Classification of Shape-Memory Polymers, Polymer Blends, and Composites

Krzysztof Strzelec, Natalia Sienkiewicz and Tomasz Szmechtyk

Abstract Since the last three decades, international research interest into the shape-memory effect in polymers has been rapidly growing. The recent progresses made in the synthesis of different types of shape-memory polymers (SMPs) significantly expanded the practical potential of their applications in such fields like microelectromechanical systems, medical and biomimetic devices, sensors, actuators, self-healing systems, etc. The present chapter is focused on the classification of shape-memory polymeric materials (SMPs), as well as the current developments and most important concepts for these types of smart polymers. The recent progress in the development of shape-memory polymer composites (SMPCs) and shape-memory polymer blends (SMPBs) is also highlighted. In this chapter, different classification criteria of SMPs with a view to polymer type and structure and external stimulus are described. Particular emphasis is placed on the factors enabling shape-memory effects, especially structure–property correlations that influence shape-memory mechanisms.

1 Introduction

Shape-memory polymers (SMPs) are a kind of very important smart polymers that have multiple shape capacities. They can be deformed and subsequently fixed into a temporary shape, which would remain stable unless they are exposed to an appropriate external stimulus such as temperature, light, pH, electric or magnetic field, and specific ion or enzyme that triggers the polymers to recover to their original shape. Usually, preparation of SMPs is conducted by conventional processing methods, e.g., injection molding or extruding. During processing, the polymer is formed into its ini-

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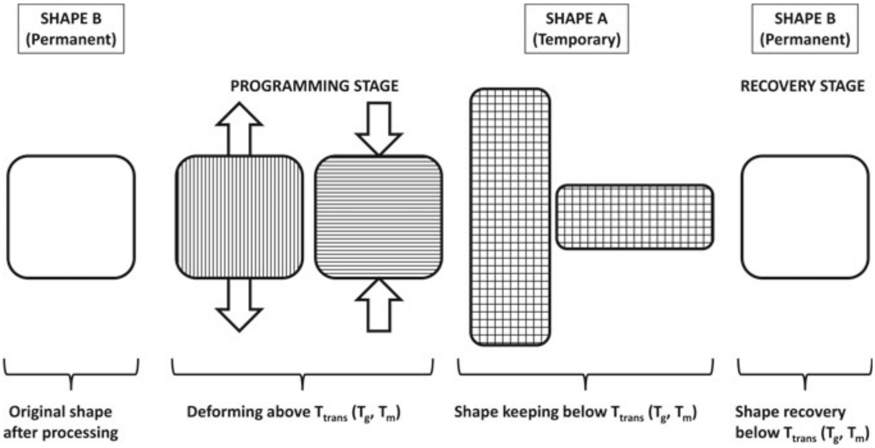

Fig. 1 Schematic representation of shape-memory effect for thermally induced process

tial permanent shape B. Afterward, the polymer specimen is deformed and fixed into the temporary shape A (Fig. 1). Polymer recovers its initial permanent shape B after application of an external stimulus [1]. In comparison with metallic shape-memory alloys, such cycle can be repeated several times in much shorter interval. Additionally, SMPs allow a much higher deformation rate between shapes A and B [2]. Apart from easy manufacturing and processing, for many applications, SMP materials are attractive substitutes to metals because of their flexibility, biocompatibility, low cost, and wide scope of modifications. Shape-memory polymer composites (SMPCs) and shape-memory polymer blends (SMPBs) have considerably enhanced the range of applications of shape-memory polymers.

The first shape-memory effect in polymers was described by Vernon et al. in the US patent on dental materials (methacrylic ester resin) [3, 4]. The first application of SMPs was heat-shrink tubing by Paul Cook at Raychem Company in the late 1950s [5]. The next important step in the development of SMPs was reported by Rainer et al. in [6], the utilization of heat-shrinkable polyethylenes [6]. This polymer was able to memorize its initial shape after irradiation with gamma rays. Also, George Odian with coworkers at Radiation Applications, Inc. in early 1960s, developed for NASA deployable space structures from polyethylene with radiation-induced memory. Besides these, only a few other studies were performed in the 1960s; however, industrial application was being widely explored as evidenced by patent literature on “heat-shrinkable” or “heat-recoverable” materials used in electrical engineering and packaging industry (Fig. 2) [5]. Starting in the mid-1990s, academic interest in the field of shape-memory polymers dramatically grew. Since then the research in SMPs has increased due to their possible and promising application in several fields such as smart textiles and apparels, medical devices, sensors and actuators, flexible electronic devices, high-performance water vapor permeability membranes, aerospace applications, and many others [7]. In recent years, a wide variety of polymers has been

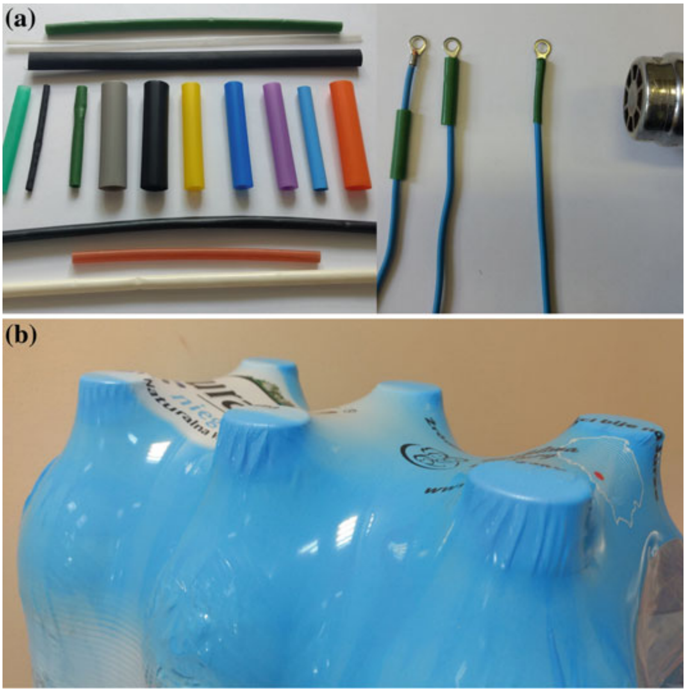

Fig. 2 **a** Heat-shrinkable plastic tubes used to insulate wires; **b** Packaging shrink-wrap foil

synthesized with shape-memory effects. A number of unique properties have been developed in different types of polymers like thermoplastics, elastomers, thermosets, polymeric blends and composites, hydrogels, and liquid crystals.

2 Classification of SMPs

With the emergence of new types of shape-memory polymers, the basic criteria for their classification were defined. The most commonly used classification of SMPs (discussed in this review) includes the three criteria: composition and structure of polymers, the type of stimulus which triggers the shaping back to the permanent phase, and the character of shape-memory function. Such integrated insight into the classification of SMPs was proposed by Hu et al. [8]. Another division into physically and chemically cross-linked SMPs, according to the nature of their netpoints, was introduced by Liu and coworkers [9]. The combined scheme of the two above classifications is presented in Fig. 3. The chemical structure of SMPs and a type of activation trigger were the main criteria for classification showed by Mather [5]. This division includes four categories. Category I and Category II are chemically cross-

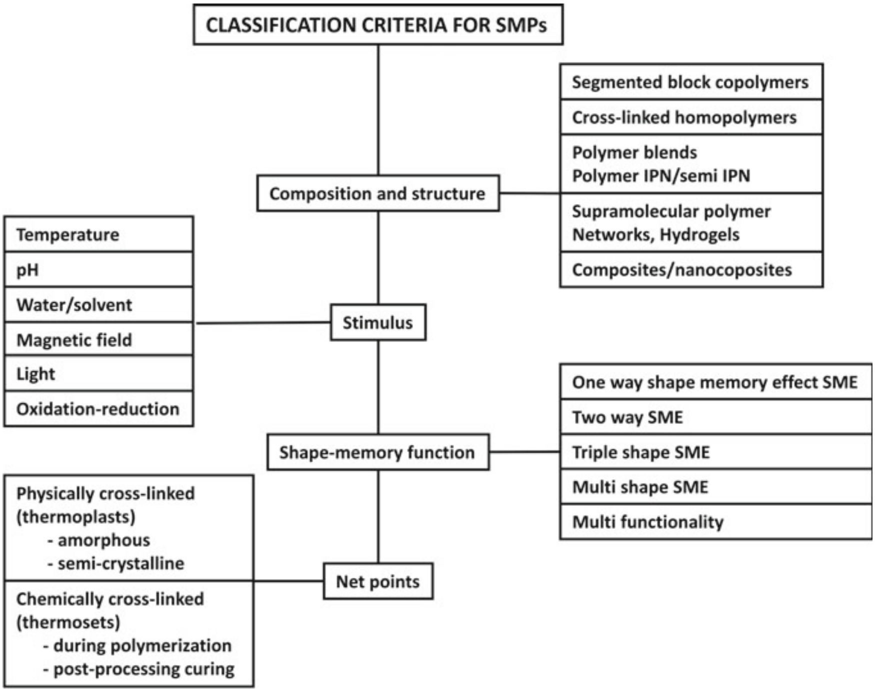

Fig. 3 Schematic view over classification criteria of shape-memory polymers

linked networks that utilize, respectively, a glass transition and melting transition for their activation. Category III and Category IV represent physically cross-linked polymers activated accordingly, with a glass transition and melting transitions.

