Thermo-Moisture Responsive Polyurethane Shape Memory Polymer for Biomedical Devices

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Abstract: Shape memory polymers (SMPs) have a number of advantages as compared with their metal counterpart, i.e., shape memory alloys, in particular for biomedical applications. The recent finding of the influence of moisture on the glass transition temperature of a polyurethane SMP, which is traditionally well-known for its thermo-responsive feature, enables us to achieve not only the so called moisture-driven for shape recovery, but also the recovery following a pre-determined sequence, i.e., programmed recovery. Utilizing these new features, we demonstrate a few novel applications of this SMP for biomedical devices, in particular, for minimally invasive surgery and cell surgery in future.

Keywords: Shape memory polymer, medical device, programmable, polyurethane, moisture responsive.

1. INTRODUCTION

Shape memory polymers (SMPs) have a number of advantages over shape memory alloys (SMAs), in particular for biomedical applications. Larger recoverable strain (well over 100%), lower density and lower cost are the most important ones among others [1]. Although photo-responsive and chemo-responsive (namely, change in pH value) SMPs are available, at present the most popular SMPs are those activated by heat, i.e., thermo-responsive SMPs. Unlike SMAs, which can be directly actuated by Joule heating, i.e., by passing an electrical current directly for heating [2], it is rather complicate to heat polymers, since they are intrinsically non-conductive in their natural form. Although electrically conductive SMPs can be realized by blending with various kinds of conductive fillers [3-9], for instance, carbon black as the simplest and cheapest filler, the actuation still cannot be triggered in a wireless manner. One of the recent developments in terms of the technologies for activating thermo-responsive SMPs is to heat SMP composites, which are mixed with magnetic particles, by applying an alternating magnetic field for induction heating [10-12]. Despite that direct wire connection is avoided, the generation of a strong enough alternating magnetic field requires an additional bulky system. Laser heating is another recent development, which is only applicable to certain transparent SMPs largely in thin wire form and requires an optic fiber for laser beam to pass through [13].

On the other hand, some SMPs have been developed to be able to recover two shapes one after another upon heating (i.e., from shape *A* to shape *B* and finally to shape *C*) [14, 15]. However, it is not easy to fabricate a SMP which can recover its original shape following a pre-determined multi-step sequence (more than two intermediate shapes), i.e., in a programmable manner.

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Recently, a new approach to trigger the recovery of a thermo-responsive polyurethane SMP has been identified [16]. This polyurethane SMP can recover its original shape upon immersing it into room temperature water, i.e., moisture-responsive, in addition to its well-known thermo-responsive feature. The moisture-driven shape recovery is due to the strong influence of moisture absorbed upon immersing into water, which can significantly lower down the glass transition temperature (T_g) of the SMP by up to over 25^{o}C [17]. Consequently, instead of heating the material to over its original T_g to trigger the actuation, the shape recovery can be initiated upon immersing into ambient temperature water due to the drop of T_g of the polymer. This finding can also be utilized as a simple and convenient approach to work out a SMP with different T_g at different locations, i.e., a SMP with a functionally gradient T_g. Consequently, the recovery can be programmed in a step-by-step manner as shown in Fig. (**1**).

With the thermo-moisture responsive feature, and the intrinsic good bio-compatibility of polyurethane, this SMP can have a wide range of bio-related applications, in particular for minimally invasive surgery and even for cell surgery. The purpose of this paper is to demonstrate some novel concepts utilizing this material for, for instance, self-tightening/self-unraveling suture, retractable stent and possibly delivering tiny devices/machines into a living cell.

2. MATERIAL BACKGROUND

The particular thermo-moisture responsive SMP is an ester-based thermoplastic polyurethane SMP obtained from the Misubishi Heavy Industries (MHI), Japan. It is prepared from diphenylmethane-4, 4’-diisocyanate, adipic acid, ethylene glycol, ethylene oxide, polypropylene oxide, 1, 4-butanediol and bisphenol A. As indicated by MHI, the T_g of this material can be tailored in order to meet the requirement of a particular application. Here, we used MM3520 and MM3550 (in pellet form), which have nominal T_g of 35^{o}C and 55^{o}C, respectively as provided by MHI, and MS-5510 (SMP solution, 30 wt% of polyurethane resin and 70 wt% of

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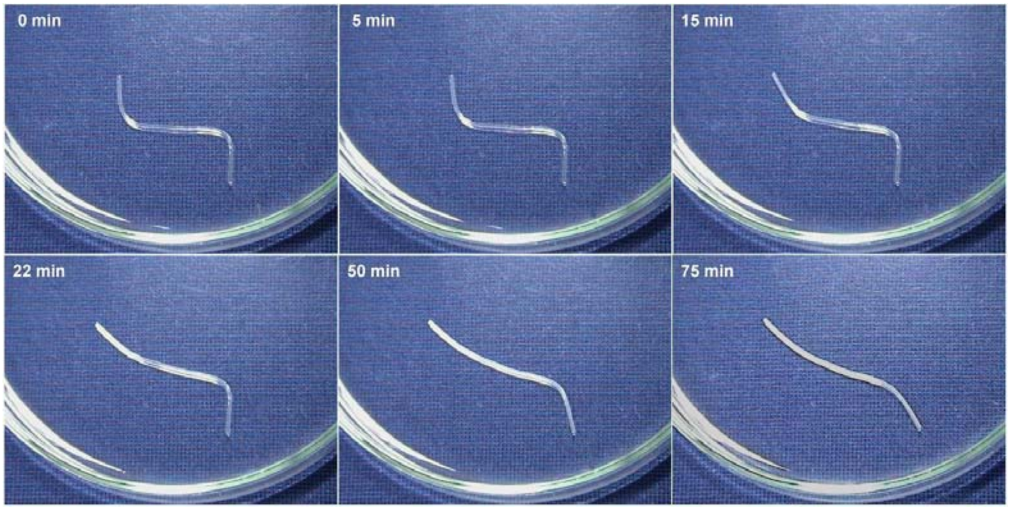


