Micro patterning atop shape memory polymers

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Micro Patterning atop Shape Memory Polymers

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Abstract

Shape memory polymers (SMP) are a new class of materials that have become popular recently due to its potential applications in fields related to engineering and medicine. Understanding how SMPs behave under different thermal or mechanical conditions will open exciting possibilities. Researchers have shown considerable interest in the thermomechanical properties of SMPs, but the behaviour is not yet fully understood. The thesis details the studies performed in this domain to better understand the thermomechanical properties of SMPs. Interesting effects like “butterfly effect” was observed and the mechanism was studied in detail.

The behavior of styrene SMPs on micro and nano indentation is studied to investigate the thermomechanical properties. The study revealed that SMPs are a feasible material for patterning in the micro and nano scale. This provides excellent opportunities to employ SMPs in MEMS/NEMS devices and the applications requiring controllable surface topography. Different patterning techniques were also investigated to demonstrate the possibility of forming the surface topography with various shapes. The results shows good agreement with the numerical simulations performed. The work was extended on Ni powder based SMP composites to study the self assembly property and its applications.

Keywords: shape memory polymer; shape memory effect; polystyrene; polyurethane; indentation; surface patterning;

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Chapter 1 Introduction

1.1 Background of shape memory polymers

Shape memory materials have been a subject under intensive investigation for some years. As compared with shape memory alloys (SMAs), which have been used in a variety of engineering and biomedical applications (Otsuka and Wayman 1998, Huang 1998, Wever *et al* 1998, Duerig *et al* 1999), the development of shape memory polymers (SMPs) is still lagging well behind, despite their many unique advantages and great potential (as will be discussed below).

Same as other shape memory materials, SMPs have the typical shape memory effect (SME). However, unlike SMAs, in which SME can only be triggered thermally or by a magnetic field, the recovery in SMPs can be driven by, apart from heat, various other external stimuli, such as, light, moisture and PH change etc. Consequently, based on the type of stimulus, SMPs can be divided into four major categories, namely, thermal-responsive SMP, photo-responsive SMP, moisture-responsive SMP and chemo-responsive SMP (Seki *et al* 1997, Otsuka and Wayman 1998). Among them, the thermo-responsive SMPs have been the major focus in the past years, which has resulted in some products commercially available at present (Yang 2007). In comparison with SMAs, SMPs have many apparent advantages, such as much higher shape recoverability (a few hundred percent of recoverable strain), lower density,

lower cost, ease in processing and control of recovery temperature, and possibility in color variation (Liu et al 2004, Liu et al 2005).

The first generation of SMP was made of polyethylene crosslinked by reaction with ionizing radiation during processing (Ota 1981). Since then, various kinds of SMPs have been developed for different applications. To name a few, poly (isoprene-butadiene-styrene), polyurethane, polyacrylamide and polystyrene series (Hu *et al* 1995, Takahashi *et al* 1996, Lee *et al* 2001, Yang *et al* 2003, Cao *et al* 2003) are some typical ones among others.

Recently, a biodegradable thermoplastic SMP has been developed (Lendlein and Langer 2002). This novel SMP is biodegradable multiblock copolymer, in which block-building segments, containing hard and “switching” segments, are linked together in linear chains. The hard and “switching” segments have significantly different thermomechanical properties. Upon heating, the “switching” segment either melts or goes through a transition. A suture made of this SMP can tighten itself in 20 s upon heating to 40°C. A more fascinating point of this SMP is that the polymer can degrade within a predetermined timeframe, so that a follow-up surgery for suture removal becomes unnecessary. Such feature should be very useful in, for instance, minimally invasive surgery.

Recently, a few new SMP systems have been developed (Lendlein and Kelch 2002). A SMP system means that a family of polymers in which macroscopic properties (for example, mechanical properties or transition temperature, T_{trans}) can be controlled by

the variation of one specific molecular parameter. Hence, it becomes convenient to tailor the properties of a SMP by a slight variation in chemical composition, so that the requirement(s) of a particular application can be met. Such kind of materials is required for applications, for instance, minimally invasive surgery. Apart from this approach, the thermomechanical behavior of a SMP can also be tailored by applying the concept of multiphase composite using the polymer as matrix. For instance, by mixing with nano-sized SiC particles, the Young's modulus, recovery force and glass transition temperature (T_g) of a SMP are significantly altered (Liu *et al* 2004).

A triple-shape memory polymer, which, upon heating, is able to switch from the first shape (A) to the second shape (B) and then to the third shape (C), has been realized (Bellin *et al* 2006). While shapes A and B are fixed by physical cross-links, shape C is by covalent cross-links established during network formation. As shown in Figure 1.1, while the final shape C is independent on the previous two shapes A and B, the intermediate shape B is also independent on shape A. The triple-shape feature together with another more important one that the thermomechanical properties of such SMPs can be adjusted over a wide temperature range should be very useful in many applications in various fields.

