5.2

Soft Shape-Memory Materials

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CHAPTER OUTLINE

5.2.1 Introduction

Mother Nature displays numerous examples of materials that can autonomously change their shape in response to external stimuli. This is seen in both the conifer pinecone and the wheat awn, where microscopic fibril orientation change accompanied by macroscopic close–open shape transition is induced by depending on hydration level (Fig. 5.2.1a and b) [1]. Despite their biological nature, this shape-changing effect is possible via noncell-mediated processes; the microarchitecture of these biological systems ultimately governs their ability to change dynamically their macroscopic shape. In nonbiological systems, researchers have created a variety of materials that have the ability to "memorize" a temporary given shape, and then "recover" to an original permanent shape when triggered by external stimuli. This "shape-memory effect" (SME) is characteristic of all shape-memory materials. SME is an extremely broad phenomenon, and a wide range of materials including polymers [2,3,4], metal alloys [5], ceramics [6,7], supramolecular systems [8,9], and their composites [10], as well as crystalline porous coordination polymers [11] have each been shown to exhibit SME. Since molecular conformational changes within these artificial systems result in macroscopic structural actuations, these shape-memory materials are not so dissimilar from living systems that change shape in response to external stimuli including the pinecone (Fig. 5.2.1c and d).

The most noteworthy and extensively researched shape-memory materials are "shape-memory alloys" (SMAs). Ölander first discovered and reported in 1932 a novel metallic transformation of gold-cadmium (AuCd) alloy, whose pseudoelasticity triggered unusual macroscopic deformation [12]. The discovery of the SME in equiatomic nickel-titanium (NiTi) alloy, which is well known as nitinol, represented a paradigm shift in the SMA field,

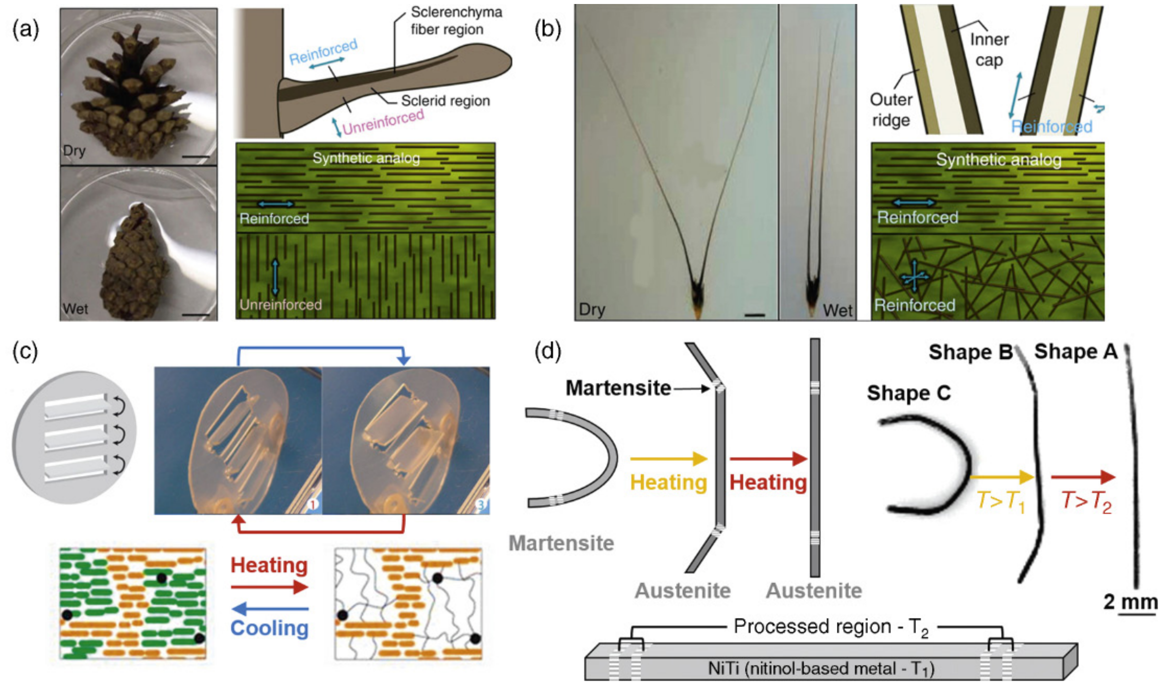

FIGURE 5.2.1 Shape-memory effect seen in Mother Nature and an artificial system. (a and b) Biological systems: (a) conifer pinecone and (b) wheat awn that smartly use fiber orientation to induce shape change [1]. (c and d) Artificial systems: (c) reversible shape-memory plastic [4] and (d) shape-memory alloys that can also actuate by changing molecular structure in response to stimulus [5].

representing a major body of both academic and industrial research. “Shape-memory polymers” (SMPs) were described just a few years later, marked by their first mention in a US patent applied by Vernon and Vernon in 1941 [13,14]. They discovered an “elastic memory” property in thermoplastic synthetic resins made of methacrylic acid ester developed for dental restoration. In this thermally induced SME, they demonstrated that polymeric materials could change shape upon pressure application and then recover their original shape upon heating. Over half a century later, “shape-memory hydrogels” (SMH) [15,16] and “biodegradable polymers” [17,18] have further represented a paradigm shift in soft shape-memory materials (Fig. 5.2.2). Since then, the area of soft shape-memory materials based on polymer and supramolecular systems has attracted tremendous attention, marked by an exponential increase in relevant scientific publications. The reasons for this impressive development are many and accompanied with some important findings including reversible SMH [19], light-induced SME [20], surface SME [21], triple-/multi-SME [22,23], temperature memory [10] as well as two-way (reversible) SME [24,25] as shown in Fig. 5.2.2. In conjunction with the rapid evolution of material science and increasingly sophisticated fabrication techniques, unique and highly functionalized soft shape-memory materials that match capabilities of SMAs and ceramics have gradually emerged. Therefore, it is no doubt that soft shape-memory materials will continue to become increasingly valuable and prominent for a broad scope of applications.

