Chapter 10

Shape-Memory Polyurethane Polymers

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Polyurethanes (PUs) are one of the most widely used polymers in research and industry. They can be synthesized from chemical sources and natural sources. PUs are a very useful class of polymers and exhibit many desirable properties that can be exploited in various applications. PUs are formed by the reaction between polyols and isocyanates. A wide variety of polyols and isocyanates are available for synthesis, and hence we can produce a large number of PUs. PUs show high mechanical strength, chemical resistance, flexibility, and resilience. One of the major advantages of some specially designed PUs is their ability to recover their primary shape, which is known as shape memory. The shape-memory effect (SME) of PUs makes them popular in biomedical, electronic, and thermal applications. The SME can be monitored using different measures such as shape fixity, recovery time, and recovery rate. Various stimuli are applied to shape-memory materials to induce shape memory. PU polymers can be modified with different nanofillers, and these fillers influence the shape-recovery parameters. PU composites are popular because of a good property–price relationship. This chapter discusses the various factors affecting the SME of PU composites and the effect of different types of fillers on the PU matrix.

Introduction

Polyurethanes: An Overview

From their first synthesis through a normal polyaddition reaction in 1937 by the genius German chemist Prof. Otto Bayer, polyurethanes (PUs) have been one of the most demanded plastics in the world. Otto Bayer is recognized as the father of PUs. PUs are a class of polymers that are widely used in industry in applications such as upholstery materials, resilience materials, and bushings. PUs are very much close to our lives, from clothes to footwear, from bedding to roofing, and from cars to the construction field. PU attributes include high mechanical strength, flexibility, and chemical and oil resistance. These properties make them a favorite candidate in a variety of aforementioned applications. PUs are interesting polymers because of their methods of synthesis and wide field of applications. The reaction chemistry of PU is simple, but it has unwanted side reactions. Generally, PUs are reaction products of an isocyanate and an oligomeric compound containing hydroxyl groups, called polyol, and often a chain extender (low molecular diol). Depending on the choice of the starting materials, the chain length, properties, and applications of PUs can be tuned. Because PUs contain reactive functionalities, they easily form blends and composites with other polymers. PU composites are used in biomedical applications because of their biocompatibility and possible biodegradability. The polyols can be derived from vegetable oils, and the PU composites made up of these polyols normally show biodegradability. Biobased PUs may be recycled, and hence it is a step toward a greener approach in PU synthesis. In addition to the aforementioned advantages, PU composites are known to possess a wide range of good intrinsic properties. The segmented structure of PUs makes them capable of memorizing the shape (shape memory). Shape-memory PUs are very important both industrially and biomedically.
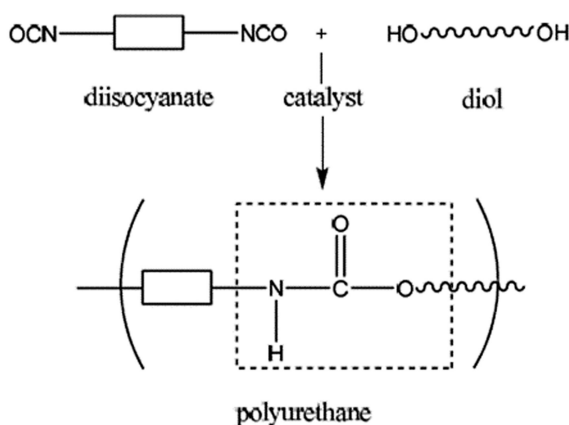
Synthesis of PUs

PUs are segmented polymers that contain two segments: hard and soft (Scheme 1).
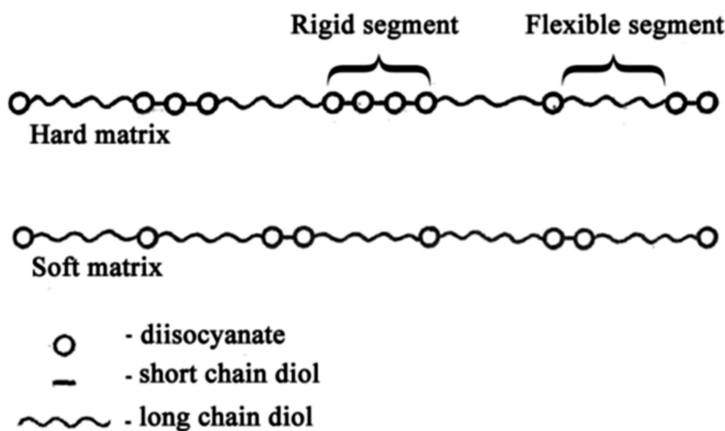
Scheme 1. General structure of segmented PUs.

The diol part constitutes the soft segment (SS), and the isocyanate constitutes the hard segment (HS). The chemical linkage in the polymer is denoted as urethane linkage (-NHCOO-) and is the most reactive moiety in the PU. There are mainly two types of PUs: polyester based and polyether based, depending on the diol part. The general synthetic route of a PU is given in Scheme 2.

Scheme 2. Synthetic route of PU from diol and isocyanate.

Biobased PUs

As mentioned previously, PUs are synthesized from polyol and isocyanates. Isocyanates are considered harmful or toxic chemicals. After the use of PU and its composites, waste disposal is a huge environmental consideration. Both incineration and landfilling are unsafe. So the synthetic route must be modified to make it environmentally friendly or green. Here comes the role of development of biobased PUs. Various methodologies have been adopted in order to make PUs greener, such as selecting biobased polyols and isocyanates, converting the byproducts into secondary materials, and considering non-isocyanate routes in the synthesis.

Fatty acids are a rich source of precursor materials for the PU industry. As a general consideration, biobased PUs contain polyols from vegetable oils. Castor oil is used in large quantities to derive polyols. Castor oil is a nonedible oil with economic importance. It contains triglycerides of hydroxyl fatty acid known as ricinoleic acid. From this oil, polyol can be derived, and the castor oil–based PU composite can be prepared with suitable isocyanate. These composites have been used in the biomedical field. Plant-oil–based polyols, including those derived from soybean, sunflower, jatropha, linseed, tung, palm, and *Sapium sebiferum* kernel oils, can also be used for the preparation of novel specific PU formulations. The strength of biobased PUs can be improved, and the resultant materials can be used for composites, polymer concrete, and marble preparation. PU concrete based on vegetable oil polyol has a splitting tensile strength of 22 MPa, a flexural strength of 50 MPa, and a compressive strength of 115 MPa, which is about 5–10 times higher than that of conventional high-strength concrete and higher or comparable to epoxy- or polyester-based concrete (*1*).

Biobased PU nanocomposites can be synthesized by adding suitable nanomaterials such as fibers, silica, graphene, carbon nanotubes (CNTs), or biomaterials. Graphene oxide (GO) can be used to modify plant-based PUs (Figure 1).

There are materials from which eco-friendly isocyanates or related compounds can be synthesized. Vegetable feed stock is a rich source of furfural. This material can be used to produce furfuryl amine, which can be converted into furfuryl isocyanate, a green precursor for PUs. We can reduce waste materials and also toxic chemicals. When such isocyanates are reacted with biobased polyols, the PUs become biodegradable and eco-friendly. The flow behavior of PU-synthesized biobased isocyanate and soybean oil–based polyol can be tuned by controlling the amount of polyol. These types of composites are non-Newtonian (*2*).

