Shape-Memory Polymers and Multifunctional Composites

Edited by Jinsong Leng · Shanyi Du

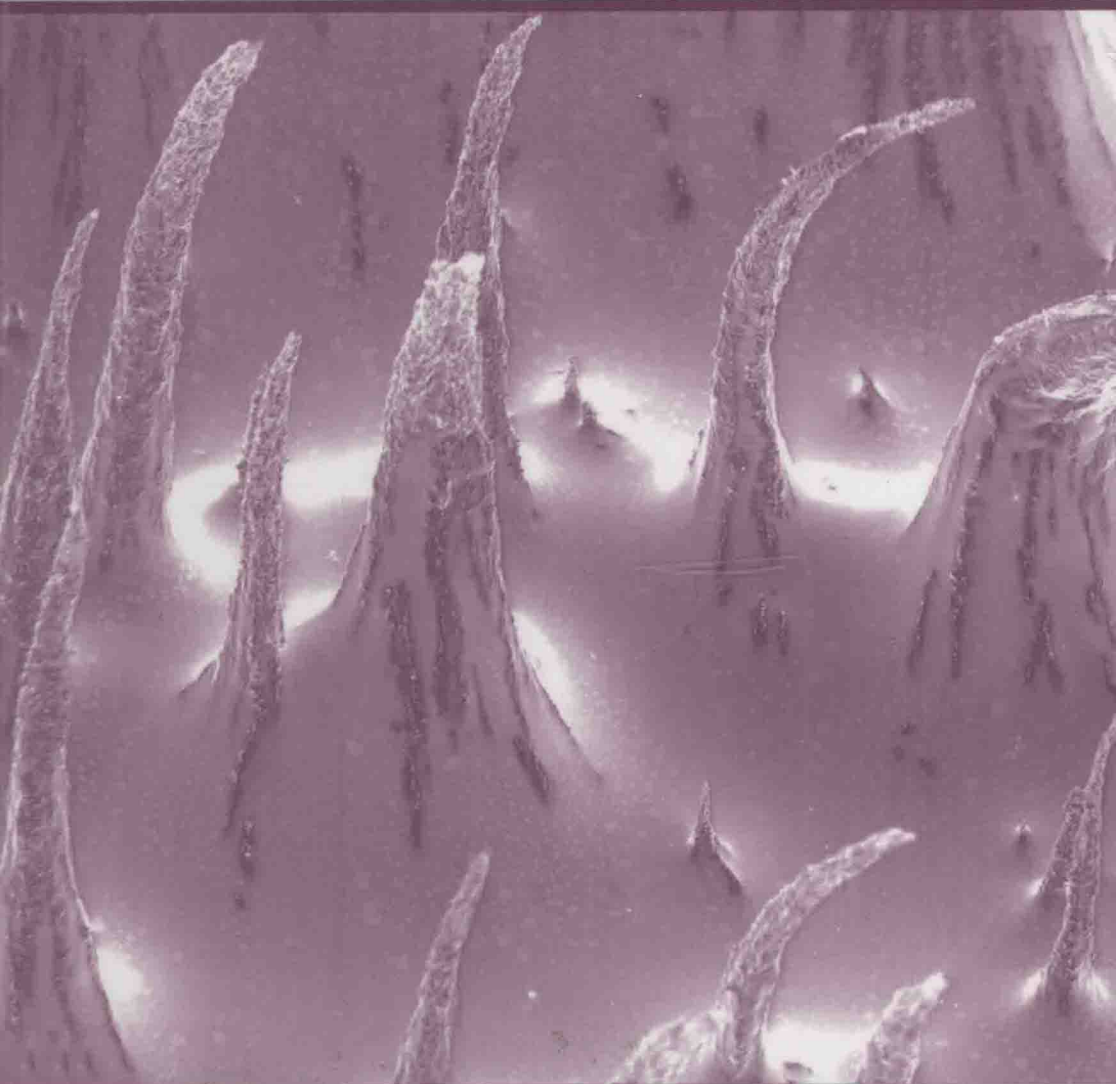# Shape-Memory Polymers and Multifunctional Composites