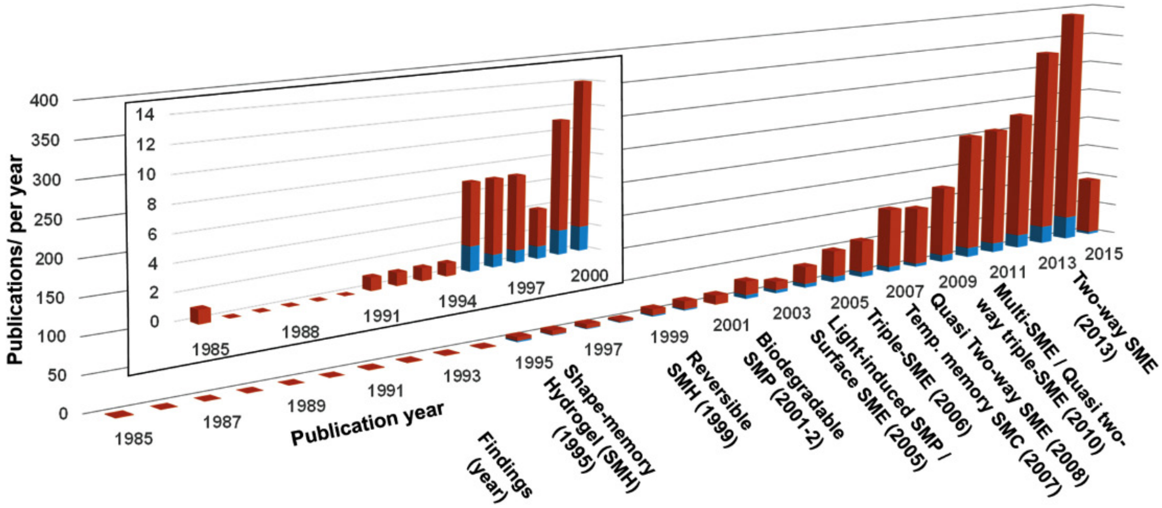

FIGURE 5.2.2 Evolution of published papers in the field of soft shape-memory systems. It shows the results for publication of a topic search for "shape-memory" polymer(s) (light gray [orange in the web version]) and gel(s) (dark gray [blue in the web version]) but not alloy(s) in ISI web of knowledge performed on May 4, 2015. It also shows some key findings addressing shape-memory polymer systems.

In this chapter, we focus on recent efforts to design and fabricate soft shape-memory materials, including both polymeric and supramolecular systems. We first classify these materials based on their micro- and nanostructure (Section 5.2.2). We then highlight how soft shape-memory materials have been applied to biomedical applications as implantables (Section 5.2.3.1), drug delivery devices (Section 5.2.3.2), and tissue engineering scaffolds (Section 5.2.3.3). In addition, we briefly discuss future trends for utilizing soft shape-memory materials for biomedical applications (Section 5.2.4).

5.2.2 Classification of Shape-Memory Materials

5.2.2.1 Polymer Network Architecture

Polymer network structures offer several parameters to tailor properties such as the chain length (molecular weight), branching (molecular shape), or composition (molecular connecting and positioning) in multicopolymer systems. In other words, the properties and functionalities are determined by material nanoarchitectonics. Generally, SMPs have been categorized by the difference in chemical structures and morphologies of the forming network, for examples chemically (or physically) cross-linked semicrystalline (or glassy) polymers. This classification is strongly related to the molecular design of SMPs, and is very useful in describing SMP systems based on thermal phase changes, known as thermally induced SME. The transition temperature (melting temperature [T_m] and glass transition temperature [T_g]) in SMPs can be tuned by precious designing of network structure (Fig. 5.2.3a). In this regard, the T_m of chemically cross-linked poly(ε-caprolactone) (PCL) can be adjusted to physiological temperature range by tailoring the nanoarchitectonics