Soy-based PUs have thermal, oxidative, and hydrolytic stability that is superior to those based on petrochemicals, and soy-based PUs could be a practicable substitute for petrochemical–urethane matrix resins for composites.
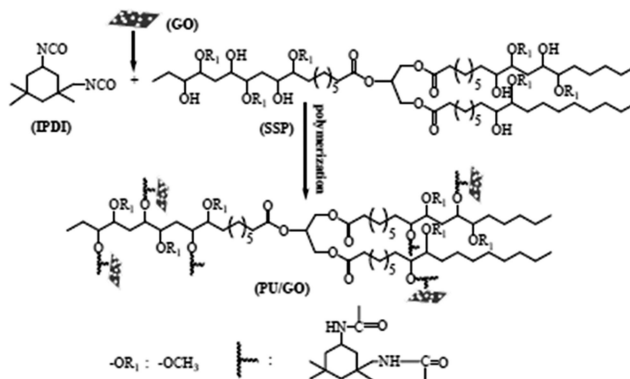

Figure 1. Biocomposites fabricated from PU with graphene as fillers. The graphene sheets are functionally attached to the PU chain.

The properties of biobased PUs can be improved by the addition of a second phase. When glass fibers are used, the mechanical properties can be improved. The physicomechanical properties of the resulting composites with glass fiber loading from 15, 30, and 50 wt % showed significant increase. The storage modulus of virgin biobased PU gets a 14-fold increase on reinforcement with 50 wt % glass fibers. The results highlight a significant enhancement in strength and modulus of virgin biobased PU by more than 260 and 480%, respectively, for a fiber content of 50 wt % (3).

When soy-based PUs were modified with glass fibers, a noticeable increase in mechanical strength was obtained. The thermal stability and durability of the biobased PUs containing molasses and lignin can be improved by adding inorganic fillers such as barium sulfate and calcium carbonate. The hydroxyl (–OH) group in the plant materials can act as a reaction site (4). Thermal and mechanical stability can be enhanced by adding natural fibers such as unidirectional sisal fibers. PU prepared from rubber seed oil can be modified by adding such fillers, and the flexural modulus and tensile strength can be enhanced. Because of the high fiber matrix interaction, the thermal properties can also be enhanced (5). The flexible PUs derived from castor oil–based polyols can be made stiff by adding cellulose nanowhiskers. In order to enhance the compatibility, the cellulose nanowhiskers can be modified and covalently bonded to a PU chain. The storage modulus can be improved by this modification. Increased cross-link density and enhanced interaction between biobased PU matrix and nanowhiskers are responsible for the increase in properties (6).

Fiber volume fraction, fiber length, and alkaline treatment can influence the mechanical and thermal properties in the case of short random banana-fiber-reinforced PU derived from castor oil. Hydrophobic coatings can be synthesized from dispersion of PU–perfluorooctyltrimethoxysilane-$nTiO_2$ hybrid in a solution containing castor oil, triethanolamine, and isophorone diisocyanate prepolymer. The degree of hydrophobicity was found to be increased from 68 to 132° as per the contact angle measurements. These composites also exhibit self-cleaning properties.

Shape-Memory Behavior: An Overview

Shape-Memory Polymers and Phases: Amorphous and Crystalline

PU polymers are very structurally interesting materials. This group of polymers can be synthesized from many different substrates, such as isocyanates, oligomers, chain extenders, or cross-link agents and catalysts.

Shape-memory polymers (SMPs) belong to the specific class of smart materials that are able to respond to proper stimuli and recover their original shape (OS). The general definition of an SMP is a polymer that is able to memorize its original permanent shape, achieve a metastable temporary shape under deformation, and return to the OS through a stimulating factor.

Specific properties of PU SMPs are able to be observed when external stimulation occurs, such as a thermal, chemical, or physical (e.g., light) factor (7). The behavior of such materials is demonstrated by the extremely wide group of materials known as PUs. PUs are predestinated as SMPs because their structure is basically built from HSs and SSs (8). The presence of these structural forms is related to the fact that PUs are made of rigid segments (isocyanates + chain extenders or cross-linkers) and flexible segments (polyols) (Figure 2) (9). The shape-memory effect (SME) of PUs is strongly associated with microphase separation of these polymers, and therefore, they exhibit the characteristic behavior of SMPs. The heterogenous structure (different HSs and SSs) within PUs may be able to control external factors (characteristic trigger). For PUs, studies show that the SS phase is related to the shape fixity of the materials, whereas the HS phase is in charge of shape recovery. In PUs, SSs can act as actuator domains, in which polymer chains or chain fragments are straightened at tension at a temperature higher than the glass-transition temperature (T_g), their position is fixed at cooling, and they are able to shrink and return to the coiled form at repeated heating. In turn, the HSs can support crystallization of the SSs (10).

The polymeric hard phase is reliable for retaining the original geometry of the SMPs. This segment may be formed by chemical cross-linking, interpenetrating networks, or the formation of crystalline phases within the PUs (11).
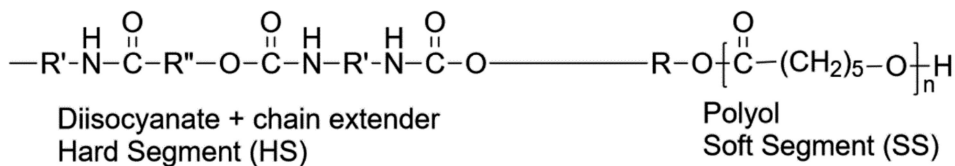

Figure 2. Microphase separation structure of PUs.

The most investigated SMPs are thermally induced materials, which are triggered by heat.

It is well-known that transition temperature (T_{trans}) usually equals T_g for SMPs possessing an amorphous phase. For polymers that contain a crystalline phase, this transition is in the region of melting temperature (T_m) (11). In line with this division, it is important to properly define the basic parameters of PUs to determine the phase T_{trans}.

Based on analysis of SMPs (12), it was proven that high crystallinity of the SSs is important for obtaining SMP. Therefore, higher crystallization of the HSs and their stable domain structure is preferred to achieve good SMP properties. Additionally, besides conventional thermal transitions (T_g, T_m), the presence of hydrogen bonds (Figure 2) could also be used to control thermal transitions in the SMP materials in PUs (13).

Shape Fixity

The shape-memory properties of PU polymers are often characterized by shape fixity, in which temporary shape can be fixed, and shape recovery, in which the permanent shape is recovered.

Shape fixity is the extent of OS being fixed for an SMP. This behavior can be described by eq 1:

$$R_f = \frac{\varepsilon}{\varepsilon_{load}} \times 100\% \ (1)$$

where ε_{load} (eq 1) represents the maximum strain under load, ε is the fixed strain after cooling and load removal, and $\varepsilon_{recovery}$ is the strain after recovery (eq 2).

