

Shape-Memory Polymers—A Class of Novel Smart Materials

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Abstract

Shape-memory polymers (SMPs) offer a number of potential technical advantages that surpass other shape-memory materials such as shape-memory metallic alloys and shape-memory ceramics. The advantages include high recoverable strain (up to 400%), low density, ease of processing and the ability to tailor the recovery temperature, programmable and controllable recovery behavior, and more importantly, low cost. This article presents the state-of-the-art regarding SMPs. First, the architecture, type, and main properties of the traditional and recently developed SMPs are introduced. Second, structural and multifunctional SMP composites are summarized and discussed. These composites greatly enhance the performance of the SMPs and widen their potential applications. Finally, current applications of SMP materials in aerospace engineering, textiles, automobiles, and medicine are presented.

Introduction

Shape-memory polymers (SMPs) are able to recover their original shape upon exposure to an external stimulus. While a reversible martensitic transformation is the mechanism behind the shape-memory phenomenon in metallic shape-memory alloys (SMAs), the shape-memory phenomenon in SMPs arises from a dual-segment system, in which one segment is highly elastic and the other is able to remarkably reduce its stiffness in the presence of a particular stimulus. SMPs can be activated not only by heat/magnetism (similar to SMAs), but also by light/moisture and even a change of pH value.¹

Furthermore, SMPs have a far higher recoverable strain (up to 400%), much lower density, more convenient processing and fabrication techniques, and properties that are more easily tailored (e.g., transition temperature, stiffness, bio-degradability, functional gradient) to better accommodate the requirements of a particular application than SMAs. In addition to these advantages, low cost—not only for the materials themselves but also in processing

and fabrication—enables the use of SMPs for a wide range of applications.^{2–6}

In this article, thermo-responsive, light-responsive, and chemical-responsive SMPs are discussed, although with a focus on thermo-responsive SMPs because they are more developed at present.

Definition and Architectures of SMPs

SMPs are able to actively respond to a specific stimulus by means of significantly changing their shape and/or maneuvering accordingly. The basic molecular architecture of SMPs is a polymer network underlying active movement.⁷ Almost all SMPs contain dual segments, where one is highly elastic, and the other is able to remarkably reduce its stiffness in the presence of a particular stimulus. The latter segment can be either a molecular switch or a stimulus-sensitive domain. Upon exposure to a specific stimulus, the switching/transition is triggered, which consequently results in the shape recovery.

As illustrated in Figure 1, the typical thermomechanical cycle of a thermo-responsive SMP consists of the following steps. (1) Form the SMP into a shape (original shape); (2) heat the SMP above its thermal transition temperature (T_{trans}) and deform the SMP by applying an external force, cool well below T_{trans} and remove the constraint to obtain the temporary shape (storage); (3) heat the pre-deformed SMP above T_{trans} at which point the SMP recovers the original shape (shape recovery).⁸

Correspondingly, SMPs are mostly dual shape in nature. One is the deformed configuration, and the other is the original shape. Their shape-memory feature is not an intrinsic material property but results from a combination of the polymer's molecular architecture and a programming procedure in order to obtain the temporary shape. To enable the shape-memory feature, a special architecture is required, consisting of net points and molecular switches that are sensitive to an external stimulus. Net points can be realized by covalent bonds or intermolecular interactions and play a role in connecting the hard segment and the soft segment in a macromolecule chain. When it is heated to an active state, soft segments can be deformed without being limited by the hard segments. Hence, they are either chemical or physical in 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 suitable polymer architectures, these domains can be formed by side chains or by chain segments linking two net points. In both cases, the temporary stabilization is caused by the aggregation of the switching segments.

Thermal-Responsive SMPs

Thermal-responsive SMPs with dual shape capability⁷ can be classified into four different categories according to the nature of their permanent net points and the thermal transition related to the switching domains:⁹

- Chemically cross-linked amorphous polymers ($T_{\text{trans}} = T_g$),
 - Chemically cross-linked semi-crystalline polymer networks ($T_{\text{trans}} = T_m$),
 - Physically cross-linked thermoplastics with $T_{\text{trans}} = T_g$,
 - Physically cross-linked thermoplastics with $T_{\text{trans}} = T_m$.
- Here, T_g and T_m are the glass transition temperature and melting temperature of a SMP, respectively.

Furthermore, these four types of SMPs are characterized by the specific dynamic thermomechanical behavior⁹ as shown in

Figure 2, where the tensile storage modulus versus temperature measured at small oscillatory deformation at 1 Hz is plotted. The storage modulus is measured by a dynamic mechanical analysis instrument. The elastic modulus of a material is the mechanical property that reflects the material's resistance to external mechanical loading, and it is determined from the stress-strain curve. The elastic modulus is composed of the storage modulus and the loss modulus, where the elastic modulus is the modulus of the elastic portion, and the loss modulus is the modulus of the viscous portion of the material.

The first type of SMP in Figure 2a is a cross-linked glassy polymer featuring a sharp glass transition at the temperature of rubber elasticity, above the glass transition temperature derived from covalent cross-linking.