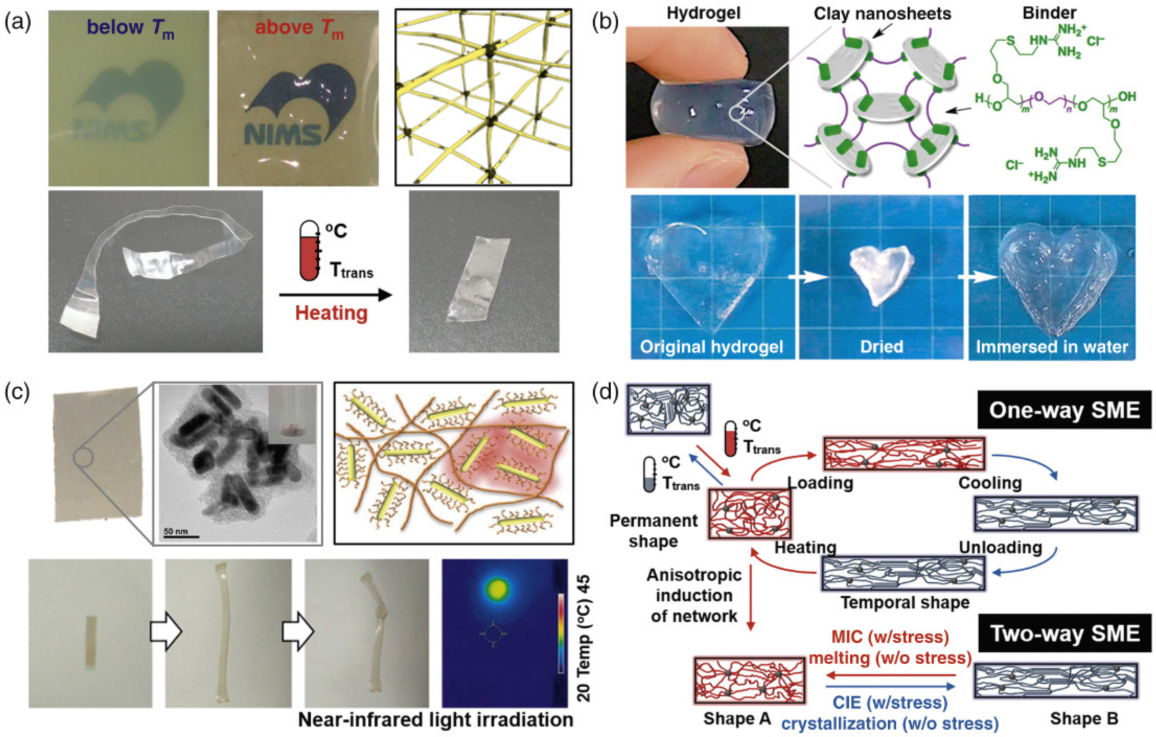

FIGURE 5.2.3 Classification of soft shape-memory materials from the viewpoint of nanoarchitectonics. (a–c) Structures and (d) molecular mechanism. (a) Chemically cross-linked polymer network, (b) supramolecular network with clay nanosheets [29], and (c) inorganic/polymer composite network system, and their shape-memory profiles [30]. (d) The nanoscale molecular mechanism for one-way and two-way SME of a cross-linked semicrystalline polymer system.

of PCL [26,27]. In addition, molecular network structures influence not only the thermal properties but also the mechanical properties and biodegradability. Therefore, there is no doubt that the concept of material nanoarchitectonics in SMP systems is crucial to the design of soft shape-memory materials especially for biomedical applications. The relationship between chemical structure and their functions in SMPs has been well addressed and widely reviewed by the Bowman group [28].

5.2.2.2 Supramolecular Network Architecture

The SME is based on the combination of structural and morphological property, and the majority of soft shape-memory materials contain permanent chemical and physical cross-linking points in their network structure as described previously. On the other hand, the supramolecular system has shown potential in a range of applications in the biomedical field due to its versatile and dynamic nature resulting from noncovalent interactions. In this regard, an alternative methodology for creating soft shape memory by reversible noncovalent interactions as cross-linking points has attracted much attention. Anthamatten and coworkers first reported that reversible noncovalent interactions can be used efficiently to fix mechanically deformed states at low temperature [31]. In this system, they utilized multiple hydrogen bonding between ureidopyrimidinone moieties to make a temporal shape, and the supramolecular material clearly showed the thermally induced SME due to the dynamic nature of hydrogen bonding. In addition, nanoscale inclusion complex formation between cyclodextrin and poly(ethylene glycol) has been employed as a molecular switch to actuate SME in the supramolecular system [32]. Despite these successes, distinct applications utilizing supramolecular interactions have not yet been fully realized, due in part to poor network mechanical properties. Recently, Aida et al. successfully fabricated moldable supramolecular hydrogels consisting of a polymeric binder carrying guanidinium ion pendants and clay nanosheets [29]. The hydrogel demonstrated excellent material properties, having formed through a multivalent salt bridge involving hydrogen bonding and electrostatic interactions. Interestingly, a supramolecular gel network can remember its shape even after drying and rewetting (Fig. 5.2.3b). High water content, mechanically tough, and shape-memory supramolecular gels with well-organized nanoarchitectonics offer different potentials over polymer network systems. Although the supramolecular shape-memory material has a relatively short history, its structural versatility and diversity should be applicable for designing a new class of biomaterials.

5.2.2.3 Composite System

As discussed above, most SMPs utilize reversible thermal phase transition induced by heating above T_m and T_g or cooling below the crystallization temperature (T_c) and T_g. However, such direct heating or cooling is often incompatible with biomedical applications *in vivo*; our bodies can only accommodate a narrow physiological range of temperatures. Instead, the transition temperature of these materials must be engineered to match that of body temperature. Another rational strategy to overcome this issue is to utilize endogenous heating that generates heat from inside material by indirect heating. In view of this, the hybridization with SMPs and other materials such as inorganic materials including (nano)particles and (nano)wires is called shape-memory composites (SMCs) and is often used to endow a special triggering switch and multifunctionality to SMPs. Through appropriately designed material, various stimuli including magnetic, optical, and electrical energies can be applied as a source to convert into thermal energy to induce phase transition. For example, remote activation of bulk and surface SMEs via near-infrared (NIR) light irradiation by using gold nanorods (AuNRs)-embedded PCL composites has been demonstrated (Fig. 5.2.3c) [30,33]. To achieve an efficient photothermal effect in response to NIR light, a high and homogeneous dispersion of AuNRs in the cross-linked PCL matrix is necessary. In fact, PCL modification with AuNRs was efficient to enhance nanoscale dispersibility and miscibility in the PCL matrix. This composite is just one example of many SMCs, and there are many excellent review articles covering SMP composites [34,35]. From those reviews, the relationship between nanostructures of composites and their functionality is highly relevant, suggesting the importance of material nanoarchitectonics in SMCs.