Characteristic parameters for materials with shape memory can be determined by thermomechanical tensile experiments with the use of a tensile testing machine, which is often equipped with a thermo chamber. Research often concerns specimens that are deformed (elongated or compressed). SMPs (especially PUs) are tested to find how the temporary shape is obtained and a recovery state is achieved. Using this procedure, shape recovery of the OS or the recovery stress is being tested. Changes in these parameters can be tested under controlled stress or strain conditions (*14*).

One of the most useful methods (next to tensile testing) to characterize the shape fixity parameter is dynamic mechanical analysis. This thermomechanical tool allows us to measure thermally induced multi-shape-memory behaviors (for example, using tension clamps and controlled-force mode) (*15*).

Shape Recovery and Recovery Rate

Shape recovery can be defined as the ability of a polymer to remember the OS from a temporary changed shape. The shape recovery rate is the percentage of the ratio of deformation recovered by the sample to the deformation taken place in this material (*11*):

$$R_r = \frac{\varepsilon - \varepsilon_{recovery}}{\varepsilon} \times 100\% \ (2)$$

Thermomechanical tests are often performed to characterize the aforementioned parameters (related to SME). Shape recovery and shape fixity can be characterized using a universal testing machine using cyclic loading/unloading mode with a temperature-controlled chamber (*16*). It is possible to characterize shape recovery as a function of cycles. Then parameter R_r can be written according to eq 3 (for strain-controlled sample):

$$R_{r(N)} = \frac{\varepsilon - \varepsilon_{recovery(N)}}{\varepsilon - \varepsilon_{recovery(N-1)}} \times 100\% \ (3)$$

where (*N*) represents the *N* cycle number of the strain after recovery, and (*N*−1) represents the strain after recovery during the previous cycle.

It is worth noting that a shape-memory characteristic strongly depends on the polymer structure, type of material (PU or other polymer), and conditions of the process (e.g., heating or cooling rates or the type of mechanical deformation).

It is essential that the study of these two basic parameters (shape fixity and shape recovery) have been measured to evaluate the shape-memory behavior of the polymers and in particular PU materials.

The Mechanism of the SME

PU heat-responsive materials are characterized by network architecture based on occurring domains of chemical or physical cross-linking (Figure 3) and switching domains connected to a T_{trans}. This characteristic temperature can be associated with the T_g or the T_m of PU (Figure 3).
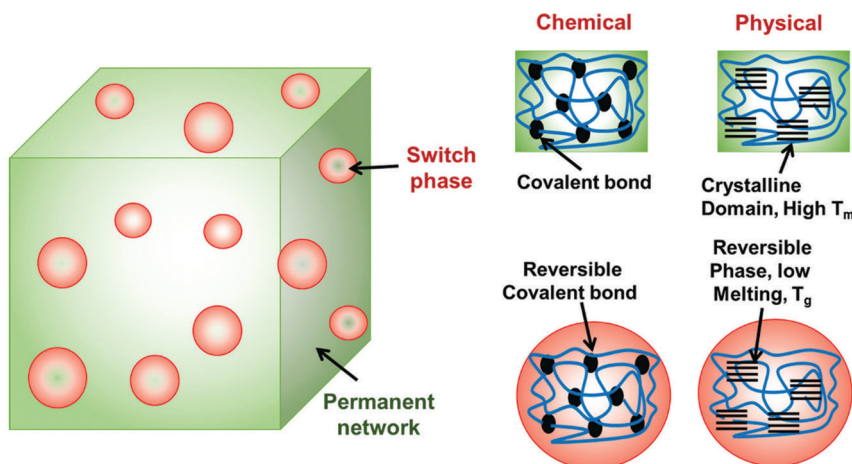

Figure 3. Schematic SMP structures containing covalent bonds or domain structure needed to obtain the SME. Reproduced with permission from reference (11). Copyright 2017 IntechOpen. The article was printed under a CC-BY license.

The shape-memory phenomenon can be observed when a shape is programmed to the temporary shape. This shape may be given by the deformation (e.g., elongation, bending) and can be acquired by preheating the material to more than T_{trans} and then cooling to less than this T_{trans} (17).

Shape-memory behavior can be observed for several polymers (elastomers, copolymers, liquid crystal polymers, or PUs). The basic programming process and recovery of a shape is shown schematically in Figure 4.
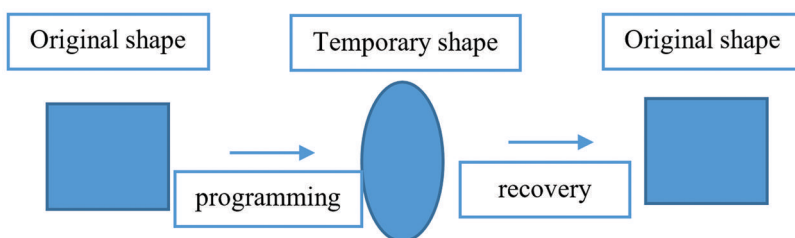

Figure 4. Schematic behavior of the thermally induced one-way SME. Reproduced with permission from reference (18). Copyright 2002 Wiley-VCH.

Figure 4 presents the different stages of a material's shape: the OS, the temporary shape (programming), and the permanent (original) shape (recovery). The first stage is programming the temporary shape of the sample. This process can be led by using, for example, a thermal factor. During the second stage, the temporary shape is programmed to obtain the appropriate sample geometry. Next, at the third step, the sample is returned to the OS during the recovery process (Figure 4) (19).

General classification of SMPs is based on single-shape or dual-shape behavior. Single-shape action is connected with an irreversible recovery mechanism in which the change of shape can be made from a temporary shape to a permanent shape only. In the case of dual-shape behavior, which is characterized as a shape-memory cycle, metastable temporary shape and an equilibrium permanent shape are distinguished (*20*).

The permanent shape is transferred to the temporary shape by the programming process. Heating the sample to a temperature higher than the switching T_{trans} results in the recovery of the permanent shape (*18*).
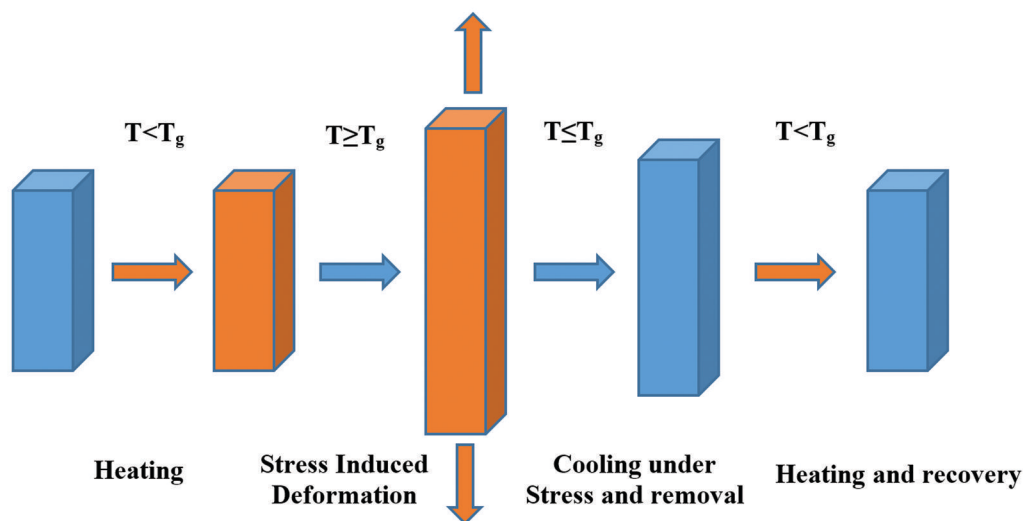

Figure 5. Thermomechanical mechanism of SMP. Reproduced with permission from reference (21). Copyright 2020 SAGE.