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Preface

Shape-memory polymers (SMPs) undergo significant macroscopic deformation upon the application of external stimuli (e.g., heat, electricity, magnetism, light, and moisture). Since the discovery of SMPs in the 1980s, international research interest in the shape-memory effect of polymers has grown rapidly in different fields. There has been a rapid development of SMPs and a number of achievements have been reported. It will not be an exaggeration to say that the appearance of the shape-memory effect in polymers is one of the revolutionary steps in the field of active materials research. Recently, the underlying behavior in response to an external stimulus, structures and applications of SMPs has increasingly drawn the attention of researchers. Due to their novel properties, SMPs can be used in a broad range of applications from outer space to automobiles, and to address challenges in advanced aerospace, and mechanical, bionic, and medical technologies.

This book aims to provide a comprehensive discussion of SMPs, covering the foundations and applications of all aspects of SMPs and their composites. Chapter 1 provides an overview of SMPs, where the different types of materials showing the shape-memory effect are described and some basic concepts are discussed. The definitions, architectures, and fundamental principles of different functions of SMPs are explained. Some examples, including direct and indirect triggering of SMPs, the light-induced dual shape effect, and triple-shape polymers are also presented. Chapter 2 presents the structural requirements and provides an overview of the variety of chemical compositions of SMPs. The synthesis, processing, and particular features of covalently cross-linked SMPs and thermoplastic SMPs are discussed in detail. Many practical applications require constitutive models that describe the three-dimensional finite deformation. Chapter 3 therefore presents thermomechanical constitutive models of SMPs based on viscoelasticity and phase transition. SMPs have been extensively studied in the last decade, especially their thermo-mechanical and electrical characterizations. Chapters 4 and 5 elaborate on these essential properties. Chapter 6 is devoted to an investigation of some actuation methods of SMPs, such as heat, electricity, light, magnetism, and moisture. These novel actuation approaches play a critical role in the development of multifunctional materials that not only exhibit the shape-memory effect but also perform particular functions. Chapter 7 elaborates on how SMP composites filled with particles or fibers may overcome the poor mechanical properties of pure SMP materials. Then, Chapters 8 through 12 present some typical potential applications of SMPs. In recent years, SMPs and SMP composites have been developed and qualified especially for deployable components and structures in aerospace. Chapter 8

describes the applications, which include hinges, trusses, booms, antennas, optical reflectors, and morphing skins. Chapter 9 discusses SMP foam technologies and identifies their potential applications in space, as well as their commercial and biomedical applications. Chapter 10 presents shape-memory fibers based on SMPs that can also be implemented to develop smart textiles that respond to thermal stimulus and may be used in future smart clothing. In recent times, a number of medical applications have been considered and investigated. SMP materials have been found to be biocompatible, nontoxic, and nonmutagenic. Chapter 11 describes SMP materials and their potential and existing medical applications. Finally, Chapter 12 presents some novel applications of SMPs, and proposes potential directions and applications of SMPs for future research and development.

Last but not least, we would like to take this opportunity to express our sincere gratitude to all the contributors for their hard work in preparing and revising the chapters. We are indebted to all members of the team as well as to those who helped with the preparation of this book. Finally, we wish to thank our families and friends for all their patience and support.

In addition, we hope that this book will be a useful reference for engineering researchers, and for senior and graduate students in their relevant fields.

Editors

Jinsong Leng is a Cheung Kong Chair Professor at the Centre for Composite Materials and Structures of Harbin Institute of Technology, Harbin, China. His research interests include smart materials and structures, sensors and actuators, fiber-optic sensors, shape-memory polymers, electro-active polymers, structural health monitoring, morphing aircrafts, and multifunctional nanocomposites. He has authored or coauthored over 180 scientific papers, 2 books, 12 issued patents, and has delivered more than 18 invited talks around the world. He also serves as the chairman and as a member of the scientific committees of international conferences. He served as the editor in chief of the *International Journal of Smart and Nano Materials* (Taylor & Francis Group) and as the associate editor of *Smart Materials and Structures* (IOP Publishing Ltd). He is the chairman of the Asia-Pacific Committee on Smart and Nano Materials. Professor Jinsong Leng has been elected as an SPIE Fellow in 2010.