5.2.2.4 Molecular Mechanism

Though various molecular or nanoscale switches can be designed into shape-memory materials to trigger phase transition, we will focus our discussion of the molecular mechanism of SME to thermally induced changes. The most common class of shape-memory material to date is a thermally induced one-way dual type. The terms "thermally induced," "one-way," and "dual" imply a stimulation method to induce SME, irreversible shape change, and the total number of programmable shapes. Therefore, one-way dual SME refers to materials that are able to shift their shape from a temporary shape to a permanent shape in an irreversible fashion. On the other hand, more sophisticated two-way and/or triple (or multi-) SMEs have also been developed recently [4,22–25]. Strictly speaking, the programming process to make a temporary shape is crucial to achieve a two-way reversible system. In a cross-linked glassy or semicrystalline SMP, how the skeleton of crystallized geometry is built and the conformation orientation of the switching domain in the polymer network is created are key factors to determine whether the system is "one-way" or "two-way" (Fig. 5.2.3c). In similar way, how many different switching domains are introduced into the polymer network or how broad transition is produced by material design are key elements to create "triple" or "multi-" SME systems. For more information, the reader is referred to a recent review by Xie and coworkers that describes the design criteria and principle regarding the new behavior of SMPs [36]. From the viewpoint of the molecular mechanism of SMPs, it is also noticed that the materials nanoarchitectonics plays an important role in deciding whether the system is a "one-way" or "two-way" or "dual," "triple," or "multi-" SME.

5.2.2.5 Material Textures and Forms

So far, we have discussed the properties of soft shape-memory materials as a function of their nanoarchitectonics. At the same time, material microarchitectonics, also known as material forms, should be tailored to specific applications as SME in material was generally treated with bulk phenomenon. As such, designing an SMP object at the submicron to microscale is challenging. In particular, the synthesis of well-regulated nanoscale structures built up as meso- or macroscopic materials remains challenging. Recent rapid evolution in SMPs has been developed in efforts to meet various requirements in diverse potential applications. As a result, not only traditional film, tube, and sponge (foam) forms, but also microparticles, surface as well as micro/nanofiber that exhibit SMEs at mesoscopic to microscopic scales, have attracted much attention (Fig. 5.2.4).

Although these forms have different object scales from nano- (nm) to centimeter (cm) and various dimensions from one-dimensional (1D) fiber to three-dimensional (3D) sponge, it is possible to fabricate these material forms with excellent shape-memory properties [37,38]. Despite unique material textures and forms with multiscale, the underlying molecular principle of SMEs is largely equivalent to that of bulk systems, suggesting similar design criteria and principles. Structural flexibility and diversity originated from material microarchitectonics may certainly promote soft shape memory for many new applications.

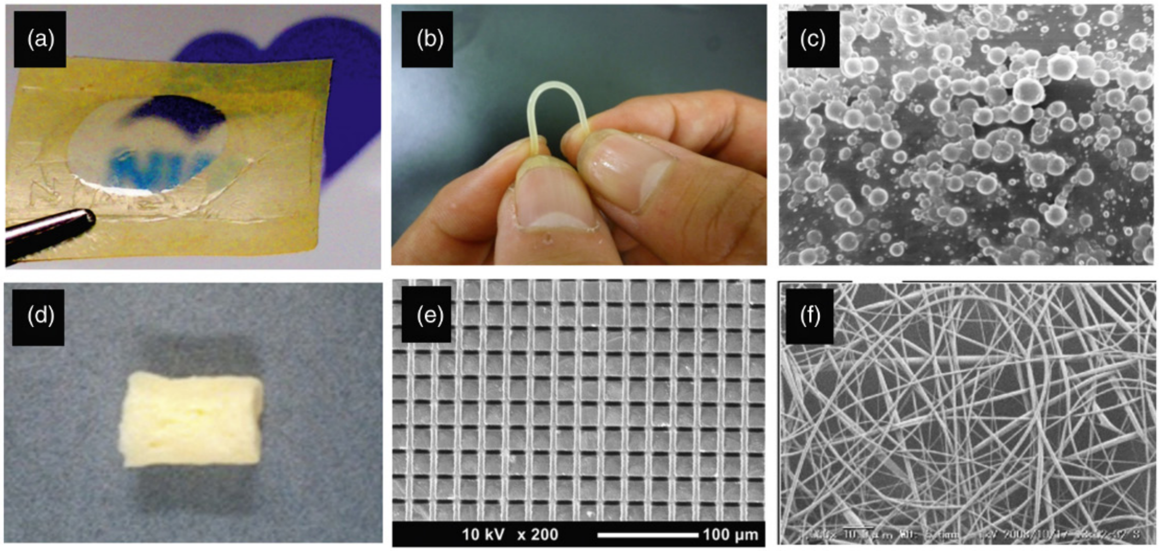

FIGURE 5.2.4 Classification of soft shape-memory materials from the viewpoint of macroarchitectonics (forms). Variants in shape-memory forms such as (a) film, (b) tube, (c) particle, (d) sponge (foam), (e) surface, and (f) fiber types. SMP platforms have various material dimensions from 1D (fiber) and 2D (surface) to 3D (sponge).

5.2.3 Biomedical Applications of Shape-Memory Materials

Representing a novel smart material, soft shape-memory materials are uniquely suited for applications in medicine and biotechnology. In 2002, Lendlein and Langer first demonstrated the concept of biodegradable thermally responsive SMP sutures [17]. In combination with publishing the excellent review article on “designing materials for biology and medicine” by Langer and Tirrell [39], many researchers are utilizing SMPs to introduce biocompatible and biodegradable implant materials through minimally invasive surgical procedures. In this section, we overview recent studies on soft shape-memory materials for biomedicine.

5.2.3.1 Implantable Devices

SMPs have most notably been promoted because of their potential in minimally invasive surgery, where a compacted device could be passed through a smaller incision and deployed to its full shape once inside the body [40]. For biomedical devices, the heating of polymer to activate SMEs has been proposed by body, temperature, optical/laser heating, and remote inductive heating [41]. As each of these thermal activation methods is possible within the body, control over SMP geometry is possible with implantable devices.