Fig. (1). Recovery of a 1 mm diameter polyurethane SMP wire in water in a sequence. The wire was produced by extrusion. The top-half wire was placed in water for a lower T_g, while the bottom-half was kept dry. The wire was then bent into a Z-shape. Upon immersing into room temperature water, the top-half of the wire recovered first and the bottom half started to recover later. (Reprinted with permission from [18]. Copyright 2005, American Institute of Physics).

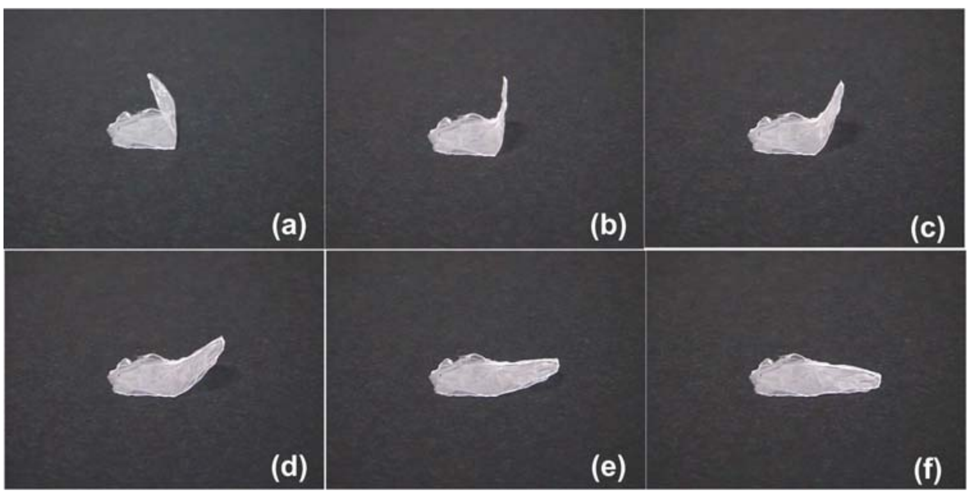


Fig. (2). Shape recovery of a 300 nm thick polyurethane SMP film upon heating.

dimethylformamide [DMF]) for preparing various kinds of samples.

For samples/devices made out of pellets, the raw material was pre-dried in a vacuum oven at 80^{o}C for 12 hours. Different shaped/sized samples were prepared by injection molding, extrusion and hot pressing following the processing procedures suggested by MHI. The thinnest wire we have prepared by extrusion was about 0.3 mm in diameter, and the thinnest film by hot pressing was about 0.5 mm thick.

In addition, we have prepared ultra-thin films down to 300 nm thick by water casting using SMP solution (in DMF) with 4wt% concentration. Fig. (**2**) reveals that the produced ultra-thin film has excellent shape memory. A piece of carbon fiber (about 7 μm in diameter, left-top inset of Fig. **3**) was immersed into SMP solution (in DMF, with 5wt% concentration). By passing a constant electrical voltage of 23 V over a fiber length of 40 mm for a while, after drying in air, micro SMP beads were formed. The exact size of these beads depends on the heating time. Typical SEM image of these beads atop a carbon fiber is presented Fig. (**3**). The wall-thickness of the zoom-in viewed bead in Fig. (**3**) is about 1.5 μm at the thickest position. Prolonged heating eventually resulted in the whole carbon fiber covered by SMP almost uniformly, i.e., a SMP wire with a very small carbon fiber core.

Porous polymers are very important in many applications, such as, in tissue engineering where they are applied as scaffold for cellular attachment and tissue development [19]. The common agents used for polyurethane to develop porous or foaming structures are organic solvents. The residues of these agents remaining in the material may be harmful to cell and tissue [20]. Utilizing the high moisture absorption capability of this polyurethane (over 4.5wt%, about half of it is free water), we used water as a non-toxic agent to develop porous SMP thin films [21]. Depending on the time of immersion in water and the late on heating temperature, different size and density of bubbles were resulted (Fig. **4**). These bubbles can even shrink or totally disappear upon heating