The second type of SMP (Figure 2b) is composed of semi-crystalline networks in which the melting transition at T_m is employed to trigger shape recovery.

The third type of SMP (Figure 2c) is a thermoplastic in which crystalline or rigid amorphous domains serve as the physical cross-links that afford high elasticity.

The fourth type of SMP (Figure 2d) is a block copolymer, of which the shape-memory transition temperature is determined by the melting transition temperature (T_{m2}) of the crystalline soft segment. Both SMPs represented in Figure 2c and 2d have crystalline hard domains, domains of the hard segment in a macromolecule, characterized by T_m . The shape-memory transition temperature of a SMP is determined by the melting transition temperature of the crystalline cross-links or soft segment.

The most important group of physically cross-linked SMPs is linear block copolymers, including polyurethanes and polyetherester.² In polyester-urethanes, oligo-urethane segments act as the hard elastic segments, while polyester is the switching segment.^{10–12} The phase separation and the domain orientation of poly(ϵ -caprolactone)-based polyester-urethanes were determined by Raman spectroscopy.¹³ A similar effect is found in copolyester-based ionomers obtained by bulk polymerization of adipic acid and mixed monomers (bis-poly(oxyethylene)) sulfonated dimethyl fumarate and 1,4-butane-diol).¹⁴ The polycarbonate segment is synthesized by copolymerization of ethylene oxide in the presence of CO_2 and catalyzed by a polymer-supported bimetallic catalyst, which yields an aliphatic polycarbonate diol. This macrodiol is further processed by the prepolymer method into a polyurethane SMP.¹⁵

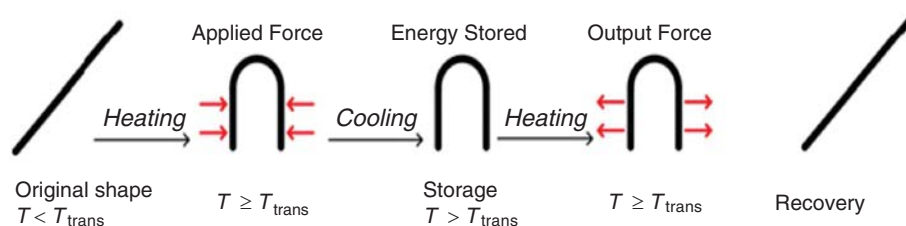


Figure 1. Schematic illustration of the shape-memory effect in a typical thermomechanical cycle. T , temperature; T_{trans} , transition temperature. Reprinted with permission from Reference 8. ©2009, Institute of Physics and IOP Publishing.