Cerebral aneurysms treated by traditional endovascular methods using noble metal (platinum)-based coils have a tendency to be unstable, due to chronic inflammation, compaction of coils, or growth of the aneurysm. In addition, with physical limitation, mechanical mismatch between hard metal and the thinned, weakened wall, aneurysms exhibit a potential for rupture. Maitland et al. addressed this issue and developed a new filling

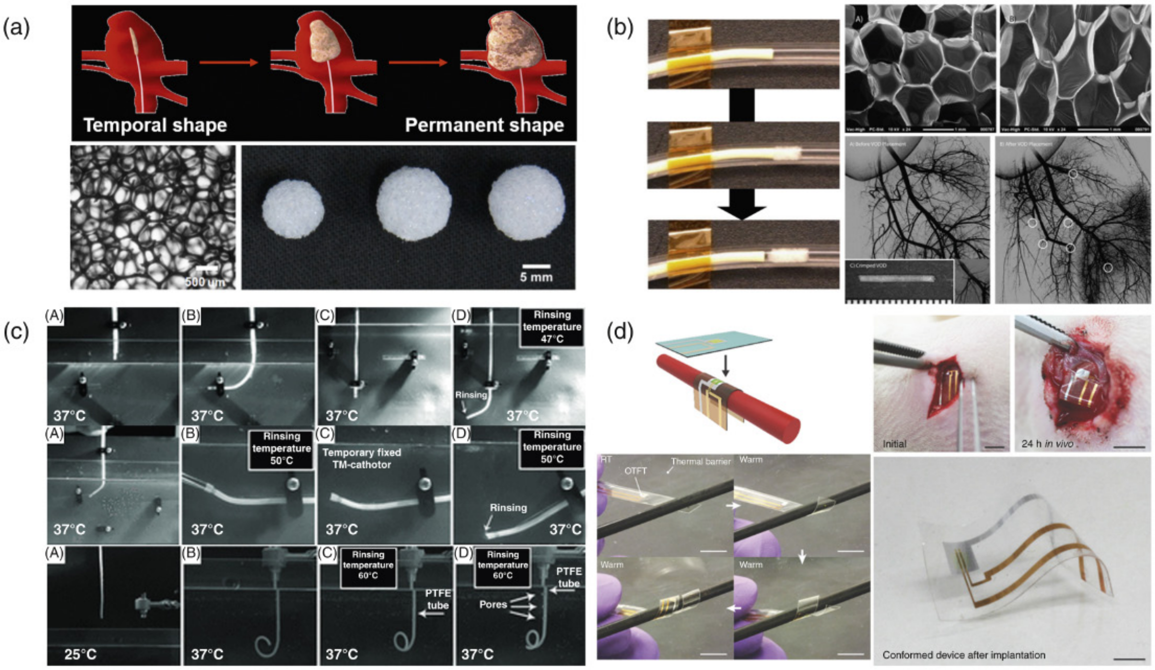

FIGURE 5.2.5 Soft shape-memory platform for functional implantable devices. (a) Closed-cell low density [42] and (b) opened-cell SMP foam devices for aneurysm filling [43]. Both SMP foam devices can deliver to the aneurysm via a catheter as a crimped temporary shape. These foams enable expansion within the aneurysm, as it recovers to its permanent shape via stimuli, and finally treated aneurysm with fully expanded foam. The reticulated foam device (b) is also capable of achieving rapid vascular occlusion in an *in vivo* porcine model. (c) Intelligent catheters based on temperature-memory effect in SMPs. Although these catheters are composed of the same material, they can operate in different ways such as (top) individually programmable, (middle) *in situ* programmable, and (bottom) intelligent drainage catheter [44]. (d) SMP-based implantable electronics. By combining SMPs and organic thin-film transistors (OTFTs), a unique form of adaptive electronics is developed, which changes their mechanical properties from rigid and planar to soft and compliant, in order to enable soft and conformal wrapping around 3D objects, including biological tissue [45].

method for the treatment of intracranial aneurysms using polyurethane-based SMP foams (Fig. 5.2.5a) [42]. The SMP foam with a crimped temporary shape is capable of expanding to fill the aneurysm sac. In particular, their developed low-density SMP foams displayed only a small expansion force, suggesting a decreased risk of aneurysm rupture upon treatment. However, the SMP foam was predominantly a closed cell structure with limited potential for full healing, which involves blood clotting and cell migration throughout the foam's inner volume space. The development of a more open-cell microstructure might further improve the healing response. To overcome this issue, they successfully fabricated low-density SMP foams with reticulated pore structure (Fig. 5.2.5b) [43]. Nondestructive reticulation of SMP foams was achieved by using a gravity-driven floating NiTi alloy pin array coupled with vibratory agitation of the foam and additional chemical etching. It was clearly demonstrated that reticulation of SMP foams resulted in a reduced elastic modulus and increased permeability while retaining their shape-memory property. They also showed the capability of a rapid vascular occlusion device in an *in vivo* experiment using a porcine model. Although further study is needed to definitively prove the advantage of reticulate structures in their system, well-regulated microarchitectonics should improve the efficacy of aneurysm healing response.

In the previously described approaches, catheters can be utilized to deliver developed SMP foams to diseased areas. Catheters are essential medical devices that can be inserted into the body cavity, duct, or vessel to treat diseases and perform a surgical procedure. Lendlein and coworkers developed a new type of intelligent catheter based on a multiblock copolymer [44]. Importantly, they cleverly adopted the temperature memory effect (TME), which is the capability of a polymer to remember the temperature where they were deformed recently, into the system [4,10]. To achieve this actuation, they used the multiblock copolymer consisting of PCL and poly(ω-pentadecalactone) selected as switching and hard segment forming components, respectively. They finally demonstrated three concepts including individually programmable, *in situ* programmable, and intelligent drainage TM-catheters to show the working principle of TME for application potential in minimally invasive medical devices (Fig. 5.2.5c). Therefore, this concept should prove powerful as TME in soft shape-memory materials enables the realization of various response temperatures with the same polymer material by simple regulation of thermomechanical processing, without requiring synthesis of the new material.