Temperature stimulating of sensitive polymers is one of the characteristic methods to describe their shape-memory properties. The schematic mechanisms of temperature-sensitive SMPs are shown in Figure 5. These programming and recovery modes are divided into several stages. At the first step, the sample is heated to more than the T_g, and force is applied to achieve proper deformation. Next, the sample is cooled with applied force to a temperature less than the T_g zone. After these treatments, the SMP sample acquires the programmed shape (PS). Then the sample is reheated to more than T_g and is able to recover to the initial shape (*22, 23*).

Generally, SMPs belong to the class of covalently or physically cross-linked materials, which can have viscoelastic properties in the specific temperature range. Figure 6 shows the basic molecular mechanism of the SME. Generally, polymer network structures contain netpoints and switchers, which are stimuli-sensitive elements (Figure 6) (*24*).

SMPs are usually built with netpoints and polymer chains that act as connectors. From a chemical and physical point of view, they can be constructed from chemical bonds (covalent) and intermolecular interactions. As represented previously in Figure 3, covalent bonds can be formed by a cross-linking reaction, and physical "cross-links" can be formed by the physical interactions with crystalline and amorphous structures (for PUs: HSs and SSs). The chains connected to the netpoints must be suitable to achieve proper orientation, especially with regard to programming shape. The possibility of deformation of the polymer chains is correlated with their elasticity and length. Switching between OS and programming deformation is possible because of the presence

of these chain segments as well as cross-linking points (net points), which play an important role in this process. Thus, the presence of both systems is essential to the process of SMP functioning (programming, recovery) of materials. The essential connections of the systems can be formed by the previously mentioned cross-linking points (chemical) and physical cross-linking. Chemical cross-links can be created by the reaction of two functional groups giving a chemical bond. In the case of physical cross-linking appearing during the cooling process, the crystalline domains can be formed and function similar to chemical cross-linking points (24). Additionally, good separation of the amorphous and crystalline phase promotes the temporary shape fixation.
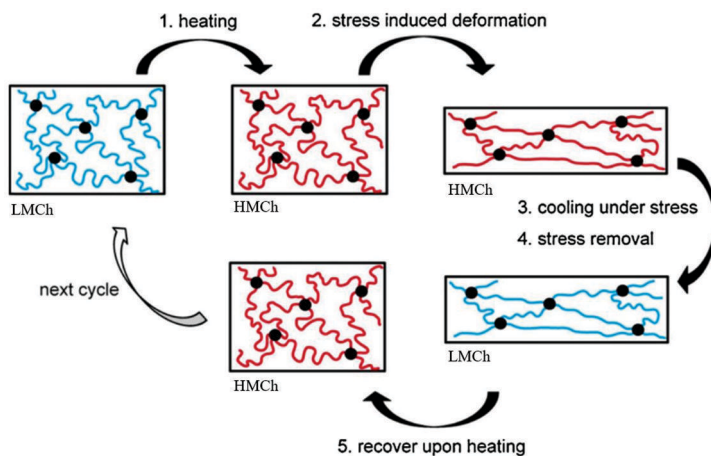

Figure 6. The molecular mechanism of the SME. ●, cross-linking nodes; LMCh, low-mobility chains (less than T_{trans}); HMCh, high-mobility chains (more than T_{trans}). Reproduced with permission from reference (20). Copyright 2015 Elsevier.
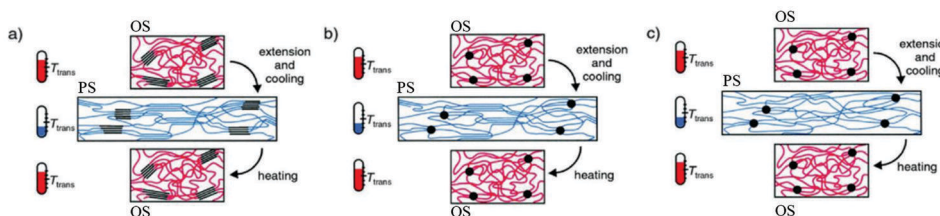

Figure 7. Polymer structures during one-way shape-memory changes. (a) Multiblock copolymer transitions ($T_{trans} = T_m$). (b) Cross-linked crystalline polymer transitions ($T_{trans} = T_m$). (c) Network structure of glassy polymer transitions ($T_{trans} = T_g$), where OS polymer chains represent OS and PS chains are programmed.

Polymeric materials that exhibit shape-memory properties may show different behavior under some temperature changes. In this case, the molecular structure of the polymer may produce some switching phenomenon.

From the thermodynamic point of view, the SME can be assigned to storage energy and release of strain energy by using entropy of the network (25). The flexibility of the polymer chain is connected to the changes of the temperature parameter. The key issue in studying SMP behavior is to characterize the T_{trans}, which plays a crucial role in programming the behavior of this type of material. At less than the T_{trans}, the polymer chains (Figure 7, OS of the polymer chains) are stable and interact as multiphase structures. Within them are present crystalline and amorphous structures

or cross-linking polymer chains. In the case of programmed deformation of shape and subsequent cooling, the characteristic segments lock the polymer in an intermediate state (Figure 7, PS of the polymer chains). The next step is heating to more than T_{trans}, and the polymer structure returns to its original state.

As was mentioned before, shape-memory PU polymers are very versatile materials that are able to recover to their original (permanent) shape from temporary shapes under an external stimulus. Additionally, SMP materials can achieve a number of temporary shapes, such as dual and multiple SMPs.

For a dual SMP, the temporary shape achievement and OS recovery are determined by a reversible T_{trans}, in which the chain mobility is limited (shape fixation) and there is also release limitation (shape recovery), when changing the temperature to less than and more than T_{trans}. It is well-known that a lot of polymers may show a dual-shape memory behavior (especially PUs) when they have one reversible thermal transition close to T_g for an amorphous polymer and T_m for a semicrystalline polymer (13).

