are less investigated.

POLYMERIC MATERIALS

Shape memory polymers (SMPs) are polymers which are able to “memorize” a permanent shape and that can be manipulated in a way that a certain temporary shape will be “fixed” under appropriate condition [4]. Thanks to a several great features, SMPs show several advantages in comparison with SMAs [26]. In particular, some of these are low density, high recoverable strain within a wide range of stimuli (by means of direct heating or by Joule heating, induction heating, infrared/radiation heating, laser heating, moisture or solvent or changes in pH value, light, etc.), as well as, transparency, chemical stability, easy chemical modification, well processability, high potential to be easy recyclable and reusable at low cost [38] and eventually, biocompatibility and biodegradability. Regarding the costs, not only the cost of raw material as well as the cost in fabrication and processing remain lower than for SMAs [26].

The first publication mentioning SME in polymers is due to L. B. Vernon in 1941 in a United States patent [39], who claimed a dental material made of methacrylic acid ester resin that could recover its original shape upon heating. Despite this early discovery, recognition of the importance of SMPs did not occur until the 1960s, when covalently cross-linked polyethylene was found to have shape memory capability [40]. Significant efforts began in the late 1980s and this trend continues to grow until nowadays. Dozens of other polymers have been designed and synthesized demonstrating shape memory properties for different applications.

Shape memory effect has been reported in many types of polymers like thermosets [41-42], thermoplastics [43-44], elastomers [45-46], hydrogels [47-48] and liquid crystals [49-50]. Despite their unique properties, the potential applications of SMPs are often limited due to their low thermal conductivity, inertness to electrical stimulus, slow light and electromagnetic stimuli responsiveness and low recovery time during actuation [5].

To overcome these difficulties new generation of shape-memory polymeric nanocomposites (SMCs) have been designed. Generally, they are produced by the incorporation of one or more nanofillers as, nanotubes [51], nanofibers [52-53], nanocrystals [54-55], etc., within the polymer matrix. The advantages of the incorporated nanoreinforcing agents are based on their high specific surface area, high stiffness and their inherent functionalities.

The SME in SMPs is based on a totally different mechanism compared to the other SMMs. In order to show SME, SMPs should be composed by two basic phases/domains, one is the “fixing” domain, and the other is the transition or “switching” domain. While the fixing domain always maintains its shape within the whole SME cycle, the switching domain changes its stiffness significantly at the presence of the right stimulus. This property is not intrinsic to the material. A combination of a determined polymer molecular structure, morphology, and a specific tailored processing known as a “programming” and “recovery” processes is needed in order to obtain SME [18]. First, the material is formed into its initial permanent shape by conventional processing methods, such as solvent casting, extrusion or injection molding. In the “programming” process, the material is deformed and fixed in a “temporary shape.” Afterwards, upon the application of an external stimulus, the material recovers its initial permanent shape, during the “recovery” process [56].

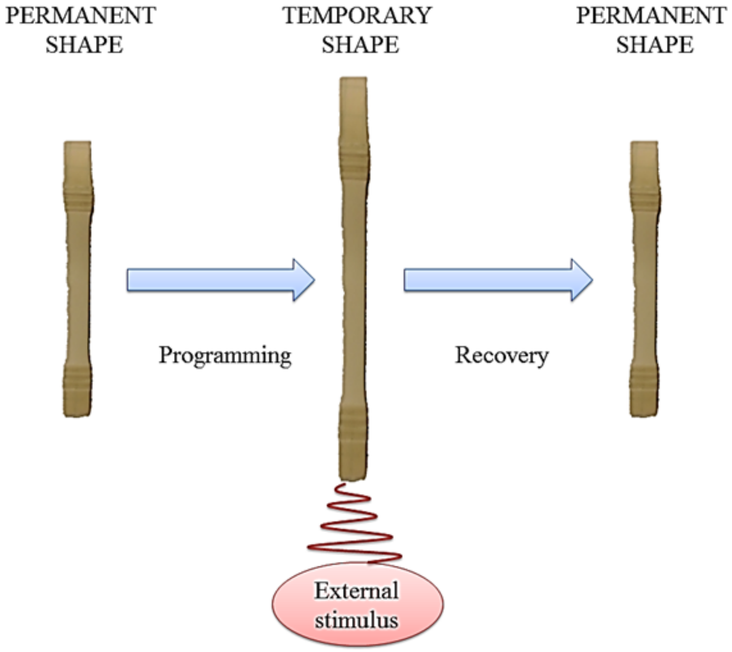

Figure 1. Schematic representation of the shape-memory effect (SME).