Soft electronic devices are capable of addressing health care problems that require chronic device implantation. In view of this, intimate conformability is essential for obtaining stable interfaces on complex surfaces such as tissues and organs. SMPs may have the potential to contribute in this field. Someya et al. developed a unique form of adaptive electronics that softly conforms or deploys into a 3D shape in response to a stimulus by exploiting the functional features of soft shape-memory materials [45]. They first fabricated SMP substrates composed of 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione, tricyclodecane dimethanol diacrylate, and *tris*[2-(3-mercaptopropionyloxy) ethyl] isocyanurate, integrated with organic thin film transistors (OTFTs) (Fig. 5.2.5d). The resulting hybrids can change their mechanical properties from rigid and planar, to soft and compliant via SMEs, in order to enable soft and conformal wrapping around 3D objects such as biological tissue. These acutely physiologically stable and active OTFTs have the potential to address challenging biomedical problems by enabling new means of creating intimate interfaces between body tissue and high performance, robust bioelectronics.

5.2.3.2 Drug-Releasing Devices

Polymeric materials have been developed into multiplatform technologies to offer biomedical materials with multifunctionality [39]. For example, in addition to a unique structural role, SMP medical devices offer biodegradability and enable controlled therapeutic drug release. Since Wache et al. first reported the development of an SMP stent as a new vehicle for drug delivery in 2003 [46], there has been much effort to design drug-eluent stents (DESs). A drug-loaded, degradable SMP stent has been demonstrated by Lendlein's group. They successfully demonstrated a first example of the potential application of such SMPs as ureteral stents [47], and the potential of drug-loaded SMPs as injectable or implantable self-anchoring implant rods, which could enable spatial fixation for a local drug release [48].

The development of releasing systems involving multiple therapeutics, macromolecular drugs, remote control, and/or spatiotemporal control over payload delivery has been addressed as a recent trend in the field of SMPs (Fig. 5.2.6). Wang et al. reported an SMP-DES developed by chemically cross-linked copolymer networks of poly(ethylene glycol) and PCL. By optimizing the molecular composition and weight of copolymers, they successfully adjusted their transition temperature to match that of body temperature. They loaded two different drugs (mitomycin C and curcumin) into their SMP network to potentially prevent in-stent restenosis of the vessel; both short- and long-term therapeutic effect was achieved by controlled dual drug release (Fig. 5.2.6a) [49]. Additionally, Zhou and

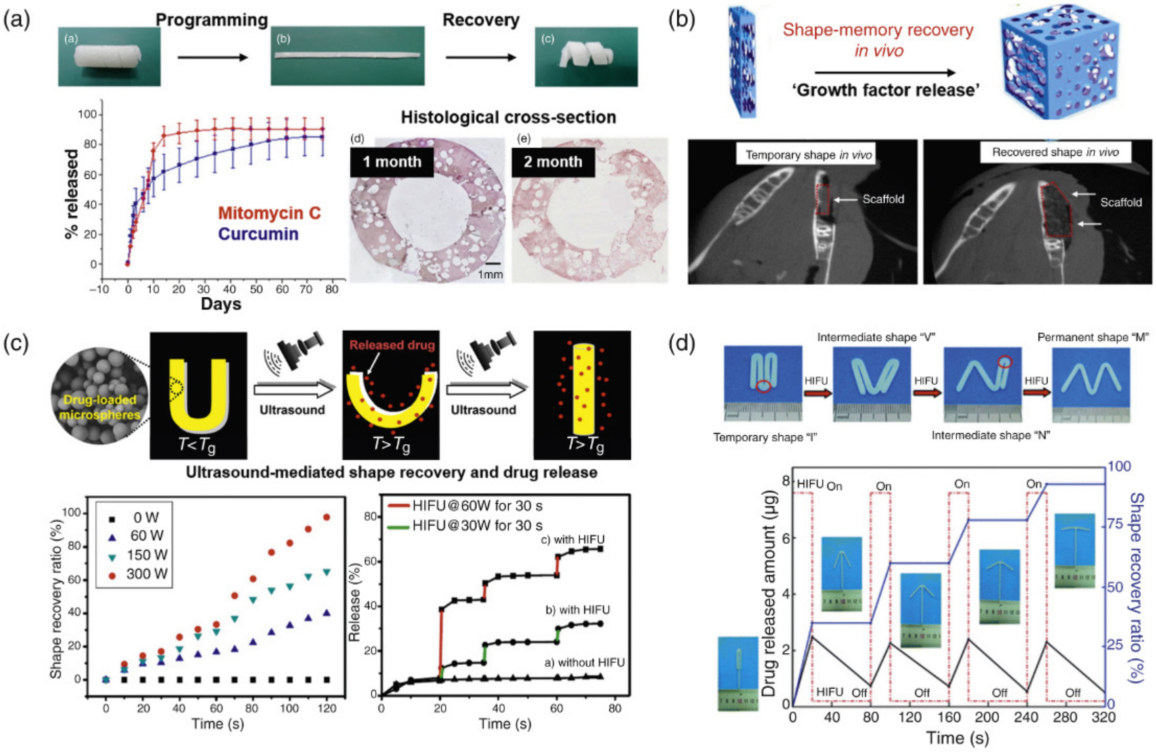

FIGURE 5.2.6 Soft shape-memory platform for functional drug delivery devices. (a) Biodegradable SMP-DES. SMP-DES shows shape recovery in response to temperature change and dual drug (mitomycin C/curcumin) release property [49]. (b) Shape-memory porous nanocomposite scaffold. This device enables the loading of growth factor BMP-2 during calcium cross-linking of sodium alginate. *In vivo* shape-memory recovery process of the BMP-2-loaded porous nanocomposite scaffold is clearly demonstrated by using cone beam computed topography [50]. (c) Biodegradable cylindrical shape-memory rod made of SMP microspheres. Shape recovery and payload protein release effects can be modulated by applying the ultrasound [51]. (d) HIFU-enabled spatial and temporal control of shape recovery and release of loaded drugs. Spatially and temporally controllable shape recovery and copper sulfate release in response to HIFU application is demonstrated [52].