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Overview of Shape-Memory Polymers

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1.1 Introduction

The ability of polymers to respond to external stimuli such as heat or light is of high scientific and technological significance. Their stimuli-sensitive behavior enables such materials to change certain of their macroscopic properties such as shape, color, or refractive index when controlled by an external signal. The implementation of the capability to actively move into polymers has attracted the interest of researchers, especially in the last few years, and has been achieved in polymers as well as in gels. Sensitivity to heat, light, magnetic fields, and ion strength or pH value was also realized in gels [1]. In nonswollen polymers, active movement is stimulated by exposure to heat or light and could also be designed as a complex movement with more than two shapes.

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Besides their scientific significance, such materials have a high innovation potential and can be found, e.g., in smart fabrics [2–4], heat-shrinkable tubes for electronics or films for packaging [5], self-deployable sun sails in space-crafts [6], self-disassembling mobile phones [7], intelligent medical devices [8], and implants for minimally invasive surgery [9–11]. These are only examples and cover only a small region of potential applications. Actively moving polymers may even reshape the design of products [12]. In this chapter, different classes of actively moving materials are introduced with an emphasis on shape-memory polymers. The fundamental principles of the different functions are explained and examples for specific materials are given.

1.2 Definition of Actively Moving Polymers

Actively moving polymers are able to respond to a specific stimulus by changing their shape. In general, two types of functions have to be distinguished: the shape-memory and the shape-changing capability. In both cases, the basic molecular architecture is a polymer network while the mechanisms underlying the active movement differ [13,14]. Both polymer concepts contain either molecular switches or stimuli-sensitive domains. Upon exposure to a suitable stimulus, the switches are triggered resulting in the movement of the shaped body.

Most shape-memory polymers are dual-shape materials exhibiting two distinct shapes. They can be deformed from their original shape and temporarily assume another shape. This temporary shape is maintained until the shaped body is exposed to an appropriate stimulus. Shape recovery is predefined by a mechanical deformation leading to the temporary shape. So far, shape-memory polymers induced by heat or light have been reported. Furthermore, the concept of the thermally induced shape-memory effect has been extended by indirect actuation, e.g., irradiation with IR-light, application of electrical current, exposure to alternating magnetic fields, and immersion in water.

Besides exhibiting two distinct shapes, an important characteristic of shape-memory polymers is the stability of the temporary shape until the point of time of exposure to the suitable stimulus and the long-term stability of the (recovered) permanent shape, which stays unchanged even when not exposed to the stimulus anymore. Finally, different temporary shapes, substantially differing in their three-dimensional shape, can be created for the same permanent shape in subsequent cycles.

In contrast to shape-memory polymers, shape-changing polymers change their shape gradually, i.e., shrink or bend, as long as they are exposed to a suitable stimulus. Once the stimulus is terminated, they recover their original shape. This process of stimulated deformation and recovery can be repeated several times, while the geometry, i.e., of how a workpiece is

moving, is determined by its original three-dimensional shape as the effect is based on a phase transition in a liquid crystalline elastomer network. Heat, light, and electromagnetic fields have been reported as suitable stimuli for shape-changing polymers.

1.3 Shape-Memory Polymer Architectures

The shape-memory effect is not an intrinsic material property, but occurs due to the combination of the polymer's molecular architecture and the resulting polymer morphology in combination with a tailored processing and programming technology for the creation of the temporary shape. To enable the shape-memory effect, a polymer architecture, which consists of netpoints and molecular switches that are sensitive to an external stimulus, is required.