Programming-recovery cycles should be repeated several times. Moreover, depending on the structure of the polymer, it is possible to fix two or more temporary shapes in each cycle [57]. SME can be utilized on surfaces (i.e., polymer coating) [58] in order to tune the surface properties by changing the shape of the polymer surface. Furthermore, bulk materials are of great interest where the polymeric material is able to change its overall shape. The properties of shape memory polymers render them attractive for a variety of application in both technical industries (i.e., aeronautics, electronics, textile and packaging) and biomedical applications (i.e., stents, scaffold, etc.).

Design of Shape Memory Polymers and Classification

As mentioned in the previous paragraph, SMPs should generally possess two structural pre-requisites: one consisting of netpoints that define a stable "network" structure or stable domain and the other one is named as switching domain, which can be influenced and change its properties by means of the external trigger and can enable fixation of the temporary shape. The first domain stabilizes the whole SMP and is responsible to retain the original shape. Indeed, the deformation of this phase is the driving force for the shape recovery. In fact, in the permanent shape, the molecular chains within the SMP are at the lowest energy (highest entropy) state. As long as this is stable, any macroscopic deformation imposed on the permanent shape would change the conformation of the polymeric chains raising the energy state of the material. At this point, thanks to the influence of the external trigger, a depression of the molecular mobility can be induced and it serves to maintain the system in high energy state. Once it is removed out by reactivating the chain mobility, with the external trigger (i.e., by heating), the entropic energy is released, driving the molecular chains back to their lowest energy state. Therefore, the materials recover their original shape [59]. In SMPs, this stable domain (network) can be achieved by the introduction of either chemical covalent bonds or physical interactions, i.e., crystallites, glassy hard domains, hydrogen bonding, ionic clusters, chain entanglements and interpenetrating networks [18, 60-61]. The netpoints should be sufficiently stable to withstand the mechanical conditions encountered in the shape memory cycles without plastic deformation; otherwise, the permanent shape would not fully recover. The second phase fixes the temporary shape by crystallization (i.e., a melting transition will lead to the shape recovery), glass transition, a transition between different liquid crystalline phases, reversible covalent or non-covalent bonds (i.e., photodimerization of coumarine [63], Diels–Alder reactions [63], supramolecular interactions [64] and dipolar interaction [65]). Furthermore, SMPs can be designed as "multimaterial" systems such as multi-block copolymer as well as covalent polymer networks can be used as components forming "multimaterial" with shape memory properties. The preparation of binary blends from two polymers by a physical process is also an efficient method for the creation of "multimaterial" systems, in which the properties of the resulting binary polymer blends can be systematically varied.

Often one of the blend component is a polymer able to provide the flexible SMP matrix. The second blend component is used for the modification of the properties of one or both domains.

The covalent polymer network approach to create "multimaterials" is applied in interpenetrating polymer networks (IPN). Here, both polymer networks are not covalently linked to each other [60]. IPN can be obtained by two crosslinking processes occurring sequentially or both at the same time by using two different, not interfering chemical reactions forming the two different networks. Each polymer network provides permanent net-points contributing to the permanent shape [66].

In literature, SMPs have been classified in several ways, for example, through the nature of the fixed or fixity bonds, the nature of the stimulus, which allows the shape memory properties, the transition able to activate the recovery process. In the next paragraphs, SMPs will be classified depending on the nature of the stimulus, which allows the shape memory properties: temperature, solvent/water and humidity, light and other stimuli (electric and magnetic field, etc.).

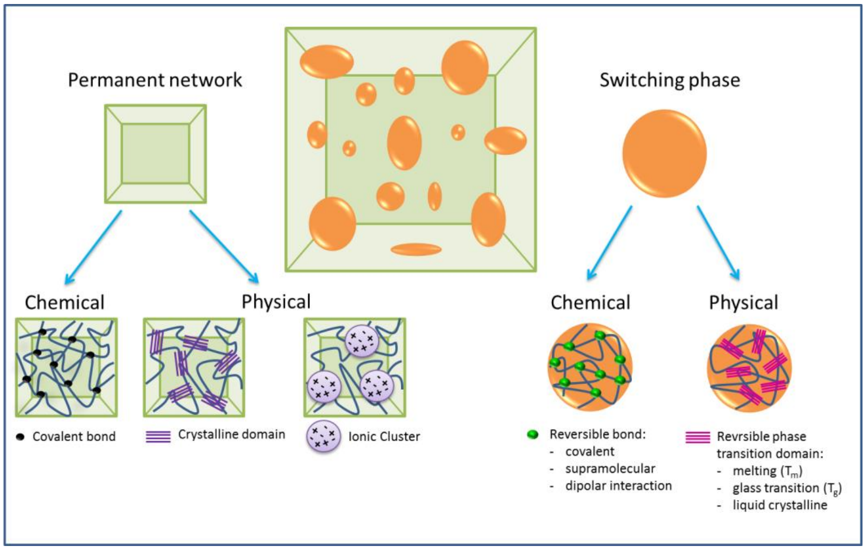

Figure 2. Schematic representation of different permanent networks and switching phases that can constitute shape memory polymers.

