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Polyurethane: A Shape Memory Polymer (SMP)

Suman Thakur and Jinlian Hu

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Abstract

Shape memory polymer (SMP) is a stimuli-responsive material with the ability to alter a programmed shape to its original shape upon triggering of an appropriate stimulus. For the past decades, SMP has dragged much interest in material field owing to its various and versatile applications. One archetypal SMP is polyurethane, which has a wide-ranging transition temperature for its shape recovery, retraction temperatures, inherent soft-hard segments, a high recoverable strain (up to 400%), high control of the softening, favorable and tunable physical properties, and so on. This chapter emphasizes on the raw materials required for the synthesis of shape memory polyurethane (SMPU), the principle of shape memory function, the design of protocol of SMPU, and their applications with future directions.

Keywords: polyurethane, shape memory, smart, stimulus sensitive

1. Introduction

Shape memory polymer (SMP) is a stimuli-responsive polymer which has an ability to fix a temporarily deformed shape and to return from the deformed shape to its original permanent shape while induced by an external stimulus such as thermal, humidity, pH, light, magnetic energy, electric field, and so on [1–5]. SMP possesses two phases viz. frozen phase or net hard phase and reversible or switching soft phase. In case of polyurethane (PU), they may have reversible amorphous or crystalline phase [6, 7]. PU has a unique structural characteristic because of the presence of inherent incompatibility due to microphase in-homogeneity in its chain molecules. It possesses a wide-ranging temperature for shape recovery, high recoverable strain (up to 400%), inherent soft-hard segments, high control on the softening and retraction temperatures with good biophysical properties [8–11]. Further, the properties including switching transition temperature like glass transition temperature (T_g) or melting temperature (T_m) can be tuned much easily by proper choice and using suitable composition

of the components during polymerization process. A large number of versatile components with different structures and properties are available for this polymerization [12]. Thus, PU is versatile with respect to its structure and properties. Further, it is available in various forms, thermoplastic, foam, elastomer, and fiber [13, 14]. Thus, among the different types of SMP, PU is a good candidate as SMP for various advanced applications. In this chapter, we focus on the raw materials required for the synthesis of shape memory polyurethane (SMPU), the principle of shape memory function, the design of protocol of SMPU, the recent research progress of SMPU, and their potential applications.

2. Raw materials for shape memory polyurethane

PU is an important subclass of polymers and it contains multi-disperse blocks of soft and hard segments in an alternative fashion. The urethane linkage (—NHCOO—) is produced by a rearrangement reaction between a diisocyanate and a polyol. The common raw materials used for PU synthesis are categorized into macroglyol, diisocyanate, and chain extender. The brief descriptions of these components are presented in this section.

2.1. Diisocyanate

It is a fundamental precursor for the synthesis of PU. Although both types of diisocyanate viz. aromatic and aliphatic are used, aromatic diisocyanates are most commonly used for SMPU. The properties of SMPU greatly depend on the structure of diisocyanate component. Thus, appropriate selection of diisocyanate component envisages the properties of SMPU. The most commonly used diisocyanates are toluene diisocyanate (TDI), 4,4-diphenyl methane diisocyanate (MDI), polymeric methylene diphenyl diisocyanate (PMDI), 3,3-dimethyl diphenyl methane diisocyanate (DDI), naphthalene diisocyanate (NDI), hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), and lysine diisocyanate (LDI).

Among them, TDI and MDI are widely used in the preparation of SMPU [15, 16]. In most of the cases, TDI is used as a mixture of the 2,4- and 2,6-isomers in 80:20 mol ratio. Similarly, MDI also has three isomers namely 4,4-, 2,4-, and 2,2-diphenyl methane diisocyanates. However, 4,4-isomer is used in most of the SMPUs [15]. Though aromatic diisocyanates have higher reactivity than aliphatic ones and obtained SMPU exhibited good thermal and mechanical properties, the former SMPU also suffers from a few inadequacies such as lower oxidation and weaker ultraviolet stabilization [17]. Therefore, the use of aliphatic diisocyanates is required, where color and transparency are important for end application.

2.2. Macroglycol

In the synthesis of SMPU, the aliphatic diols or polyols with a molecular weight of 400–5000 g mol^{-1} are mainly used as macroglycols. The long-chain macroglycol containing low functionality provides elastomeric soft SMPU, whereas the short-chain macroglycol with high functionality forms rigid SMPU. Various types of macroglycol such as polyester, polyether, polycarbonate, hydrocarbon, and so on are used in the synthesis of SMPU. However, the

polyester and polyether macroglycols are mostly used among them. Polyester macroglycol provides high flexibility, which is very useful in SMPU. However, the ester groups are easily hydrolyzed by alkali, thereby weakening the performance of SMPU in special biological application under alkaline condition [18]. A few of polyester polyol macroglycols such as polycaprolactone, polycarbonate, and so on demonstrate high hydrolytic stability in alkaline condition too. On the other hand, polyether macroglycol contributes some specific properties such as metal chelation, hydrophilicity, crystallinity, surface activity, and so on. In addition to that, different dendritic or hyperbranched polyols are also used to prepare SMPU. Among all, the crystalline polycaprolactone diol (PCL) and polyethylene glycol (PEG) are widely used for SMPU as macroglycol.

2.3. Chain extender

Several low-molecular-weight (generally below 500 g/mol) diols, diamines, and amino alcohols are used as chain extenders for the synthesis of SMPU [18–20]. The most commonly used chain extenders are ethylene glycol, 1,4-butanediol, 1,6-hexanediol, diethylene triamine, and diethanol amine. The chain extender is generally used to increase the chain length and the molecular weight of SMPU. The amine chain extender reacts rapidly and increases the crosslinking density of SMPU by bridging with biuret linkages in case of SMPU thermoset, whereas diol chain extenders sometimes required organometallic catalysts to obtain SMPU. On the other hand, multifunctional and highly branched chain extenders like trimethylol propane, glycerol, triglyceride ricinolate, hyperbranched polyol, and so on are used to prepare hyperbranched structure in SMPU.