The triple SMPs are able to memorize three shapes (two temporary shapes and one permanent shape). This behavior can be seen also in multiple SMPs, in which more "metastable stages" are remembered. The dual SMP exhibits only one thermal transition for one temporary shape, whereas the triple (or multiple SMP) is based on one broad thermal transition or at least two separated thermal transitions (13). The basic triple shape-memory cycle mechanism is presented in Figure 8.
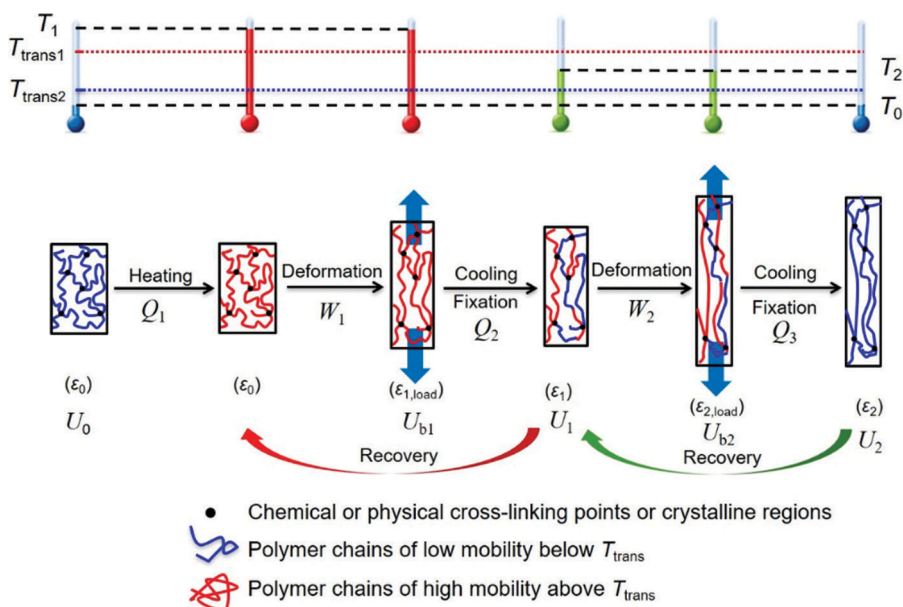

Figure 8. The molecular mechanism of a triple shape-memory cycle. Adapted with permission from reference (13). Copyright 2019 Elsevier.

At the first step of the triple shape-memory cycle, the sample must be heated to temperature T_1 (Q_1) and then deformed (W_1). In the next step, the sample is cooled to temperature T_2 under the deformation force.

The first temporary shape, called (ε_1), is the achieved metastable state after removing the external force from the sample. Next, the material is deformed (W_2) and cooled to temperature T_0,

and the second metastable state is achieved (U_{b2}). The second temporary shape (ε_2) can be formed when the force is removed. The sample can recover from (ε_2) to (ε_1), the first temporary shape, and from (ε_1) to (ε_0) and the OS when it is heated (*13*).

Factors Affecting the SME

SMPs are a class of controlled and programmable materials, and their behavior depends on many factors. These materials can exhibit the SME under different factors, including thermal, light, magnetic, electric, microwave, and chemical ones. (*8*).

One of the most important factors influencing the properties of an SMP is the cross-link density of the polymeric material. It was proven that a higher cross-link density of the polymer increases shape-recovery values. Preparing SMPs with good shape-memory properties should be controlled by the cross-linked density of the final polymeric product (*26*).

On the other hand, to achieve physical cross-links in materials with SMP properties, the presence of at least two different domains with different thermal transitions (such as in PUs) or some other block copolymers is needed. The polymeric domains with the highest thermal transition can behave as cross-linking points and are responsible for the permanent shape, whereas the regions with lower thermal T_{trans} can be responsible for the switching segments (*26*).

The shape-memory properties can be linked by the degree of crystallinity of the PU polymers. It was proven that higher recovery stress depends on a higher degree of crystallinity, but recovery rate and shape recovery decreased with increasing the degree of crystallinity (*19*).

Shape-memory properties depend on many factors, including mechanical stress/strain mode, temperature, and strain rate, as well as structural factors and chemical or physical cross-links (flexibility of the polymer chains). More specific SMPs depend also on many factors such as the programming step and the triggering process parameters.

The Influence of T_g or T_m on SMP Properties

The most important transition characteristics for SMP materials are the two thermal transitions: T_m and T_g.

T_{trans} is usually equal to T_g for amorphous SMPs or T_m for a crystalline SMP. These parameters can be characterized by standard thermal analysis techniques such as differential scanning calorimetry or dynamic mechanical analysis (*11*).

The shape-memory process of the polymer material is presented as a shape-memory cycle in Figure 9. The basics steps of the SMP material are described in the literature as programming, storage, and recovery (*27*). At the first step, it is necessary to program the shape of the polymeric material and apply force to achieve the optimal sample deformation at more than the T_{trans}. This is an easily executable manipulation because material is in the viscoelastic state at more than the T_g. After this programming stage, this structure needs to be fixed under the appropriate level of strain and time, so fixed SMPs must be cooled to less than T_g. The last step of the memory cycle is called the recovery, when the temperature of the material is rising and the sample returns to the previous (original) state. This type of SMP property is characteristic for shape-memory materials sensitive to temperature changes (Figure 9) (*27*).
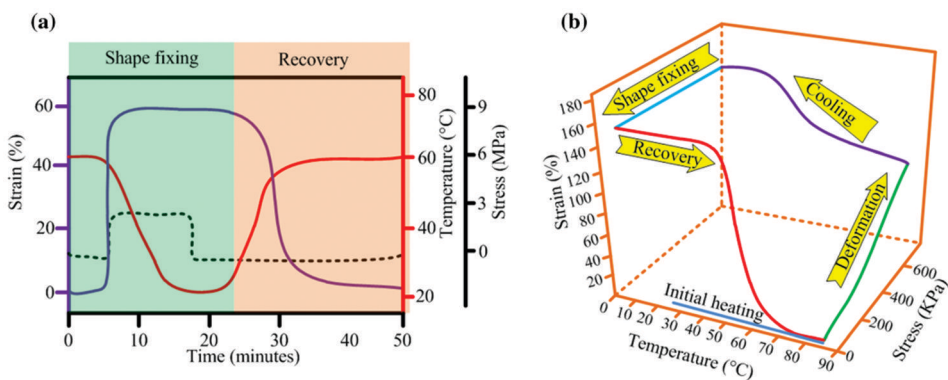
Figure 9. The molecular mechanism of the SME. (a) Two-dimensional graph (strain vs stress vs time vs temperature). (b) Three-dimensional graph. Adapted with permission from reference (27). Copyright 2020 Springer.
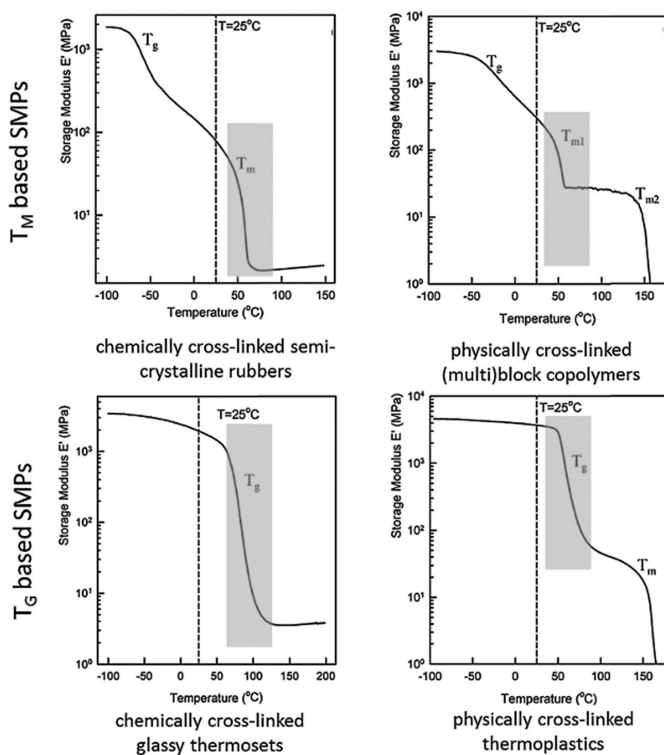

Figure 10. T_m and T_g of different types of SMPs (the gray area represents switching of the SMP). Adapted with permission from reference (28). Copyright 2015 Elsevier.

