



Self-expanding stents based on shape memory alloys and shape memory polymers

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ABSTRACT

A stenotic vessel can be opened using net-shape tubes called “stents” leading to the restoration of the bloodstream. Compared to the commonly used stainless steel stent, self-expandable stents have some advantages. They do not suffer from the risks of damage to the vascular tissue due to the balloon expansion. Moreover, overexpansion for compensating the elastic recoil is not needed, and there is no constant force applied on the artery until the occlusion of the device by the artery stops. However, the stent cannot restore the original dimensions of the vessel in the case of calcified plaques. Self-expandable stents can be utilized for the treatment of atherosclerotic lesions in the carotid, coronary, and peripheral arteries. Shape memory alloys (SMAs), mainly NiTi (nitinol), are employed for self-expandable vascular stent applications. Nitinol is widely applied for medical devices and implants due to its excellent fatigue performance, mechanical properties, and biocompatibility, which make this alloy suitable for long-term installations. Other materials used for self-expandable cardiovascular stents are shape memory polymers (SMPs). Shape memory effect is triggered by the hydration of polymers or temperature change preventing the collapse of small blood vessels. This review has focused on the mechanisms and properties of SMAs and SMPs as promising materials for stent application.

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1. Introduction

The development of SMPs is the result of scientists' desire for the production of next-generation functional materials exhibiting interesting characteristics. As a result of various potential applications as well as facile manufacturing, blend and composite polymers, especially SMPs, have greatly desirable among researchers [1-4]. This technology provides the possibility to produce desired polymer architectures that can be tailored by the conditions of thermo-mechanical programming to

fabricate high-performance polymers with sophisticated characteristics required for special applications [5-7]. Upon an external stimulus exposure, SMPs are able to transform their temporary shape to their original shape, which is known as the shape memory effect (SME). Due to the dual- or multi-shape capability, these promising materials can be used in different applications such as drug carriers, self-deployable space structures, intelligent medical devices, stents, self-assembling mobile phones, smart fabrics, etc. The external stimulus for SME includes light, direct or indirect heating, solvent exposure, or changes in pH. Using a combination of careful thermo-mechanical programming and polymer

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morphology, SME is achieved [8, 9].

A gold-cadmium alloy was the first material whose shape memory effect was discovered by Chang and Read in 1951 [10]. Before them, Vernon reported a type of SME in a dental material based on methacrylic acid resin in 1941 [11]. An equimolar alloy of Ni and Ti, called nitinol, with shape memory properties was reported first by Buehler et al. [12] in 1963. Ti and its alloys have been considered as proper materials for implants due to their good performance in body [13-15]. In continuation of materials with the SME, a number of ceramics and metallic alloys were found by researchers to have the SME behavior [16-18]. The SME in shape memory alloys is based on the reversible thermal transitions between the martensitic phase formed at low temperature and the austenitic phase formed at high temperature [18]. NiTi, CuAlNi, and CuZnAl are the most popular SMAs among all shape memory alloys due to their performance indexes [19].

SMPs exhibit better properties compared to SMAs in many respects. For example, their recoverable strain is greater, they can be processed easily, and they are lighter and cost-effective. Furthermore, they have easily tuned properties and they are responsive to various stimuli [8]. A heat-shrinkable polymer based on covalently cross-linked polyethylene (PE) was developed in the 1980s, exhibiting SME properties. In this polymer, the permanent shape is because of covalent cross-links, and the switching process results from the melting of PE crystallites [20]. Later on, various SMPs based on polynorbornene [21, 22], poly(vinyl alcohol) [23, 24], and polyurethanes [25, 26] were developed.

SMPs have the capability to recover up to 10% of apparent permanent deformations as well as the typical peculiarities related to metals such as workability, stiffness, resistance, and so on. In the common mechanical world, health was the first field where SMAs were utilized extensively since some SMAs have been found to be almost perfectly biocompatible. The most evident examples of SMAs potentials are orthodontic wires and aortic stents, which are part of everyday life [27]. This article summarizes the mechanisms, properties, and application of SMAs and SMPs as stents and most important steps in their development are studied.