coworkers reported a delivery of a macromolecular object using a smart porous nanocomposite scaffold to repair a mandibular bone defect (Fig. 5.2.6b) [50]. The fabricated scaffold consists of chemically cross-linked PCL and hydroxyapatite nanoparticles that is an SMC system, and succeeded in preparing highly interconnected pores of scaffold using a sugar-leaching method. Furthermore, to load macromolecular objects into the system, they adopted a coating layer of calcium alginate and bone morphogenetic protein-2 (BMP-2) on the porous SMP framework. The developed SMP scaffold displayed good shape-memory recovery in both *in vitro* and *in vivo* environments, and they found that it promoted new bone generation in the rabbit mandibular bone defect model.

Zhang and coworkers recently reported biodegradable shape-memory cylindrical rods offering a unique structure [51]. In this research, chitosan functionalized poly(lactic acid-*co*-glycolic acid) microspheres containing lysozyme as a model payload were first prepared by the emulsion method, and a macroscopic cylindrical-shaped rod was then fabricated by directly sintering the drug-loaded macrospheres (Fig. 5.2.6c). By employing high-intensity focused ultrasound (HIFU), the temporal and simultaneous regulation of SMEs and payload release of the 3D cylindrical rod were remotely operated. Moreover, these two processes are controllable and could be manipulated by varying acoustic power and insonation pulse duration. Additionally, Xia and Zhao proposed a new concept and modality enabling the simultaneous control of SMEs and release of loaded drug by utilizing a unique feature of HIFU [52]. To achieve this, they selected poly(methyl methacrylate-*co*-butyl acrylate) copolymer as a matrix component because of the biocompatibility and easy tunability of its transition temperature. They clearly showed that the HIFU-triggered shape recovery process can be spatially and temporarily controlled, allowing the SME to manifest in selected regions on demand, endowing SMPs with the capability of adopting multiple intermediate shapes and synchronizing the release of loaded drugs in a switchable manner (Fig. 5.2.6d). From these studies, it is clear that drug-releasing ability is applicable for not only medical device applications but also tissue engineering and regenerative medicine, suggesting the importance of combinations with other functionalities.

5.2.3.3 Tissue Engineering

The advent of biodegradable SMPs spurred the investigation of their use as a vehicle for tissue engineering. Tissue can be grown on collapsible SMP scaffolds *in vitro* and then delivered into the body using minimally invasive techniques to initiate repair or reconstruction of tissue organs. In addition to the biocompatibility and biodegradability of scaffold, the shape memory will surely open the door to new applications in tissue engineering.

Success in bone tissue engineering, especially in the treatment of critical-sized craniomaxillofacial bone defects, requires conformal matching between the scaffold and the tissue defects. Toward this, Grunlan et al. developed an SMP scaffold exhibiting an open porous structure and a “self-fit” ability [53]. They produced a porous cross-linked PCL network by the solvent casting/particulate leaching method using a fused salt template. To enhance the bioactivity, a polydopamine coating was conducted onto the wall of porous cross-linked PCL frameworks. The scaffold became malleable and showed “self-fit” ability after pressing into an irregular model defect (Fig. 5.2.7a). In addition, they successfully demonstrated that polydopamine-coated scaffolds exhibited superior bioactivity, osteoblast adhesion, proliferation, osteogenic gene expression, and extracellular matrix deposition after hydroxyapatite mineralization. In this system, polydopamine coating is an additional value to the SMP scaffold but clearly showed enhancement bioactivity without loss of original SMP property.

Cell responsiveness to its surrounding mechanical cues has been the subject of active research. In spite of a considerable amount of ongoing research, current efforts are centered on rather static patterns. Due to the dynamic nature of the regeneration processes, static substrates seem to be deficient in mimicking changing physiological conditions, such as development, wound healing, and disease. Surface SMEs can provide a dynamic change of micro- and nanotopographical property to adhered cells [27,56,57], and may have the potential to be powerful tools for regulating cell functions and fate. In this