Figure 1.1 Series of photographs illustrating the triple-shape effect in a SMP tube (Bellin *et al* 2006).

1.2 Innovative applications of SMPs

With these unique properties, SMPs are gradually gaining more attention in recent years. Some applications, for instance, in active devices, self-deployable structures, micro-system assembly and remote actuator etc, have been proposed and tested (Hayashi 1993, Hayashi *et al* 1994, Tobushi *et al* 1996, Chiodo *et al* 1999, Monkman 2000, Koerner *et al* 2004). Utilizing the extremely large recovery strain in SMPs, some novel devices and micro devices for MEMS or medical applications can be realized.

Wache *et al* (2003) fabricated expandable SMP stents by injection molding, extrusion and dip coating for drug delivery. One of the major advantages of this kind of stent is that during processing, the drug is introduced into the polyurethane SMP, so that the risk of complications is reduced. Figure 1.2 illustrates the working principle of this stent. First, the stent is pre-deformed (stretched) at a temperature above its glass transition temperature (T_g). The deformed shape is then fixed, and subsequently, cooled to below T_g . After the constraint is removed, the deformation is retained as long as the temperature is kept to below T_g . Recovery can be activated upon heating when the stent is placed at the required location. The stent can be applied as a drug delivery system in the cardial area with the minimally invasive effect. It also reduces the chance of restenosis and thrombosis. Applications in other organs, such as, the trachea, oesophagus and urethra, have also been proposed.

A remotely actuated polymer nanocomposites have been recently developed (Koerner *et al* 2004). The unique nanocomposite fabricated by uniform dispersion of 1-5 vol.% of carbon nanotubes (CNT) in a thermoplastic elastomer can store strain energy and subsequently release it through remote means (infrared photons source). Non-radiative

decay of infrared photons absorbed by the CNT raises the internal temperature, melting strain-induced polymer crystallites, which act as physical crosslinks that secure the deformed shape and remotely trigger the release of the stored strain energy. Furthermore, the directionality of the recovery can be controlled. Figure 1.3 qualitatively depicts the shape-recovery of the polymer nanocomposite. As the infrared absorption is very strong, the release is initially confined to the near-surface region of the ribbon resulting in non-homogeneous strain recovery within the ribbon and consequently causing it to “curl” towards to the infrared source within 5 seconds.

Figure 1.2 Schematic of working principle of a stent made of polyurethane SMP. Left: prior to shape recovery; right: after shape recovery (Wache *et al* 2003).

Figure 1.3 Shape recovery towards an infrared source (Koerner *et al* 2004).

More recently, it has been demonstrated that SMPs can fully recover from nano-scale deformation upon heating. It sheds light on numerous potential applications in

nano-actuation, nano-manipulation, active surface texturing, data storage, and nano-fluidics (Nelson et al 2005).

1.3 Objective and scope

After a literature review on SMPs, their current applications, in particular for medical applications, some possible directions for applying this material are identified.

1.3.1 Objectives

This project aims

- To investigate the thermomechanical properties of the styrene SMP and its response upon indentation;
- To systematically study the feasibility of using SMP for patterning, in particular on micro and even nano scale;
- To modify the technique of patterning atop SMP using different sized and shaped micro/nano indenters.
- To numerically investigate and predict the surface patterning by styrene SMP. A general quantitative theory is proposed for this technique, so that features with well controlled shape and size can be produced.
- To improve the properties of the SMP, so that better performance can be achieved. (Appendix)

- To fabricate and characterize SMP and SMP composites. Ni powders are used to produce SMP composites with reversible micro/nano brush that is resulted from self-assembly of long SMP/Ni column. Attapulgate, a kind of nano-sized tube-like crystalline clay, are used as the filler for reinforcement. (Appendix)

1.3.2 Scope

At present, there is still a lack of understanding of the thermomechanical properties of this SMP. As such, a systematical investigation by means of thermal test, thermomechanical test and indentation test will be carried out. The knowledge obtained in these tests also serves as the platform for later studies on patterning atop SMPs.

Utilizing the ultra high recoverable strain in SMPs, one may realize different patterns on different scales by various techniques. In the course of this study, indentation will be used as a simple approach to produce single feature or array atop SMP on different scales. A general quantitative theory is proposed for this technique, so that features with well controlled shape and size can be produced.

Reversible micro/nano brush can also be fabricated from self-assembly of long SMP/Ni column on top of SMP. As a styrene polymer, the strength of SMP itself may not be high enough for some engineering applications. By reinforcement, one can get higher stiffness and actuation stress. Attapulgate will be used as the filler for reinforcement.