2. The shape memory cycle in SMPs

Generally, the shape memory cycle involves four stages. First, the material is deformed then is cooled (stage 1-2). The stages 3 and 4 are fixing and recovery [28]. At the first stage, the deformation of the sample to a predetermined strain or stress is done at its deformation temperature (T_d). Due to heating above T_d which is above the switching or transition temperature of T_{trans} , molecular switches are opened and the shape deformation can occur. Thereafter, the sample is cooled from T_d to a set temperature of T_s under pre-strain constraint. T_s is below the T_{trans} , and the deformation history (strain) is stored during the cooling stage. At this stage, the switches become closed and a temporary shape is fixed. At the third stage, a stress-free condition is obtained due to the release of the initial deformation constraint at T_s . At the last stage, the opening of the molecular switches occurs by heating again above T_{trans} . This stage is the unconstrained recovery under stress-free condition, and the sample achieves its initial permanent shape again. Experimental conditions, geometric considerations, and material properties can affect the whole SM cycle time [29, 30].

3. Mechanism of shape memory effect in polymers

SMPs are elastic networks possessing suitable molecular switches responding to stimuli and can form physical cross-links when the temperature is below a critical temperature leading to the temporary shape fixing. Their permanent shape is determined by linking chain segments

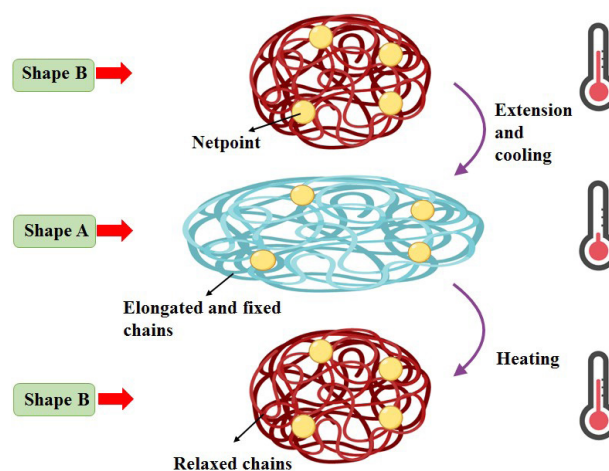


Fig. 1. Shape memory effect in polymers.

by net points of either covalent bonds or physical nature such as crystallites. The SME is considered as an entropic phenomenon [31]. In the permanent macroscopic shapes, the molecular chains are thermodynamically stable and their entropy has the highest value. A less stable state with lower entropic is obtained when a macroscopic deformation is applied due to the changes in molecular chain conformation. This entropic state is kinetically trapped while the material undergoes cooling below T_{trans} because the molecular chains freeze and the new conformation of the chains is fixed. Heating above the T_{trans} increases the mobility of molecules resulting in the release of strain energy and getting back to the original shape with the highest entropy and lowest energy (Fig. 1) [30]. Therefore, switch segments fix the temporary shape in SMPs. It should be mentioned that the SME could not be achieved by segmental switching alone. A precondition required for an ideal process of shape recovery is the inhibition of long-range slippage of chains leading to the macroscopic deformation. Thus, the net points should have sufficient stability to resist the thermo-mechanical conditions in order to experience complete recovery. These net points might be either chemical crosslinks by covalent bonds or physical interactions such as chain entanglements, ionic clusters, hydrogen bonding, glassy hard domains, or crystallites. While net points with physical interactions provide reprocessability, a complete recovery is not offered due to weak interactions. On the other hand, an almost complete recovery is achieved by strong chemical crosslinks, but reprocessability is not obtained [28].

4. Mechanism of shape memory effect in alloys

Shape memory alloys possess two stable phases that have various crystal structures and characteristics. The phase formed at high temperature is austenite (parent phase) with the crystal structure of body centered cubic. The phase formed at low temperature is martensite that has a lower symmetry crystallized in monoclinic, orthorhombic, or tetragonal structure. Twinned and de-twinned forms are two forms that the martensite assembly can appear.