2.1 Classification by Polymer Structure

Almost, all polymerization methods can be used to synthesize SMPs, including addition, condensation, free-radical and photochemical polymerization, and radiation reaction [9]. The shape-memory effect of the polymer can be achieved through the generation of strong interaction among the polymer chains. Usually, elastic entropic forces result from the presence of physical or chemical netpoints, which can be achieved by covalent bonds or intermolecular interactions. This kind of polymeric materials must present an adequate morphology in order to show this behavior [10]. Taking into account the cross-linking characteristics, composition, structure, morphology, and type of polymer materials, SMPs are often classified into four different polymer structures: chemically cross-linked, physically cross-linked, polymer blends, and polymer composites [11].

Generally, the molecular structure of SMPs consists of two practical parts, cross-links with chemical or physical nodes (hard segments), and switching segments. The cross-linked elements of structure allow for the memorization of the original permanent shape. The hard segments may be of physical or chemical nature, such as chemical cross-links, crystals, glassy domains, or chain entanglements [12]. The switching segments are the polymer chains between network nodes that undergo the reversible shape change (Fig. 4) [5]. The soft segments work as reversible molecular switch at transition temperatures. These segments can be either amorphous or crystalline, and therefore the transition temperature (T_{trans}) is glass transition temperature (T_g) and a melting point temperature (T_m), respectively. Chemically cross-linked SMPs can be obtained by a suitable cross-linking chemistry, which are referred to as thermosets. Physically cross-linked ones require a polymer morphology consisting of segregated domains, which is typical for thermoplastics [10].

2.1.1 Chemically Cross-Linked Polymers

For the chemically cross-linked polymers (thermosets), the polymer network is built from the polymer chains connected by covalent bonds, which are more stable than the physical cross-linking network and show an irreversible nature [13, 14]. When the covalent bonds are introduced into polymer matrix, the programmed shape of polymer cannot be further changed. Covalent netpoints can be obtained during polymerization by the cross-linking of linear or branched polymers as well as (co)polymerization/(co)polycondensation of one or several monomers, in which one has at least trifunctional. The other methods rely on postprocessing cross-linking of polymer chains. The physicochemical properties of the network can be adjusted by the choice of monomers, their ratio and functionality, and the cross-link content. Additionally, these properties can be controlled by the curing conditions and curing time. Several types of SMPs are also synthesized by synthesis route, which involve copolymerization of monofunctional monomers with oligomeric difunctional cross-linkers [10]. Such AB copolymer networks possess increased toughness and elasticity at room temperature. AB copolymer network with T_{trans} based on T_g was obtained by copolymerization of various acrylates with poly[(l-lactide-*ran*-glycolide)]dimethacrylate [13]. Similar covalently SMP AB copolymer network with melting transition T_m used as switching transition for the shape-memory effect was prepared by copolymerization of *n*-butyl acrylate with semicrystalline oligo[(ε-hydroxycaproate)-*co*-glycolate]dimethacrylates [15].

Typical examples of SMP networks prepared during polymerization processes are styrene copolymers, thermosetting polyurethanes, polyacrylates and polymethacrylates, PE/poly(vinyl acetate) copolymer, and epoxides. The thermosetting SMPs, like for example cross-linked styrene-based SMP and epoxy SMP, in contrast to thermoplastic SMPs with poor thermal and mechanical properties, are generally used for large-scale structural materials. Copolymerization of styrene with various co-monomers is the key to obtaining shape-memory materials with enhanced flexibility and a huge variety of network architectures [16]. For example, shape-

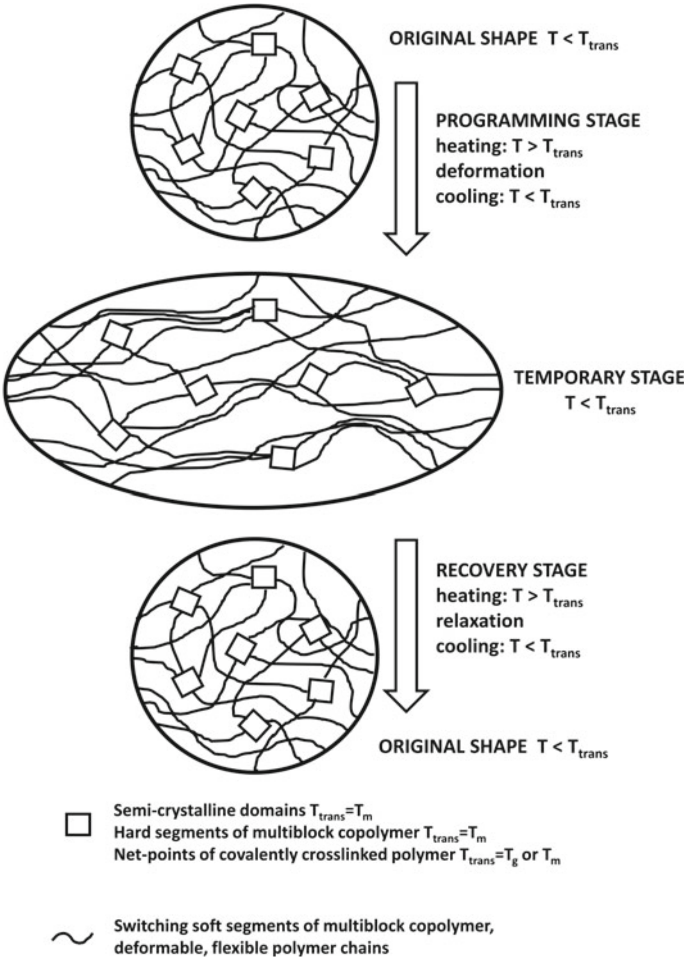

Fig. 4 Molecular mechanism of thermally induced shape-memory effect for different types of SMPs

memory effect has been reported for copolymer of styrene, corn oil and divinylbenzene [17], and *trans*-poly(1,4-butadiene)-polystyrene copolymer [18]. Also, polyacrylates and polymethacrylates are of interest as shape-memory materials due to their ease of preparation, their simple phase behavior, and the possibility of easily tuning their key characteristics. (Meth)acrylates with a wide variety of ester functionalities are commercially available, and many of them can be copolymerized by radical polymerization in bulk or in solution [13]. The acrylic monomers which are predominantly used for synthesis of SMP networks may have (1) network segments, (2) a switching segment, and (3) a cross-linker. For example, SMP networks were synthesized from poly(methyl methacrylate-*co*-butyl methacrylate) copolymer cross-linked with tetra(ethylene glycol) dimethacrylate [19]. Apart from being built up by the main chain of poly((meth)acrylates), the switching segment can also be introduced as side chains or as long-chain cross-linkers by the use of (meth)acrylic ester macromonomers based on oligo(ε-caprolactone), PEG, and poly(lactide-*co*-glycolide) [13]. As cross-linkers, multifunctional (meth)acrylates include (meth)acrylates of polyols (ethylene glycol, butylene glycol, glycerol), trimethylolpropane, and acrylamides which are often employed. There are several reports on the SMPs based on the polyethylene oxide (PEO), cross-linked with maleic anhydride, glycerin or dimethyl 5-isophthalates [17]. Also, interpenetrating polymer network (IPN) of polyethylene oxide/poly(methyl methacrylate) (PMMA) was reported [20]. PEO/PMMA IPN systems show shape-memory properties with two transition temperatures: T_m of PEO and T_g of IPN.

Chemically cross-linked SMPs can be also synthesized by polyaddition and polycondensation reaction. Shape-memory behaviors were observed for thermosetting polyurethanes. Hu et al. reported the influence of the molecular weight on shape-memory behavior in polyurethane films [21]. Glycerin and 1,1,1-trimethylolpropane were applied as cross-linker for polyurethanes [12, 22, 23]. A clear improvement in creep and increase in recovery temperature have been observed due to the application of cross-linking [24]. Hybrid polyurethanes, cross-linked with Si–O–Si linkages, were made by Xu and coworkers [25]. Thermosetting polyurethanes were prepared by grafting of polyacrylamides and polyacrylates or by introducing hydrophilic groups into the cross-linked polyurethane backbone. Such networks showed both shape-memory and hydrogel properties [17].