Temperature Responsiveness

The shape memory behavior of thermally-activated SMPs is generally triggered by heating the specimen above a specific transition temperature (T_{trans}) belonging to the switching domain. The most important transitions, which are used for thermally-activating SMPs are: the melting/crystallization transition ($T_{trans} = T_m$) and the glass/rubber transition ($T_{trans} = T_g$) [4].

The T_m can be utilized in chemically crosslinked rubbers, in semicrystalline polymeric networks as well as in physically crosslinked polymers (i.e., copolymers with a low melting temperature phase, which is responsible for the switching, and a high melting temperature phase, which constitutes the permanent network) [67]. Indeed, one possibility for the shape fixation is the crystallization of the switching domain. The melting of this phase will lead to the shape recovery of the SMP. Most of these SMPs are based on polyolefins (including ethylene copolymers i.e., ethylene vinyl acetate), polyethers, or polyesters (in particular polycaprolactone, PCL). Hereby two different mechanisms related with T_m have been developed: The first concept is based on the strain induced-crystallization. In particular, the strain induced-crystals act as thermo-responsive switching domain responsible for fixing the temporary shape. The other strategy is based on the melting of the crystalline switching domain of a two-component system such as blends [43], block copolymers [68] as well as polyurethanes [69]. Polyethers are a polymer class, which feature typically low melting temperatures, which makes them promising materials for the switching domain on SMPs. For instance, polyethylene oxide was utilized as soft block (switching domain) in segmented multiblock copolymers with poly(ethylene terephthalate) hard block (stable domain) [70]. In segmented materials, an increase of the soft block content, resulted in higher T_{trans} due to the better crystallization of the soft block. Low melting aliphatic polyesters are probably the most often utilized soft block (in particular PCL). These soft blocks have also been applied in polyurethane systems [69]. Lower molar masses of the polyester results in lower T_{trans}, so that temperature (40ºC) in the region of the human body temperature could be achieved [54]. Additionally, polymer blends containing PCL have been previously reported in the context of SMPs. The biodegradability of the soft PCL blocks opens the possibility to design SMPs for biological applications [71].

In a similar way, the T_g can be utilized in chemically crosslinked thermosets as well as physically crosslinked thermoplastics. Polymeric materials with a T_g above room temperature can be utilized. Within this context, large varieties of different materials have been investigated. In comparison to the SMPs based on T_m, in general, when T_g is used as T_{trans}, a slower shape recovery is shown due to the broad glass transitions (representing a second order phase transition). Consequently, these SMPs are not ideal for applications where a sudden shape recovery is required. On the other hand, the slow recovery makes them interesting candidates for certain biomedical applications [72]. Different studied show that is possible to reduce the broadness of T_g. For example, epoxy resins, as a classical thermoset, were also utilized as SMPs based on T_g [73]. Rousseau et al. [74] reported that, the T_g could be tuned out by the thermoset composition between 31ºC and 93ºC and that a higher crosslinking density resulted in a faster shape recovery of these materials. Polyurethanes (PUs) containing a switching domain with a glass transition instead of a semicrystalline switching domain can also feature SME, as previously reported in literature. In contrast to the shape memory PUs based on T_m, these systems are transparent and are more prone to biodegradation due to the absent crystallinity of the switching domain [75]. Classical thermoplastic elastomers like PUs or EVA feature an excellent processability. However, the lack of chemical crosslinks lead to inferior properties compared with covalently crosslinked polymer. Indeed, latter materials show higher recovery stresses and higher cyclic recoverable strains [76]. Most methacrylate-based covalently crosslinked shape memory polymers are based on the T_g of the soft domain [77]. These materials are also interesting for bio-applications due to their biocompatibility and biodegradability [78].

Another biocompatible and biodegradable polymer that show shape memory effect based on its T_g is the polylactic acid (PLA), but its intrinsic brittleness limited the shape-memory effect for wide application. Zhang et al. [79] found that melt-blending PLA with biodegradable polyamide elastomer (PAE) can change the mechanical properties of PLA. With the PAE contents increasing, the elongation at break of blends increased and the brittle behavior of PLA changed as a ductile behavior. PAE domains act as stress concentrators in system with the stress release locally and lead to energy-dissipation process. They will prevent breaking of PLA matrix under high deformation, and lead to

PLA molecular orientation. When the temperature is above to the T_g of PLA, at about 60ºC, the shape memory behavior can be activated [79].