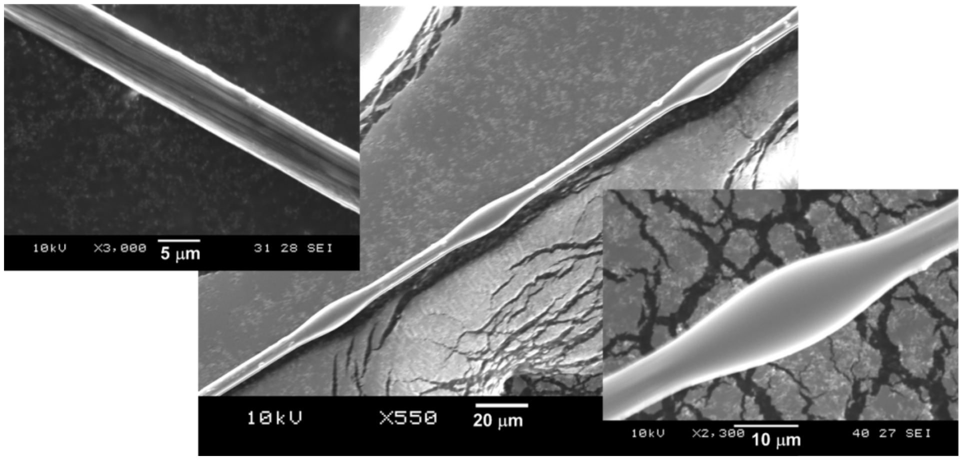
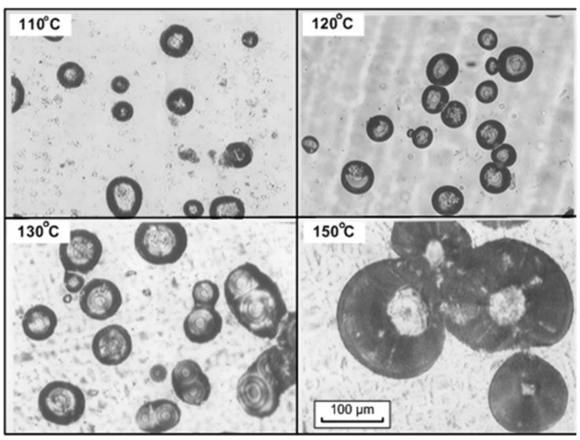


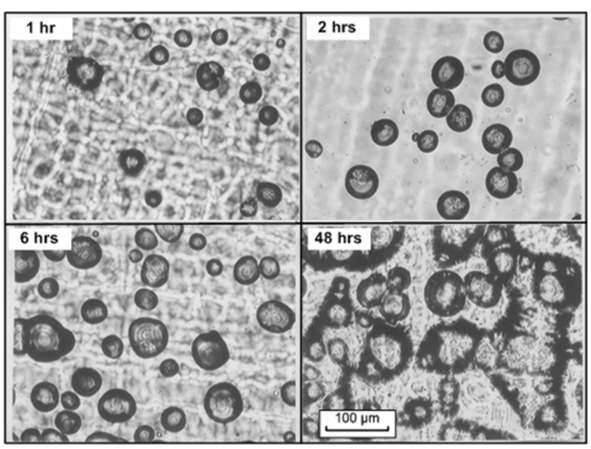
Fig. (3). SEM image of micro polyurethane SMP beads. Left-top inset: carbon fiber; right-bottom inset: zoom-in view of a bead.

(Fig. **5**). This is a very useful feature, since these bubbles may be used to store medicine inside as micro reservoirs. Upon heating or immersing into water, the medicine can be *pumped* out due to the shape recovery (shrinkage) of these bubbles.

Thin film SMP with magnetic chains inside using Fe_3O_4 powders (nominal particle size, <5 μm, purity 98%) has been produced [22]. The chains were formed in three steps. First,

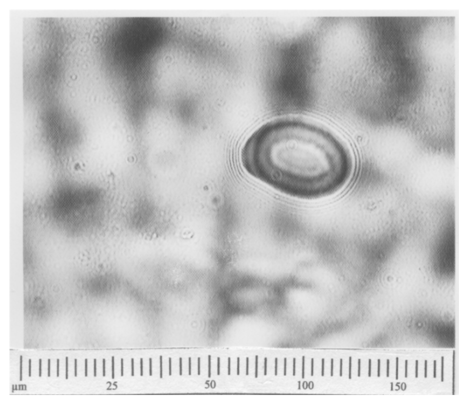


(a)

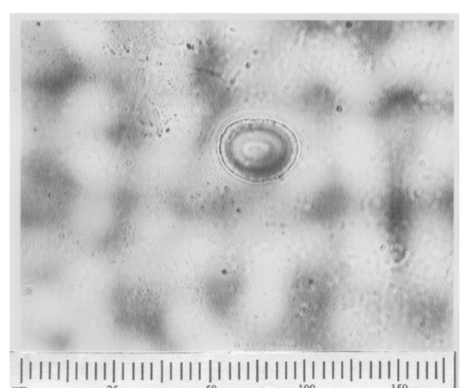


(b)

Fig. (4). Porous SMP films using water as non-toxic agent. (**a**) Heating at different temperature after immersing in room temperature water for two hours; (**b**) immersing in water for different period of time and heated at 120°C. [21].



(a) Initial bubble



(b) After subsequent heating

Fig. (5). Soaked for two hours initially, heated to 102°C and subsequently heated to 80°C. [21]