1.4 Outline of the thesis

The outline of the thesis is as follows:

Chapter 1 briefly introduces SMPs and the objectives of this project.

Chapter 2 is an extensive literature review on SMPs and their applications.

Chapter 3 investigates the thermomechanical properties of the styrene SMP and micro and nano indentation tests on this SMP.

Chapter 4 studies the feasibility and advantages of using SMP for patterning on macro and micro scales by indentation.

Chapter 5 presents the theory to numerically model the patterning on macro scale by indentation.

Chapter 6 illustrates and compares the numerically predicted and the experimentally measured surface patterning results.

The thesis is concluded in chapter 7 and some future work directions are outlined.

SMP composites are discussed in the Appendix.

Chapter 2 Literature Review

A systemic review on SMPs, their composites and applications is presented in the first part of this chapter. The types of available SMPs and their typical shape memory and thermomechanical properties are described. After that, the fabrication and characterization of SMP composites filled with various types of fillers for the improvement of thermomechanical response, electrical conductivity and other properties are reviewed. Next, innovative applications, including minimally invasive surgery are discussed. The second part of this chapter is about various approaches for micro/nano fabrication and patterning using polymers. The last part is about the finite element modeling of polymer.

2.1 SMPs and their composites

2.1.1 Shape memory effect (SME) and mechanism

Shape memory materials are stimuli-responsive materials which are capable of changing their shape upon exertion of an external stimulus. The external stimulus could be water, light, temperature, stress and PH (Lendlein and Kelch 2002, Wei *et al* 1998, Jung *et al* 2006, Yang 2007, Yang *et al* 2006).

Water-driven functionally gradient SMPs have been realized in PU-based SMPs, which are normally a thermal responsive one, and their composites (e.g. mixed with carbon

nano powder) (Yang *et al* 2006, Huang 2005). In these materials, the temporary shape is programmed by conventional methods. When immersed into water, moisture diffuses into the PU polymer and acts as a plasticizer, resulting in shape recovery (Figure 2.1). The T_{trans} can be lowered from 35°C to below ambient temperature.

Figure 2.1 Water-driven recovery in sequence. (Huang *et al* 2005)

Recently, Jung *et al* (2006) synthesized a water-responsive SMP by introducing hydrophilic and hydrophobic groups into the soft and hard segments of PU block copolymer respectively. Shape-fixing was made at the post melting temperature of hydrophilic crystals, followed by quenching into a dry-ice bath. The shape recovery was triggered by immersing the sample in the water (Figure 2.2).

Figure 2.2 Example of water-sensitive shape recovery. (Jung *et al* 2006)

Light-induced stimulation in SMPs can be realized by incorporation of reversible

photo-reactive molecular switches (e.g. Lendlein *et al* 2005). This unique characteristic not only is the independence upon any temperature effects but also can be actuated remotely. The permanent shape is determined by the cross-links of an amorphous polymer network. In programming, the polymer is deformed under the irradiation of ultraviolet light (wavelength > 260 nm), subsequently, new covalent netpoints are created and the temporary shape is fixed. The permanent shape is recovered upon irradiation with ultraviolet light of wavelength < 260 nm by means of the cleavage of the cross-links.

Thermal-responsive SMPs can be either thermoset or thermoplastic with a chemically or physically cross-linked network structure, which permits a rubbery plateau at a temperature above T_g . The majority of SMPs is thermo-responsive, such as, polyurethane (PU) and polystyrene (PS) SMPs. The permanent shape (the original shape) can be setup by molding, casting, or coating. The SME in a thermomechanical cycle is as follows (Figure 2.3).

- a. The SMP sample can be easily deformed at a temperature above T_g and then cooled down to form the temporary shape. This process is called programming. If the SMP sample is deformed at a low temperature (below T_g), it is called cold programming.
- b. The removal of the constraint results in a very small elastic shape recovery, but the temporary shape is largely maintained.
- c. This temporary shape can be held until shape recovery is activated upon reheating to over T_g . Cooling down the SMP to below T_g does not induce any significant shape change.

The SME cycle is fully repeatable and the temporary shape could be different each time and not necessarily related to each other.

Figure 2.3 Illustration of SME. (Yang 2007)

SMPs are elastic polymer networks that are equipped with suitable stimuli-sensitive switches (Marc Behl and Andreas Lendlein 2007, Lendlein A. and Kelch S. 2002, Lendlein A. *et al* 2005). The polymer network consists of molecular switches and netpoints (Figure 2.y1). The netpoints determine the permanent shape of the polymer network and can be of a chemical (covalent bonds) or physical (intermolecular interactions) nature. Physical cross-linking is obtained in a polymer whose morphology consists of at least two segregated domains, as found for example in block copolymers. Here, domains related to the highest thermal transition temperature (T_{perm}) act as netpoints (a hard segment), while chain segments in domains with the second highest thermal transition T_{trans} act as molecular switches (a switching segment). If the working temperature is higher than T_{trans} , then the switching domains are flexible, resulting in an entropic elastic behavior of the polymer network above T_{trans} . If the sample has been

previously deformed by application of an external stress, it snaps back into its initial shape once the external stress is released. The molecular mechanism of the SME is illustrated for the thermally induced SME in Figure 2.4. The SMP network consists of covalent netpoints and switching segments based on a physical interaction.