Regarding high temperature SMPs for new applications, the engineering polymer polyetheretherketone (PEEK) can be modified to reveal shape memory properties as well. Indeed, it was revealed that it was practically feasible to program PEEK at room temperature and to lower the recovery temperature from its melting temperature range to around its T_g only by varying the programming temperature [80]. However, the strains that can be achieved with PEEK are rather small (30%), and the shape memory behavior is relatively poor due to creep issues. In contrast, dual and triple shape memory polymers can be prepared from sulfonated PEEK ionomers and a high temperature fatty acid salt, in particular sodium oleate (NaOl) [81]. Therefore, metal salts of sulfonated PEEK exhibited triple shape memory behavior, where two temporary networks are shown: one from the glassy state of the ionomer and the other from the NaOl crystals. While the ionic nano-domains due to the ionic or dipolar interactions between metal sulfonate groups provide the permanent network [81].

The switching phase, able to fix the temporary shape, can also be based on thermo-reversible bonds. An example of covalent thermo-reversible covalent bond is the Diels-Alder reaction and its corresponding retro-Diels-Alder reaction. Raquez et al. [63] synthesized cross-linked semicrystalline PCL-based polyesterurethane systems by thermo-reversible Diels–Alder reactions, and they showed that this system exhibits one-way and two-way shape-memory properties.

Instead of thermo-reversible covalent bonds, supramolecular interaction can be also utilized for the design of a reversible network. For this purpose, several possibilities exist: hydrogen bonds, ionic interactions or metal ligand interactions. Briefly, the design of shape memory polymers based on hydrogen bonds mostly depend on two binding motifs: the pyridine moiety [82] and the ureidopyrimidine unit [83]. The pyridine moiety can form inter- or intramolecular hydrogen bonds to the urethane group [84]. These interactions can be reversibly broken and, thus, they can interact as the temporary network. In order to increase the strength of the hydrogen interaction, the ureidopyrimidine unit can be installed within the polymeric structures. Due to the quadruple-hydrogen-bonded dimer a strong interaction could be achieved [85]. Regarding the other thermo-reversible supramolecular interactions, ionomers represent another approach. These unique materials exhibit physical and mechanical properties that are profoundly different from their non-ionic analogs. The most common strategies to obtain ionomers are the neutralization of sulfonated polymers with zinc salt [87-88] and the integration of the ionic group by carboxylic acid [86]. This behavior is attributed to the strong interactions that they are able to form because of coulombic difference in potential between ionic charges. While the morphology of ionomers is not fully understood, it is generally accepted that ionic groups coordinate with counter ions to further self-assemble into phase separated nano-domains (ionic clusters) thus forming a reversible ionic network [86]. The inter-chain interaction formed the permanent network, whereas the dipolar interactions between the dispersed phase of crystalline salt and the ionomer itself resulted in the temporary network. In addition, metal-ligand interactions provide a thermo-reversibility that can be used for the design of shape-memory polymers [89]. Thanks to the development of reversible covalent and non-covalent chemistry, opportunities for designing switching domains or segments at the molecular level have emerged. While phase transitions are largely related to a thermal effect, molecular switches bring more options in terms of triggering mechanisms.

Moreover, it is also important to emphasize that for certain application direct heating methods are not applicable and a solution can be found using indirect trigger methods. Therefore, electrical, magnetic, optical, acoustic and chemical energies can all be converted into thermal energy and cause heating within the materials. Normally, it is necessary to incorporate functional fillers into a SMP matrix in order to achieve the energy transformation, i.e., carbon fiber, carbon nanotubes, carbon nanofibers, metal powder, etc. [59]. In the next sections, non-thermal triggers are briefly described.

Solvent/Water/Humidity Responsiveness

Only few SMPs responsive to solvent/water/humidity (also called chemo-responsive) have been reported in the literature. The programming procedure for the water-responsive SME is basically the same as that in the thermo-responsive SME. However, instead of heating to above the T_{trans} to activate the SME, the approach applied to trigger the water-responsive SME is to soften/dissolve the switching domain or, the transition temperature of the switching domain can be lowered below room temperature [19, 90]. Indeed, solvent molecules can have a plasticizing effect on polymeric materials, and they can then increase the flexibility and the macromolecule chains mobility of SMPs [91]. On the other hand, it is possible to design a special dual-component material, which has a switching component that can be softened by a particular chemical agent under its working environment. Instead of softening, in dual-component materials, shape recovery may be induced by removing (dissolving/swelling) the switching component, so that the elastic component can freely release the elastic energy stored during the programming [19].