2.4. Catalyst

The isocyanates especially the aromatic ones are highly reactive, so catalyst is generally not needed in such cases. However, catalyst is required for synthesis of aliphatic isocyanate containing SMPU and at low temperature. Also, the reaction rate rapidly decreases when the steric hindrance increases, mainly on the substitute in higher alcohols. In such cases, catalyst is required. These catalysts are mainly divided into two categories viz. amino (basic) and organometallic compounds. The commonly used amine catalysts are triethyl amine, triethylenediamine (TEDA), dimethylethanolamine (DMEA), dimethylcyclohexylamine (DMCHA), and so on. Similarly, organometallic catalysts are mercury, lead, tin, bismuth, and zinc-based organo-complexes. However, these catalysts are toxic and hence they have disposal problems which hinder their uses. Nowadays, bismuth and zinc carboxylates, alkyl tin carboxylates, oxides and mercaptide oxides such as dibutyl tin dilaurate (DBTDL), dioctyltin mercaptide, stannous octoate, dibutyltin oxide, and so on are used successfully [21].

3. Properties and characterization of shape memory polyurethane

Transition temperature (T_{trans}), shape fixity (R_f), shape recovery ratio (R_r), maximum recoverable strain (ε_{max}), and maximum recovery stress (σ_{max}) are the important parameters that are used to describe shape memory effects of a polymeric material [22].

Shape fixity: Shape fixity is the extent of a temporary shape being fixed for an SMP. It is also known as strain fixity or shape retention. The shape fixity is thus equal to the percentage of the ratio of fixed deformation to total deformation (Eq. (1))

$$R_f = \frac{\varepsilon}{\varepsilon_{\text{load}}} \times 100\% \tag{1}$$

Shape recovery: Shape recovery is defined as the ability of a polymeric material to memorize the original shape from a temporary deformed shape. Therefore, the shape recovery is the percentage of the ratio of deformation recovered by the specimen to the deformation taken place to the specimen (Eq. (2))

$$R_r = \frac{\varepsilon - \varepsilon_{\text{recovery}}}{\varepsilon} \times 100\% \tag{2}$$

Recovery rate: This parameter describes the speed, that is, the rate of recovery from a programmed shape to its original shape upon triggering of a proper stimulus. It can also be said as the speed of recovery process or shape recovery speed.

T_{trans} is usually equal to T_g for an amorphous SMPU or T_m for a crystalline SMPU. This is generally measured by standard thermal analysis techniques such as differential scanning calorimetry (DSC) or dynamic mechanical analysis (DMA). Conveniently, a shape memory cycle (SMC) as mentioned in **Figure 1** is performed in order to determine R_f and R_r, the changes of sample dimension are manually measured, and R_f and R_r are calculated with the measured data using Eqs. (1) and (2), respectively. However, a mechanical testing equipment with a climate chamber (possess heating and cooling facilities) is the best choice to evaluate ε_{max} by elongating the testing sample to its failure at T_{trans}. In addition to that, the SMC using such thermo-mechanical analyzer can precisely evaluate different shape memory parameters such as R_f, R_r, σ_{max}, and shape recovery rates. This method can accurately record the time progress of temperature, stress, and
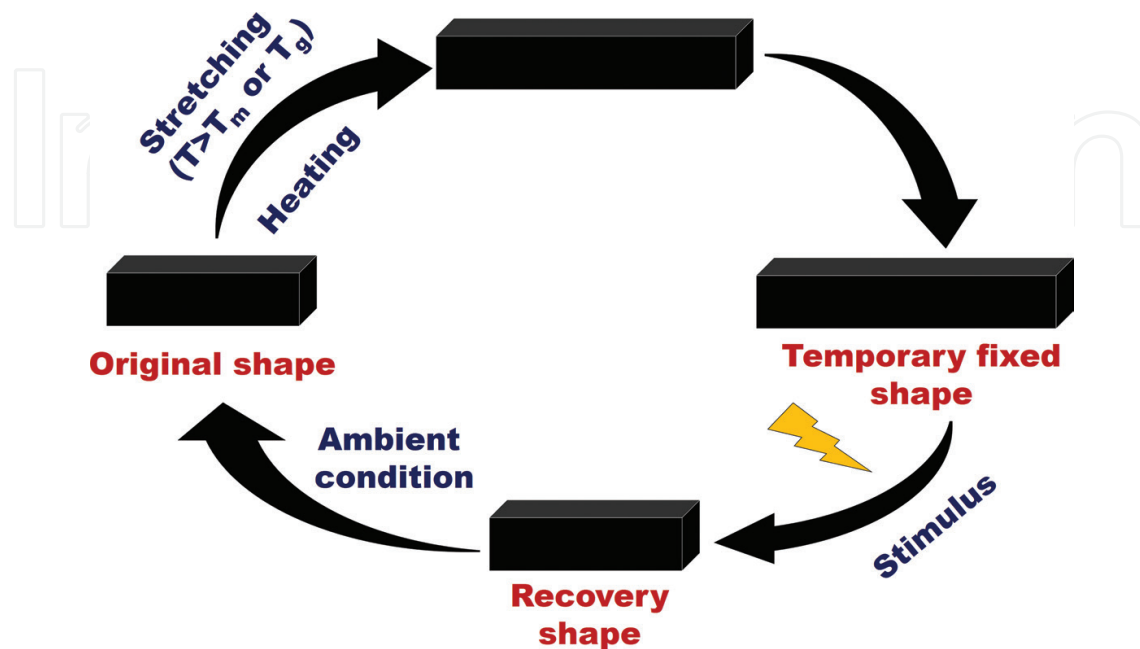

Figure 1. Thermomechanical cycle of SMPs.