The permanent shape in such a polymer network is determined by the netpoints that are cross-linked by chain segments (Figure 1.1). Netpoints can be realized by covalent bonds or intermolecular interactions; hence, they are either of a chemical or a physical nature. While chemical cross-linking can be realized by suitable cross-linking chemistry, physical cross-linking requires a polymer morphology consisting of at least two segregated domains. In such a morphology, the domains providing the second-highest thermal transition, T_{trans}, act as switching domains, and the associated segments of the multiphase polymers are therefore called "switching segments," while the
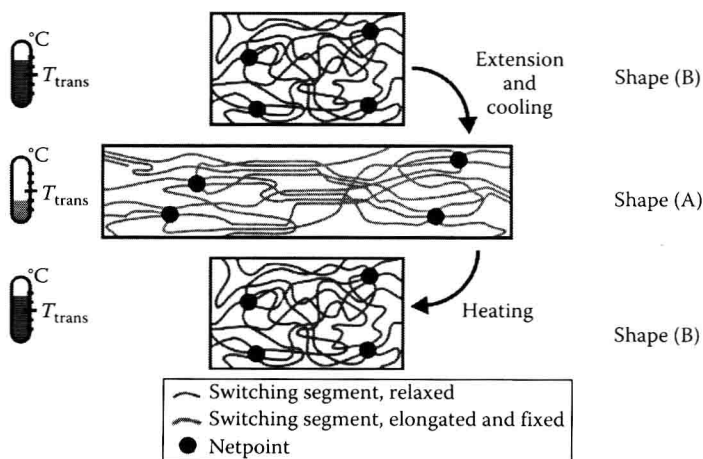

FIGURE 1.1
Molecular mechanism of the thermally induced shape-memory effect. T_{trans} is the thermal transition temperature of the switching phase. (Adapted from Lendlein, A. and Kelch, S., *Angew. Chem. Int. Ed.*, 41(12), 2034, 2002. With permission.)

domains associated-to-the highest thermal transition, T_{perm}, act as physical netpoints. The segments forming such hard domains are known as "hard segments." These switches must be able to fix the deformed shape temporarily under conditions relevant to the particular application. In addition to switching domains, they can be realized by functional groups that are able to reversibly form and cleave covalent cross-links. The thermal transition, T_{trans}, related to the switching domains can be a melting transition (T_m), or a glass transition (T_g). Accordingly, the temporary shape is fixed by a solidification of the switching domains by crystallization or vitrification. In suitable polymer architectures, these switching domains can be formed either by side chains that are only connected to one netpoint and do not contribute to the overall elasticity of the polymer, or by chain segments linking two netpoints and contributing to the overall elastic behavior. In both cases, the temporary stabilization is caused by the aggregation of the switching segments. Recently, blends of two thermoplastic polymers having shape-memory capability were presented, in which the segments forming the hard and the switching domains consisted of two different multiblock copolymers.

Functional groups that are able to reversibly form and cleave covalent bonds controlled by an external stimulus can be used as molecular switches providing chemical bonds. The introduction of functional groups that are able to undergo a photoreversible reaction, e.g., cinnamic acid (CA) groups, extends the shape-memory technology to light, which acts as a stimulus.

Shape-memory properties are quantified in cyclic stimuli-specific mechanical tests [15,16] in which each cycle consists of the programming of the test specimen and the recovery of its permanent shape. Different test protocols have been developed for the programming and recovery (see Chapter 3) from which the shape-memory properties are quantified by determining the shape-fixity ratio (R_f) for the programming and the shape-recovery ratio (R_r) for the recovery process. In thermally induced shape-memory polymers, the determination of the switching temperature, T_{sw}, characterizing the stress-free recovery process can be included in the test protocol.

1.3.1 Thermally Induced Dual-Shape Effect

1.3.1.1 Thermoplastic Shape-Memory Polymers

An important group of physically cross-linked shape-memory polymers are linear-block copolymers. Block copolymers with $T_{trans} = T_m$, and where polyurethanes and polyether-ester are prominent examples for such materials, are reviewed by Lendlein and Kelch [15]. In polyesterurethanes, oligourethane segments act as hard segments, while polyester, e.g., poly(ε-caprolactone) ($T_m = 44°C–55°C$) forms the switching segment [17–19]. The phase separation and the domain orientation of poly(ε-caprolactone)-based polyesterurethanes could be determined by Raman spectroscopy using polarized light [20]. In polyesterurethanes where poly(hexylene adipate) provides the switching