Shape-memory properties are exhibited by different types of polymers, such as copolymers, rubbers, thermoplastics, and thermoset materials.

The switching transitions (at the melting area temperature) can be observed in semicrystalline and physically cross-linked polymers as well as in chemically cross-linked rubbers (Figure 10). In turn, when the switching transition is connected with the T_g, it can be used for describing shape-memory properties of chemically cross-linked thermosets as well as of physically cross-linked thermoplastics (28).

The T_{trans} for the thermoplastic and thermoset polymers is localized in the T_g range (gray region) (Figure 10). For the cross-linked rubbers and block copolymers, the T_{trans} is rather localized at the T_m appropriate for one of the blocks of the block copolymer and its T_{m1} Figure 10 (27). These basic types of polymers are the primary types of materials that can exhibit the SMP properties described in this chapter.

PU polymers belonging to the thermoplastic elastomers exhibit good processability. These materials have low levels of chemical cross-links, but because of physical cross-linking, thermoplastic PU elastomers possess properties similar to classic covalent cross-linked elastomers (28).

PUs and Their Shape-Memory Composite

PU is one of the best examples of SMP and is known to regain 100% of its shape if it is stretched to more than its T_g and then cooled to fix the new shape. It can be reheated to more than the start of the glass transition zone, which facilitates complete recovery of its original form.

SMP Composites of PU and Carbon Derivatives

A variety of stimuli-responsive composites may be obtained by the blending of PU with carbonaceous materials such as CNTs, graphene, and carbon black. The SMEs can be enhanced by the addition of carbonic fillers. The limitations of virgin SMPs can be minimized by the incorporation of fillers. Being low-density particles in the regime of nano dimension, carbon derivatives are highly preferred to act as fillers. The anisotropic nature of CNTs assists in attaining exceptional thermally and electrically conducting SMP composites (29). High surface area, easy synthetic strategy, flexibility, and superior mechanical strength make graphene nanoparticles sufficient fillers for providing high thermal conductivity (30). Carbon black also acts as a conductive filler and is available at a cost lower than that of graphene and CNTs.

CNTs as Fillers

Many research groups have investigated the effect of incorporation of CNTs in PU matrix. When CNT was added to PU in an amount ranging from 0.5 to 5%, there was a reduction in the resistivity of the material, depending on the amount of CNT; these composites were highly strain-sensitive. At a lower percentage of CNT, the PU composites could exhibit only delayed recovery of shape. SMPs have a distinct behavior in the presence or absence of electrical actuation. A high step up in shape recovery was noticed at a higher content of CNT (31). An outstanding improvement in the shape-memory properties was obtained when PU formed a hybrid with CNT and montmorillonite. The dispersion of CNT could improve the mechanical properties and crystallization in the case of composites and was higher than that of the pristine PU. Both shape fixity and shape recovery can be obtained at this synergic effect, eventually resulting in exceptional thermomechanical properties (32). A flexible methodology, spray deposition, was used to fabricate nanocomposite in which CNT layers are incorporated into thermoplastic PU. This novel technique is feasible in tuning the number of layers of CNT, and localized actuation is possible in composite. A complete shape recovery was possible in 30 s at 40 V, and the composite can be treated as a potential material for numerous actuation applications (33). Melt mixing can be adopted for the fabrication of CNTs embedded in ester-based PU. A good dispersion of CNTs resulted in very fast shape recovery, and the trigger temperature could be decided by manipulating the T_g of the matrix (34). Melt mixing is a simple synthetic strategy for the preparation of polymer-blend nanocomposite containing polylactic acid

and CNTs. The obtained nanocomposite displayed PU, an enhancement in the electroactive shape-memory behavior (35). A shape recovery of 98% and a fast recovery time of 9 s were shown by multiwalled CNT-reinforced PU prepared by solvent casting. These composites show significant applications in actuator applications (36).

Electroresponsive shape-memory devices can be constructed by adding functionalized CNTs in the PU network (37). The electroactive materials can also be synthesized from polypyrrole and Multiwalled CNT coated with polypyrrole (Figure 11).
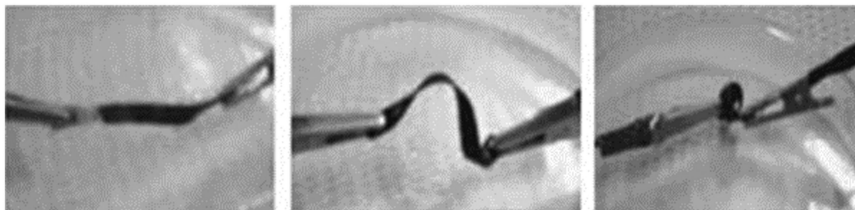

Figure 11. The electroactive shape-recovery behavior of PU/multiwalled nanotube composites. The pictured transition occurs within 10 s when a constant voltage of 40 V is applied. Reproduced with permission from reference (35). Copyright 2013 Elsevier.

The SME of PUs can be diminished by the addition of carbon nanofibers. When carbon nanofibers with a diameter of 60–200 nm and a length of 30–100 nm were incorporated in the PU matrix as fillers, the SME diminished, and this can be attributed to the interference of the fibers on the SS crystallization (38). HSs can also exhibit SME when clay is included as a filler (39). PU SMPs can be used as UV-protection materials (40). Treated cotton fabric can be dispersed in PU solution containing multiwalled CNTs. The resulting material will have sufficient water permeation and UV protection.

Graphene as a Filler

Graphene sheets and CNTs can act as a conductive network in an epoxy-based PU matrix, and this versatile shape-memory composite finds potential applications in optics and aerospace technology. The following diagram shows the scheme for the overall fabrication process (Figure 12) (41).