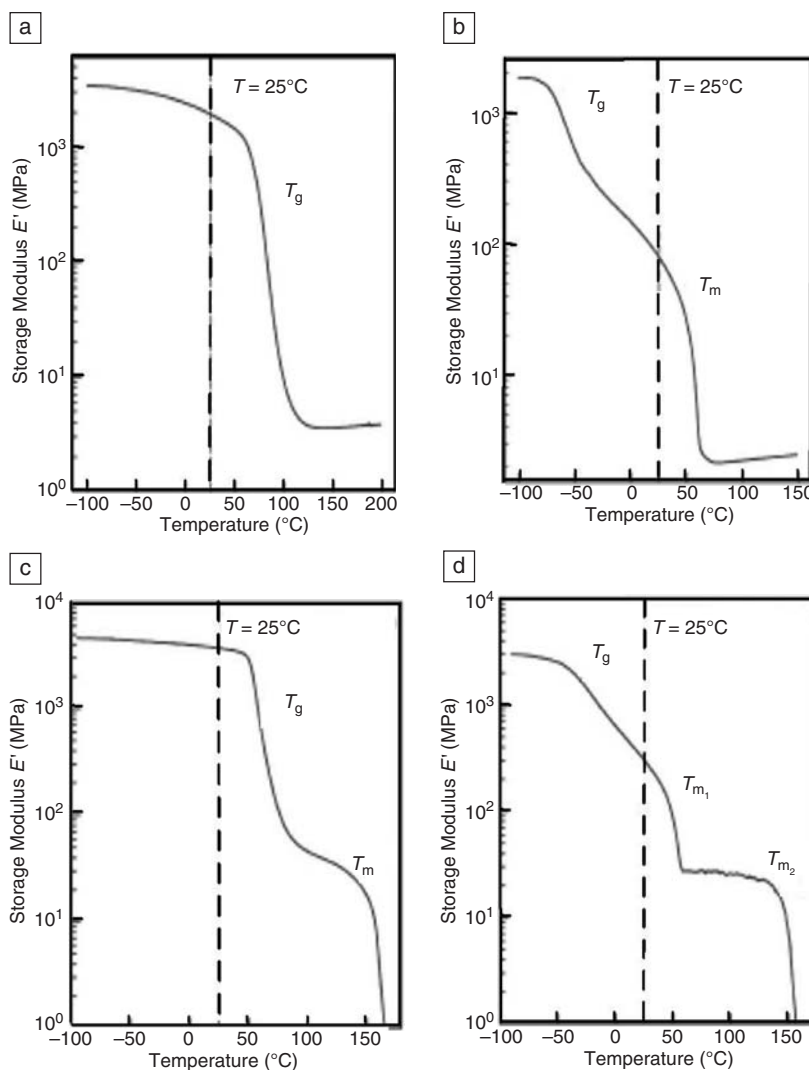


Figure 2. Four types of shape-memory polymers (dual shape effect) depicted as a function of their dynamic thermomechanical behavior. Plotted is the tensile storage modulus (E') versus temperature as measured using a small oscillatory deformation at 1 Hz for (a) chemically cross-linked amorphous polymer networks ($T_{\text{trans}} = T_g$); (b) chemically cross-linked semi-crystalline polymer networks ($T_{\text{trans}} = T_m$); (c) physically cross-linked thermoplastics with $T_{\text{trans}} = T_g$; and (d) physically cross-linked thermoplastic ($T_{\text{trans}} = T_m$). T_{trans} is the transition temperature; T_g is the glass transition temperature; T_m is the melting temperature; T_{m1} is the melting transition temperature of the cross-links; and T_{m2} is the melting transition temperature of the soft segment. Reprinted with permission from Reference 9. ©2007, Royal Society of Chemistry.

Covalent net points 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 at least one must be tri-functional where the monomer has three functional groups in its chemical structure. Depending on the synthesis strategy, cross-links can be created during synthesis or by post-processing. Subsequently, the shape recovery can be triggered by the melting of crystallites, which can be controlled by the trans-vinylene content. In a polymer network, the trans-vinylene works as a cross-linking agent. With an increasing amount of cross-linking agents, the crystallinity of material decreases.¹⁶ Additionally, shape-memory properties also are influenced by the monomer component.¹⁷

The other synthesis routes to obtain polymer networks involve the copolymerization of monofunctional monomers with low molecular weight or oligomeric bifunctional cross-linkers.¹⁸ The copolymerization of monofunctional monomers of low molecular weight with oligomeric bifunctional cross-linkers enables AB copolymer networks, obtained from the copolymerization of diethyleneglycole with *t*-butyl acrylate, with increased toughness and elasticity at room temperature.¹⁹ This type of SMP is a cross-linked glassy polymer featuring a sharp glass transition temperature derived from covalent cross-links. The shape-memory effect is determined by its cross-linking nature.

Covalently cross-linked polymers also can be synthesized by polyaddition or polycondensation reactions. Polyurethane networks prepared by the prepolymer method using diisocyanate and 1,1,1-trimethylol propane provides covalent cross-links, whereas poly(tetrahydrofuran) provides the switching segment.²⁰ In the two-step process, the prepolymer is formed by the reaction of poly(butylene adipate) with diphenylmethane diisocyanate and afterward reacts with the hyperbranched polyester Boltron H30.

Light-Responsive SMPs

Light-induced stimulation of SMPs has been realized through the incorporation of reversible photoreactive molecular switches. Upon irradiation with light of a suitable wavelength, a cycloaddition reaction occurs among these light-sensitive moieties. Irradiation with a different wavelength results in cleavage of the newly formed bonds.

Independence of shape recovery from any temperature effect has been achieved in light-responsive SMPs.⁵ Here, light of different wavelengths is used for the fixa-

tion of the temporary shape and for shape recovery. For example, on the molecular level, this is realized by the incorporation of photosensitive molecular switches, such as cinnamic acid or cinnamylidene acetic acid. When irradiated by light of a suitable wavelength (λ), the photosensitive functional groups form covalent cross-links with each other in a [2 + 2] cycloaddition reaction. Light-responsive SMPs consist of two components on the molecular level: molecular switches and coiled polymer-chain segments. Upon exposure to light, two molecular switches are cross-linked to form a circle in which two segments are involved. In the course of programming, the polymer is strained and then irradiated by ultraviolet light of $\lambda > 260$ nm so that new covalent bonds are created to fix the strained chain segments in their uncoiled conformation. These newly formed covalent bonds can be cleaved and the permanent shape recovered when the sample is irradiated by light with $\lambda < 260$ nm.

The photosensitive groups have been incorporated into two alternative polymer network structures, a graft polymer network and an interpenetrating polymer network. For a light-responsive SMP with a graft polymer network, the photo-reversible covalent cross-links are formed through molecular switches that are grafted onto the polymer network. For a light-responsive SMP with an interpenetrating polymer network, the photo-reversible covalent cross-links are formed through molecular switches that interpenetrate the polymer network. In both cases, the permanent shape is determined by permanent net points, which cross-link the chain segments of the amorphous polymer networks.⁵

Chemo-Responsive SMPs

Indirect actuation for shape recovery by means of lowering the transition temperature of SMPs has been demonstrated in commercially available polyurethanes^{21–24} and polystyrene.^{25,26} When immersed into a special chemical liquid (e.g., a solvent), solvent molecules diffuse into the polymer sample and act as a plasticizer, resulting in shape recovery (Figure 3).²² In polyurethane, it was revealed that the lowering of T_g depends on the amount of absorbed moisture, which, in turn, depends on the immersion time. The molecules first diffuse into the polymer network, then have a plastic effect on the polymer and lower T_g of the polymer. With T_g of the polymer is below the temperature of the environment, shape recovery will occur. On the other hand, the shape recovery of a polystyrene SMP was observed upon immersion into N, N-dimethylformamide