strain. An example of a typical SMC is shown in **Figure 2a**. Instead, the SMC may also be demonstrated in a three-dimensional (3D) diagram as shown in **Figure 2b**. In this 3D diagram, the three axes are temperature, strain, and stress. Especially, time information is absent there. This absence does not impede the determination of R_f and R_r. Basically, the use of such a 3D diagram is very well known in the literature. The absence of time information may be moderately
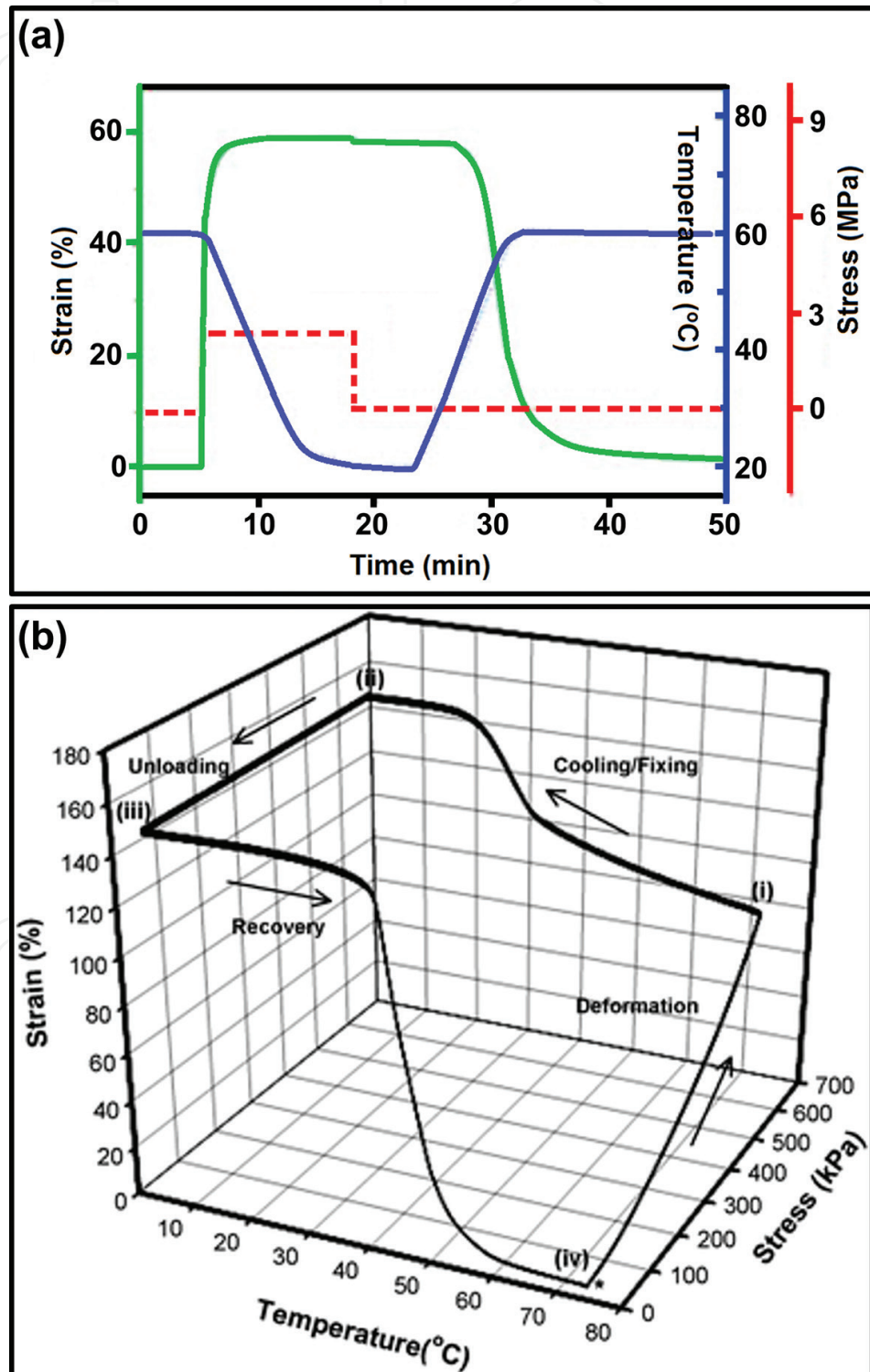

Figure 2. Shape memory cycle test: (a) 2D diagram (reproduced with permission from Ref. [2]) and (b) 3D diagram (reproduced with permission from Ref. [3].

unfavorable for a more sophisticated experiment of SMC. For example, if the testing sample is annealed under a constant stress at any stage of the experiment, the information about the annealing time and the strain reaches equilibrium or not during the annealing process would not be known. The rapid strain recovery rate V_r can also be calculated from the strain curve in the recovery portion of the SMC (**Figure 2a**), the time derivative of the strain as defined in Eq. (3)

$$V_r = \frac{\delta\varepsilon}{\delta t} \times 100\% \tag{3}$$

4. Mechanism of shape memory behavior of SMPs

It is well known that the segmental motions of the polymer chains ceased on cooling the polymer below T_g, but the motions start dramatically above this T_g. Basically, the polymers are transformed from a glassy state to a rubbery-elastic state during this transition. In this state, if uniaxial stress is applied for a short period of time, then the entanglement of polymer chains prevents a large-scale movement of chains, resulting in the storage of entropic energy. However, if the application of stress occurs over a longer period of time, the relaxation process can take place and that causes chain slippage and bulk flow of polymer chains. Thus, the reversible macromolecular deformation can be achieved by using network chains as a kind of molecular switch. At a certain dose of external applied energy (stimulus), the chains are flexible at a temperature above the T_{trans}, whereas their flexibility below T_{trans} is limited. Thus, the freezing of the molecular motion of the amorphous zone or the crystallization of the crystalline zone of the polymers prevents the molecular chains from immediately reforming the coil-like structures and instinctive recovery of the original shape, that is, programmed shape is fixed. Therefore, the stability of molecular orientation depends on the strength of interaction between the macromolecular segments and on the conformations of the chains constituting a polymer. The stretching of molecular chains leads to a drop in entropy, which can be compensated for by the cooling process, where the internal energy is decreased. Again, when the system is heated, the oriented polymer chains are softened from their glassy state or melted from the crystals, and thereby molecular chains relax the orientation to form more stable, coiled conformations. Such relaxation or shrinkage of the molecular chains caused shape recovery [23]. Therefore, the elastic strain energy produced during the deformation process is the driving force for shape recovery in SMPU. The molecular mechanism of shape memory behavior of SMPUs is shown in **Figure 3**.