A micro honeycomb formation of graphene-CNT framework in PU matrix possesses shape-memory behavior including a recovery ratio of 90.6% and shape fixity of 95.6% (42). The solution casting method can be used to produce PU nanocomposites with different ratios of polycaprolactone and graphene sheets. These nanosheets avoid stress transfer, which further results in a high shape-recovery ratio (43). PU-based shape-memory composites can be prepared by a two-step synthetic method with epoxy and GO. GO co-valent networks offer potential shape-memory behavior (44). The effect of reduced GO sheets in a PU matrix on shape-memory behavior was studied by conducting tensile stress-strain cyclic investigation, and it was found that nanocomposites display higher shape-recovery ratio than does neat PU (45). In situ polymerization of PU having diselenide bonds and functionalized GO was done to generate self-healing shape-memory nanocomposite. Self-healing behavior of the composite was attained under near infrared irradiation. The composite could also reach approximately 90% in shape fixity as well as shape recovery. Figure 13 shows the healing process (46).
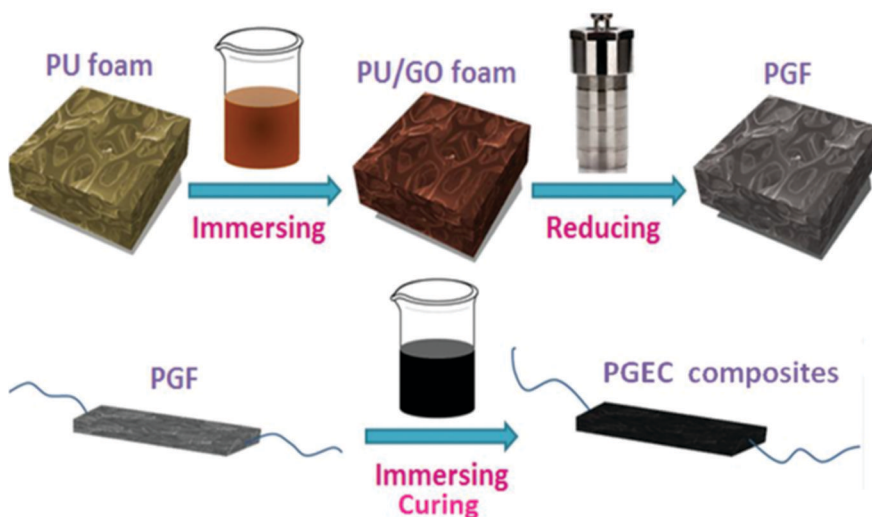
Figure 12. Overall fabrication process of the PU graphene foam/epoxy/CNT composites. (1) Immersion of a commercial PU foam into GO solution with hydrazine. (2) Assembly of graphene sheets on the PU skeleton by in situ chemical reduction of GO. (3) Immersing PU graphene foam into the mixture of CNTs and epoxy resin. (4) Curing. Reproduced with permission from reference (41). Copyright 2016 Elsevier.
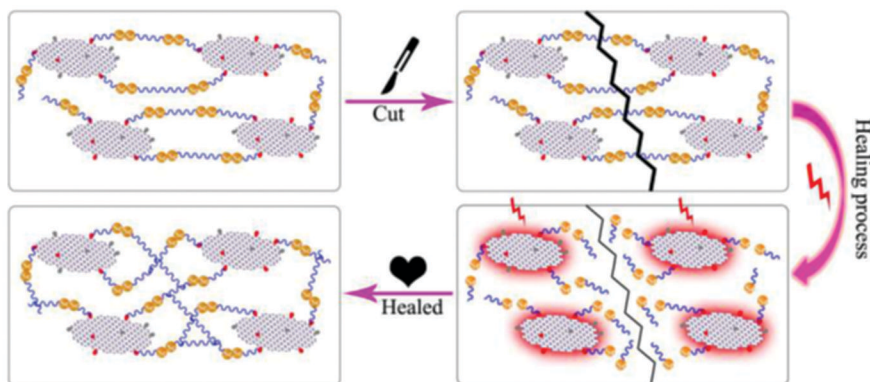

Figure 13. Schematic showing the possible healing mechanism of a composite of polyurethane/ functionalized graphene oxide containing diselenide bonds under near-infrared light. Reproduced with permission from reference (46). Copyright 2018 Elsevier.

Carbon Black as a Filler

A conductive material, carbon black was used as a filler in PU to obtain nanocomposite that reacts to both thermal and electrical stimuli. An excellent shape recovery of 94% for thermal- and 98% for electroactuation was reported (47).

It can be concluded that the addition of carbon derivatives as fillers enhances the thermal, physical, and shape-memory behavior of PU composites. These exceptional stimuli-responsive nanocomposites find tremendous applications in various fields such as aerospace, optics, and biomedical devices.

SMP Composites of PU and Biomaterials

SMPs are promising biomaterials because of their biocompatibility and material processability. Because these SMPs are derived from conventional polymers, they satisfy the general requirements for a biomaterial such as being nontoxic, noninflammatory, and compatible. Polymers such as polycaprolactone-, polyglycolic acid–, and polylactic acid–based PU composites were found to have potential applications in tissue engineering, drug delivery, and biomedical implantations (48). Poly(L-caprolactone)-based (PCL-based) PU composites are known to possess SME. Segmented PUs containing SSs with lower molecular weight exhibit shape-memorizing properties.

Fabrication of bone scaffolds was done by combining PU with polyethylene oxide and gelatin, and excellent printability was observed. PU–polyethylene oxide scaffolds have better shape-memory properties such as shape recovery and shape fixity when compared with gelatin composite. Nontoxicity as well as biodegradability of the synthesized scaffolds offers superior surgical measures for bone tissue engineering (49). A biodegradable polymer blend using PU from isosorbide as the SS and polycaprolactone as the HS was fabricated. Analyzing the shape memory featuring 30% PU/polycaprolactone gave better results (50). Electrospun PUs containing polyols demonstrate shape-memory behavior and are used for tissue engineering and drug delivery. Cell proliferation tests were conducted on human cardiac fibroblast cell lines, and the composites were found to be active as nanofibrous scaffolds (51). Shape-memory photoresponsive implants were prepared by the addition of yak hair melanin to biodegradable PU. Biomedical applications were tested via in vitro analysis by choosing mouse fibroblast cells and human mesenchymal stem cells (52). Plasma immersion ion implantation was performed to improve the surface wettability and biocompatibility of PU. Collagen was coated on PU, and in vitro toxicity was tested by implanting on mice. It was proven that collagen coating appreciably enhanced the biocompatibility of PU, making it an outstanding material for implantation (53). The salt-leaching phase inverse method was used to fabricate a porous structure of PU for tissue engineering. Bone repair and cell proliferation was studied in osteosarcoma MG-63 cells, and the results proved the efficiency of these scaffolds for application in tissue engineering (54).

PU composites are promising materials in the field of bioscience because of their SME. They can be implanted in the body in a folded or contracted form and can regain shape as the target position is reached. This unique property when combined with their biocompatibility and biodegradability creates a significant role in biomedical applications (Figure 14) (55).
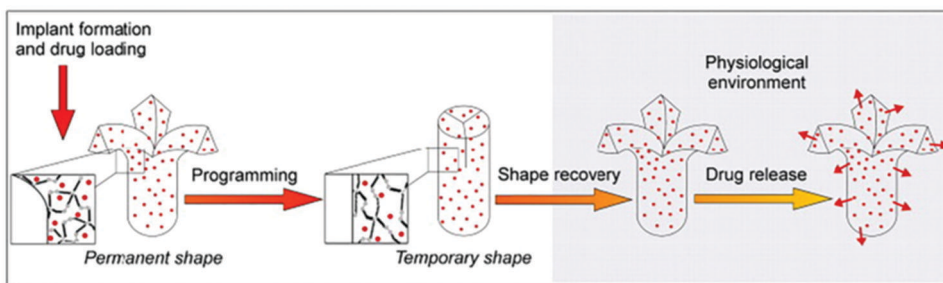

Figure 14. Operating mechanism in drug delivery. Reproduced with permission from reference (55). Copyright 2019 Elsevier.