(DMF), as shown in Figure 4.²⁶ Furthermore, the solubility parameter of the solvent plays an important role in shape memory recovery.²⁷ A different strategy for water-actuated SMPs has been realized in polyether-urethane polyhedral oligomeric silsesquioxane block copolymers.²⁸ Here, low molecular weight poly(ethylene glycol), or PEG, was used as the polyether segment. Upon immersion into water, the PEG segment dissolves, resulting in the disappearance of T_m and recovery into the permanent shape.

Shape-Memory Polymer Composites

Pure SMPs, in general, exhibit low strength and stiffness and produce an elastic modulus of only 10 MPa. Thus incorporation of reinforcement fillers has been investigated to improve their properties for diverse applications.

Reinforced SMP Composites

The reinforcement can improve mechanical properties and environmental resistance and turns the SMP into a high-performance structural material. Both particles and fibers can be used as reinforcements to achieve higher stiffness.²⁹ The elastic modulus increases by approximately a factor of three, after loading with 40 wt% SiC.³⁰ The most recent development is to use nano-sized carbon fillers.³¹ Incorporation of 3.3 wt% multi-walled carbon nanotubes (CNTs) into polyurethane SMPs results in an increase of the recovery stress by 200%. After several cycles of training, the nanocomposites retain a high shape recovery ratio (more than 90%).³² Generally, the shape recovery ratio of thermoplastic SMP bulk ranges from 80–90%, while that of thermoset SMP bulk is approximately 95%.

Koerner et al.³³ compared polyurethane SMPs reinforced with CNTs and carbon black. The nanocomposites display increased shape fixity, which is defined as the capability of maintaining the deformed temporary shape. The CNT-reinforced materials show almost 100% shape recovery as compared with the carbon black-reinforced materials, which exhibit only a limited shape recovery ratio of around 30%. The difference in behavior of the two materials is attributed to the interactions between the anisotropic CNTs and the crystallizing polyurethane switching segments.³³

Furthermore, continuous fiber-reinforced SMP composites play an important role in improving mechanical properties for applications. An increase in failure stress of 140% and a decrease in recovery ratio of 62% are reported³⁴ as a result of an addition