Regarding humidity/water responsiveness, in literature are reported different strategies in order to obtain humidity/water-activated SME. One strategy is the plasticizing effect of water of the polymer matrixes. In fact, water molecules, which diffuse into the polymeric sample, disrupt the intramolecular hydrogen bonds and then mobilize the previously vitrified chains, thereby shifting the T_g to lower temperatures and allow for room temperature actuation [92]. Yang et al. [93] reported that water-absorbed in shape memory polyurethanes can be split into two parts, namely, free water and bound water. They showed that free water absorbed into the polyurethanes has negligible effects on the T_g and the uniaxial tensile behavior, while bound water significantly reduces the T_g in an almost linear way and it has significant influence on the uniaxial tensile behavior [93]. The shape memory effect associated with the lowering of transition temperature has also been shown for polyurethanes composites reinforced with carbon nanotubes [94]. In all cases, the shape memory effect was reported to be slow, with recovery taking at least 140 min. Furthermore, in these cases, strain recovery is limited to water and it could not be triggered by only moisture due to their very low moisture absorption. Chen et al. [95] synthesized novel moisture-sensitive shape memory polyurethane based on pyridine derivative. They showed that the mechanism of moisture-sensitive SME is based on the dissociation or disruption of hydrogen bonding in the pyridine ring, induced by moisture absorption.

A different strategy for humidity/water-induced shape memory effect can be realized by incorporating a hydrophilic or water swellable component into the structure [96]. In this way, the shape recovery can be greatly accelerated [97-98]. Mei-Chin Chen et al. [99] developed a biodegradable water-activated stent, made of chitosan films cross-linked with an epoxy compound with shape-memory properties. The raw materials used in the fabrication of the developed stent are relatively hydrophilic and a subsequent immersion in water led to rapid hydration and recovery in a short period of 150 s. The hydrophilic component could be a polymeric component belonging a copolymer or a blend as well as hydrophilic filler, organic as much as inorganic [100-102]. Wu et al. [103] developed an enzymatically degradable nanocomposites with water-activated SME by using hydrophilic cellulose nanocrystals (CNCs) and hydrophobic poly(glycerol sebacate urethane). The presence of CNCs improved the mechanical properties and thanks to the water absorption/desorption, the elastic modulus of the material can be reversible changed. This is because CNCs are hydrophilic and absorb a higher amount of water, increasing the water content in the polymeric matrix. Thus, the incorporation of CNCs into the polymeric matrix, triggers the water-activated SME in the corresponding nanocomposite. Wu et al. [104] successfully synthesized composites with excellent water-activated SMEs by using clay as switching component and thermoplastic polyurethane (TPU) as the matrix.

Light and Others Stimuli

Another stimulus that can be used as trigger, in order to activate SME, is the light. Light can be used as a precise stimulus by selecting suitable wavelengths, polarization directions, and intensity, allowing non-contact remote. A wide range of polymeric materials have been found to change different properties in response to light [62, 105]. From the view point of the mechanism of light-activated SME, light-responsive SMPs can be divided into two categories. The first approach, also the most obvious way, is to heat above the T_{trans} via photothermal effect. In this case, generally, light is used only for the shape recovery process but is not involved in the processing of fixing the temporary shape. In order to achieve effective heating when exposed to light, the SMPs should contain some kind of additive or filler that is not only a strong light absorber but also presents high efficiency to convert optical energy to heat through non-radiative energy decay of excited electrons. The nanofillers could be organic dyes, ligands, gold nanoparticles, gold nanorods, carbon nanotubes and graphene for example [106-111]. This kind of light-activated SME is essentially a thermally-activated mechanism because the thermal effect is still involved to activate the shape-memory behavior. Photothermal SMPs have the advantages of fast response (from a few seconds to a few minutes) and good shape memory properties, just as those thermally-activated. The second approach has a different mechanism based on the use of a reversible photochemical reaction without any other energy conversion. Actually, the most extensively studied photo-responsive polymers in the literature include light responsive moieties based on azobenzenes, spiropyrans and spirooxazines and groups undergoing [2 + 2] cycloaddition upon light irradiation such as cinnamic esters, coumarin and diarylethenes [112-123]. In the case of photo-crosslinking reaction, light takes action in both processes of temporary shape fixity and permanent shape recovery. After deforming the polymer to a temporary shape, light at a certain wavelength is applied to induce the photo-crosslinking of the SMP. Therefore, this photo-induced network structure formed with polymer chains in a deformed state is able to retain a certain degree of deformation after removal of the external trigger. For the recovery of the permanent shape, light at a different wavelength is used to de-crosslinking the polymeric network [62, 124]. Other stimuli can be used in order to activate SME such as electric and magnetic fields, pH, etc.

Electro-activated SMPs are materials that respond to an applied electric field by changing their size or shape. They have attracted rapidly expanding scientific and technological interest, due to their potential applications in sensors and actuators, robotics and artificial muscles, optical systems, drug delivery, space, ocean and energy storage applications [125]. Electro-activated SMPs are divided into two types: ionic type [125] and dielectric type [126]. In the first type the electro-responsiveness is a result of an electric field driven mobility of free ions to create a change in the local concentration of the ions within the material. The ionic type includes the conducting polymers [127], the ionic polymers [128], and polymer gels [129], as well as the so-called ionic polymer–metal composites [130]. They require low actuation voltages but suffer low deformations and response rates, while they also normally operate under wet conditions. Dielectric type materials, whose deformation is induced by electrostatic forces developed between two electrodes, comprise the dielectric elastomers [131] and the electrostrictive polymers [132]. They exhibit fast response and high deformations and they operate under dry conditions, but they require high activation electric fields [91, 113].