At a high temperature, the rubber modulus of SMPU is lower, which makes the orientation of SMPU chains more feasible. So the deformation is much easier at high temperature. On the contrary, deformation at a lower temperature is tougher as glassy state modulus of the SMPU is high. However, the orientation of SMPU chain will withstand at a higher degree due to the slowdown of the relaxation process. Therefore, higher glassy state modulus (E_g) will offer higher shape fixity during concurrent cooling and unloading, where a higher rubber modulus (E_r) will offer higher elastic recovery at a higher temperature. Shape memory effect can thus be described by mathematical modeling as follows [24]:
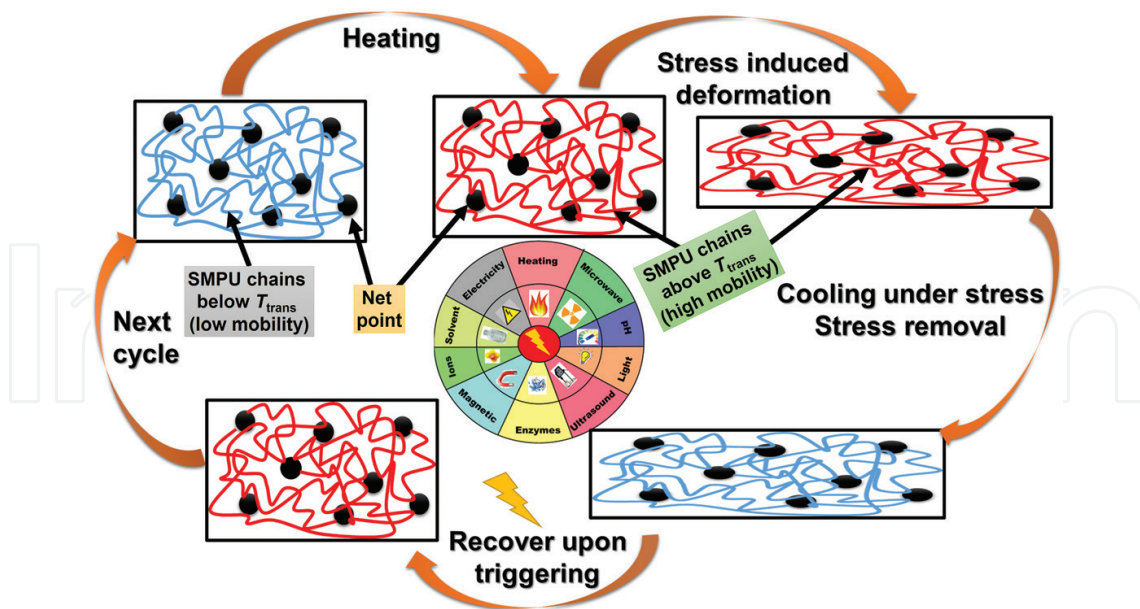
Figure 3. The molecular mechanism of the shape memory effect under different stimuli. Black dots: net points; blue lines: SMPU chains below T_{trans} (low mobility); red lines: SMPU chains above T_{trans} (high mobility).

$$R_f = (1 - \frac{E_r}{E_g}) \tag{4}$$

$$R_r = \frac{(1 - f_R)}{\left[\left(\frac{1 - E_r}{E_g}\right)f_\alpha\right]} \tag{5}$$

where f_R is the viscous flow strain and f_α is the strain when $T >>> T_s$. A high elastic ratio (E_g/E_r) offers easy shaping of SMPs at $T > T_s$ and provides a great resistance to deformation at $T < T_s$. The polymer should have thus greater E_g/E_r. The fixation of the temporary shape is caused by strain-induced crystallization and strain-oriented reorganization. The processing conditions of SMPs have also an effect on the shape memory behavior, as there may be a variation in modulus under different processing conditions. A significant variation of rubbery modulus in SMPU was observed when cooled at different rates. Further, the recovery ratio increased with the increase of deformation speed with decreasing maximum strain. T_s of SMPU could be tuned over a wide range of temperature from −30 to +100°C by using different structures and compositions of the components like diisocyanate, polyol (macroglycol), and chain extender. Further, the shape memory effect can be monitored by the proper choice of nature and the amount of reinforcing nanomaterials.

5. Criteria and designing protocol for a desired SMPU

As mentioned earlier, the presence of two different "segments" (a permanent or a hard segment and a switching or a soft segment, which can be influenced by the external trigger) is

essential to obtain shape memory effect in SMPs. The hard phase is responsible for retaining the original shape of the whole SMP. This hard segment can be attained through chemical crosslinking in the polymer network, incorporation of interpenetrating networks or crystalline phases (**Figure 4**). The switching segment temporarily fixes the programmed shape by a glass transition, crystallization, a transition between different liquid crystalline phases, reversible covalent or non-covalent bonds (e.g., photodimerization of coumarin, Diels-Alder reactions, and supramolecular interactions).