SMPs based on epoxy polymers are a high-performance thermosetting resin possessing a unique thermomechanical property together with excellent shape-memory effect [10]. The epoxy SMP was synthesized from an epoxy resin, hardener, and additional linear epoxy monomer, by Leng et al. [26]. With the increase of active linear epoxy monomer, the T_g of such tailored network ranges from 37 to 96 °C. Shape-memory network was enabled by reaction of 3-amino-1,2,4-triazole with epoxidized natural rubber catalyzed by bisphenol-A [13]. The transition temperature of this network is the T_g, which could be controlled by the 3-amino-1,2,4-triazole content in the range between 29 and 64 °C [27]. The shape-memory IPN networks can be also prepared through successive polyaddition and polymerization. The example of such IPN is a system obtained from polyethyleneglycol dimethacrylate blended with star-shaped poly[(rac-lactide)-*co*-glycolide], which is first photopolymerized and later, the polyesterurethane network is formed using isophorone diisocyanate [13]. T_{trans} can be adjusted between −23 and 63 °C [28].

Another method of preparation of chemically cross-linked SMPs is a subsequent cross-linking of a linear or a branched polymer [14, 17, 29]. The SMPs created by postprocessing can be divided into two groups: cross-linked by means of cross-linking agent and cross-linked by electromagnetic radiation. An example of the first method is the application of peroxide to cross-link the linear polymers [11, 29–31]. Liu and coworkers used a dicumyl peroxide to cross-link semicrystalline polycyclooctene obtained by ring-opening metathesis polymerization containing unsaturated carbon bonds [32, 33]. The electromagnetic radiation with different wavelengths (γ-radiation, UV, neutrons, e-beam) is often used to cross-link polymers during postprocessing processes. The abovementioned polyethylene cured with gamma rays obtained by Rainer in 1964 was one of the first SMPs [6]. The γ-radiation has been also used to generate SMPs based on poly(ε-caprolactone) and its blends with poly(methyl vinyl siloxane) [11, 34]. Application of UV radiation to cross-linking SMPs requires incorporation of photo-initiators or light-sensitive monomers. For example, a covalent network with shape-memory properties was synthesized from poly(lactide-*co*-glycolide) and polyhedral oligomeric silsesquioxanes (POSS) using tetrathiol as cross-linking agent and 2,2-dimethoxy-2-phenylacetophenone as radical photo-initiator [35]. The use of functional, light-sensitive monomers, for example, monomers with acrylic groups, allows easy control of the initial shape and degree of cross-linking of the network formed by photo-curing [36, 37].

2.1.2 Physically Cross-Linked Polymers

For the physically cross-linked SMPs, the formation of phase segregate morphology is the fundamental mechanism behind the thermal-induced shape-memory behavior of these thermoplastic materials [10]. The molecular switch and physical cross-link are provided by separate phases of the polymer. A notable difference between physical and chemical cross-linking is that in the physically cross-linked polymers it is possible to remold the fixity phase after reaching the temperature at which the physical bonds disappear [11]. Physically cross-linked polymers can be further classified into linear polymers (block copolymers and high-molecular-weight polymers), branched polymers, and polymer complex [10]. Another classification takes into account the presence of the SMP amorphous or crystalline switching segments.

In glassy SMPs with amorphous switching segments, the hard amorphous domains act as physical cross-link via van der Waals forces, polar–polar interactions, hydrogen bonding, and other weak interactions. The T_g of the soft segments represents the transition temperature T_{trans} and is responsible for SME [38]. The shape-memory behaviors of this type SMPs depend on the chain length, structure, and arrangements of soft segment. Segmented amorphous shape-memory polyurethanes (PU) are the most important class of this type of SMPs. The hard segments of linear PU are formed either from a long-chain macro-diol with a higher thermal transition temperature or from diisocyanates and chain extenders [13]. The T_g of thermoplastic polyurethanes can be controlled in a wide range by using different kinds of monomers (aromatic or aliphatic diisocyanates) and chain extenders (low-molecular-weight diols or diamines) and by adjusting their amounts [17]. Precise control of PU composition and structure of soft and hard segments are necessary for effective shape-memory effect. The glassy hard segments, except physical cross-linking, should maintain the shape of material through hydrogen bridges or polar interaction. The soft segments could freely absorb external stress by unfolding and extending PU chains in these domains. The synthetic route for long polymer polyurethane chains (soft segments) and highly polar (hard) segments is based on the two-step procedure. In the first step, a polymeric diol reacts with diisocyanate to form the prepolymer. Next, this prepolymer reacts with low-molecular-weight chain extenders, like diols or diamines [39–42]. Another method of obtaining shape-memory polyurethanes based on joining block copolymers was proposed by Lendlein et al. [43]. He prepared SMPs with tunable T_{trans} between 14 and 56 °C, from copolymers of lactic acid with other monomers. Besides polyurethanes, many other SMPs with amorphous switching segments have been reported. Both homopolymers and their blends, like poly(methyl methacrylate), polynorbornene, poly(methylene-1,3-cyclopentane), poly(vinyl chloride) [17], as well as, numerous block copolymers like, for instance, poly(lactic-*co*-glycolic acid), allow to obtain separated phase systems [44, 45]. In the case of copolymer SMPs, the blocks from co-monomer with the highest transition temperature act as the hard segments (fixity phase), while the other ones are the soft segments (switching phase). In the case of SMPs prepared by copolymerization, the appropriate selection of monomers allows improvement in other properties like biodegradability, hydrophilicity, solvent absorption and diffusion, toughness, transition temperature, or activation shape-memory time [11].

The second group of physically cross-linked SMPs comprises polymers with crystalline switching segments. The temporary shape of these materials is fixed by crystallization of the soft domains, which occurs below T_g. The transition temperature region corresponding to T_m (melting of crystalline domains) is narrow, in contrast to the SMPs, with amorphous switching segments, which often show broad transition temperature range and usually requires difficult to achieve precise combination of soft segments [17]. Various physically cross-linked semicrystalline SMPs were reported. Typical examples are biodegradable poly(L-lactide-*co*-ε-caprolactone) [46], poly(ethylene oxide-*co*-butylene terephthalate) [47], and polystyrene-*co*-poly(butadiene) [38]. However, the largest group in this category are the thermoplastic segmented shape-memory semicrystalline polyurethanes. Polycaprolactone-diol (PCL-diol) has been extensively used for the synthesis of PU with crystalline soft phase [48]. The hard segments were incorporated in 4,4′-diphenylmethane diisocyanate (MDI)-based PU by application of such monomers as 1,4-butanediol [49], 4,4′-bis(2-hydroxyethoxy)biphenyl (BEBP) or 4,4′-bis(2-hydroxyhexoxy)biphenyl (BHPP) [50], and 1-octadecanol [51, 52].

2.1.3 Segmented Block Copolymers

Shape-memory effect in segmented block copolymers is based on different transition temperatures (T_g or T_m) of co-monomers [11]. The transition temperatures determine, which co-monomer will be switching phase (lower temperature) and which one will be fixity phase (higher temperature). Well-known example of switching phase co-monomer is lactic acid as PLA, but it cannot provide optimal SME without appropriate fixity phase. Only combined with ε-caprolactone as poly(l-lactide-*co*-ε-caprolactone) (PCLA) [46] or with glycolic acid as poly(lactic-*co*-glycolic acid) (PLGA) [44] shows superb SME. Similar relation between phases is also observed in polyurethanes, where reaction between diisocyanate and diol allows to obtain fixity phase with urethane groups and switching phase of oligoester [39–43]. Strong interactions between dipoles and hydrogen bonds ensure polarity of fixity phase, high enough to use PLA, or even polycaprolactone (PCL) as switching phase. Another example of segmented block copolymer with shape-memory effect is poly(ethylene terephthalate) (PET) as fixity phase with poly(ethylene dioxide) (PEO) as switching phase [47].

2.1.4 Cross-Linked Homopolymers

Shape-memory homopolymers have fixity phase and switching phase as block copolymers, but the difference lies in the presence of both amorphous and crystalline regions in one polymer. While crystals act as fixity phase and provide shape, physical bonds of amorphous chains (switching phase) react to appropriate temperature and reshaping occurs. Example of shape-memory homopolymer is semicrystalline PLA, which in addition to being SMP also is biocompatible and biodegradable [46, 53–55]. Unfortunately, shape-memory effect of PLA is limited to narrow temperature range. Also compared with the performance of polymer blends, block copolymers, and interpenetrating polymer networks, shape-memory effect of PLA homopolymer is limited.