Magnetic-activated SMPs show magnetic-activated SME with the change in an applied magnetic field [133]. They are composites of elastomers (magnetically active elastomers) or gels (magnetically active polymeric gels) filled with small magnetic particles [134]. They are also called magnetoelastic or magnetostrictive polymeric composites. Magnetic-active elastomers are composites of high elastic polymeric elastomers filled with small nano- or micro-sized magnetic particles [135]. When a magnetic field is applied to the composite, all forces acting on the magnetic particles are transmitted to the elastomeric matrix resulting in the shape change of the sample [91]. Magnetic-active polymeric gels, also called as ferrogels, are super-paramagnetic particles filled swollen networks [136-137]. The finely distributed ferromagnetic particles are attached to the flexible network by adhesive forces, resulting in direct coupling between magnetic and mechanical properties of the magnetic-active polymeric gel [91-113].

pH-responsive polymeric systems provide the possibility to fabricate tailorable ‘‘smart’’ functional materials; hence they have found many potential commercial applications, such as in controlled drug delivery, personal care, industrial coatings, etc [138]. pH-responsive polymeric systems are polymers whose solubility, volume, configuration and conformation can be reversibly manipulated by changes in external pH. Indeed, a polymer is considered as pH-responsive when it features moieties that are capable of donating or accepting protons upon an environmental change in pH [139].

Ultrasound is the high-frequency waves created by mechanical oscillations of a piezoelectric material when an alternating current is applied. Ultrasounds can provoke shape changes in polymeric materials due to the unique heating mechanism based on polymer chain shearing and friction activated by ultrasonic energy [113]. Ultrasound is used in many different fields including ultrasonic devices for object detection and distance measurements, for imaging in medicine and for cleaning, mixing and accelerating chemical processes in industry [140-141].

SHAPE MEMORY EFFECT CHARACTERIZATION

During the last years, various methods for the characterization of SME have been used. In this context, a wide variety of different procedures such as the determination of the polymer’s shrinkage, the application of simple bending tests, compression tests (i.e., in case of SMP foams), three-point flexural tests, application oriented tests (e.g., for SMP textiles or medical devices), cyclic and thermo-mechanical as well as photo-mechanical or magneto-mechanical tensile tests have been reported in the literature for quantification of the shape-memory properties on the macroscopic level [142]. Furthermore, several test methods focusing on the examination of the SME on the micro- and nano-scale have been described [143-144]. Two key values for quantification of SME in polymers have been introduced describing the ability of fixing the temporary shape, called strain fixity ratio (R_f), and the ability of recovering the original shape, called strain recovery ratio (R_r). In the next paragraph, a brief overview about the main cyclic thermo-mechanical tests for macroscopic quantification of SME is given as example.

Thermo-Mechanical Cycle Experiments

One of the most powerful test methods for quantification of the SME of SMPs are the thermo-mechanical cycle experiments [145]. These can be defined as continuous and repeatable testing protocol for studying the SME of polymers. Besides thermo-mechanical cycles allow accurate simultaneous control of physical parameters such as strain, stress and temperature, during programming and recovery, in contrast to other testing methods. Such experiments are typically performed with a conventional tensile machine equipped with a thermo-chamber enabling an accurate temperature control during mechanical deformation of the specimen (programming) and recovery [18, 54]. Alternatively, dynamic mechanical thermal analyzer (DMTA) can be applied, which allow conducting experiments in tensile and bending mode [44, 146]. It is possible to divide thermo-mechanical cycle experiments in different methods according to the geometry of the test setup as reported bellow.

Cyclic Thermo-mechanical Tensile Tests follow tailored test procedures. These test procedures consist to a programming step, where the temporary shape is fixed, and a recovery step where the permanent shape is recovered. The programming step can be performed under stress-controlled or strain-controlled conditions and the recovery step can be carried out under stress-free conditions or under constant strain. Several thermo-mechanical testing parameters influence the shape-memory properties, such as the applied strain, the strain rate, cooling and heating rates, number of operates cycles (N) as well as the applied temperatures, to stretch or deform the sample (T_d), to fix the temporary shape (T_{fix}), and to recover the original shape, the switching temperature (T_{sw}). The programming procedure can be performed based on different test protocols, such as cold drawing process ($T_d < T_{sw}$) or a heating-stretching-cooling process ($T_d = T_{sw}$). In general, the programming step is composed by three steps, (1) heating of the sample to the T_d and deforming of the specimen with a defined strain rate; (2) cooling to T_{fix} with a certain cooling rate, while the elongation is kept constant for the fixation of the temporary shape; (3) unloading the applied stress at T_{fix} resulting in the fixed temporary shape. After the temporary shape is fixed the recovery process can be initialized in step (4) consisting on heating from T_{fix} to T_{sw} with a constant heating rate, allowing the recovery of the original shape when performed under stress-free conditions.