The reversible transformation of SMAs from the austenite phase to the martensite phase is the base of their functional properties. When there is no loading, austenitic phase transforms into different martensite variants (up to 24 for nitinol) upon cooling, which results in twinned martensite. This transition between the two phases is time-independent and does not proceed by the diffusion of atoms, because atoms need small movements in the crystal lattice for the transition. The transformation occurs over a specific temperature range related to the type of the alloy system [27, 32]. Fig. 2 shows the transformation cycle and name of each point. Stress and/or temperature hysteresis is observed in the austenite to martensite phase transformation. M_s and M_f during heating

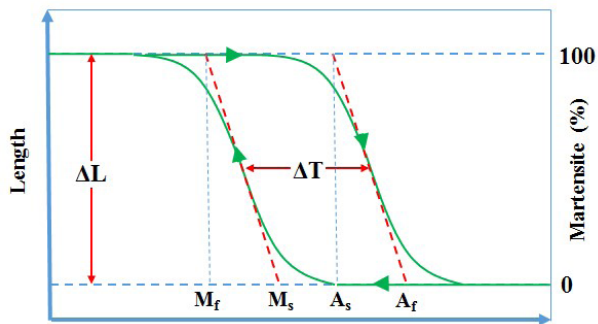


Fig. 2. Thermal hysteresis in SMAs.

represent the starting and finishing temperatures of the transformation, whereas A_s and A_f during cooling indicate the beginning and finishing temperatures of the reverse transformation, respectively.

In some NiTi alloys, the phase transition occurs in two steps upon cooling. In these alloys, austenite first transforms into a trigonal structure called the R-phase, and then by the reduction of the temperature, it changes into martensite. Three ways exist for achieving the sequential transformation of austenite-R-martensite: addition of a third element such as Fe, aging of the alloys with a higher Ni content and cold work [33].

Since the 1970s, the intermediate transformation of austenite-R has gained the physicists' attention and material scientists. The σ - ϵ -T responses show a narrow hysteresis as a result of the austenite-R transformation, and a noticeable change with cycling is not seen through the transformation range. Due to small transformation strains exhibited by austenite-R, excellent fatigue properties are obtained. Considering this property, these alloys are very attractive for being used in actuator applications.

Stress-induced phase transitions can also occur in SMAs besides the transformations by changing temperatures. The transformation to martensite can be achieved by applying a strain to the sample at temperatures above the A_f . When the applied stress reached a critical value of σ^M , the transformation to martensite is started. In this case, the austenite phase transformation to the de-twinned martensite results in a macroscopic deformation. By applying the load, twinned martensite can be de-twinned, martensite can be reoriented or the de-twinned martensite orientation can be changed with the change in the applied load direction.

The SME is observed in SMAs when they are deformed at low temperatures while retaining the apparent plastic deformation during the unloading step. The original shape is recovered by heating above A_f due to transforming in austenitic [34]. Fig. 3 schematically demonstrates the SME in shape memory alloys showing the stress-strain-temperature diagram. The starting point is from the reference configuration at zero stress and a given temperature. Slope 1-2 shows linear elastic behavior of the material when the stress is increased, then at plateau 2-3, plastic deformations develop at constant stress. However, after the deformation reaches a saturation value, SMA demonstrates a new linear elastic branch with a further increase of the load unlike the typical plastic deformation (slope 3-4). At point 5, a residual strain exists after unloading. This residual deformation can be recovered by the increment of the temperature to a characteristic temperature without applying a load, which is presented in points 6-7. Finally, the complete recovery of the initial material state is possible if the temperature is reduced to the initial temperature [35, 36].

5. Shape memory alloys for vascular stents

The stent implantation during transluminal coronary angioplasty can treat coronary arterial stenosis. In 1994, the Food and Drug Administra-

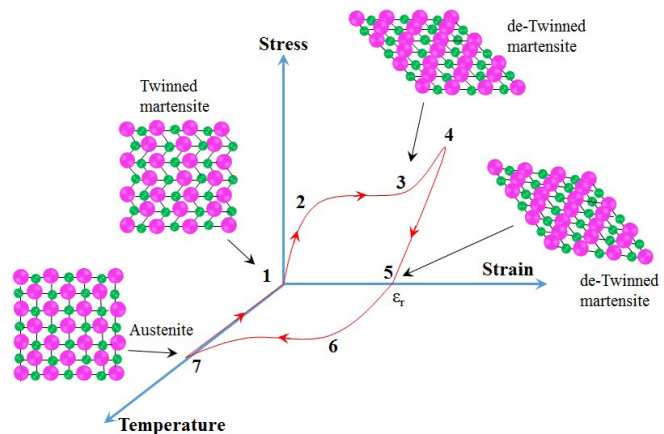


Fig. 3. Shape memory effect in SMAs.

(FDA) approved the application of coronary stents expanding by balloons. However, a metallic stent was the first clinically applied in 1986. Thereafter, many investigations have been carried out to develop stents with enhanced materials and design. Schematic illustration of vascular stents performance is shown in Fig. 4.