segment, and a hard segment is formed by the 4,4'-diphenyldiisocyanate and the 1,4-butanediol, the influence of the M_n of the switching segment as well as the hard segment content on the shape-memory properties were investigated [21]. The R_f increases with the increasing M_n of the switching segment but decreases with the increasing hard segment content. At the same time, the R_r decreases with the increasing M_n of the switching segment and the increasing hard segment content. Fibers from polyesterurethanes exert significantly higher recovery stress in the fiber axis when compared to the polymer films [22]. The exchange of the chain extender 1,4-butanediol with ethylenediamine can result in improved values of the R_f as urea-type bonding of the ethylene diamine can restrict the chain rotation and strengthen the physical interactions between the polyurethane segments [23]. Additionally, the shape-memory properties of polyurethanes can be enhanced by the addition of a second soft segment in small amounts so that segmented polyurethanes are obtained; e.g., 5 wt% of poly(ethylene glycol) can be added during synthesis to the poly(tetramethylene glycol) [24]. The addition of N-methyldiethanolamine as a cationomer in the hard segment of the segmented polyurethanes from poly(ε-caprolactone), 4,4'-diphenylmethane diisocyanate and 1,4-butanediol, simultaneously improved the R_f and the R_r. This effect is attributed to an improved switching segment crystallization [25]. A similar effect was found in copolyester-based ionomers obtained by the bulk polymerization of adipic acid and mixed monomers of bis(poly(oxyethylene)) sulfonated dimethyl fumarate and 1,4-butanediol [26]. The storage modulus of the rubbery plateau was significantly increased with increasing ionomer content and recovery rates of up to 95% were determined. Melt blending of an elastomeric ionomer based on the zinc salt of sulfonated poly{ethylene-r-propylene-r-(5-ethylidene-2-norbornene)} and low molecular mass fatty acids results in polymer networks in which the nanophase-separated ionomer provides the permanent network physically cross-linked by the zinc salt, and the fatty acids provide nanophases, whose melting triggers the shape recovery [27]. Polycarbonate segments containing polyurethanes were synthesized by the copolymerization of ethylene oxide in the presence of CO_2 catalyzed by a polymer-supported bimetallic catalyst, which yields an aliphatic polycarbonate diol. This macrodiol was further processed by the prepolymer method into a shape-memory polyurethane [28].

Thermoplastic multiblock copolymers with polydepsipeptide- and poly(ε-caprolactone)-segments providing shape-memory capability were synthesized via the coupling of oligodepsipeptide diol and oligo(ε-caprolactone) diol (PCL-diol) using a racemic mixture of 2,2,4- and 2,4,4-trimethylhexamethylene diisocyanate (TMDI). The multiblock copolymers were developed for biomedical applications and are supposed to degrade into less harmless degradation products than polyester-based materials. In the polymer molecules, the PCL block has the function of a switching segment forming the switching domains, that fix the temporary shape by crystallization [29].

Recently, binary polymer blends from two different multiblock copolymers with shape-memory capability were presented, whereby the first polymer component provided the segments forming the hard domains and the second, the segments forming the switching domains [30]. In both multiblock copolymers, a poly(alkylene adipate) mediator segment was incorporated to promote their miscibility as the hard segment poly(p-dioxanone) (PPDO) and the switching segment poly(ε-caprolactone) (PCL) are nonmiscible. All polymer blends investigated showed excellent shape-memory properties. The melting point associated with the PCL switching domains T_m, PCL, is almost independent of the weight ratio of the two blend components. At the same time, the mechanical properties can be varied systematically by the blend composition. In this way, a complex synthesis of new materials can be avoided. This binary blend system providing good biodegradability, a variability of mechanical properties, and a T_{sw} around the body temperature is thus an economically efficient, suitable candidate for diverse biomedical applications.