The polymer must deform to a desirable extent on heating at a certain temperature without any other change of its performance. This certain temperature is known as switching temperature (T_{sw}), which may be a T_g or a T_m of switching segments of the polymers. Here, it is necessary to mention that if the T_{sw} is nearer to the human body temperature, then the polymer is very useful for biomedical applications and T_{sw} as T_m is preferable over the T_g, as the former is a sharper physical property than the latter. Upon reheating above the T_{sw}, the oriented chains in case of an amorphous polymer or a crystalline polymer in the network restore the random coil conformation resulting in a macroscopic recovery of the original shape. So they have two different segments or phases in the structures: one is a net point or hard or fixed phase and the other is a soft or reversible or switching segment. Thus, the hard segment serves as a pivoting point for shape recovery and the soft segment could mainly absorb external stress applied to the polymers. They should also possess highly strain fixity rate and strain recovery rate.

The programming like applied strain or deformation rate and extent are also influenced by the shape memory effect of the polymers. The recovery ratios increased with an increasing deformation speed and with a decreasing maximum strain. Thus for good shape recovery,
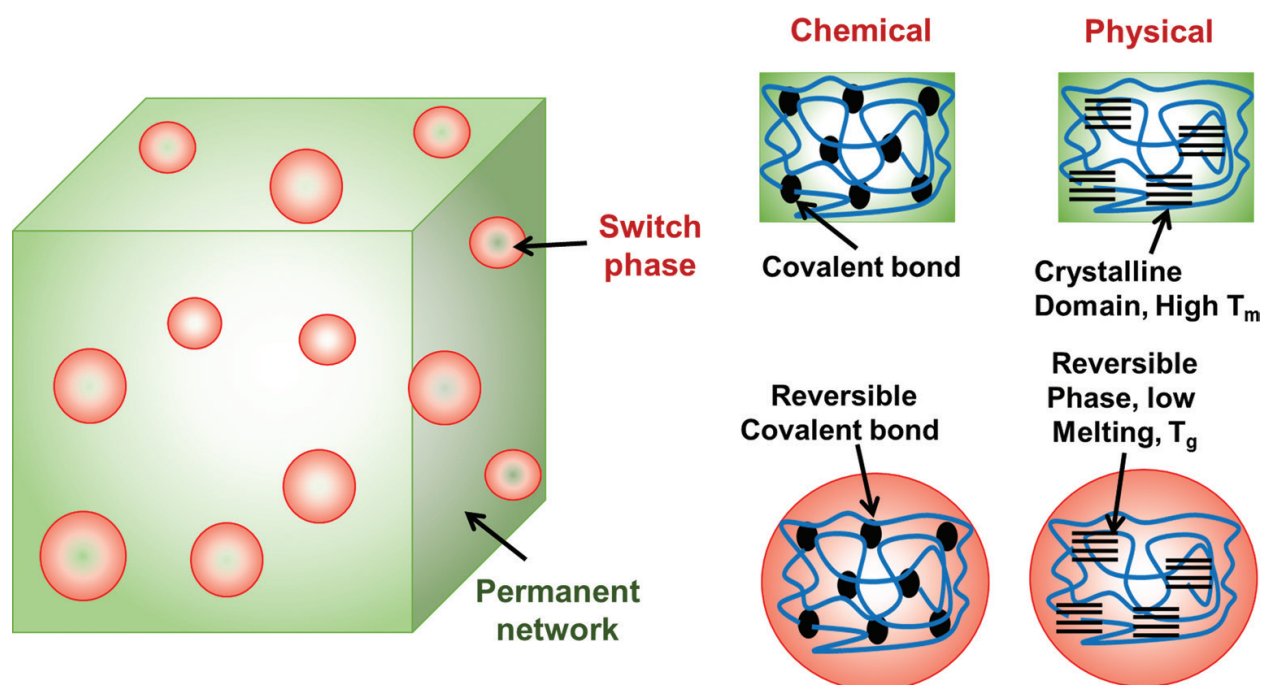

Figure 4. General structure of SMPU containing a "permanent network," which controls the shape and a "switch phase," which can be triggered by external stimuli.

deformation speed must be fast, while overall deformation should be low. The recovery stress of SMPs increased with the decrease of stretching rate, an increase of stretching temperature, and stretch ratio. The recovery stress of SMPU largely depended on the degree of interfacial interaction. The effective SMPs can be obtained when the hard segments retain the whole shape through inter-/intra-attractions (H-bonding or dipole-dipole interaction) in SMPs chain and the soft segments freely engross external stress by extending and unfolding the molecular chains. If the interactions in the hard segments are broken at high stress, the shape memory effect will be lost and the original shape cannot be restored. Hence, the controlling of composition and the structure of hard segments and soft segments are very much required to obtain desired shape memory effect.

SMPs are designed in such a way so that a large change in elastic modulus above and below T_g of the switching or amorphous phase will occur. They also have micro-Brownian movement of the chain molecules at a temperature above T_g, though rubber elasticity will present within T_g to T_m range due to limited molecular motion of the frozen or crystalline phase. Below T_g, the deformation is fixed due to the frozen Brownian motion of the chains. The shape can be recovered by reheating at an elevated temperature due to the recovery of the elastic force or the strain generated during the deformation.

For crystalline SMPU, T_m can be taken as at T_s instead of T_g, as a large change in elastic modulus above and below T_m of the soft segment is possible. Further, thermoplastic SMPU with the mesogenic unit in the structure has a high value of modulus compared with conventional SMPU [25]. Crystalline state, glassy state, entanglement network, or crosslinking network can be used as a fixed structure memorizing the original shape, that is, frozen phase, the reversible phase must have a large drop-in-elastic modulus on heating at T_s. The selection of T_s depends on the temperature at which the elastic modulus is the highest.