2.1.5 Polymer Blends, Polymer IPN/Semi-iPN

There are two types of polymer blends with shape-memory effect: miscible and immiscible. Both of them are interesting for industrial applications, due to the fact that blending is easily implementable and can provide enhancement of mechanical and thermal properties. Miscible blends can be made from semicrystalline polymers like PCL and polydioxanone [56] or from semicrystalline and amorphous polymers like polyurethanes based on PCL with poly(vinyl chloride) [57] or phenolic resin [58]. Although miscibility theoretically causes one T_g of blend, different concentrations of each polymer in various regions differentiate local T_g. Immiscible blends like PCL matrix with poly(styrene-*b*-butadiene-*b*-styrene) (SBS) [59] or PLCA with PLGA [25] also represent shape-memory polymers.

Specific blends of miscible polymers with interlaced networks are known as interpenetrating polymer networks (IPNs). They can also exhibit shape-memory properties if aforementioned T_g issue is solved in similar way as for other miscible polymers. IPNs based on PLGA polyurethanes with poly(ethylene glycol) (PEG) dimethacrylates were proposed by Zhang et al. [28]. Other IPNs with acrylates were made of PMMA with PEO, where shape-memory effect was based on melting of PEO crystals, and poly(methyl methacrylate-*N*-vinyl-2-pyrrolidone) with PEG, where shape-memory effect was provided by hydrogen bonds [60, 61].

2.1.6 Supramolecular Polymer Networks, Hydrogels

SMPs obtained via supramolecular chemistry are based on non-covalent interactions such as hydrogen bonds, dipole–dipole bonds, or van der Waals forces. Great numbers of these interactions can provide better stability of polymer structure and act as fixity phase [62]. Despite this, thermal-induced dissociation of hydrogen bonds also provides shape recovery of the structure [63]. Also, supramolecular SMPs have distinctive dynamics of shape change response. Most notable studies on supramolecular SMPs include solutions with ureidopyrimidinone (UPy) in polyurethane elastomers [64] or polyacrylate copolymers [63]; α-cyclodextrin (α-CD) and polyethylene glycol (PEG) in PEG-α-CD [65]; PEG and acrylates in PEG-PMMA-*co*-(*N*-vinyl-2-pyrrolidone) [60, 61], PEG–PMMA-*co*-acrylic acid [66], and PEG–polymethyl acrylate [20]; and pyridine in polyurethanes [21].

Hydrogels, as polymers with hydrophilic groups, are able to change their structure, thanks to ability of absorbing significant amounts of water. Temperature is a stimulus, which has important role in mechanism of shape change. There are two types of hydrogels behaving conversely: lower solution critical temperature (LSCT) hydrogels and higher solution critical temperature (HSCT) hydrogels. While LSCT hydrogels are swollen at temperatures lower than LSCT and shrunken at temperatures higher than LSCT, HSCT hydrogels have inverted characteristic (swell above HSCT and shrink below HSCT) (Fig. 5).

First shape-memory hydrogels were obtained from stearyl acrylate [67], but shape-memory effect was not obtained immediately in both states. After achieving SMP

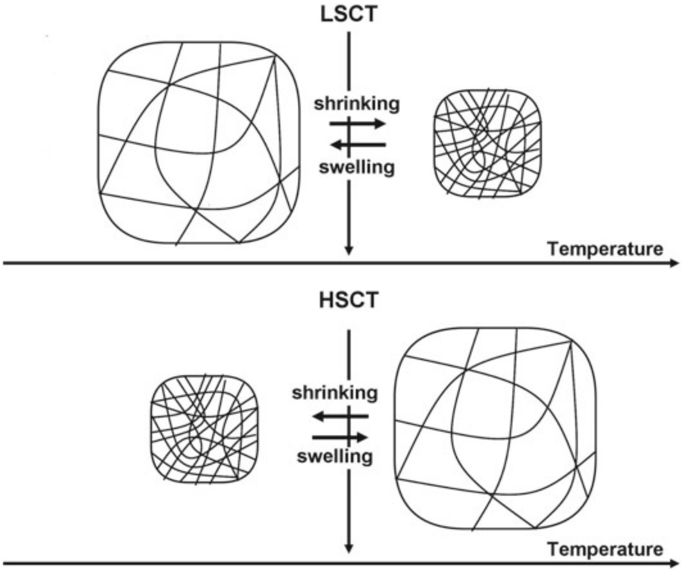

Fig. 5 Swelling/shrinking mechanism of shape-memory hydrogels

as swollen hydrogel, exchange of stearyl acrylate to methyl acrylate was necessary to create hydrogel with shape-memory effect in both (shrunken and swollen) states [68]. Other polymers common in hydrogel synthesis are polyacrylamide (PAAm) and poly(vinyl alcohol) (PVA). While PAAm is very useful in drug delivery, shape-memory effect of PVA is hindered by cleavage of hydrogen bond above 60 °C and in consequence, unstable structure of PVA [69, 70]. Success of PAAm results from its LSCT, which is close to temperature of human body, and from modulated gel technology technique [53] using interpenetrating networks of PAAm with *N*-isopropylacrylamide (NIPAAm), which provides shrinkage of hydrogel at elevated temperature.

2.1.7 Composites/Nanocomposites

Shape-memory polymer composites (SMPCs) differ from other structures because of fillers and nanofillers influence on shape-memory effect. SMPs have intrinsic low mechanical strength and shape recovery stress, which have largely restricted their applications [71]. A small amount of micro/nano-sized fillers can significantly improve these properties of SMPs. SMPCs not only exhibit improved mechanical properties and shape-memory properties but also possess novel properties like multi-shape-memory effect, indirect SME, gradient SME, two-way SME, and complicated movement SME, indirectly triggering SME [71]. SMPCs can also enable or enhance thermal stimuli-active effects, include electroactive effect, magnetic-active effect, water-active effect, and photoactive effect. Zheng et al. [72] reported poly(l-lactic acid fillers) (PLLA) matrix with shape-memory effect improved by β-tricalcium. Another PLLA composites with hydroxyapatite [73] and chitosan [44] also exhibit better shape-memory effect than PLLA homopolymer. Increased stiffness and decreased recoverable strain were observed for SMPs reinforced with glass and Kevlar [17]. Conducting SMPCs were prepared by blending carbon black or a conducting polymer with the SMP [74–76]. Incorporation of 3.3% of carbon nanofibers resulted in 200% increase in recovery stress of the SMPCs [77]. Application of carbon nanotubes or carbon black of similar size for reinforcement of polyurethanes gave the nanocomposites with increased shape fixity [78]. SMPCs with shape-memory effect triggered by magnetic field were obtained using magnetic nanofiller like Fe_2O_3 with a shell of oligo(ε-caprolactone) or Ni–Zn ferrite particles [79, 126] .

2.2 *Classification of Shape-Memory Function*

Shape-memory polymers may have different kinds of shape-memory effect. The most common memory effects are the one-way and two-way shape-memory, multi-shape, and multifunctionality.

2.2.1 One-Way Shape-Memory Effect SMP

The procedures in one-way shape-memory effect (1W-SMPs) consist of programming and recovery of a shape. Depending on chemical structure of polymer, its behavior can differ significantly. In Fig. 6, the process of programming and recovery of a shape is shown in a schematic way. In the beginning, a programming process is carried out during which the shape-memory polymer is subjected to such action to obtain its permanent shape. In the next stage, the SMP is distorted and the intentional temporary shape is fixed. The whole this process is based on heating up the sample, deforming, and cooling the sample, or as it is possible drawing the sample at a low temperature. Shape-memory effect is inducted by heating up the sample above a transition temperature (T_{trans}), and the recovery of SMP is observed. Solidification of the material is possible during cooling down the polymer below transition temperature; however, no recovery of the temporary shape is observed—what is called a one-way shape-memory effect. During next programming, including mechanical deformation, the polymer can obtain a temporary shape again but this new temporary shape is not identical as the first temporary shape. The best example of materials which have a thermo-responsive one-way shape-memory effect are hydrogels with hydrophobic, crystallizable side chains, and cross-linked poly(vinyl alcohols) [80, 81]. Hydrogels prepared from copolymerized acrylic acid and stearyl acrylate cross-linked with methylenebisacrylamide have a really strong temperature dependence in their mechanical properties. Polymers obtained in this reaction behave like tough polymers in temperature below 25 °C, but above 50 °C softening enables the materials to be extended up to 50%. 1W-SMPs behavior of poly(cyclooctene) that was cross-linked through a free-radical reaction using dicumyl peroxide was reported [32, 33]. What is important is the establishment of a provisional shape on cooling as well as quick improvement to the basic form upon heating. Besides, it was also proposed that cross-linked poly(cyclooctene) reveals crystallization-induced elongation and melting-induced contraction on heating, which can be explained by thermo-reversible actuation. The melting temperature of sample (T_m) can be customized by change of the quantity of dicumyl peroxide used for the cross-linking stage. Poly(cyclooctene) has a stable molten–rubbery plateau above the T_m, which provides effortless deformation and reacts as the transition temperature for shape-memory step, as well as a crystallization temperature (T_c) close to room temperature that lets fast crystallization process and efficient fixing of a temporary shape [82].