Figure 2.4 Molecular mechanism of the thermally induced SME. T_{trans} = thermal transition temperature related to the switching phase. (Lendlein A. and Kelch S. 2002.)

To display shape-memory functionality, the polymer network has to be temporarily fixed in a deformed state under environmental conditions relevant to the particular application. This requires the deformed chain segments, which are under external stress, to be reversibly prevented from recoiling, and is achieved by the introduction of reversible netpoints as the molecular switches. These additional netpoints can be formed by physical interactions or by covalent bonds. Physical cross-linking is obtained by vitrification or crystallization of domains related to T_{trans} . These switching domains can be formed either by the chain segments driving the entropic elastic

behavior themselves or by side chains, whose aggregation is able temporarily to prevent recoiling of the chains, whose aggregation is able temporarily to prevent recoiling of that chain's side chains or the side chain segments themselves. Reversible covalent cross-linking is obtained by attaching functional groups to the chain segments. Controlled by an external stimulus, these functional groups must be able to form covalent bonds reversibly by reaction with each other or suitable counterpart functional groups.

2.1.2 Thermomechanical properties and thermal stability

Thermomechanical properties are very important in evaluating a SMP. Cyclic thermomechanical test is a standard approach for the characterization of the shape memory properties. A typical stress-strain-temperature relationship is illustrated in Figure 2.5 (Tobushi *et al* 1992, Tobushi *et al* 2001). The thermomechanical test is performed via the following steps.

- a. At a temperature T_h ($> T_g$), the SMP specimen is loaded to a pre-determined maximum strain (ε_m).
- b. The SMP sample is held with ε_m fixed and cooled to a new temperature T_l ($< T_g$).
- c. The stress is reduced to zero at T_l . Upon unloading, only a very small elastic strain is recovered. ε_f is the remaining strain after the applied stress is fully removed.

- d. The sample is reheated from T_l to T_h without applying any external stress.

The pre-strain is almost fully recovered with only a very small strain ε_i left at

T_h .

Figure 2.5 Scheme of a thermomechanical test. (Tobushi *et al* 2001)

Figure 2.6 DSC result of a PU SMP. (Yang 2007)

The glass transition in SMPs occurs over a temperature range, in which the soft segments wiggle around to form the conformation entropically favored and the heat capacity of SMP increases by an order of magnitude. Figure 2.6 is the differential scanning calorimetry (DSC) curve of a PU SMP (MM3520, from Misubish Heavy Industry [MHI], Japan) in a fully thermal cycle. T_g is defined as the median point of the glass transition range in the heating ramp.

Thermogravimetric analysis (TGA) test can be used to investigate the thermal stability of SMPs. Figure 2.7, a typical TGA result of MM3520, reveals that there is only a slight weight loss before heating to 260°C, which is largely attributed to the evaporation of moisture. Hence, 260°C is defined as the decomposition temperature of this SMP (Yang 2007).

For a perfectly elastic material the stress and strain are perfectly in phase. Instead of deforming reversibly upon loading, a perfectly viscous material flows. Under dynamic loading, its stress-strain curves are out of phase by 90° since the strain is proportional to the changing rate of the stress. The SMPs behave in a way combining both, i.e. they simultaneously react elastically and flow to some extent. Therefore, their stress and strain curves are out of phase by a phase angle (δ) which is less than 90°. Dynamic mechanical analysis (DMA) can be used to measure the amplitudes of stress and strain as well as δ . The storage modulus, the loss modulus and tangent delta can be recorded against the temperature. The storage modulus is the modulus of the elastic portion of material while the loss modulus is the modulus of the viscous portion. Tangent delta is

defined as the ratio of the loss modulus over the storage modulus indicating the damping capability of a material (Yang 2007).

Figure 2.7 TGA result of a PU SMP. (Yang 2007)

Figure 2.8 DMA result of PU SMP. (Yang 2007)

Typical DMA result of a PU SMP (MM3520) plotted in Figure 2.8 reveals that the storage modulus, which corresponds to the stiffness of the material, decreases sharply in the glass transition region. The ratio of storage modulus in the glass state to that in the rubber state is up to 200~300 in this SMP. Furthermore, tangent delta reaches its maximum of about 1.45 during the glass transition. The temperature corresponding to the peak of tangent delta is an alternative definition of T_g (Yang 2007).