Bending test. There are two types of tests that are based on bending the polymeric samples in order to characterize the SME. One is called “simple bending test” and the other one is the so-called “three-point flexural test.” Bending tests are preferred in brittle materials, since the interpretation of the tensile test result is difficult due to breaking of the sample near the clamps. Additionally, large deflections can be achieved at modest strain levels. Another aspect to be mentioned is that several applications require information obtained by the bending rather than the tensile properties of the samples [142]. In a bending test the sample is bent to a certain angle at T_d and it is kept in this shape. The deformed sample is cooled to a lower temperature, T_{fix}, and the remaining stress is released. In the last step, the sample is heated up to the T_{sw} and the recovery of the permanent shape is recorded in terms of a series of deformation angles depending on T [147-148].

The three-point flexural tests is able to provide values for the elastic modulus in bending, flexural stress, flexural strain, and the flexural stress–strain response of the tested material, *i.e.*, the determination of strain recovery and stress recovery ratio [146, 149-150]. Compared to uniaxial cyclic tensile tests the main advantage of simple bending tests and three-point flexural tests are the rather simple specimen preparation and testing. The maximal deformation in three-point flexural tests is significantly lower than in tensile tests. While in tensile tests it is possible to reach values up to about 200% of deformation (depending on the instrument used), in three-point flexural tests, the maximal deformation is only about 20–30%. In tension or compression, thermal stresses arise from constrained thermal expansion or contraction, leading to difficulties in separating the various mechanisms during deformation. Upon cooling, after tensile deformation, the applied stress can increase at a fixed strain, while in the flexural deformation the thermal contraction is not as severely constrained [18, 147].

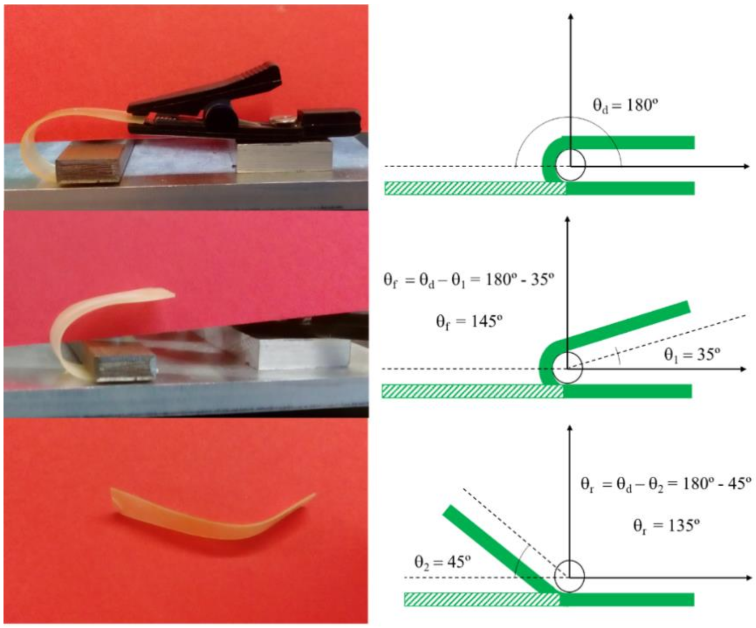

Figure 4. Schematic representation of simple bending test.

Cyclic Thermo-mechanical Compression Tests. A compressive stress reduces the length of the sample by the uniaxial application of two plates on the sample. Various sample geometries with two opposite planar surfaces can be tested in a compression test. Cyclic thermo-mechanical compression tests have been mainly applied for porous test specimens [142]. Indeed, such foams can be subjected to large compressive strains, above

90% depending on the foam morphology and density considering that many applications of foams involve compression. In a standard compression test of foams, bending of the pores occurs during the elastic regime, which can be followed by buckling, as represented by a stress plateau at increasing strains [151]. In such a cyclic thermo-mechanical test, the foam is inserted in the temperature controlled testing machine and subsequently increasing the temperature to T_d in order to perform compression of the foam at the programmed strain rate. Next, the foam is cooled maintaining the compressive stress until T_{fix}. The compressive stress is then unloaded to obtain the temporary shape of the sample. While cooling, thermal contraction occurs, leading to an additional compression of the SMP foams. Consequently, the sample would lose contact to the compression plates, if cooled under constant strain conditions below T_{trans}. By heating the foam under stress-free conditions the recovery strain is obtained, while the evolution of the recovery stress can be observed by heating under constant strain conditions [152-153]. The parameters R_f and R_r are calculated in the identical manner as for cyclic thermo-mechanical tensile tests [142].