As a result of excellent fatigue performance, mechanical characteristics, and biocompatibility, NiTi is widely utilized as materials for medical devices and implants requiring long-term installations [37]. The NiTi-based stent was introduced in 2003, which was perhaps the most famous application of this alloy in medical devices, using the super-elastic behavior of the alloy [38]. The stent is a miniaturized cylindrical elastic device used for the support of diseased arteries. Nitinol is utilized in about 25% of all the stents implanted in arteries. The diameter of self-expanding shape memory alloy stents is larger than that of target arteries. In order for the device to work easily under standard environmental conditions, A_f is set to a small value below the body temperature. The stent is constrained to a rig to inhibit the premature release, and after the installation, it is removed. After a short time of installation, the stent attains its final configuration [39, 40].

An essential property for any biomaterial is biocompatibility, particularly for NiTi, which has the possibility of Ni release. Ni has been proved to have immune-sensitizing, carcinogenic, and toxic effects. However, NiTi is extremely stable and shows very different biocompatibility properties in comparison with Ni alone. In general, some studies have shown that the NiTi alloys exhibit even more biocompatibility than stainless steel [41]. Its good biocompatibility is originated from the more-rapidly oxidized Ti resulting in the formation of protective TiO_2 film on the surface, which prevents the release of Ni-ion and provides corrosion resistance [42]. However, the body fluid is highly corrosive and the corrosion resistance is not provided by just the TiO_2 layer. Therefore, it is required to modify the surface of NiTi devices to improve surface corrosion resistance and develop implant-safe conditions [43, 44].

Compared to common engineering metals, NiTi alloys show non-standard fatigue and fracture responses due to microstructural evolutions resulting from stress and/or heat and the complex various phases [45]. Consequently, well-known standard fatigue testing procedures and theoretical models cannot be applied, and there is still a lack of universal description for the fatigue behavior of NiTi [45, 46]. In order for nitinol to be more fracture-resistant, recent studies focused on optimizing the applied geometry [47, 48].

For the improvement of the biocompatibility of anodized NiTi, Mohammadi et al. [49] coated the alloy with chitosan-heparin nanoparticles. The results show that the chitosan-heparin coating had the ability

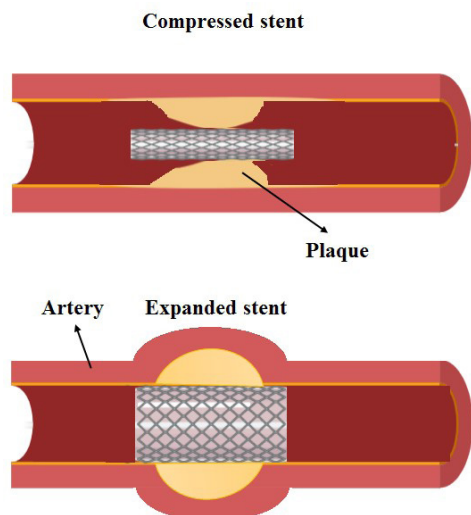


Fig. 4. Schematic illustration of vascular stents performance.

to prevent the nickel ion release, while the ion release was observed in the anodized sample without coating. Furthermore, heparin was released in a controlled manner from the coating, resulting in the remarkable enhancement of blood compatibility. The cell compatibility of the coated specimens was confirmed by the attachment and proliferation of HU-VECs.

Lotkove et al. [50] used plasma immersion ions to dope Si into intravascular NiTi stent. According to the results, the stress required for the stress-induced martensite formation under loading was reduced by surface modification. The hysteresis was also increased upon unloading. It could be concluded that the Si-doped self-expanding stents are a promising material for peripheral vascular treatment. Park et al. [51] also reported that Ta-coated NiTi stent developed by ion-induced plasma sputtering showed enhanced biocompatibility and radiopacity. The improved radiopacity was stated to be due to the large thickness and the large X-ray absorption coefficient of the Ta coating layer. Additionally, Ta coating was believed to improve the attachment and proliferation of endothelial cells.

Park et al. [52] investigated the influence of the TiN on endothelial cell function on the NiTi alloy and its corrosion resistance. In contrast to bare NiTi, TiN-coated samples showed effective prevention of the Ni ions release, promotion of focal adhesion formation, actin cytoskeleton, and amino acid metabolism, improved inflammation regulation, and enhanced energy metabolism.