Figure 2.9 shows the engineering strain vs. engineering stress relationship of a PU SMP (MM3520) at room temperature, in which the SMP is in the glass state, at different strain rates. It shows that similar to that in mild steels, after a small linear elastic deformation, this material experiences a distinct upper yield point, followed by an apparent plateau and then hardening. The yielding-plateau phenomenon is similar to the well-known Luder band phenomenon, in which necking and propagation can be observed upon stretching (Yang 2007).

Figure 2.9 Engineering strain vs. engineering stress relationships of a PU SMP in glass state. (Yang 2007)

The stress-strain response in Figure 2.10 reveals the typical viscoelastic properties of a PU SMP (MM3520) at $+15^{\circ}\text{C}$, where the SMP is in the rubber state. At all strain rates, the maximum elongation strain is above 600%, but the exact stress-strain curve is highly strain rate dependent. At a high strain rate of 0.1/sec, the curve closely resembles that in the glass state, while at low strain rates the curve is dominated by creep, i.e., the extension increases continuously under about a constant force (Yang 2007).

Figure 2.10 Engineering strain vs. engineering stress relationships of a PU SMP at $T_g + 15^{\circ}\text{C}$. (Yang 2007)

2.1.3 SMP composites

A significant drawback of un-reinforced SMP materials is their low stiffness as compared with metals and ceramics. It results in a relatively small recovery force. In order to improve their strength and stiffness, one may reinforce SMPs with fillers. By adding in different fillers, other properties of SMPs can be improved.

2.1.3.1 Reinforced SMPs

Preliminary work has been reported in Liang *et al* (1997) on reinforcing a PU SMP with glass fiber and Kevlar. The SMP composites were prepared by blending the PU SMP melt or 30% DMF SMP solution with fillers. It was found that the reinforcements increase the ultimate strength and the Young's modulus, but reduce the elongation limit at room temperature dramatically even when loaded with a very small volume fraction of fillers. Moreover, the continuous fiber reinforced PU SMPs were found to be anisotropic, without SME in the fiber direction. In addition, recovery after bending was found to be limited. On the other hand, SME persists in all discontinuous fiber reinforced SMP composites in all directions.

Thermosetting SMP-based composites have been investigated for deployable space structures (Gall *et al* 2000, Cadogan *et al* 2002, Abrahamson *et al* 2002). Reinforced with fibers, these composites exhibit not only excellent shape memory and environmental durability, but also good stiffness and strength. The mechanisms in interaction between SMP and reinforcement fibers have been studied. These fiber-reinforced SMP composites have some apparent advantages over shape memory alloys and shape memory ceramics. Lower density, higher elastic strain capability and lower processing cost are some among others. Both stiffness and recovery stress of thermosetting SMP-based composites are found to be dramatically improved by filling with different fibers.

One of the interesting progresses in recent years is SMP nanocomposites. Gall *et al* (2002) fabricated some SMP nano-composites by adding SiC nano-particulates (average diameter: 300 nm) into a thermosetting epoxy-based SMP matrix. These SMP composites with different weight fractions of SiC nano-particles have been

characterized at macro and micro-scales. The results show that the presence of SiC nano-particles can remarkably reduce T_g and the temperature range of transition process. The micro-hardness and elastic modulus of the nanocomposites increase with the concentration of SiC particles. Figure 2.11 shows the hardness/modulus of the SMP composites with different SiC weight percentages. The bending force in constrained recovery of a SMP composite filled with 20% weight fraction of SiC increases by 50%. On the other hand, unconstrained strain recoverability of the SMP nanocomposites characterized by bending tests depends on the weight fraction of SiC. With below 40% weight fraction of SiC, the SMP nanocomposites can fully recover a pre-strain of up to 10%.

Figure 2.11 Load-depth curves of composite materials with different weight fractions of SiC. (Gall *et al* 2002)

In the SiC nano-particles filled SMP composites, the nano-particles store a finite compressive stress, which can be determined by measuring the changes in the lattice parameters of the SiC particles by X-ray diffraction methods. The stored compressive stress is almost completely released upon strain recovery induced by heating (Gall *et al* 2004).

As a special note, mechanical properties of polymers with magnetic chains have been

investigated experimentally and numerically (Coquelle *et al* 2006).

2.1.3.2 Electrically conductive SMPs

Conductive polymers can be realized in two ways. One is to produce a polymer that is intrinsically conductive. Heeger *et al* received the Nobel Prize in Chemistry in 2000 for developing these intrinsically conductive polymers (ICPs). However, commonly used ICPs, such as polyacetylene, polyaniline and polypyrrole, have a typical value of conductivity around $10^{-10} \sim 10^{-5}$ S/m only. They are expensive and difficult in preparation, in particular in polymerization (Cotts and Reyes 1986). The other approach is to dope or load with conductive fillers, e.g. graphite, carbon powders and metallic particles. Due to very low cost and convenient in fabrication (requires only conventional processes in preparing polymers), the later approach is more popular in engineering practice (e.g. Jäger *et al* 2001).