From the study of shape memory effect with the molecular structure, it has been observed that high crystallinity of the soft segment region at room temperature is a necessary prerequisite for SMPU [26]. Thus, the most important thing to be required for developing SMPU is to achieve maximum crystallization and stable hard segment domains. To achieve this, various attempts have been made. These include incorporation of the mesogenic unit such as 4,4'-bis (2-hydroxy ethoxy) biphenyl [27], ionic group [28], long alkyl chain [29], and so on. Further, the studies of Kim et al. suggested that large ratio of E_g to E_r is essential for obtaining good shape memory effect [29]. This can be easily achieved by using crystalline soft segments, for example, polycaprolactone diols; mesogenic moiety, for example, hydroxy-substituted biphenyls; and ionomers, for example, dimethylol propionic acid as the components of SMPU.

6. Application of shape memory polyurethane

SMP has myriad of advanced applications in different fields from daily life uses like textile to biomedicals. These applications include artificial organs like muscles, smart catheter, drug-delivery systems, biosensors, auto-repairing automobile parts, smart textile, self-healing

materials, smart suture, and so on. In this section, we described the detailed application of SMPU in the different advanced areas.

6.1. Industrial applications of SMPU

SMPUs are already widely used as heat-shrinkable polymer tubings, films, and so on. The utilization of SMPU provides easier processing compared to other used polymers in such application [30]. As a consequence, these materials found a wide range of applications, for instance as a safety tag [31] or as a self-deploying chair [32].

6.2. Biomedical applications of SMPU

SMPs are also well suitable for the use in different biomedical applications, even though several requirements must be addressed and a range of problems must be overwhelmed for advanced application in this field [33]. For example, one major issue with thermo-responsive SMP is the heating of it inside the human body. Various approaches are developed to overcome this problem. One route is the use of noncontact triggering stimulus such as infrared (IR), lasers, and so on [34, 35]. These can heat SMP inside the body at the accurate location. Another way is the incorporation of magnetic nanoparticles in SMP. This magnetic nanoparticle can be triggered by an external magnetic field for the selective heating of the SMP. Biocompatible and nontoxic nature of SMP is also a crucial concern for biomedical applications. In this regard, it is pertinent to mention that the several SMPUs are developed, which are biocompatible. Generally, PCL, PEG, and polylactic acid-based SMPU are found to be nontoxic and biocompatible [36–38]. Besides these academic studies, DiAPLEX is a commercially available SMPU which also showed biocompatibility. Such biocompatible SMPU can be utilized in several biomedical applications, such as endovascular devices (clot-removal devices, aneurysm occlusion devices, and vascular stents), repair of cardiac valves, tissue engineering, orthopedics, orthodontics, endoscopic surgery, kidney dialysis, photodynamic therapy, and so on.

Thermo-responsive SMP-based mechanical clot extraction devices to treat ischemic stroke was reported by Maitland et al. [39]. Their fabricated catheter is photothermally activated, so it can easily remove the clot and finally relieve of the ischemia. Moaddeb and coworkers invented SMPU-based devices for treating heart failure patients suffering from various levels of heart dilation [40]. Such heart dilation is treated by reshaping the heart anatomy with the use of SMPU. The concept of biodegradable thermo-responsive SMP sutures was showed by Lendlein and Langer [41]. The suture was fabricated using oligo(ε-caprolactone)diol-based SMP. An abdominal wound in a rat was loosely sutured using the SMP fiber, and then heated to body temperature to achieve wound closure (**Figure 5a**). SMPU provides an alternative to traditional materials used for the treatment of dental malocclusions. Also, SMP arch wire in orthodontic braces for aligning teeth is more aesthetically appealing than a traditional metallic arch wire. These features were studied by Jung and Cho [42]. They used extruded SMP wire, which was attached to stainless steel brackets bonded to teeth in a dental model. When heated, the teeth slowly moved into alignment (**Figure 5b**).
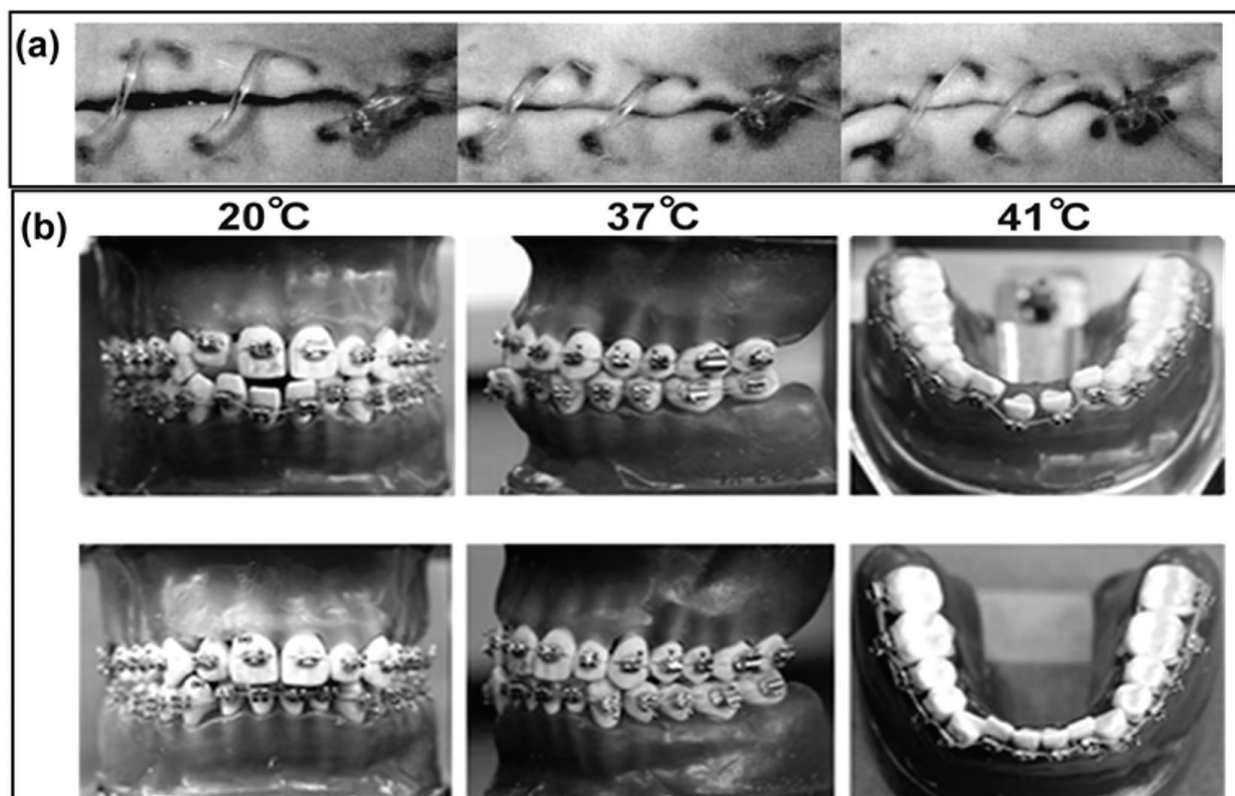
Figure 5. (a) Biodegradable SMP suture for wound closure. The photo series from the animal experiment shows the shrinkage of the suture as temperature increases (reproduced with permission from Ref. [41]) and (b) photographs of the orthodontic appliance (top) before and (bottom) after treatment. The movement of the misaligned teeth due to a lateral force originating from the shape recovery of the SMP arch wire is seen (reproduced with permission from Ref. [42]).