2.2.2 Two-Way Shape-Memory Effect SMP

Recently, two-way convertible shape-memory polymer materials (2W-SMPs) are greatly advisable for many applications [83–85]. Nowadays, some polymers have been investigated for two-way shape-memory properties, such as liquid crystal elastomers and photo-deformation polymers. Variety from the mechanism of 1W-SMPs, the 2W-SMPs process in liquid crystal elastomers and photo-deformation materials is imputed to the conversion of anisotropic polymer chain conformation and

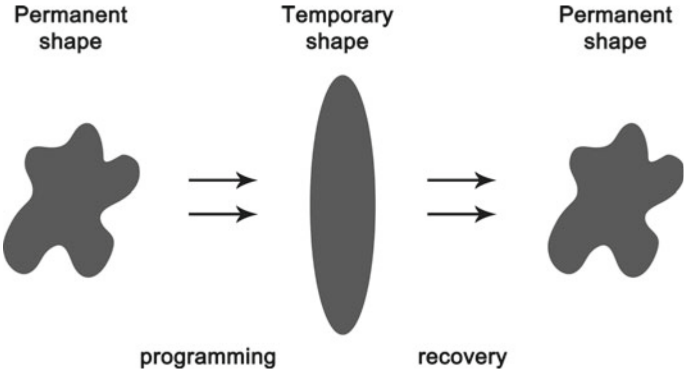

Fig. 6 Schematic picture of the thermally induced one-way shape-memory effect

light-stimulated phase transitions (Fig. 7) [86–89]. Shape change gel layer is one of the samples with a thermally caused two-way shape-memory effect. Discussed gels include two types of layers: a thermosensitive control layer and a substrate layer which is not sensitive to changes in variables temperature. The first one consists of an ionic gel prepared from the *N*-isopropylacrylamide and sodium acrylate cross-linked with *N, N′*-methylenebisacrylamide. During the temperature exceed of 37 °C, the control layer shrinks while the substrate layer does not change. For connecting both varied layers, one part of the control layer includes cross-linked copolymer which is exposed to an aqueous solution of acrylamide. Next, the acrylamide is polymerized by the use of a radical initiator to form diffuse chains. The pronounced variation in shape of gels is convertible, and the system can reverse between two defined shapes depending on the reaction conditions (below or above the transition temperature) [90] (Fig. 8).

Wang et al. reported the application of homopolymers and copolymers of ε-caprolactone and ω-pentadecalactone with cocrystallizable monomeric units for the composition of 2W-SMPs. The thiol–ene cross-linking system exposed two-way reversible 2W-effects under stress-free and stress conditions. The propulsion temperature of the two-way shape-memory effect under stress-free condition can be adapted in an extensive scope using suggested prepolymers by photo-cross-linking with a multifunctional cross-linker [91].

The shape-memory elastomer with a pre-stretched in stencil is checked. Designed material shows 2W-SM effect in reply to alterations in temperature without the need of an unchanged permanent exterior load [92]. Chen et al. prepared laminated composites with SMPs membrane and elastic polymers membrane. It is 2W-SM behavior in which the mechanism of shape-memory is ascribed to the release of elastic strain of SMP layer upon heating, and the recovery of elastic strain caused by the bending force of substratum membrane upon cooling [93].

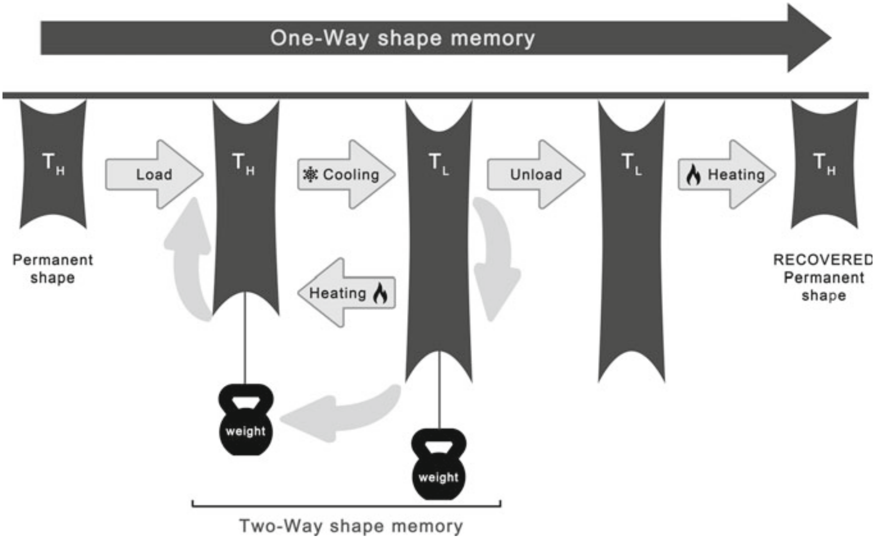

Fig. 7 Schematic showing the difference between the one-way and two-way shape-memory effects

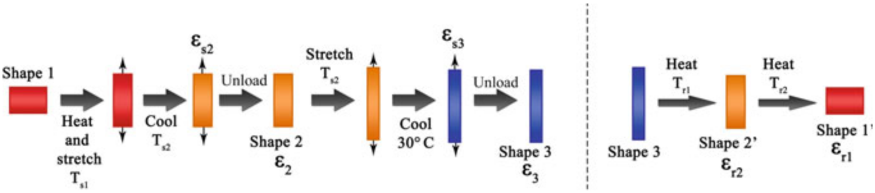

Fig. 8 Schematic of multi-shape-memory effect

2.2.3 Triple-Way Shape-Memory Effect SMP

Triple-way shape-memory polymers (3W-SMPs) can change forms twice and can fix two shapes compared to its permanent and initial shape. The 3W-SMPs comprise a cross-linking phase and two independent phases related to two different conversions which contain programming and recovery cycles. The programming stage of 3W-SMPs commences with heating the sample above both transitions and inducing distortion. Next, maintain the deformation while cooling the polymer to fix form at a temperature between the two conversions. Ware et al. reported a novel 3W-SM system contained both permanent covalent cross-links and supramolecular hydrogen bonding cross-links. The described effect comes into being from the connection of the glass transition of methacrylate copolymers and the dissociation of self-complementary hydrogen bonding moieties providing easy control of both glass transition temperature (T_g) and cross-link density [94]. Bellin et al. have shown the 3W-SM effect in systems containing two crystalline switching phases, while others have linked an amorphous phase with a crystalline switching phase [95]. Recently, Xie and coworkers have shown quadruple shape-memory utilizing the broad transition of perfluorosulfonic acid ionomers [96]. The composites capable of being the 3W-SMPs stand to increase the complexity of appliances utilizing the shape-memory effect by enabling multistage complex recovery profiles were prepared [97, 98]. Recently, the 3W-SM epoxy composites consisting of two layers of well-separated glass transition temperatures have been successfully synthesized. The various amounts of nanosilica particles entered into the matrix are able to cause different glass transition temperatures of the epoxy composites [99–101]. The application of 3-aminopropyltriethoxysilane as a chemical modifier for graphene oxide into silanized polyurethanes gives two different molecular weights and chemical compositions by sol–gel reactions. The research has proven that the materials act as multifunctional cross-links as well as supporting fillers and significantly enhanced the glassy and rubbery state moduli, glass transition temperature, and 3W-SM properties [102].

2.2.4 Multi-Way Shape-Memory Effect SMP

In last time, it has been shown that polymers with a wide thermomechanical transition temperature range can have a multi-shape-memory effect what is related to a shape recovery process with one or more intermediate shapes between the temporary shape and permanent shape. Actually, such a condition for the multiple SME is not necessary, the use only one single transition to gain that as well. It is possible because one single transition should be considered as a combination of many small transition steps, so in fact, the multi-SME is a common property of polymers [95, 96, 103, 104].