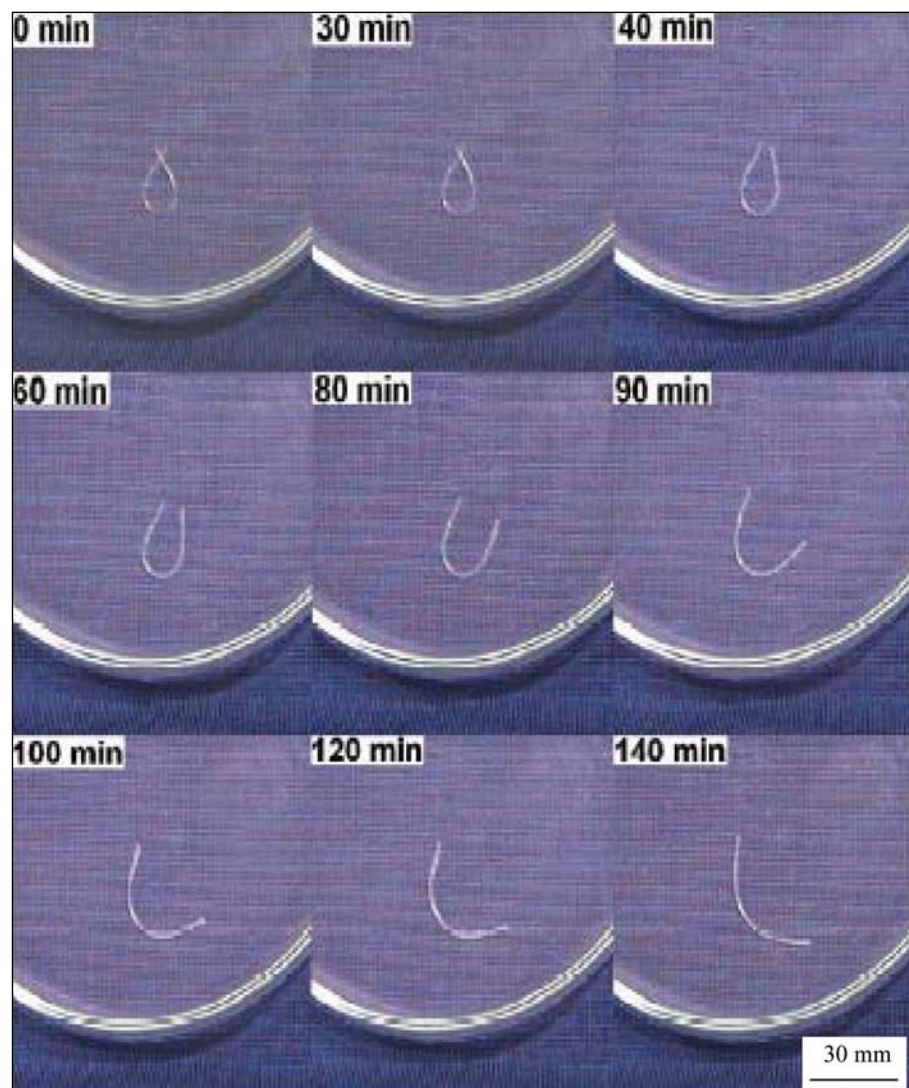


Figure 3. Water-driven actuation for the shape-memory effect. A shape-memory polyurethane with a circular temporary shape is immersed into water. After 30 minutes, the recovery to the linear permanent shape begins.²¹ Reprinted with permission from Reference 21. ©2005, American Institute of Physics.

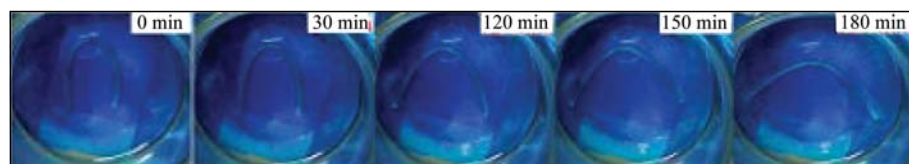


Figure 4. Shape recovery in a 2.88-mm diameter shape-memory polymer wire in dimethylformamide. The wire was bent into an "n" shape. Reprinted with permission from Reference 25. ©2008, Wiley-Vch Verlag GmbH & Co.

of 50 wt% of glass fiber after injection molding. A similar trend is reported in SMP composites blended with carbon fibers.³⁴ It is of vital importance that the impregnation process used to combine the reinforcing

fiber with SMPs is conducted in such a way that each fiber in each yarn bundle is completely wetted by the matrix. In addition to improved stiffness, other advantages of short fiber-reinforced SMPs are light

weight, possible electrical conductivity (if a conductive filler is used), enhanced wear resistance, and improved dimensional stability.

Multifunctional SMP Composites

The state-of-the-art in the fabrication of SMP composites is to load them with fillers for multiple functionality and/or to apply alternative activating techniques. The first SMPs were based on the thermally induced dual shape effect. Since then, the external stimulus has been extended from direct heating to other methods (e.g., indirect thermal actuation or other direct actuation after blending with other stimulus-sensitive groups at the molecular level). In addition, some of these materials can be made biofunctional and/or biodegradable. Such multifunctional SMP composites enable tailored properties and thereby a wider range of applications.

Electrically Conductive SMP Composites.

Conductive SMP composites have been produced by blending in various kinds of conductive fillers, such as CNTs, short carbon fibers (SCFs), carbon black, metallic powders (e.g., Ni powder, even aligned in chains, which occurs upon the application of an external magnetic field during the curing progress of the shape-memory polymer), or a conductive polymer. The composites are suitable for electrically induced actuation by means of Joule heating, which can be controlled remotely.³⁵

After nitric acid and sulfuric acid treatments, 5 wt% multi-walled CNTs were loaded into a polyurethane SMP. The composite can be heated for shape recovery by applying a 60 V electrical current.³⁶

Actuation of a styrene-based SMP blended with carbon black and SCFs had been demonstrated by applying 25 V.³⁷ It was found that the carbon black were distributed homogeneously within the polymer matrix and served as interconnections with the SCFs. The SCFs are rigid long aggregates of carbon that help the formation of conductive networks.³⁸ Subsequently, carbon black is incorporated into the SMP, and the actuation of this type of composite has been realized by electrical resistive heating.³⁹

Alternatively, a slight improvement in electrical conductivity can be achieved by adding a small amount of electromagnetic Ni powder into a polyurethane SMP/carbon black composite, and significant improvement is achieved if Ni chains are formed after application of a weak static magnetic field.^{40,41} By adding in 0.5 vol% Ni powder and aligning them into chains in a SMP filled with carbon black, the

electrical resistivity is reduced by more than 10 times, in comparison with the same sample but with randomly distributed Ni powder. As shown in Figure 5, at 0.5% volume fraction of Ni micro powder, the chained sample (with dimensions of 40 mm × 15 mm × 0.6 mm and a resistivity of 12.18 Ω cm in the chain direction) can be heated from 20°C to 55°C by applying 6 V to trigger full shape recovery. These dimensions correlate with the electrical resistance of composites. (Upon application of the same voltage, the resistive Joule heating that is used to induce the shape recovery is determined by the electrical resistance.)