Witkowska et al. [53] coated composite surface layers (a-C(Ag)+TiO₂) on NiTi using ion beam assisted deposition. It was found that the produced hybrid surface exhibited improved corrosion resistance, surface roughness, altered surface free energy, and wettability, as well as decreased platelet activation, aggregation, and adhesion compared to the uncoated alloy in the initial state. Therefore, these properties offer great benefits for cardiac applications.

Bakhshi et al. [54] developed a polymeric coating based on poly(carbonate-urea) urethane (PCU) and polyhedral oligomeric silsesquioxanes (POSS) for being applied on the nitinol stent using electrohydrodynamic spraying. According to the results, the POSS-PCU coating on the stent surface could improve biocompatibility and enhance surface resistance. Moreover, the peel strength was improved by surface modification before and after degradation.

6. Shape memory polymers for vascular stents

SMPs are used in various possible applications due to having great functionality in SME. The most important applications include engi-

neering, textile, medical, and spacecraft applications. In medical applications, SMP is used as actuation, fixation, and deployment such as cardiovascular stents [55]. Small blood vessels can be protected from collapse, owing to the shape memory effect triggered by hydration of polymers or the temperature change [56, 57].

There is the possibility of artery re-narrowing and occlusion after 6 months using metal stents. These stents must overcome some limitations including thrombogenicity, compliance mismatches, low stiffness, and low flexibility. These devices have been investigated in terms of materials improvement, and the most attractive candidates are biodegradable SMPs [58-61]. Igaki-Tamai stent was one of the first biodegradable shape memory polymer stents. This SMP stent is consisted of poly-L-lactic acid (PLLA), which can recover its shape in 20 min at 37 °C [62]. A bi-layered device composed of PLLA and polyglycolic acid (PLGA) is another example of the biodegradable shape memory stent, which fully degrades at biological environments [63].

Drug delivery systems are gaining increasing significance for the treatment of human diseases [64, 65]. For the prevention of in-stent restenosis, drug-eluting stents (DESs) have been developed recently. It has been found that the restenosis rate can be reduced by local drug delivery. The used drugs in these stents are mainly antibacterial and antiplatelet drugs [66-68].

Yakacki et al. [55] prepared a shape memory polymer using photopolymerization of poly(ethylene glycol) dimethacrylate and tert-butyl acrylate for cardiovascular applications. It was found that crosslink density and T_g highly affected the storage of the stent at room temperature. It was also demonstrated that the crosslink density influenced the stent pressurized response. The prepared SMP showed extensive thermomechanical and shape memory responses to meet the special requirements of cardiovascular devices with minimal invasion.

Biswas et al. [69] developed a biodegradable polyurethane/ two-dimensional platelets nanohybrid SMP for smart biomedical applications such as self-expanding stents. They found that the overall crystallinity in the nanohybrid SMP decreased due to the strong dipolar interaction between polymer chains and nanoclay resulting in remarkable enhancement of flexibility and toughness required for most implants. In addition, the nanohybrid thermal stability improved by the barrier created by the silicate layers of the nanoclay. Therefore, the developed shape memory nanohybrid demonstrated good shape memory property at physiological temperature favored for biomedical applications.

Small et al. [70] presented a novel prototype device comprised of a polyurethane-based SMP stent and a shape memory polymer embolic foam that was attached to the outside of the stent for fusiform aneurysms endovascular embolization. The stent had the role of maintaining an open lumen in the artery and the aneurysm lumen is filled with the embolic foam. An expansion of the foam at body temperature was accompanied by the controlled expansion of the stent in the suitable orientation/location by laser heating. Additionally, for the provision of the control over actuation, a stent with higher elastic modulus and T_g could construct a more rigid structure for supporting the embolic foam. They reported that the laser heating possibly affects the preperipheral arterial tissue adversely by direct heating or heat transfer from the device to the blood cells or surrounding tissue. The blood flow convective cooling was stated to be able to alleviate the adverse thermal effects. However, in localized areas, the blood flow is decreased by the device. By optimization of the device, the laser power amount required for expansion, and the consequent adverse effects can be minimized.

The thermo/moisture response of a polyurethane-based SMP was investigated by Sun et al. [71] for possible surgery inside living cells. Polyurethane SMP has been traditionally recognized for its thermo-responsive behavior. Recently, it has been found that moisture can influence its glass transition temperature, enabling us to understand the shape recovery after a pre-determined sequence and the water-driven shape

recovery. These characteristics are in favor of delivering tiny micro/nano devices for surgery in living cells through a hole with a very small size.