1.3.1.2 Covalently Cross-Linked Shape-Memory Polymers

Shape-memory polymer networks providing covalent netpoints can be obtained by the cross-linking of linear or branched polymers as well as by (co)polymerization/poly(co)condensation of one or several monomers, whereby one has to be at least trifunctional. Depending on the synthesis strategy, cross-links can be created during the synthesis or by postprocessing methods. Besides cross-linking by radiation (γ-radiation, neutrons, e-beam), the most common method for chemical cross-linking, after processing, is the addition of a radical initiator to polymers. An example of this is the addition of dicumyl peroxide to a semicrystalline polycyclooctene obtained by ring-opening methathesis polymerization containing unsaturated carbon bonds [31]. Here, the shape-memory effect is triggered by the melting of crystallites, which can be controlled by the *trans*-vinylene content. With increasing cross-linking density, the crystallinity of the material decreases. A melting temperature of 60°C was determined for pure polycyclooctene with a 81 wt% *trans*-vinylene content resulting in a shape recovery of these materials within 0.7 s at 70°C. The conversion to T_{trans}, when temperature is increased, can be monitored by the addition of a mechanochromic dye based on oligo(p-phenylene vinylene). Previously formed excimers of the dye are dissolved at this point and a pronounced change of their adsorption can be observed [32].

The other synthetic route to obtain polymer networks involves the copolymerization of monofunctional monomers with low molecular weight or oligomeric bifunctional cross-linkers. In a model system based on a styrene copolymer cross-linked with divinylbenzene, the influence of the degree of cross-linking on the thermomechanical properties has been investigated [33]. By increasing the amount of the cross-linker from 0 to 4 wt%, T_g increased

from 55°C to 81°C accompanied by an increase of the gel content from 0% to 80%. The copolymerization of monofunctional monomers of low molecular weight with oligomeric bifunctional cross-linkers results in AB copolymer networks of increased toughness and elasticity at room temperature [34]. In nanoindentation studies of AB copolymer networks obtained from the copolymerization of diethyleneglycol with *t*-butyl acrylate, the increase of T_g and the rubbery modulus with increasing cross-linker addition could be confirmed [35]. From the copolymerization of various acrylates with amorphous poly[(L-lactide-ran-glycolide)]dimethacrylate, AB copolymer networks with T_{trans} based on T_g could be obtained, whose T_{sw} could be varied between 9°C and 45°C by the choice of the comonomer ratio. In copolymers with ethylacrylate as comonomer, values of R_f and R_r were higher than 97% and 98.5% while they were not influenced by the comonomer content. In similar AB copolymer networks prepared by copolymerization of n-butyl acrylate and semicrystalline oligo[(ε-hyrdroxycaproate)-co-glycolate]dimethacrylates, covalently cross-linked shape-memory polymer networks with $T_{trans} = T_m$ were obtained [36]. Here, the low T_g of butyl acrylate domains, as additional soft segment, contributes additional elasticity to the material at temperatures relevant for potential applications. The T_m of the oligo[(ε-hyrdroxycaproate)-co-glycolate] segments correlates with the T_{sw} and could be adjusted by the variation of the molecular weight and the glycolate content of the switching segment.

The photopolymerization of poly(ε-caprolactone) acrylate macromonomers with polyhedral oligosilsesquioxane (POSS) moieties located precisely in the middle of the network chains built polymer networks with $T_{trans} = T_m$ based on the T_m of the oligo(ε-caprolactone) segments [37]. In polymer networks with a POSS content of 47 wt%, a second rubbery plateau could be determined, which has been associated with the physical interactions of the POSS moieties.

Covalently cross-linked polymer can also be synthesized by polyaddition or polycondensation reactions. In polyurethane networks prepared by the prepolymer method using a diisocyanate and 1,1,1-trimethylol propane to provide covalent cross links and poly(tetrahydrofuran) to provide the switching segment, the T_{sw} could be controlled by the variation of the T_m of the precursor macrodiol, while the elastic properties were adjusted by the cross-link density [38]. High degrees of cross-linking were obtained by using hyperbranched polyesters providing the multiol component [39]. In the two-step process, the prepolymer was formed by the reaction of poly(butylene adipate) with diphenylmethane diisocyanate, which, afterward, reacted with the hyperbranched polyester Boltron H30 (hydroxyl number equal 470–500 mg KOH/g). In such polymer networks shape recovery rates of 96%–98% were determined.

Shape-memory polymer networks were also prepared using the addition reaction of oxiranes. Shape-memory properties were enabled by the cross-linking reaction of 3-amino-1,2,4-triazole with epoxidized natural rubber