Magnetic SMP Composites. After incorporating ferromagnetic materials in SMPs, an alternative magnetic field may be applied to achieve induction heating. Mohr et al.⁴² realized such remote and wireless actuation by incorporating ~20–30 nm iron (III) oxide nanoparticles into a polyurethane SMP. Iron (III) oxide nanoparticles were coated with silica to improve their dispersion within the SMP matrix. The shape-memory effect was evi-

denced by the shape change from a corkscrew-like spiral temporary shape into a flat permanent shape, when subjected to a magnetic field strength of 30 kA m⁻¹. Fe₃O₄ (40 wt%) was added into polyurethane SMP (15 mm × 2 mm × 0.5 mm). Shape recovery was completed within 20 seconds. The specific loss of power of the particles was determined to be 30 W g⁻¹ at 300 kHz and 5.0 W, which is within acceptable limits.⁴³ This magnetic actuation approach also has been carried out by the incorporation of Ni-Zn ferrite particles within a thermoset SMP.⁴⁴

The magnetic SMP has several advantages:

1. By carefully selecting particle materials with a certain ferromagnetic Curie temperature, one can fully eliminate the possible danger of overheating.
2. Virtually any complex-shaped device can be activated because heat is self-produced.
3. Actuation can be triggered in a remote and wireless manner so that this technique is applicable to embedded devices, such as medical devices inside a human body.^{45–47}

Infrared Light-Induced SMPs. In addition to the aforementioned approaches, thermo-responsive SMPs can be heated by illumination with infrared light.³³ Infrared light-induced polyester-urethanes reinforced with CNTs or carbon black of similar size display a remote thermal response. In this manner, this type of response also has been achieved for polystyrene SMP composites filled with carbon black.⁴⁸

An alternative is to embed an optical fiber into a SMP for indirect heating. This concept has been demonstrated in a laser-activated polyurethane medical device.^{49–51} Another example is a styrene-based SMP embedded with surface-modified optic fiber. The optic fiber is treated by an aqueous solution of sodium hydroxide, and the cladding is removed. In this manner, the input light may be transmitted from the side of the optical fiber, in addition to transmission from the end of the optical fiber. The input light was emitted from the optical fiber to indirectly heat the polymer.⁵²

Applications of SMPs

Given these advantages, SMPs have been used in many areas. Here, we briefly summarize some typical applications in aerospace engineering as well as the textile, automobile, and biomedical industries.

Applications in Aerospace Engineering

Thermally responsive SMPs have been developed to meet current and future aerospace engineering requirements due to their advantages such as low cost, controllable recovery behavior, light weight, and space-qualified and reliable shape recovery. These characteristics make them particularly well-suited for both small and large space applications, such as in hinges, booms, deployable optical systems, mirrors, antennae, flexible reflectors, SMP foam deployable structures and morphing structures.^{8,53}

A deployable hinge consists of two curved shells that are made from a fiber-reinforced SMP composite placed together in opposing directions.⁸ Figure 6 shows the deployment process of the prototype of a solar array that was actuated by a SMP composite hinge made of a thermoset SMP reinforced with carbon fiber. The solar arrays were suspended on a setup that simulated a zero-gravity environment. Heated by 20 V, the hinge was bent to a storage angle of 90° by the application of an external force at a temperature of 80°C. After fixing the storage shape at room temperature, the SMP hinge was heated again by applying the same voltage. The solar array deployed from 90° to ~0° in approximately 80 s.

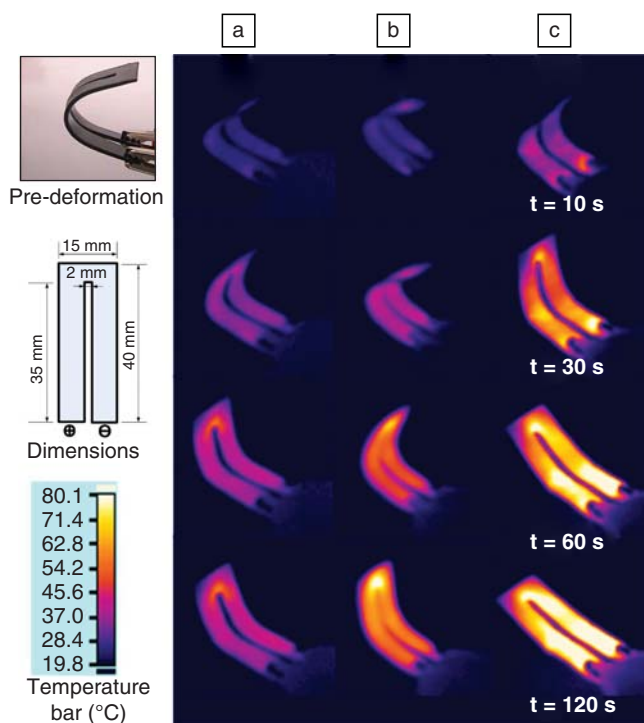


Figure 5. Sequence of shape-memory recovery behavior and the temperature distribution in a demonstrated sample, as recorded by an infrared video. Top-left inset: pre-bent shape; middle-left inset: dimensions of sample. Bottom-left inset: temperature bar (in °C). Sample (a) 10 vol% of carbon black only; sample (b) 10 vol% of carbon black, 0.5 vol% of randomly distributed Ni; and sample (c) 10 vol% of carbon black, 0.5 vol% of chained Ni. Reprinted with permission from Reference 37. ©2008, American Institute of Physics.