Prathumrat and coworkers prepared benzoxazine–urethane copolymers with multiple shape-memory behaviors. These polymers exhibited great shape fixity values of 70–96% for the first temporary shape and 83–99% for the second temporary shape. Regarding shape recovery, synthesized copolymers also had significant values of 88%–96% for the first temporary shape and 97–99% for the original shape. What is important is that the proper curing conversion influences the multiple shape-memory behaviors of copolymers—curing conversion at roughly 70% was adequate for this sample to demonstrate a multi-shape-memory effect [105].

Poly(*l*-lactide) (PLLA)/poly(methyl methacrylate) (PMMA) blends with wide glass transitions are known as an optional matrix to design multiple shape-memory polymers. The temperature range of the symmetric 50% PLLA/50% PMMA blend softly moved from 70 to 90 °C for stretching temperatures increasing from 65 to 94 °C, and certify for a meaningful temperature memory effect. In the case of asymmetric compositions with 30 and 80% PMMA, polymer also presented a “temperature memory effect”; however, the symmetric blend greatly was revealed as the most effective composition for multiple shape-memory applications. The symmetric blend can be a really interesting material for future developments because its programming step designed with two successive stretchings within the wide glass transition provided high multi-shape-memory effect with tunable intermediate shapes [106].

2.3 Classification of Shape-Memory Polymers by Type of Stimulus

Shape-memory polymers (SMPs) as a type of significant stimuli-responsive materials can receive their original and initial shape upon exposure to external stimuli. The SMPs are stimuli-sensitive polymers with the ability to transmit a large recoverable deformation upon the application of external impulses. So far, known methods of stimulus can be generally divided into heat, electricity, light, magnetism, moisture, etc. Nowadays, SMPs are attracting increasing international research attention and there is huge progress in developing stimuli-responsive shape-memory polymers with potential applications in many fields such as biomedical devices, aerospace, textiles, bionics engineering, and energy, electronic engineering.

2.3.1 Stimulation by Temperature

The characteristic thermo-responsive SMPs are really universal, frequent, and occurring for polymers [32, 33, 107, 108, 109], in which vitrification or crystallization of polymer chains is adapted as a momentary cross-link to stabilize the change in the dimension of forms and the shape recovery is induced by heat [110]. Thermo-responsive SMPs can gain their original and initial figure and form when they are warmed above T_g for amorphous polymer and above T_m for crystalline polymers. The characteristic thermomechanical cycle of SMPs is illustrated in the following steps in Fig. 9 [60, 61, 111]. The whole process consists of formation of the SMPs into an original shape, and next stage should be heating the SMPs above the thermal transition temperature (T_{trans}) (depending on the type of polymer it is a glass transition temperature (T_g), or a melting temperature (T_m)), and change of shape of the SMPs using an external force and finally cooling under T_{trans}.

French CdF Chimie Company first developed polynorbornene with a T_g range of 35–40 °C what next was introduced to the industry by the Japan Nippon Zeon Company [13, 112]. Styrene-butadiene SMPs with T_g of about 60–90 °C were synthesized by the Asahi Company [113]. Furthermore, the Cornerstone Research Group (CRG), Inc. has expanded some thermosetting SMPs [114], which comprising a one-part epoxy SMP with a T_g of about 90 °C, a two-part epoxy SMP with a T_g

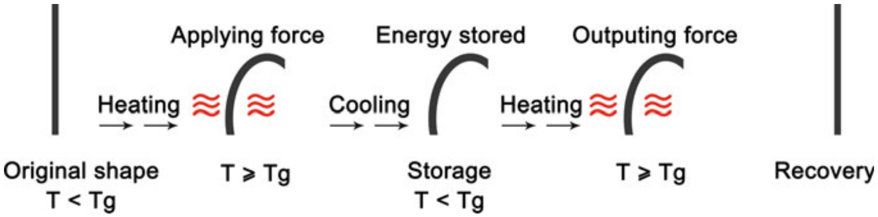

Fig. 9 Schematic of shape-memory effect during a typical thermomechanical cycle

of about 104 °C, and also a cyanate ester SMP with a high T_g range from 135 to 230 °C. Moreover, Composite Technology Development (CTD), Inc. has proceeded a thermosetting epoxy SMP with a T_g of about 113 °C. In addition, it is known that a series of thermoplastic polyurethane SMPs is commercially available from Mitsubishi Heavy Industry, with the T_g ranging from 40 to 55 °C. Lamm et al. prepared sustainable epoxy resins derived from plant oils with thermo- and chemo-responsive SM maintenance which were obtained using plant oils and cellulose nanocrystals (CNCs). Epoxidized soybean polymers (PESBMA) were grafted from CNCs using surface-initiated atom transfer radical polymerization (SI-ATRP) where the polymer was combined with P(ESBMA-co-SBMA) copolymer. P(ESBMA-co-SBMA) has a T_g of 13 °C, versus 20 °C for CNC-g-PESBMA [115]. Truong et al. [116] prepared thermo-responsive SM poly(ε-caprolactone) (PCL) networks with multiple pendant double chains at both link ends which are used to cross-link with multi-thiol compounds via photo-initiated thiol–ene reactions. SM features can be also changed through modification in the number of alkene side groups at the poly(ε-caprolactone) and thiol cross-linker structure. The developed thermoset materials exhibit great thermo-responsive shape-memory efficiency by changing the operating temperature below or above the melting temperature of crystalline poly(ε-caprolactone) segments, which changes in the range of 34–40 °C, and the highest shape retention and recovery factors can get 98–100% [117].

2.3.2 Stimulation by PH Changes

In this section, shape-memory material-stimulated pH change will be shown. The change of polymer properties occurs when in present ionizable functional groups' material gets ionized and obtains charge in certain pH. The shape-memory polymer chains between like-charged groups lead to repulsion force and from here widen their dimension and finally at the moment when the pH changed, the repulsion disappears and the materials come to the original shape and position. The reversibility and changes to this material can be treated as a disadvantage that comes into being with the use of pH-responsive materials because it commonly needs solvent replacement, which is not good for the environment. Despite these restrictions, pH-responsive polymers have shown promise in many areas such as drug delivery and microprocessing [82]. pH-sensitive SMPs were prepared by cross-linking the β-cyclodextrin-modified alginate (β-CD-Alg) and diethylenetriamine-modified alginate (DETA-Alg). The pH reversible β-CD-DETA inclusion complexes operate as a convertible phase, and the cross-linked alginate serves as a fixing phase. It is shown that this material can be processed into temporary shape at pH 11.5 and recover to its initial shape at pH 7. The recovery relation and the fixity ratio were accordingly 95.7 ± 0.9% and 94.8 ± 1.1% [118]. Han et al. proposed to use pH as a stimulus for SMPs for its convenience and safety in medical applications because the shape transition pH value is almost to that of our body fluid and this pH-triggered shape-memory effect is convenient and safe to use. It is also indicated a polyurethane with a pH-sensitive SM effect. First, a series of polyurethanes were successfully synthesized through solution polymerization of polyethylene glycol, dimethylolpropionic acid (DMPA), and 4,4′-diphenylmethane diisocyanate (MDI). These polymers PEG-*i*-MDI-DMPA ($i = 20, 30, 40\%$) and *i* represent the weight content of PEG in the polymers. The results of SM testing showed that the PEG-30%-MDI-DMPA has both the 3-SM effects. In PEG-30%-MDI-DMPA, the glass transition of PEG and the association and disassociation of carboxylic dimers act as two switches to control the 3-SM conversion, while the carboxylic dimer is affected by pH values to associate in acidic solutions (at pH 2) and dissociate in alkaline solutions (at pH 9) to induce the pH-sensitive shape-memory [119], which developed pH-responsive SMPs by blending poly(ethylene glycol)-poly(ε-caprolactone)-based polyurethane (PECU) with functionalized cellulose nanocrystals (CNCs). CNCs were functionalized with pyridine (CNC-$C_6H_4NO_2$) through hydroxyl substitution of CNCs with pyridine-4-carbonyl chloride and with carboxyl groups (CNC-CO_2H) via 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) conjunctived surface oxidation. At a high pH, the CNC–$C_6H_4NO_2$ had inviting interactions from the hydrogen bonding between pyridine groups and hydroxyl moieties at a low pH, the interplays reduced, or disappeared due to the protonation of pyridine groups, which are a Lewis base. The shape-memory function of the nanocomposite network was only dependent on the pH variation of the environment [99–101]. Xiao et al. reported novel multi-responsive polyacrylamide-(PAAm)-based cross-linked copolymer (PAAm-TSMP) hydrogel which is characterized by pH-sensitive and photo-sensitive at the same time. pH-sensitive of hydrogel is possible by adding active group in the structure (positively and negatively ionized). Polyacids and polybases are the only available groups because the first ones accept protons at low pH, producing gel shrinkage, while polybases donate protons at high pH (Fig. 10) [120].