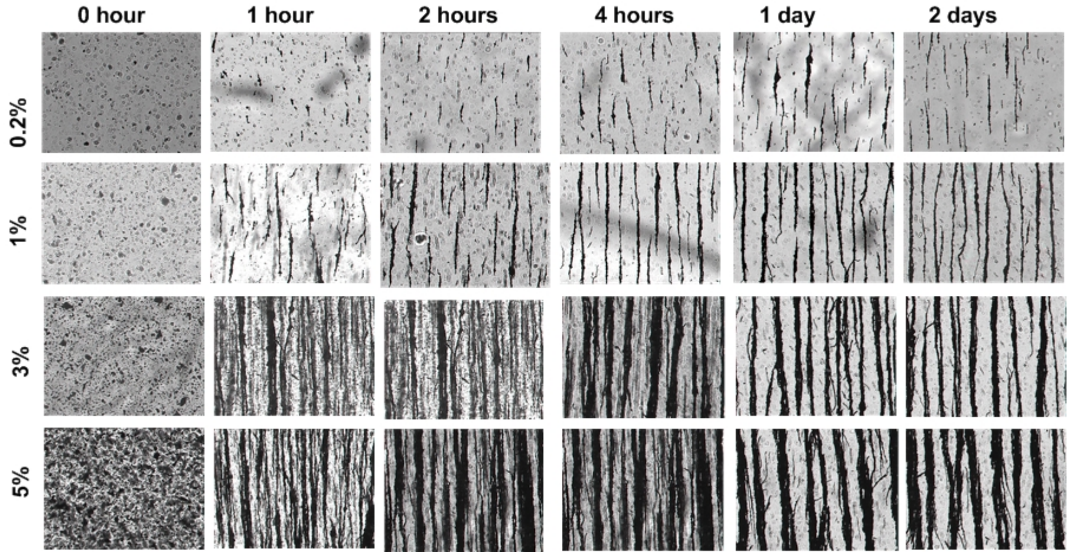
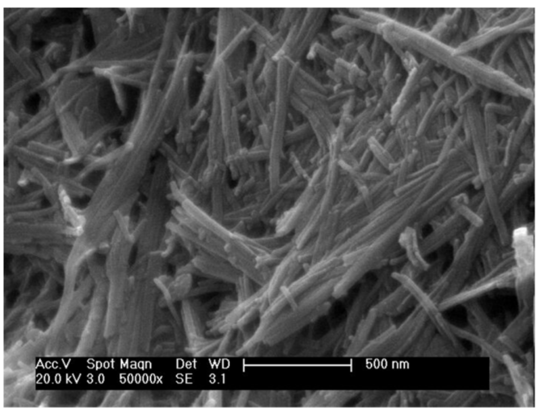
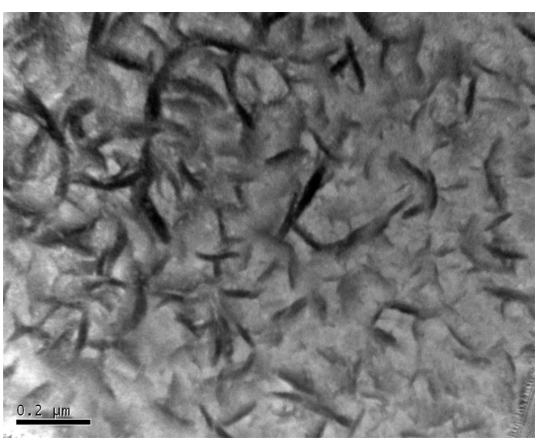


Fig. (6). Formation of magnetic chains [22].



(a)



(b)

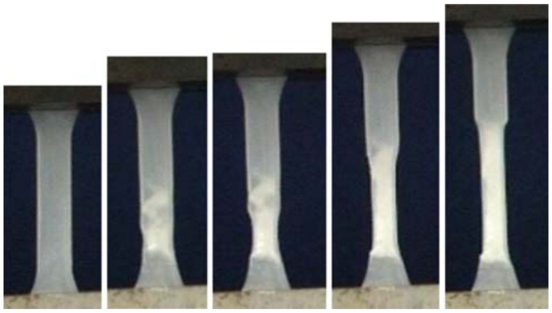
Fig. (7). SEM images of attapulgite (playgorskite) clay (**a**) and its dispersion in SMP (**b**).

the Fe_3O_4 powders were mixed with the polyurethane SMP solution. The well-stirred solution was cast on a glass surface and then a magnetic field was applied by using two pieces of magnets for a certain period of time. Fig. (**6**) reveals the formation process of these magnetic chains at different concentration of Fe_3O_4 powders. The last step was to dry the thin film at 80°C. It is also possible to form vertical protrusive chains atop a SMP substrate if a vertical magnetic field is applied. Such magnetic SMPs could be used for induction heating (by applying an alternating magnetic field) for shape recovery, or for guided patterning of particles or cells in tissue engineering.

It should be pointed out that it is possible to achieve excellent electrical conductivity for Joule heating for shape recovery by blending with various types of electrical conductive fillers and the moisture-responsive feature still remains in these composites [5]. Heat treated and non-treated attapulgite (playgorskite) clay (which is a kind of nano sized fabric) (Fig. **7**) has been used for reinforcement [23]. Uniform dispersion of the clay within the polymer matrix has been observed. Since the clay is electrically non-conductive, extremely cheap and biocompatible, it is a cost-effective alternative for enhanced performance.

It should also be pointed out that right after fabrication all samples, in particular those thin wires and thin films, should be stored in an air-tightened box and then keep in a dry cabinet to prevent the possibility to be wetted by even the moisture in air.

In addition, according to our previous study, the recovery stress in this SMP could be as high as 1.5 MPa [1,24], which is much lower than that of shape memory alloy, but more or less comparable to that of normal organic tissues. The recoverable strain of this SMP (pure) is over 100% [1]. In order to ensure a uniform deformation, it is recommended to deform the SMP at a high temperature (e.g., 15°C above T_g) to avoid the Luder band phenomenon. As show in Fig. **8a**, the appearance of Luder band, which propagates from one end towards the other end of the sample upon stretching, causes the deformation non-uniformity, i.e., one side is deformed much more than that of the other in the middle of stretching



(a)

(b)

Fig. (8). Uniaxial tension at low temperature (**a**) and shape recovery upon heating (**b**). Luder band phenomenon is observed upon stretching. However, upon heating, the recovery is more or less uniform.

process. However, unlike that in shape memory alloys [25], the transition temperature (T_g) of SMP is more or less independent on the amount of pre-strain. Thus, upon heating, the shape recovery occurs simultaneous everywhere (Fig. **8b**).