The percolation theory (Jäger *et al* 2001) can be used to describe the dependence of the electrical resistivity on the volume fraction of conductive fillers. The percolation threshold is a critical value, which indicates the transition of the material from insulating to conductive.

Li *et al* (1999) have reported some preliminary results of PU SMP/carbon black composites, which were prepared by a solution-precipitation process, followed by compressive molding. The percolation threshold was obtained at 20% weight fraction of carbon black. Beloshenko *et al* (2005) investigated the electrical resistance behavior of an epoxy polymer (EP) with thermoexpanded graphite (TEG) and thermoexpanded-kaolin (TEG-kaolin) mixture fillers. They found a sudden increase of volume resistivity of EP-TEG in the glass transition temperature range. Because

additional kaolin powder forms a dense network from the TEG particles, the absolute value of volume resistivity of EP-TEG-kaolin in deformed state is decreased. Single-wall carbon nanotubes (SWNT) was found not only can improve mechanical properties but also increase electrical conductivity to a polymer resin (Haggenmueller *et al* 2000). Kymakis *et al* (2002) reported that as the SWNT concentration increases from 0 to 20 wt%, the conductivity of the resulting polymer films increases by five orders of magnitude. The enhancement in conductivity attributes to the introduction of conducting paths to the polymer. The percolation threshold was reported to be 11 wt%. Koerner *et al* (2004) utilized heat-treated multiwall carbon nanotubes (MWNT) dispersed in a thermoplastic elastomer to make an electrically induced actuator and found that the anisotropic nature of the MWNT is critical for providing percolative behavior at low volume fractions. Another electroactive SMP nanocomposite incorporating MWNT was presented by Cho *et al* in 2005. At 60V, the surface temperature of the nanocomposite with 5 wt% MWNT could reach as high as 100°C in 100 seconds (Figure 2.12).

Yang (2007) fabricated and systematically characterized electrical conductive PU SMPs (MM 5520) blended with carbon black (CB) nano-powder. The percolation threshold was found at about 6 vol% (Figure 2.13). For the composites with a low volume fraction of carbon powders (e.g., <4%), the carbon aggregates in the SMP matrix are relatively more separated. Large gaps between the conductive carbon aggregates present significant physical barriers to electron flow, so that almost no conductive channel can be formed in the material. As the volume fraction of conductive filler reaches the percolation threshold, the gaps between conductive carbon aggregates are reduced. Some carbon aggregates even directly contact each other. The SME of these composites was demonstrated (Figure 2.14).

Figure 2.12 Electro-active shape-recovery behavior of PU-MWNT (5 wt%) composites. (Cho *et al* 2005)

Figure 2.13 Electrical resistivity vs. volume fraction of carbon powders. (Yang 2007)

Figure 2.15 plots the stress-strain curves of the uniaxial tensile tests of the SMP composites loaded with different weight percentage of carbon black at room temperature. With the increase of carbon black, the yielding strength is significantly increased. Figure 2.16 plots the ratio of the recoverable strain against the volume fraction of carbon black. It reveals that the carbon black has limited effect on the shape recovery ability of SMP at a lower volume percentage. However, with the increase of carbon black to over 13%, the trend in decrease of the ratio of the recoverable strain becomes significant. Figure 2.17 plots the recovery stress against temperature in the constrained recovery test. It reveals that the loading of carbon black significantly increases the maximum recovery stress. With the increasing

volume fraction of carbon black, the decrease of recovery stress upon further heating becomes slow after the maximum stress is reached. This is because carbon black restricts the viscous flow in SMPs (Yang 2007).

Figure 2.14 Shape memory effect in conductive PU SMP (13 vol%) at 15 V. (a) Temperature distribution taken by an infrared camera, (b) shape recovery upon passing an electrical current. (Yang 2007)

Figure 2.15 Stress-strain curves at room temperature. (Yang 2007)

At this point, we may conclude that carbon black can not only improve the conductivity of SMP, so that actuation can be achieved by applying voltage directly, but also reinforce the polymer.

Figure 2.16 Ratio of recoverable strain against volume fraction of carbon powders.
(Yang 2007)

Figure 2.17 Recovery stress as a function temperature. (Yang 2007)

As a special note, more recently, a combination of carbon black and tubes has been proposed for making conductive polymers (Drubetski et al 2007). However, no significant improvement was found.