Tissue engineering is one of the large application areas of SMPs. The introduction of biodegradable SMPU urged the study of their usage for minimally invasive tissue engineering. Usually, tissues can be grown on SMPU-based scaffolds and incorporated inside the body through minimally invasive techniques (e.g., catheter). The scaffold is implanted to initiate the repair or reconstruction of tissues or organs in the affected area of the body. The SMPU-based-implantable embolic devices and stents demonstrated potential endovascular tissue engineering applications. Such biodegradable SMPU scaffolds can also be applied in pharyngeal mucosa reconstruction, bone regeneration, and organ repair. Different research groups have investigated the use of thermally responsive SMPUs as an extracellular matrix for in situ growing of various tissues. In this context, Rickert et al. reported the growth of cells on a biodegradable PCL-based SMP [43]. Rat pharyngeal cells are grown on a porous and smooth surface of the SMP to study the prospect of reconstructing the mucosa of the upper aerodigestive tract. Neuss et al. also investigated the cell-growing behavior of human mesenchymal stem cells, human mesothelial cells, rat mesothelial cells, and L929 mouse fibroblasts, on a similar PCL-based SMPU [44]. They found that mesothelial cells create an anti-adhesive surface layer, which may support abdominal repair or regeneration. Mesenchymal stem cells, the precursor cells of bone, fat, cartilage, and muscle, may support bone regeneration and the construction of adipose tissue. Furthermore, they also found that the use of heat as a stimulus did not affect the majority of adherent cells. SMPU/carbon nanotube

composites also showed good MG63 cell differentiation ability, which showed its potentiality as an alternative biomaterial for bone regeneration in a comprehensive manner [45].

6.3. Textile application of SMPU

SMPU can be made in the form of fibers (macro-, micro-, and nanofibers), solutions, films, and foams for textile and apparel applications, such as non-woven materials, coatings, finishing, lamination, weaving, and knitting [46–49]. Various methods such as wet spun, melt spun, dry spun, and electrospun are used for the production of SMPU fiber [50–53].

Shape memory films and foams have a number of applications in laminated smart fabrics [54, 55]. The functions of SMP films applied to textiles include waterproofing, water vapor permeability (WVP), seam sewing, crease recoverability, and crease fixing [56, 57]. SMPU has a potential for making breathable fabrics due to its good WVP sensitivity. Jeong et al. studied the WVP properties of SMPUs, and breathable fabrics were invented by coating the SMPU membranes on a fabric substrate [26]. Mondal and Hu also designed SMPU-coated fabrics, which abruptly increased WVP properties at room temperature (T_r) compared to low temperature [58]. These results suggested that the breathable textiles require possessing a high WVP at higher temperatures and a low WVP at lower temperatures. Additionally, Mondal and Hu incorporated a small percentage of carbon nanotube in SMPUs and then coated on cotton. They reported that the fabricated cotton fabric provided excellent UV protection, along with a required WVP and wearing coziness [58]. In addition to that, Chen et al. also investigated adjusting the size and shape of the free-volume holes in a fabricated membrane to control the WVP by adjusting the temperature [59]. Further, Mondal and Hu attempted to find the influence of hydrophilic groups and crystalline soft segments on the WVP of SMPU films [60]. They found that the WVP increased with the increase of PEG due to the enhancement of hydrophilicity. However, PCL or polytetramethylene glycol-based SMPUs have low WVP because of the increased interaction among the polymer chains.

Hu et al. also fabricated a fabric-based thermoelectric generator using coating of waterborne PU composite on yarn [61]. They reported that this coated fabric showed satisfactory thermoelectric performance and good processability. In addition to that, medical stockings are also fabricated using SMPU for the treatment of chronic venous disorders [62–64]. This SMPU-based stocking allows controlling or managing the pressure exerted in a wrapped position and also produces extra pressure (up to 50%) by simply heating the stocking. This type of stocking possesses a great potential to overwhelm the restriction of conventional stockings. It can be used as a smart wound-care product, during the course of compression therapy. Self-healing textiles are also developed using SMPU. In this context, Hu et al. fabricated stimuli-responsive fiber using SMPU which showed 94% healing efficiency [65].