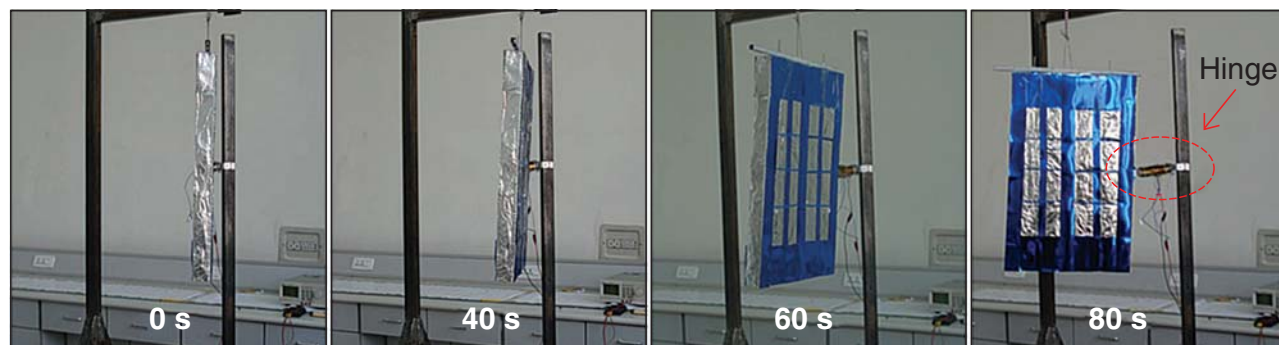


Figure 6. Shape recovery process of a prototype of a solar array actuated by a shape-memory polymer hinge. Heated by an applied voltage above 80°C, the hinge was bent to a storage angle of 90°, then cooled back to room temperature at 0 s; 20 V is applied at 40 s; the shape-memory polymer composite (SMPC) hinge starts to recover from its temporary shape; at 80 s, the SMPC hinge regains its original shape. Reprinted with permission from Reference 8. ©2009, Institute of Physics and IOP Publishing.

An SMP-based boom has been realized to meet the requirements for the fabrication of a lightweight boom.⁵⁴ A lightweight extendible boom has been identified to support a micro-propulsion attitude control system (a three-axes pulsed plasma thruster system designed by the Air Force Research Laboratory), of which the objective is to demonstrate attitude control.⁵⁴ The SMP composite boom has been designed with principal structural members and a central element, SMP composite single-tape longerons, with a number of embedded heaters that function as the primary deployment mechanism. (In aircraft construction, a longeron is a thin strip of wood or metal to which the skin of the aircraft is fastened. Longerons are attached to the ribs in the case of a wing, or frames in the case of the fuselage. Longerons often carry loads and help to transfer skin loads to internal structure.) Embedded aero heater design elements, discretely located within each longeron, were included to store and recover the packaging strain energy in a similar manner as the EMC hinge.⁵⁵ Flexibility in the design elements, such as alteration of the heater dimensions, the cross section of the longeron, and/or the architecture of the composite laminate, allow for a variety of boom layouts to be explored within a given spacecraft class. This flexibility enables a deployable structure to be developed, which specifically and efficiently meets mission requirements.

Preliminary efforts of SMP composite technology have been focused on the fabrication and applications in lab-scale mirrors, deployable optic reflectors, and truss structures.^{56,57}

Applications in the Textile Industry

Several kinds of SMPs can be employed to prepare SMP fibers. They include shape-

memory polyurethanes (including modified shape-memory polyurethanes that incorporate ionic or mesogenic components into the hard segment phase), polyethylene terephthalate-polyethylene oxide copolymer, polystyrene-poly(1,4-butadiene) copolymer, polyethylene/nylon-6-graft copolymer, triblock copolymer made from poly(tetrahydrofuran) and poly(2-methyl-oxazoline), and thermoplastic polynorbornene. Other polymers that show the shape-memory effect by cross-linking after spinning, such as polyethylene, poly(vinyl chloride), and polyethylene-poly(vinyl chloride) copolymer, can also be used.^{58–60}

The main forms of SMPs applied in textiles, clothing, and related products include shape-memory fibers, shape-memory yarns, shape-memory fabrics, and shape-memory chemicals. Shape-memory chemicals are emulsions that are used for preparing shape-memory fabrics. There are three components: shape-memory polyurethane, water, and an emulsifying agent.^{61,62} The woven fabric having a high T_g can be applied to the collars, cuffs, and shoulder pads of utility shirts.^{58,63}

Shape-memory fabrics include woven, knitted, braided, and nonwoven fabric.⁶⁴ The fabric easily returns to its original shape when heated above the switch temperature, even if it has been wrinkled or severely deformed. Therefore, the fabric can be applied in collars and cuffs, which need to keep their shape, and for elbows and knees, which need to recover their shape if wrinkled.⁶⁵

Automotive Applications

With the development of active and intelligent materials, SMPs have been used in automotive engineering. Many interesting areas of application have been developed,^{66–73} such as reconfigurable

storage bins, which is a structural component comprising of a SMP material configured to undergo a change in the modulus of elasticity upon receipt of an activation signal and results in a change in shape of the structural component. The advantages of SMPs include shape-memory behavior (deployable structures and morphing structures), ease of manufacturing (in comparison with shape-memory alloys, of which the manufacturing requires more than 1000°C and high pressure), high deformation strain (up to 400%), and low cost (the price of SMPs is as low as \$10 per pound, while that of traditional shape-memory materials is more than \$250 per pound).