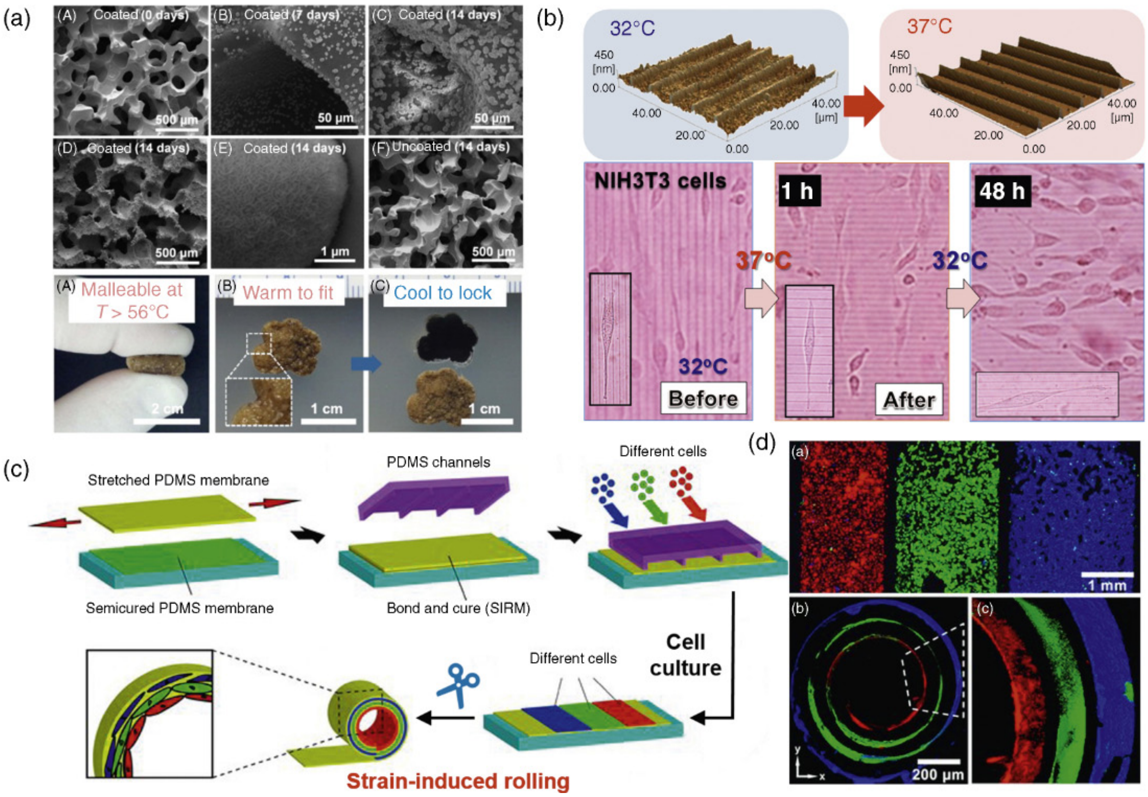

FIGURE 5.2.7 Soft shape-memory platform for functional tissue engineering scaffolds. (a) Bioactive self-fitting SMP scaffold for bone tissue engineering. SMP scaffold can be used as a template for apatite mineralization, and exhibits an open porous structure and the capacity to conformally “self-fit” into irregular defects [53]. (b) Surface shape-memory platform for mechanobiological control of cell functions and fate. Shape-memory surface transition can dynamically regulate cellular morphology, orientation, and movement [54]. (c) Stress-induced rolling bilayer membrane for 3D vascular tissue engineering. This platform enables one-pot fabrication of tubular structures with multipole cell types forming different layers of the tube walls [55].

approach, the adjusting transition temperature to physiological temperature range is a most important technical issue. Uto et al. successfully designed cross-linked PCL tailored nanoarchitectonics, providing dynamic mechanical cues in response to 5˚C temperature difference (32°C and 37°C) [26,27]. They also demonstrated that orientation modes as well as rotational movement of cells could be dynamically regulated in a desired manner using surface SMEs (Fig. 5.2.7b) [54].

Soft shape-memory material is also applicable as a scaffold to 3D vascular tissue engineering. Zhang et al. proposed a versatile, one-pot strategy for depositing different types of cells in 3D to mimic tubular structure in vascular tissue [55]. Their strategy to fabricate tubular structures with layered walls made of multiple types of cells is called the stress-induced rolling membrane (SIRM) technique. The SIRM device is fabricated by bonding two elastic membranes together (Fig. 5.2.7c). After mechanical scratching of substrate, flat-to-tube shape transition was induced by rolling, generated from the device's internal stress. They found that the 3D vascular mimic structures composed of both randomly or highly oriented endothelial cells, smooth muscle cells, and fibroblasts was fabricated in a one-pot process by using SIRM technique. This technique may not consist of SMEs, but this unique idea should be incorporated into designing soft shape-memory materials. Furthermore, this strategy will enrich the toolbox for 3D micro-/nanofabrication by initially patterning in 2D and transforming into 3D.

5.2.4 Conclusions and Perspectives

Although our understanding of design principles and mechanisms in soft shape-memory material, including polymer and supramolecular systems, has been rapidly and dramatically improved, there are only a few examples of materials exhibiting SMEs commercially available. In conjunction with rapid technological evolution of this field and interdisciplinary study, unique and highly functionalized soft shape-memory material and actuation principles have started to appear. The recent developed concept, which is a thermally driven reversible and bidirectional shape-memory effect (rbSME) platform, is useful in the creation of future biomedical devices [25], although the actuation temperature range, accuracy, and operation mode must continue to be improved. In addition, deformable, programmable micro-optics has been developed by combining surface SMEs and micro-optics [58]. Since it has been clearly demonstrated that these rewritable and switchable optics worked as SMP holograms, they may prove applicable to the biomedical field as new thermal actuated smart devices. Origami-inspired nanotechnology and manufacturing is another hot topic in materials science. By combining with SMPs and origami-inspired technology, a new concept sequential self-folding robot was developed [59,60]. Composite sheets composed of laminating several layers including SMPs work as building blocks to achieve highly sophisticated robotic movements. These results may indicate the importance of not only materials design but also system design into how assembled architectonics are operated. Here, we picked up and discussed on a number of featured and unique examples, but many other materials and principles have been extensively reported. However, there is no doubt that the unique characteristics and functions of shape-memory materials are a direct result of material nanoarchitectonics, and that soft polymer and supramolecular systems satisfy a different set of applications than those of hard shape-memory systems such as alloys and ceramics. Moreover, SMPs are one of the most fascinating polymer classes, and will accelerate the development more rapidly and discursively. In this situation, to establish more practical and valuable systems using soft shape-memory materials, we should always ask how can nanoarchitectonics express functions and the principle be used technically.

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