SHAPE MEMORY POLYMERS APPLICATIONS

The interesting properties of SMPs make them good candidates for many applications, from industrial to biomedical application, self-healing materials using the SME as well as application in aerospace field [81, 124, 154]. SMPs have been applied in commercial products as early as the 1960s in the form of heat-shrinkable polyethylene tubes used as wire wraps for the purpose of electrical insulation [155-156]. Over the past three decades, reports of SMPs activated by different stimuli and exhibiting a variety of features have been increasingly published. In many applications, SMPs have some limitations compared to metallic materials, especially due to the low mechanical properties of polymers. In order to improve the mechanical properties as well as to obtain smart multifunctional materials, many researchers reported new shape memory nanocomposites filled with different types of reinforcement [157].

Many applications of SMCs in aerospace field have been reported in the literature [4]. In this area, SMPs have one decisive advantage, i.e., their lightweight. The lightweight of the applied materials is one of the most crucial issues in the design of new systems in aerospace. SMPs are of great interest for low-cost self-deployable structure [157-158], i.e., solar arrays, solar sails, sunshields, or radar and reflector antennas [124, 159-161]. Beyond this sector many other potential applications in different areas are reported in the literature, but in this chapter, we will focus more on the potential applications in the biomedical field, whereby there have been many advances in recent years [56, 162].

Shape memory polymers have tremendous applications in biology and biomedicine. For this application field, several requirements must be fulfilled and a range of problems must be overcome [163]. As a matter of fact, these requirements for biomedical applications are related to the biocompatibility and non-toxicity [164], biodegradability [165], sterilizability [166], specific mechanical properties [167], and a trigger adapted to the human body [56, 163, 168]. As explained in the previous paragraphs, thermally-activated SMPs must be heated above their characteristic T_{trans} to induce their shape change. For SMPs with T_{trans} close to body temperature, actuation can be accomplished by simply placing the SMP into the body. However, if the T_{trans} required is higher than the body temperature, addition of fillers to the SMPs has enabled several heating schemes using external energy sources to selectively heat the SMPs into the body [133]. Small et al. demonstrated photothermal actuation using IR laser light [169]. Moisture-activation of SMPs has been demonstrated by Chen et al. [95], in which the solvent depresses the glass transition temperature of the material via plasticization. Therefore, actuation can be achieved at the body temperature. This technique is feasible for deployment of SMP medical devices in body fluids. One of the most important design considerations of any material for potential biomedical applications is biocompatibility, which is the ability of the material to perform *in vivo* with an appropriate host response [56]. Preliminary biocompatibility results of polymeric materials for biomedical applications were widely reported in the literature [170]. For example, the first commercially available SMPs from Mitsubishi Heavy Industries, Ltd. (Nagoya, Japan), which are now distributed through a subsidiary (DiAPLEX, Ltd.), are polyurethane-type SMPs [171-173]. Other published biomedical academic studies on SMPs include PCL, PLA-polyurethanes, PEO based shape memory polymers that were found to be non-toxic [166, 174-175]. If these basic requirements are fulfilled, shape memory polymers can be applied in several biomedical applications such as SMP-based medical devices [175-177] (SMP-based stents, clot removal devices, aneurysm occlusion devices, etc.), SMP-based drug delivery devices [178-180] and SMP-based biomaterials for tissue engineering [181-183] (i.e., scaffold for vascular tissue, for bone tissue, etc.) [162]. The first example of fully biodegradable body thermo-responsive SMP stent were based on poly(L-lactic acid) (PLLA) and poly(glycolic acid) (PLGA) bilayers [184]. Beilvert et al. reported in a recent study that natural starch, without chemical grafting, can now be considered for manufacturing innovative biodegradable devices for less-invasive surgery.

CONCLUSION

In this chapter, a comprehensive overview of recent developments and progress in shape-memory materials has been presented. In particular, shape memory polymers and nanocomposites are one the of most important class of multi-responsive smart materials providing excellent and new opportunities for scientific developments in the field of polymer synthesis and functionalization, molecular architecture design, processing of polymer blends and interpenetrating networks and multifunctional materials. Indeed, within the last few years, tremendous efforts were devoted to the area of stimuli-responsive materials, driven by the need for precisely controllable material properties. Due to the high degree of control, external stimuli as triggers that induce changes of the physical properties of polymeric materials proved to be a very promising approach. The interesting properties of SMPs make them good candidates for many applications, from industrial to biomedical application, as self-healing materials with SME as well as application in aerospace field.

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