As a typical example, SMPs have been used in an airflow control system to solve a long-standing issue in automobile design.⁷¹ Airflow over, under, around, and/or through a vehicle can affect many aspects of vehicle performance, including vehicle drag, vehicle lift and downward force, and cooling/heating exchange. A reduction in vehicle drag reduces the consumption of fuel. A vehicle airflow control system, which comprises an activation device made of SMP material, actively responds to the temperature and alters the deflection angle accordingly.^{74–77} Thus, the airflow is under control based on changes in the environment.

Applications in Biomedicine

Biocompatible and degradable SMPs with appropriate mechanical properties could be developed for novel medical devices.¹ Currently in the animal testing stage, large bulky devices could potentially be introduced into the body in a compressed temporary shape by means of minimally invasive surgery and then be expanded on demand to their permanent shape to fit as required. In the same way,

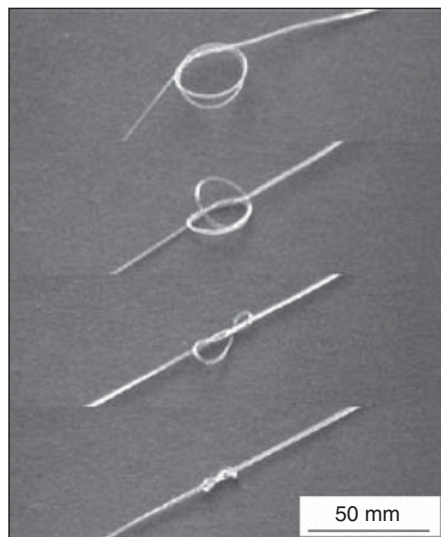


Figure 7. A fiber of thermoplastic shape-memory polymer was programmed by stretching about 200% at 40°C. After forming a loose knot, both ends of the suture were fixed. The photo series shows, from top to bottom, how the knot tightened in 20 s when heated to 40°C. Reprinted with permission from Reference 1. ©2002, American Association for the Advancement of Science.

complex mechanical deformation could be performed automatically instead of manually by the surgeon.

A challenge in endoscopic surgery is the tying of a knot with instruments and sutures to close an incision or open lumen. It is especially difficult to manipulate the suture so that the wound lips are pressed together under the right stress. When the knot is fixed with a strong force, necrosis of the surrounding tissue can occur.⁷⁸ With a weak force, scar tissue, which has poorer mechanical properties, forms and may lead to hernias.⁷⁹ A possible solution is the design of a smart surgical suture, whose temporary shape will be obtained by elongating the fiber under a controlled stress. This suture can be applied loosely in its temporary shape; when the temperature is raised above T_{trans} , the suture will shrink and tighten the knot, applying the optimum force (Figure 7). This procedure is currently being tested on animals.

Additional experiments have been carried out to test the feasibility of this concept. The highly elastic shape-memory thermoplastics were extruded into monofilaments. A sterilized suture was programmed under sterile conditions by exerting a controlled stress on the extruded fiber and subsequent thermal quenching.^{1,79} This feasibility study sug-

gests that this type of material has the potential to influence how implants are designed and could enable new surgical devices in the future. Strong, elastic, and biodegradable, it could be fashioned into thread for stitches that tighten themselves and then melt away as the body heals. Furthermore, these threads have been realized in self-tightening with shape-memory effect. However, current techniques are required for improving stress recovery and cycle time, which are two main limitations of SMPs in comparison with SMAs.

Conclusions

Here, we present a brief summary of three primary aspects of shape-memory polymers (SMPs): materials background of SMPs, SMP composites, and applications of SMPs. This article serves as a short introduction to this class of shape-memory materials, which are still under development but have already demonstrated promise in many areas.

The various SMP classes were first reviewed. They were defined as thermal-responsive SMPs, light-responsive SMPs, and chemo-responsive SMPs. SMP research was initially founded on the thermally induced shape-memory effect. This concept has been extended to other stimuli by addressing stimuli-sensitive groups on the molecular level. Subsequently, reinforced and multifunctional SMP composites were introduced where reinforcement and functional filler materials were incorporated, respectively. Finally, many applications ranging from the aerospace to biomedical industries have been proposed for the use of SMPs.

We have recently witnessed rapid development in SMPs. The advantages of SMPs have attracted attention from academic researchers as well as industrial engineers. Although a number of applications have been identified, many more SMP products are currently being developed. With the further development of currently available SMPs and the emergence of new types of SMPs, the range of applications is expected to expand more widely in the near future.

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