2.3.3 Stimulation by Water/Solvent

Yang et al. discovered this particular effect. The glass transition temperature (equal to 35 °C) of an ether-based polyurethane shape-memory polymer (SMP) has been found to decrease significantly after immersion in water. The results reveal that the hydrogen bonding between N–H and CO groups is weakened by the absorbed water. Moreover, the H_2O absorbed into the SMP can be in two forms (free water and the bound water). Bound water notably reduces the T_g in a linear way and has an influence on the uniaxial tensile behavior, while the effect of free water is negligible [121]. Also, Du and coworkers studied recovery time of poly(vinyl alcohol) in different solvents, and the results presented that the best recovery time for water is immersed. This kind of stimulation of shape-memory polymers is very interesting because it does not need to apply heat to obtain shape-memory conversion [122]. Diffusion of water, acetone, and ethanol into a polyether urethane matrix has been studied by Ghobadi et al. It was revealed that even after 1 week, putting the samples in the corresponding solvent baths, neither enthalpy relaxation nor monomer release could occur because of the lack of hydrophilic groups. Dry and physically (hydrolytically) aged samples have been conducted to different maximum strains and different holding times. It could be

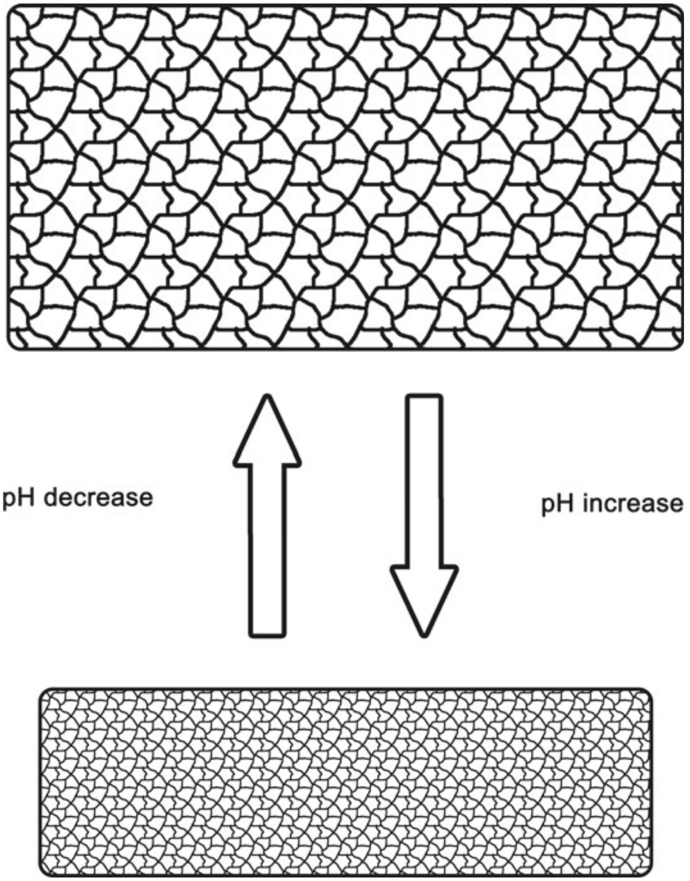

Fig. 10 Swelling and shrinkage properties in ionic-based hydrogel by change in pH

indicated that the shape fixation of physically (hydrolytically) aged polymers do not differ from dry samples. However, physical (hydrolytic) aging resulted in an obvious better and faster shape recovery ratio as a result of additional physical cross-links [123].

2.3.4 Stimulation by Magnetic Field

Magnetic field-sensitive polymer can be achieved by preparing nanocomposites loaded with specific magnetic nanoparticles. The magnetic nanofillers produce heat when they are subjected to magnetic field. The shape of nanocomposites is obtained in the same way as that in the thermally inducted one. Recovery of shape is fixed by the Joule effect at a time when the sample is exposed to exterior magnetic field.

Via magnetic fields can induce internal heating within SMP composites containing magnetic nanoparticles (Fe_2O_3, Fe_3O_4, Ni, etc.) [47, 79, 124] which are known as ferromagnetic shape-memory polymers. This type of composites can actuate at higher frequencies (up to 1 kHz) because the actuation energy is transmitted via magnetic fields and is not hindered by the relatively slow heat transfer mechanism [125]. Iron oxide (Fe_3O_4) particles are known as magnetic fillers which induce heating when exposed to a magnetic field. Incorporating them into an SMP is a known practice to fabricate a shape-memory composite for which the shape recovery can be actuated remotely via magnetic field. Leng et al. analyzed that the micro-sized Ni powder formed chains under a weak external magnetic field, which can strengthen significantly the electrical conductivity in the chain direction. Schmidt et al. and Zrinyi et al. added magnetite to poly(butyl acrylate), polylactide, and polycaprolactone matrixes [126–128]. For instance, Fuhrer and coworkers used magnetosensitive particles in shape-memory hydrogels [129]. One class of biodegradable polymer composite was elaborated with an electrospinning process using poly(ε-caprolactone) (c-PCL) as the basis and carbon nanotubes as the supplement coated with Fe_3O_4. The fibers showed an excellent SM behavior stimuli by hot water and by an alternating magnetic field [130].

2.3.5 Stimulation by Light

Light stimuli shape-memory polymer has meaningful advantage in comparison with the thermal stimuli shape-memory polymer which results from the fact that photoactivation does not produce tissue damage as could be produced by heat treatments. Thanks to this behavior, light activation is very attractive for biomedical application. Jiang et al. reported that there are three kinds of photoresponsive molecules [131]. The division created by them is as follows: molecules which have ability to change their configuration from *trans* to *cis* and contrariwise at the time when they are exposed to UV light, and molecules obtained by cationic inducted polymerization and photoresponsive molecules. The configuration capable of producing shape-memory effect with photo-reactive molecules is presented in Fig. 11. Black dots in Fig. 11 mean molecules which are the switch phase and the covalent bonds between polymer chains are the fixity phase. When the sample is in the presence of electromagnetic radiation $\lambda > \lambda_{\mathrm{trans}}$, the photo-reactive molecules form dimers that are accountable to fix the temporary shape and dimension. At the moment when the shape-memory polymer is exposed to another radiation $\lambda < \lambda_{\mathrm{trans}}$, it can recover its original shape (Fig. 12). Lu et al. developed a photoactive SMP by incorporating boron nitride and carbon nanotube, which reportedly have a synergistic effect, into an epoxy-based SMP. The use of these additives improves the thermal conductivity of the material and its infrared light absorption, while the transferred nitrides aided in the heat transfer to the SMP matrix, resulting in faster shape-memory recovery [132]. Inam and coworkers reported that infrared light can be used to produce indirect shape-memory polymer matrix with addition of carbon black or carbon nanotubes. These reinforced nanofillers increase the thermal conductivity of the polymer. The behavior of these

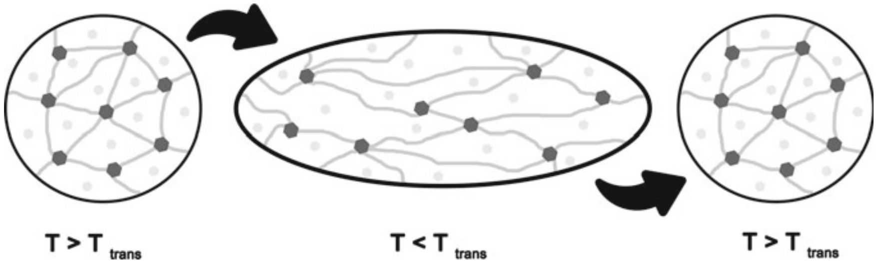

Fig. 11 Occurring processes in shape-memory polymer stimulated by magnetic field

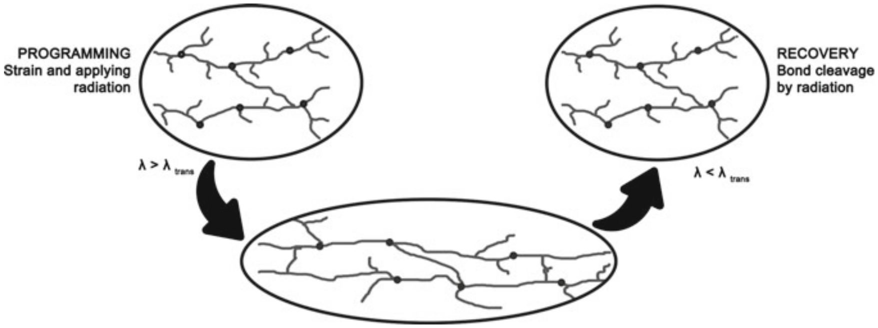

Fig. 12 Molecular mechanism of photoinduced shape-memory effect at various states

polymers is analogous to the thermal-induced shape-memory mechanism but the recovery appears when the polymer is irradiated with infrared light [133]. Shou et al. also developed near-infrared (near-IR) light-responsive SMPs by incorporating gold nanorods (AuNRs) into a poly(ε-caprolactone) matrix [134]. The second method, as reported by Lendlein et al., involves the introduction of cinnamic groups, which can be set in motion by ultraviolet light (UV). In research applied, two other configurations of cinnamic acid in polymer matrix permitted obtained SM network stimulated by light [135].