3. DEVICES AND DEMONSTRATION

As discussed above, this SMP has a number of unique features and can be easily fabricated into almost any shapes and sizes, and even with tailored properties for a particular application. Since it is also biocompatible [26], as it is polyurethane based, it can be safely used for bio-devices.

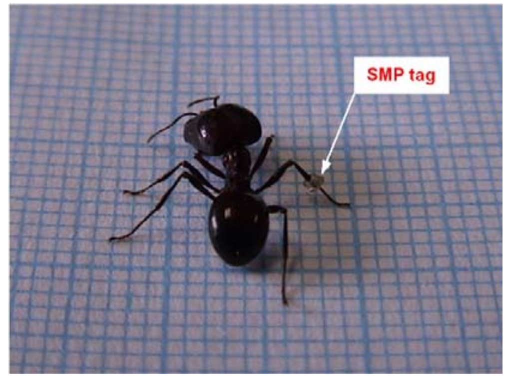


Fig. (9). SMP micro tag. (Reprinted with permission from [27]. Sage Publications).

Fig. (**9**) shows a living ant with a micro tag, which is made of the SMP, mounted on one of its legs. First, a through hole was drilled out at the center of a piece of SMP thin wire in its length direction. Subsequently, the small hole was expanded at 50^{o}C (15^{o}C above T_g of this SMP, which is 35^{o}C) by inserting a tapped rod (with a significantly bigger diameter than that of the hole) into the hole. After cooling back to room temperature, the rod was removed and an expanded *ring* was obtained. This *ring* was then mounted to one of the legs of a living ant. Upon heating to 35^{o}C, the *ring* shrank and held firmly to the leg as a permanent tag. This is a simple example to demonstrate how to utilize the shape memory behavior of this SMP in a simple device. As the maximum stress is limited (actually rather gentle and compatible to tissue), there is no need to worry about the possible damage to the leg due to over stressing. This is an apparent advantage as compared with that in shape memory alloys. After cooling back to ambient temperature, the tag becomes much harder, so that it becomes difficult to be deformed. As such, accidental loose/slip could be largely prevented.

SMP suture has been proposed for self-tightening of knots for, for instance, minimally invasive surgery [28]. Limited by the space for maneuvering in minimally invasive surgery, it is a rather difficult task to tighten these knots even for the experienced surgeons. Self-tightening SMP suture provides a simple solution to overcome this difficulty. Fig. (**10**) shows the knot-tightening sequence of a SMP wire. A piece of 0.75 mm diameter SMP wire was heated to 60^{o}C,

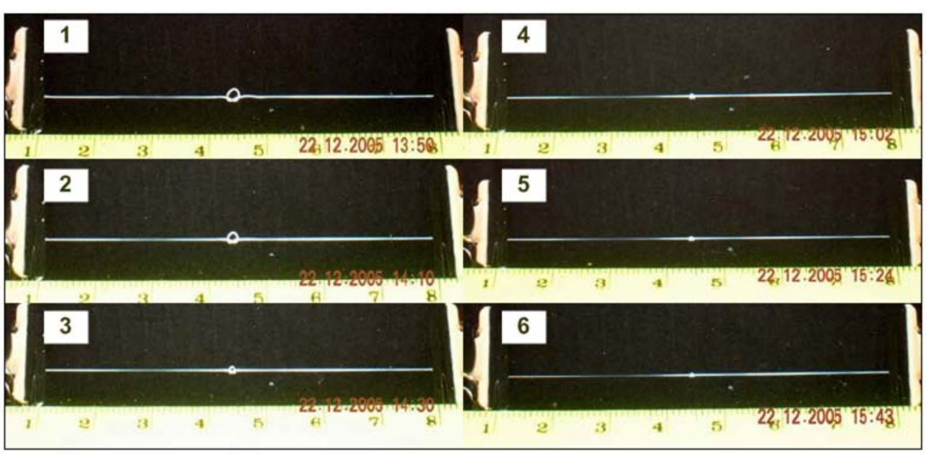


Fig. (10). Self-tightening of a SMP wire upon immersing into room temperature water. (Reprinted with permission from [24] SPIE).