2.1.3.3 Magnetically inductive SMP

Recently, several researchers investigated the properties and potential applications of SMP nanocomposites filled with magnetic particles for noncontact inductive heating to trigger shape recovery (Buckley *et al* 2006). The applied magnetic particles may consist of an iron(III)oxide (Fe_2O_3) core in a silica matrix (SiO_2) and homogeneously distributed in a SMP matrix and a biodegradable multiblock copolymer (PDC). In Figure 2.18, the SME of the mentioned composites with 10 wt% particle content is demonstrated. The maximum achieved temperature was 88°C . Magnetically triggered shape memory composites enable surgeons to perform mechanical adjustments in a noncontact mode. Hence, they have a high application potential in, for instance, smart catheters or intelligent implants. Furthermore, PDC as a degradable biomaterial and with a transition temperature slightly above body temperature is suitable for medical applications.

Figure 2.18 Series of photographs showing the SME. The applied alternating magnetic field is 258 kHz and 30 kA/m. (Mohr *et al* 2006)

Razzaq *et al* (2007) filled a PU SMP with different amount of magnetic particles and experimentally investigated their electrical and magnetic properties. The experimental results showed that the thermally induced shape recovery of the composites could be achieved at a low frequency and low field strength electromagnetic field (i.e. 50 Hz and 4.4 kA/m).

Because of the predominant hysteresis loss in inductive actuation of SMP composites, self-thermoregulation can be achieved by tailoring the particle Curie temperature to prevent overheating in medical applications (Buckley *et al* 2006). Other advantages include:

- Power transmission lines leading to a SMP device are eliminated;
- More complex device shapes are possible;
- Selective actuation of specific device area is possible by impregnating only the desired areas with magnetic particles;
- Remote actuation allows for the possibility of implantable devices that can be later actuated by an externally applied magnetic field.

These open the possibility for an entirely new class of SMP devices, such as tissue scaffolds for tissue regeneration (Figure 2.19).

Figure 2.19 SMP devices actuated by inductive heating. (a) Flower shaped device shown in collapsed and actuated form.(b) SMP foam device shown in collapsed and actuated form. (Buckley *et al* 2006)

2.1.4 Applications of SMPs

One of the early applications of the SMPs is heat shrinkable tubes reported by Ota (1977). SMPs are able to store a large strain deformation and subsequently deploy in restricted environments. This property has resulted in the development of SMP for deployable space structures (Gall *et al* 2000) and medical devices (Metcalf *et al* 2003, Maitland *et al* 2000 and 2002, Yakacki *et al* 2007, Lee *et al* 2000, Lee and Fitch 2000). Large bulky and complex devices could be introduced into the body in a compressed and simply temporary shape by means of minimally invasive surgery and subsequently be expanded on demand to their permanent shape to fit as required (Lendlein and Langer 2002).

Figure 2.20 Schematic representation of SMP microactuator. (Maitland 2002)

Laser-activated SMP medical devices for endovascular treatment of ischemic stroke and cerebrovascular aneurysms have been proposed by Maitland et al (2000). The SMP adopted is photo-thermal responsive. The mechanical removal of thrombi is an approach to overcome the limitation of traditional tPA (tissue plasminogen activator) for treating ischemic stroke. The injection-molded SMP microactuator device (Figure 2.20) has been developed as a possible therapy. The SMP microactuator mounted on a diffusing optical fiber is delivered through a catheter distal to the thrombotic occlusion in its straight form. Then it is deployed via optical heating into its coil shape at the location of occlusion. After the device is fully deployed, both the microactuator and the thrombus are removed from the vessel, restoring blood flow. The same laser-activated SMP technology can be applied in designing a fast embolic coil release system, in which the release can be completed in a second or less. As shown on Figure 2.21a, the delivery device with the coil is ready for deployment. The SMP around the coil can be

mechanically relaxed to its extruded diameter when it is heated to above the transition temperature. The SMP remains in the expanded state after the laser-coupled thermal energy is turned off and the SMP cools below the transition temperature, Figure 2.21(b). The preliminary feasibility of the optomechanical stroke treatment device using SMP and a laser coupled by an optical fiber was demonstrated in vitro by Small et al (2005). They successfully captured an artificial blood clot within a water-filled bifurcated vessel model under flow.

Figure 2.21 Schematic representation of an embolic coil release microgripper.
(Maitland 2002)

Hampikian et al (2006) reported a composite SMP with tantalum filler to increase the radio-opacity (Figure 2.22). This discovery shows the possibility to visualize the SMP microactuator for medical applications.

Sokolowski et al (1998) developed a new class of self-deployable structures named cold hibernated elastic memory (CHEM). PU SMPs poses valuable characteristics, such as high biocompatibility, unique mechanical properties and an ability to transit at body temperature. The CHEM utilizes PU-based SMPs in open cellular (foam)

structures (Figure 2.23) for endovascular intervention procedures and was investigated in vivo by Metcalfe et al (2003). It is concluded that CHEM is non-cytotoxic, non-mutagenic and poorly thrombogenic and can achieve permanent occlusion of arteries, where it completely fills the vascular lumen. It is also promising to modify some properties of the material to design new tools to prevent recanalization and recurrences after endovascular treatment of aneurysms.