6.4. Anti-counterfeiting application of SMPU

SMP security label film is made from SMPU. SMP security label film can store embossed logo/text shape information in the synthetic-paper-like film, and release these information when exposed to stimuli (**Figure 6**). This kind of SMP security label is just not only an exclusive anti-counterfeit label but also a tamper evidence label [66]. These labels are used for security label, tamper evidence, security packaging, security ticket, and so on.
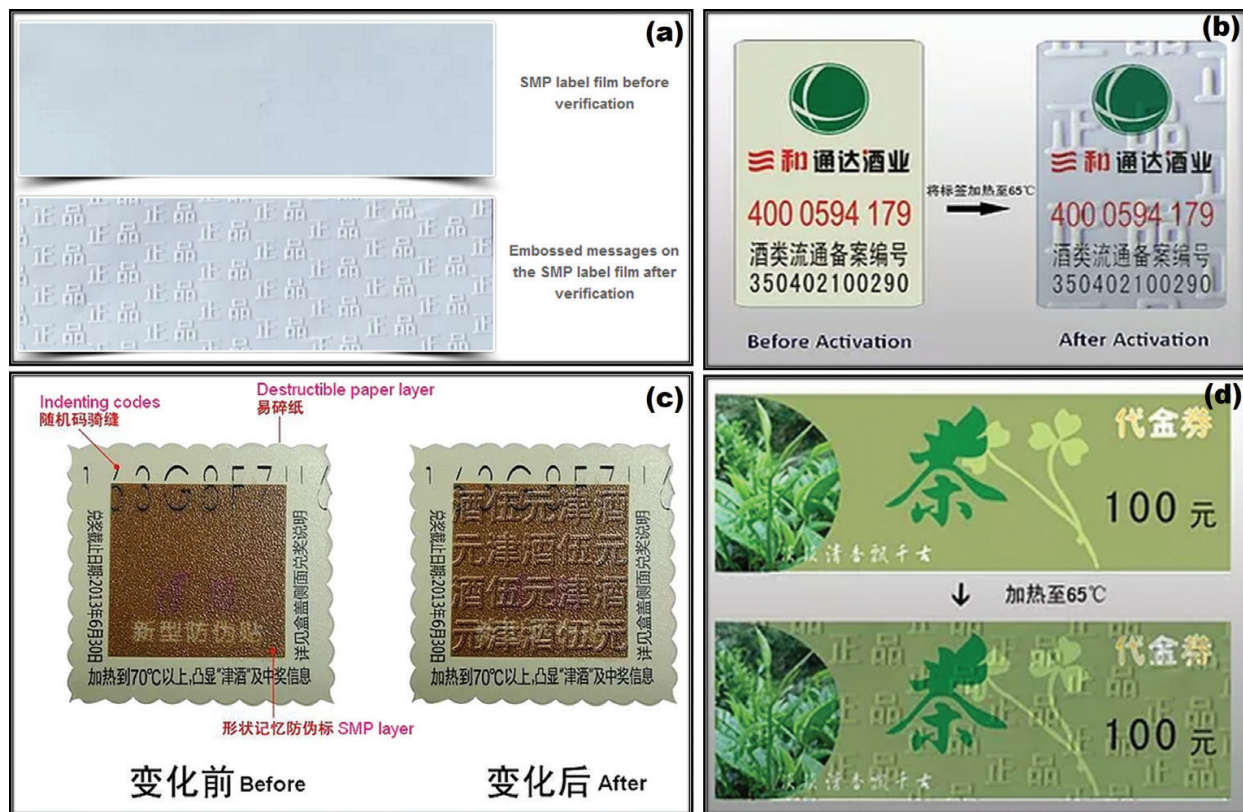
Figure 6. SMP in the anti-counterfeiting application (a) and (b) security label film, (c) tamper evidence label, and (d) security ticket. Adapted from Ref. [66].

7. New development and future trend

Even though an enormous progress in the field of SMPU is already done, several future directions and related challenges still remain, which may be considered in future research:

a. The fabrication of medical devices based on biocompatible and biodegradable SMPU is of great interest owing to the important impact on human health. Various materials are developed such as self-tightening sutures, scaffolds for tissue engineering, drug-delivery systems, implants for minimally invasive surgery procedures, synthesis of protein-polymer or DNA-polymer conjugates for therapeutic self-retractable and removable stents, and so on. Here, the main challenges of concern are the rate of degradation of SMPU (enzymatic or hydrolytic), their degree of toxicity, mechanical solicitation, and so on.

b. Three-dimensional printing of smart materials is another attractive field to be developed imminently. The change in the shape upon triggering of external stimuli provided a concept for the development of unique "four-dimensional (4D) printing" procedure. This may pave a way for the production of actuators to develop self-evolving structures, soft robotics, anti-counterfeiting system, and 4D bioprinting materials. Some technological and design restrictions are still unsolved such as inadequate choice of properly usable polymer, the existence of microstructural defects in SMPU, and materials real-time adapting; such problem can be addressed in future.

c. The design of SMPs-based self-cleaning, self-healing, and self-adapting materials is also gaining much interest over the last few years. These materials have shown their potential for the elaboration of load-bearing aircraft components, self-cleaning and light-guided windows, flexible solar modules (polymer solar cells), smart textiles, bionic robot, and so on. The production of SMPU with improved durability and good mechanical properties will further improve the performance in the field. In this regard, SMPU composite may be a choice to develop such smart materials.

d. The energy-harvesting SMPs (solar energy) and chemical-responsive SMPs (chemical reaction energy) also carved a distinct attention of both academic and commercial researchers. The molecular-, gas-, or sound-detectable materials can be defined as forthcoming materials. In addition to that, wireless and remote-controllable SMPs are another class of devices to be produced using different magnetic and light-actuated composites and piezoelectric-containing materials.

e. Despite their multi-applicability and a wide range of properties, the direct transfer from the laboratory to industrial scale remains a challenge. In this context, the main problems are associated with the complexity of shape memory effect. These are affected by many factors such as the programming step and the triggering process parameters. In addition, quick and versatile manufacturing processes are also desirable, while focusing on the use of cost-effective and eco-friendly raw materials, and ensured profit gain, and so on.

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