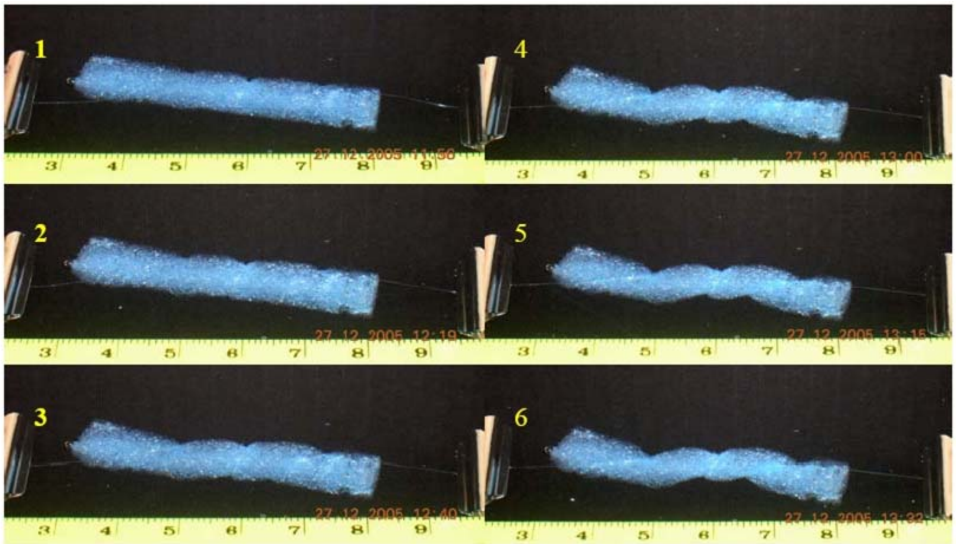


Fig. (11). Self-tightening of a SMP wire wrapped around a sponge upon immersing into room temperature water. (Reprinted with permission from [24] SPIE).

which is 25^{o}C above the T_g of this SMP, and then stretched by 50%. After cooling back to room temperature, a loose knot was made and the two ends of the wire were fixed inside a container. Subsequently, the container was filled with room temperature water (about 22^{o}C). 20 minutes later, apparent shrinkage of the knot was observed. After another 20 minutes, the knot became much smaller, and eventually, the knot was fully tightened. Fig. (**11**) further demonstrates the tightening procedure of the same type of SMP wire (again 50% pre-stretched) initially loosely wrapped around a sponge with both ends fixed. Different from other SMP sutures, since this SMP is thermo-moisture responsive, the suture can be pre-stretched at above T_g (60^{o}C in these experiments) easily, and then recover it original shape upon immersing into room temperature water, i.e., self-tightening upon absorption of water. As heating is avoided, the advantage of this SMP suture is apparent. A perfect wireless approach in inducing shape recovery is achieved. By reducing the diameter of the SMP wires (currently 0.75 mm wires were used), quick reaction should be achievable. On the other hand, by coating the thin SMP with a layer, that is degradable within a particular environment after a certain period of time, one can control the time for the recovery to happen.

Various types of self-expandable stents are widely used in these days. Previously, stainless steel was the dominant material for stents. In recent years, NiTi shape memory alloy becomes an alternative. At present, various polymer (including biodegradable and/or shape memory polymers) stents or polymer coated stents become popular and/or under development [29, 30]. A catheter is normally used to deliver a stent into the required location and then to release the stent. The expansion of the stent can be done by means of mechanical (elastic) expansion or the shape memory effect for shape memory materials. However, once the stent is in place, in general, it is very difficult to be removed. On the contrary, a retractable stent is meant for easy-to-be-taken-out. This can be realized by using the thermo-moisture responsive SMP.

A piece of thin film polyurethane SMP (0.5 mm thick) was fabricated, pre-stretched by 50%, and then wrapped into a round tube shape (Fig. **12a**). The tube was mechanically folded into star-like shape (Fig. **12b**). This folded tube, which had a much smaller diameter, could be delivered into the required location by a catheter. The expansion of the stent could be done in a standard mechanical manner (Fig. **12c**). After a certain period of time, the SMP, which was placed inside a water container (an environment similar to that inside a human body), absorbed water, which subsequently triggered the shape recovery. Hence, the tube shrank and its diameter reduced significantly (Fig. **12d**). Finally, it was ready for being taken out.

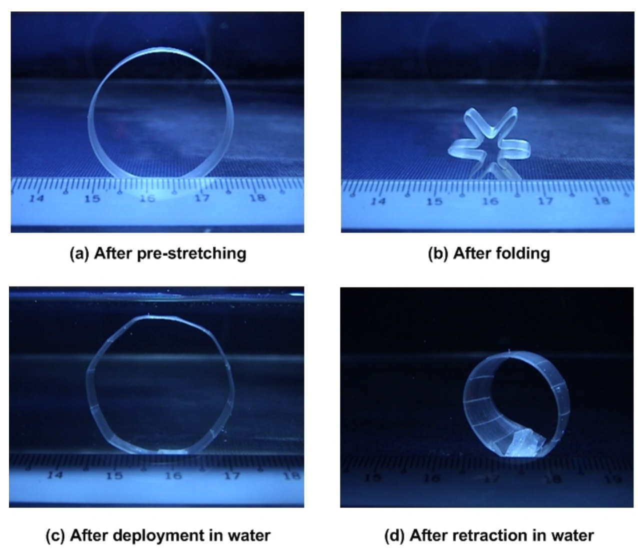


Fig. (12). Retraction of a pre-deformed polyurethane SMP STENT in water. (Reprinted with permission from [24] SPIE).