SMP Composites of PU and Nanoclays

Nanoclays are a well-known filler for the polymer modification. Nanoclays are technically layered alumino silicates having a two-dimensional structure. These layered silicates have a general

chemical formula of $(Ca, Na, H)(Al, Mg, Fe, Zn)_2(Si, Al)_4O_{10}(OH)_{2-x}H_2O$, where x represents the amount of water. There are two categories of nanoclay: natural and synthetic. A variety of nanoclays such as cloisite, attapulgite, kaolinite, bentonite, montmorillonite, hectorite, laponite, vermiculite, and saponite are being used as fillers in polymer matrix. Nanoclay can be used as a reinforcing agent or as a modifier for PUs because of its biocompatibility, noncorrosive nature, flame retardance, and nontoxicity.

SMP Composites of PU and Other Nanoparticles

PU composites with SMEs can be prepared by adding suitable fillers, including metal nanoparticles such as gold and zinc oxide and biobased nanofillers such as cellulose nanofibers and crystals (56). Among biobased fillers, cellulose is the most commonly used material for composite preparations that have SME. It is possible to improve the rigidity of the shape-memory composite by adding a small amount of nanocellulose. A large number of research reports suggested that when nanocrystals were introduced during the PU polymerization, cellulose nanofibrils were covalently linked to the PU polymer. Cellulose has polar groups that can interact with PU. Cellulose-reinforced shape-memory PU markedly improved the stiffness of the polymer while no obvious shape-memory properties decreased (57).

Gold nanorods can be employed to induce the shape-memory response in commercial PUs using the seed-mediated process. Composites were activated with near-infrared radiation. The shape-memory response was controlled by altering the irradiation time and intensity and the gold nanorod loading. Higher loading and high intensity favor high shape recovery. The recovery and thermal stability of the composites were not as much when compared with the unmodified PU composites (58).

Aluminum nitride was tested as a filler in PU-based SMPs even though it did not influence the structure or cross-linking in PU or enhance the thermal stability. The strain fixity rate, which is the ability of the specimens to fix their strain, was improved slightly in the presence of aluminum nitride filler, but the final recovery rate of the shape-memory measurement decreased (59). Biodegradable composites of PU were tested with a self-expandable stent with iron oxide as the filler. The nanocomposites had high fixing ratios at more than 99% and recovery ratios at more than 82% at both 37 and 40 °C. Cytotoxicity and in vitro degradation showed the nanocomposites had good biocompatibility and biodegradability. Poly(D,L-lactide-co-ε-caprolactone)urethane/Fe_3O_4 nanocomposites display immense promise for vascular stents with dual-responsive SMEs, favorable mechanical properties, biocompatibility, and biodegradability.

In the biomedical field, shape-memory PUs are widely used as stents. Figure 15 shows a shape-memory PU stent (thin wall tube). First the stent is expanded and then folded into a star shape for delivery by a catheter. When the required location is reached, the stent can be mechanically arranged in a traditional way. Because the stent is surrounded by room-temperature water and it is made of this PU, eventually, it will shrink back into OS and can be easily removed (60, 61).

As shown by Huang, one of the wings of a toy airplane that was made of conductive shape-memory PU was joule-heated to change its shape from curved into flat for wing morphing, which is a function required for high aerodynamic performance, in particular in unmanned aviation vehicles (62).

PU can be modified by inserting PCL and 20 wt % ZnO nanoparticles. Composites prepared by the solution-casting method showed improved mechanical strength and shape recovery. The composites were prepared by adding from 5 to 30 wt % ZnO. However, only 20 wt % was successful

in the shape recovery. This can be attributed to the replacement of the −C=O group in SSs by ZnO, and there was an obstacle for HSs to interact with SSs. More freedom was attained for the PCL component, incorporating particles as the nucleating agent of PCL chains and increasing the crystalline domains of the SS. The occurrence of these two phenomena can offer an optimized point to improve both the modulus and shape-recovery properties (63).
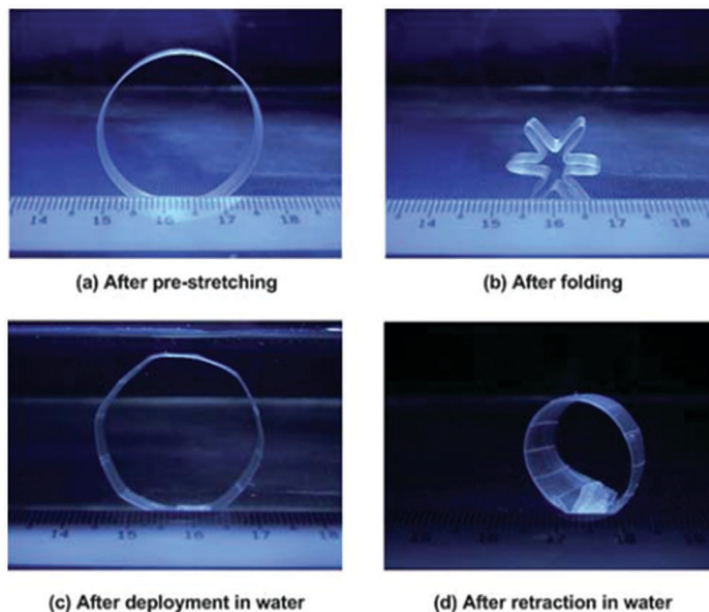

Figure 15. Self-retractable PU SMP stent. Reproduced with permission from reference (60). Copyright 2010 Royal Society of Chemistry.

Applications of Shape-Memory PUs

Biobased PUs and shape-memory PU composites have many applications in different fields. The biomedical field and industry are mainly taking advantage of two properties, biocompatibility and shape memory, of PU composites.

Some of the medical applications of shape-memory PU composites include:

- Vascular stents with shape memory as a drug delivery system;
- A specially designed spoon handle, designated for the physically handicapped;
- Construction of hematology-related products and devices;
- Materials for orthopedic and dental applications;
- Bandages and artificial skins;
- Wound closure; and
- Components of cardiac pacemakers and artificial hearts.

Conclusion

Many interesting and useful advantages of stimuli-responsive SMPs described in this chapter have been developed in many industrial applications such as automotive, aerospace, electronics, textile, biomedical, and other commonly used products. This review chapter was focused on the developments in PU SMP materials and composites. PU materials exhibit good shape-memory properties because of their microphase segregation, which is connected to their chemical structure

and physical interaction between HSs and SSs. These advantageous features of PU materials can be enhanced by the addition of various types of nanoparticles. One of the new features in producing PU SMP materials is the 3-D printing method. Using this technique, it is possible to produce polymer devices with unlimited geometries in which shape-memory properties can be incorporated (*64*).

It is worth remembering that when designing shape-memory PU materials, it is necessary to design an appropriate production technique while focusing on the use of cost-effective and eco-friendly materials.

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