2.3.6 Stimulation by Oxidation/Reduction

SM effect in hydrogels is mostly stimulated with use of a redox reaction [136]. Aoki et al. prepared cellulose derivatives by esterification of cellulose acetate (CA) with mercaptoacetic acid (MA). The CA-MA samples thus synthesized showed a sol–gel transition in solution and a shape-memory behavior formed through adequate redox treatments due to the reversible, cross-linking association and dissociation between mercapto groups [137]. Studies showed that host (poly(acrylic acid) (pAA) modified with beta-cyclodextrins (pAA-β-CDs))—guest (ferrocene (pAA-Fc)) are complementarity and multipoint cross-links have cooperative roles in forming the supramolecular polymer hydrogel. The reversible gel–sol transitions were achieved by adding an oxidant (NaClO aq.) and then a reductant (glutathione, GSH). What is more interesting is that the self-healing property of the hydrogel can be controlled by redox reactions. This study represents the first example of self-healing of supramolecular polymeric materials based on host–guest interactions and will further prompt the applications of host–guest recognition motifs in advanced supramolecular polymeric materials [138]. Moreover, redox-stimuli shape-memory matrix was obtained by cross-linking β-cyclodextrin-modified chitosan (β-CD-CS) and ferrocene-modified ethyleneimine polymer (Fc-PEI). The obtained β-CD-CS/Fc-PEI has two cross-links: convertible redox-sensitive β-CD-Fc complexes and covalent cross-links as fixing stages. The analyses showed that studied system can be processed into interim forms as needed in the reduced state and recovers its initial shape after oxidation reaction. In both cases, the recovery ratio and the fixity relation are more than 70% [139].

2.3.7 Multifunctionality

Multifunctionality is a set of material properties, which contains shape-memory effect and at least one other functionality (e.g., optical, permeable, thermal chromic, biodegradable) non-linked with SME [140]. Combining SME with phase-changing materials (PCM) can result in wrinkle-free textiles. Addition of active fillers like carbon black or carbon nanotubes to SMP will provide actuation through electric field [75, 76]. Similar actuation in magnetic field can be obtained with magnetically active fillers like iron oxide [79, 107]. Also, drug delivery systems made of SMP and drug are examples of multifunctionality. Radio-opacity of medical can be obtained via adding barium sulfate or zirconium oxide [141]. All types of modifications can provide attractive multifunctional SMP. The variety of multifunctional SMPs results from unique requirements, which are designed for certain applications.

3 Main Applications of SMP

Shape-memory polymers possess great functionality in shape-memory effect, and natural consequence is their wide range of possible applications. Most notable of them are in four fields: spacecraft, medical, textile, and engineering. Medical applications benefit from functions of SMP such as deployment, fixation, and actuation.

Deployment function plays an important role in SMP foams, which can be useful in treatment of aneurysms, especially embolic treatment [142]. Idea of SMP foam usage as device is still in the test phase, but delivery of compressed foam and its size increase after laser stimulation are still interesting solutions. Another application of deployment function in medicine is SMPs as cardiovascular stents [143]. They provide protection of small blood vessels from collapse, thanks to SME triggered by temperature change or polymer’s hydration [144, 145]. On the other hand, intracranial aneurysms can be treated with special SMP coils as blood flow reducers, which are able to help in formation of thrombus [146].

Fixation function of SMPs is useful in SMPU-PCL orthodontic wires, which are competitive alternative for traditional, metallic wires [147]. Their main advantage is better aesthetic appearance in comparison with metallic ones. SMP wires also provide low density, transparency, easy processing and, of course, high shape recovery. Another application, which benefits from fixation function of SMPs, is medical casts. Rousseau et al. proposed SMP medical cast with adjustable diameter and ability to fit the shape to broken limbs. These casts also provide easy and low-cost processing, recyclability, permeability, and lightweight [148]. Actuation function is usually related to artificial muscles, which in case of SMPs can be used in endovascular thrombectomy. Takashima and coworkers [149] obtained nitinol-core/SMP-shell artificial muscle with preprogrammed and thermally activated corkscrew form. This kind of micro-actuator can be very promising for clot and thrombus removal. SMPs with actuation function are versatile solutions, similarly attractive for spacecraft and engineering fields. Harris et al. reported liquid crystal elastomers (LCE) with shape-memory effect allowing to obtain mechanical energy from light energy [150]. These SMP actuator devices are obtained from azobenzene units in twisted and densely cross-linked structure, which results in high elastic modulus ($\approx$1 GPa) at room temperature. Other possible applications attractive for spacecraft and other engineering fields are systems like micro-valves and micro-transducers [151, 152] which are microelectromechanical systems (MEMS) providing temperature-adjustable flow through the tube. Also, stimuli-responsive SMPs can be suitable in applications such as antennas in spacecraft, morphing wing structures, or wrinkle-free fabrics [153].

Self-healing is another SMPs function, which can be widely applicable. Self-healing mechanism of SMPs can be based on reverse plasticity [154] or combination of different shape-memory effects in two-component blends called SMASH (shape-memory assisted self-healing) [155].

Group of SMPs dedicated for textile industry is based on special fibers—shape-memory fibers (SMFs). The SMFs can be obtained via different spinning methods (melt, dry, and wet) and their uniqueness results from outstanding temperature-response performance in their elastic modulus and recovery parameters [51, 52]. These properties allow to use SMFs in many textile applications, which are presented in Fig. 13.

4 Conclusion

Shape-memory polymers are one of the most intensively developing areas of materials science and technology providing excellent opportunities for scientific discoveries in the field of molecular design, polymer synthesis, functionalization and processing of polymer blends, copolymers, composites, and nanocomposites. The properties of SMPs, such as easy processing, large recoverable strains, tunability, low weight, different types of external switching stimulus, easy to control a wide range of transi-

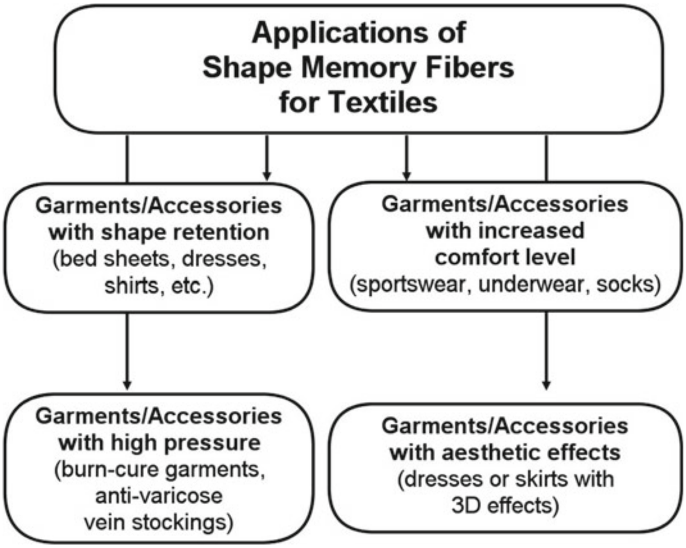

Fig. 13 Classification of shape-memory fibers' applications with examples

tion temperatures, switching at body temperature, biocompatibility, and biodegradability, makes them superior in comparison to shape-memory alloys. Due to these excellent properties and the low-cost and commercial availability of most of the polymers used as shape-memory materials, the applications of SMPs will increase in near future, within the numerous, new fields, like, for example, biomedical smart materials, advanced mechanical sectors, mechatronic, and power generation. However, great research efforts are still required to obtain SMPs with precisely controlled response and better durability and reliability over those offered by currently available technologies. In order to increase the versatility of SMPs, it is necessary to solve the major drawbacks of SMPs, which are associated with their relatively lower recovery stress/forces, long response time, lower cycle life, and weak material stability.

In this chapter, the literature reports on shape-memory polymers have been reviewed highlighting the classification of shape-memory polymeric materials and most important concepts for these types of smart materials. The main emphasis was put on the development of many types of SMPs categorized by the different classification criteria, with particular regard to polymer type and structure, shape-memory function, and external stimulus.

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