In addition to reinforcement, since attapulgite clay is also capable to quickly absorb a great amount of water, it can be filled into SMP for speed-up the moisture induced shape

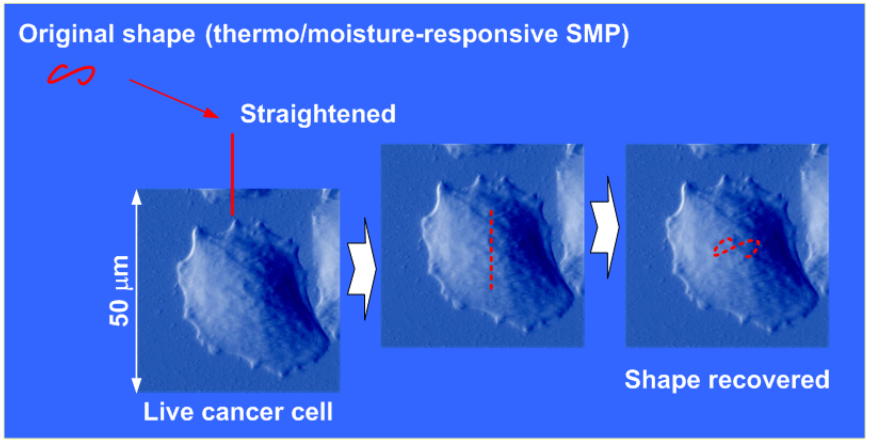


Fig. (13). Delivery of a piece of S-shape thermo-moisture responsive SMP wire into a living cell (illustration).

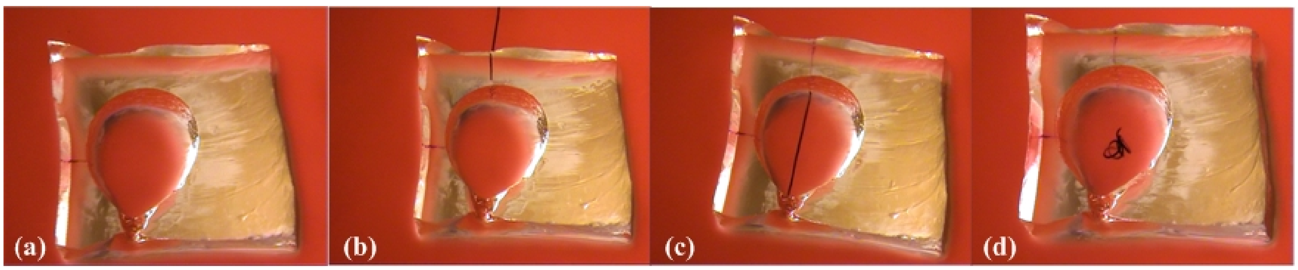


Fig. (14). Demonstration of the concept of delivering a coiled SMP wire (0.5 mm diameter) into the hole inside a hydrogen gel. (**a**) A piece of gel with a hole inside room temperature water; (**b**)-(**c**) delivery of a piece of straightened SMP wire into the hole inside gel; (**d**) recovery of SMP wire inside the hole.

recovery. It should be pointed out, although fast reaction to water/moisture might be an advantage in some applications [31], in some others, such as in the above case of retractable stent and the next application, a slow/delayed reaction is more suitable.

The shape memory phenomenon in ultra-thin polyurethane SMPs down to 300 nm thick has been confirmed (Fig. **2**), which sheds light on the possibility of realizing tiny devices working inside a living cell or for cell surgery. Tiny polymer devices down to a couple of microns in size, which can be well fitted into a cell, have been fabricated. Despite that such devices can be operated by a laser beam in water in a non-contact fashion [32, 33], the delivery of such devices into a living cell is still an unsolved problem. Thermo-moisture responsive SMP could be the right solution to this problem. As illustrated in Fig. (**13**), a piece of ultra-thin thermo-moisture responsive SMP wire can be deformed (straightened in this particular case discussed here), and then inserted into the cell. Upon absorption of water inside the living cell, the original S-shape is recovered. Fig. (**14**) demonstrates this concept at micro scale, in which we used hydrogen gel with a hole inside to represent a living cell. The hydrogen gel was placed in water for full expansion before a straightened SMP wire was inserted into the hole. The shape recovery (coiled shape) of the SMP wire was achieved due to the moisture-responsive feature of this polyurethane SMP.

Patterned surfaces are highly in demand for the enhanced efficiency of many existing drugs and enabling the construction of entirely new therapeutic modalities [34]. Patterned surface can also remarkably alter the surface tension for tailored adhesion. Recently, SMP has been demonstrated as a promising material for surface patterning of a variety of shapes at from macro scale down to nano scale in a cost-effective and convenient way [35, 36].

In addition, Fig. (**15**) shows one piece of micro reversible SMP composite chain (which is among a mass of such chains atop a SMP substrate). The vertical chain (around 35 μm in diameter) was produced from polyurethane SMP solution mixed with Ni micro powders (about 5 μm in diameter) (Fig. **15a**). Upon heating, the chain became soft. The soft chain deformed in responding to an applied magnetic field. After cooling back to room temperature and the subsequent removal of the magnetic field, the curved chain persisted and became rather rigid (Fig. **15b**). The chain was able to fully recover its original shape upon heating (Fig. **15c**).

Apart from protrusive reversible chains, different sized/types of wrinkles can be produced based the principle of thermal mismatch induced buckling of a thin elastic layer atop a soft substrate [37]. The general procedure is as follows. First, slightly pre-stretch (5% is enough) a piece of SMP at above its T_g, and then cool it back to room temperature. After coating with a very thin layer of elastic metal (e.g. a few nm of gold), heat the SMP to above its T_g for shape recovery. Subsequently, strip-type of wrinkle is formed atop SMP as shown in Fig. (**16**). Without pre-straining, labyrinths-type of wrinkle is produced when heated to the melting temperature of the SMP (Fig. **17**).