Xue et al. [72] developed biodegradable block co-polymers SMPs based on poly(ϵ -caprolactone) (PCL) and Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) for fast self-expanding stents. They found that the stent containing 25 wt% PHBV exhibited complete self-expansion within 25 s at 37 °C. This performance is much better for the best developed biodegradable stents. Thus, the non-cytotoxic, biodegradable SMP containing 25 wt% PHBV exhibited great thermal expansion property at body temperature proper for fast self-expandable stents.

Baer et al. [73] investigated the expansion, collapse pressure, and thermomechanical properties of neurovascular stent prototypes based on MM7520 polyurethane SMP. According to the results, with the increment of temperature from 32 °C to 47 °C, the collapse pressures of the stents decreased. At temperatures higher than 47 °C, collapse pressures reached a plateau. At body temperature, the stents showed full collapse pressures values larger than 4.7 psi. After crimping, full recovery was obtained by the stents. Their axial shortening and radial expansion ratio were 1.1% and 2.7, respectively. This investigation revealed the promising application of this SMP as neurovascular stents.

The expansion of an SMP stent was simulated and modeled by Liu et al. [74]. The results showed that the shape memory polymer stent could exhibit a stable and soft expansion in the body. Moreover, by applying a higher recovery temperature and a lower heating rate, higher expansion can be achieved. It was shown that the result of the recovery radius fitting function could well describe the performance of the SMP stent according to the recovery temperature and characteristic recovery ratio. The model was proposed to be proper for assisting the design of SMP stent.

Ansari et al. [75] developed PCL/PU SMP and studied its properties in combined torsion-tension loading for the cardiovascular stent application. They found that the stress-strain behavior of the SMP was significantly affected by the increment of the temperature. In the combined loading, normal strain recovery and angle recovery were influenced by high pre-torsion loading and high pre-stretch, respectively. Minimum elastic recovery was achieved at pre-torsion and pre-stretch of 25% and 720°, respectively. The reduction of recovery finished temperature (RFT) was mostly affected by the heating rate among other parameters. In the combined torsion-tension loading condition, these findings can help to develop novel shape memory polymer structures with enhanced performance in biomedical applications.

Jia et al. [76] developed biodegradable self-expanding vascular stents based on PLA using 3D printing. The prepared stent was able to obtain a temporary compressed shape easy for implantation. The stent could keep the temporary compressed shape at ambient temperature, which makes their storage possible. The stent had also excellent shape fixity. The compressed printed stent could expand to its initial shape by heating after implantation. By taking advantage of both self-expansion of biodegradable PLA and tailored design of 3D printing, cardiovascular disease can be effectively treated by the vascular stent.

Lin et al. [77] developed vascular stents based on PLA by the 4D printing technique with negative Poisson's ratio structure. It was shown that shape recovery of the stents was as high as 98% and they had the ability to expand narrow blood vessels within 5 seconds. However, some limitations were observed in the shape memory stents such as the high T_g value of the shape memory PLA although serious vessel injury has not been observed.

7. Conclusion and future insights

SMA's have attracted the attention of many scientists due to their fascinating properties providing their infinite applications. However, a few

devices made of SMA have found a place in the market and their commercial use is limited for very precise aims. Currently, the most important applications of these type of materials are in medicine such as stents and orthodontics appliances, micromanipulators, and robotic actuators. Although the application of such compounds in the medical field is continuously growing and has become almost a standard, the certification for biocompatibility is a major issue for biomedical implants. Thus, the development of more biocompatible materials has found a ground to be investigated. Ongoing research on more functional materials ensures the continuity of SMA's for medical issues.

Biodegradable SMPs can be adapted to the various requirements for biomedical applications. Furthermore, some of their properties, such as biodegradability, flexibility, biocompatibility, chemical stability, and their potential for drug delivery, will encourage the research on the development of SMPs. Various applications including tissue engineering, scaffolds for aesthetic or reconstructive surgery, and biomaterial-assisted therapies require such a combination of biodegradability, functions, drug delivery capability, and shape memory. Presently-used multimaterial systems in these fields are not able to fulfill the needs; therefore, materials that possess all these functions will be of great interest.

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