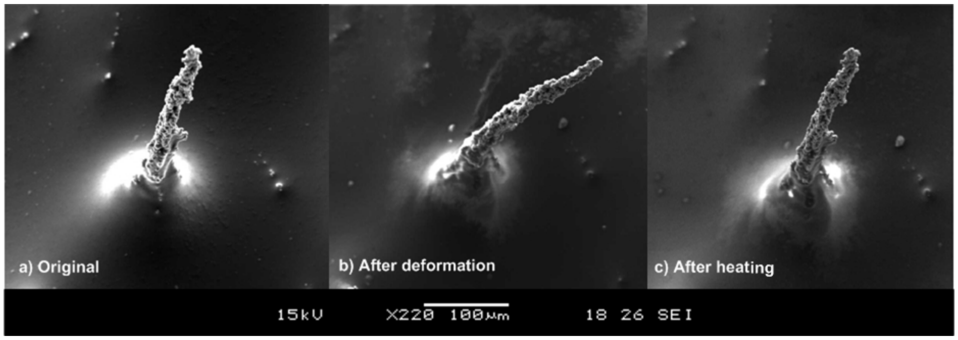


Fig. (15). Reversible vertical chain.

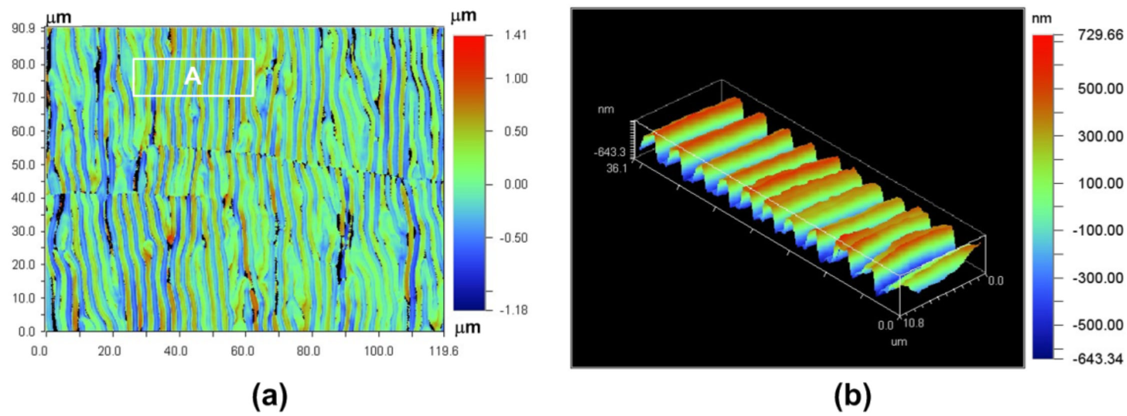


Fig. (16). Wrinkling (strips) atop 5% pre-strained SMP after shape recovery (**a**), and a zoom-in view of area A (**b**). The image is obtained by 3-D Wyko surface scanning.

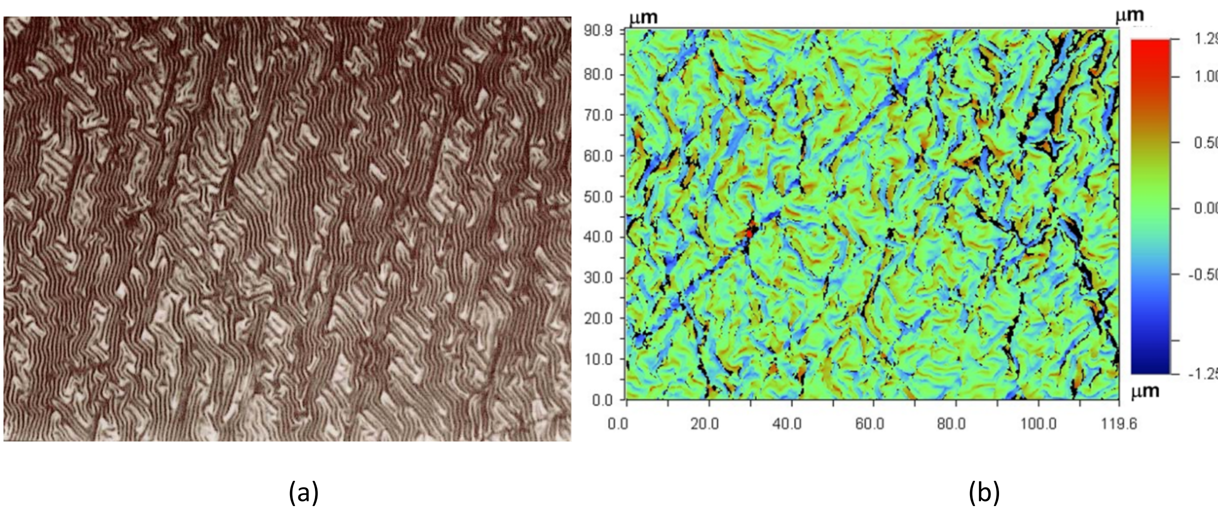


Fig. (17). Wrinkles (labyrinths) atop SMP without pre-straining. (**a**) Optical image; (**b**) 3-D Wyko surface scanning.

4. CONCLUSIONS

Since the polyurethane SMP is biocompatible, it is intrinsically suitable for biomedical applications. Given the unique thermo-moisture responsive feature and together with the apparent convenience in processing and fabricating into a variety of sizes and different shapes, as presented in Section 2 of this paper, it is expected that this material should have a great potential for novel biomedical devices, with easily tailored properties to meet the requirements of a particular application. A few novel devices are demonstrated to prove the feasibility of some concepts, in particular, for minimally invasive surgery and cell surgery.

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