Figure 2.22 Fluoroscopic image of 3% Ta-filled SMP coils. (Hampikian *et al* 2006)

The concept of vascular stents as a means of maintaining the lumen of the diseased vessel segment until healing taken place was introduced by Charles Dotter in 1969. The utilization of SMP developed by TU Berlin allows the application of a fully polymeric stent for the first time (Wache et al 2003). Wache et al (2003) manufactured a PU based polymer stent with shape memory behavior that can be applied with minimally invasive effects. They concluded that the PU SMP stent improves the stent as drug delivery system in a cancer therapy. The benefits of the PU SMP stent are less costly in

manufacturing as compared with metal stents and a reduced risk of complications. Another SMP stent made of tert-butyl acrylate (tBA) and dimethacrylate (DEGDMA) and poly(ethylene glycol)n dimethacrylate (PEGDMA) was designed and investigated for cardiovascular stenting applications (Yakacki et al 2007) (Figure 2.24). The results revealed that the SMP stent can be fabricated to maintain shape storage at room temperature and fully activate at body temperature. The glass transition and rubbery modulus of the SMP can be varied independently of each other, which provide a platform for independently varying recovery properties and mechanical properties once implanted.

Figure 2.23 Deployed and stowed CHEM structures. (Metcalf *et al* 2003)

Figure 2.24 Recovery of SMP stent. (Yakacki *et al* 2007)

Other than the above applications in medical, active disassembly is another application of SMPs. Chiodo et al (1999) conducted an initial investigation on active disassembly of mobile phones. The liquid crystal display (LCD) bracket of a mobile phone with an original shape as shown in Figure 2.25a was molded from polyurethane SMP. At a high temperature, the SMP bracket is deformed and assembled with the LCD. The position

of LCD in Figure 2.25b is the intended configuration after assembly. Figure 2.25c shows that the SMP bracket is fixed with LCD and other components upon cooling by cold bathing. If disassembly is needed, reheating the SMP bracket is an efficient way that triggers shape recovery of the SMP bracket, so that LCD is rejected in a nondestructive way (Figure 2.25d). SMP is demonstrated to be an efficient and low cost way to ensure reliable active disassembly not only with minor change in the product design but also without any destruction to the product components.

Figure 2.25 Active disassembly using polyurethane SMP. (Chiodo *et al* 1999)

Figure 2.26 Illustration of fabrication and operation of a SMP-based micro-fluidic reservoir. (Gall *et al* 2004)

SMPs have been proposed for applications in Micro-ElectroMechanical Systems

(MEMS) or Bio-MEMS. Figure 2.26 illustrates the fabrication and operation of a SMP-based micro-fluidic reservoir, which can be used to store liquid chemicals (Gall *et al* 2004). Figure 2.26a shows a circular section made of SMP with a smooth surface. Micro-channels are machined into the surface of SMP by laser cutting or multilayer soft-lithography method (Figure 2.26b). A reservoir for the chemicals is built at the end of the micro-channel by indenting SMP at a temperature above T_g (Figure 2.26c and d). Then, the surface is covered with a glass slide to seal the reservoir (Figure 2.26e). Upon heating the reservoir to induce shape recovery, the fluid in the reservoir flows down from the micro-channel (Figure 2.26f).

2.2 Nano/micro fabrication and patterning

Controlled reversible changes in surface texture and topography are of interest to many applications, including information storage, optical communication devices, micro-fluidic instruments for drug delivery, and smart tribological surfaces for friction and wear control (Zhang *et al* 2006). So far the surface texture and topography of shape memory materials which have been investigated previously are mainly on shape memory alloys (SMAs) (Ni *et al* 2004, Liu *et al* 2005). Polymer brushes are found to be useful as new adhesive materials (Raphael *et al* 1992; Ji *et al* 1993), protein-resistant biosurfaces (Amiji and Park 1993), chromatographic devices (Van Zanten 1994) as well as many other applications.

2.2.1 Patterning using polymer

The topography of a polymer surface is of fundamental importance to many

applications, for instance, fabrication of polymer electronic and optoelectronic devices, fluidic channels, sensor coatings, and biotechnology applications (Chou *et al* 1999, Kwon 2006, Müller – Buschbaum 2006, Senaratne *et al* 2005).

Self-organized anisotropic structures can be formed atop polymer thin films (Kwon 2006), for instance, by heating a polymer to above its glass transition temperature within perpendicularly aligned corrugated elastomeric molds (Figure 2.27).

Figure 2.27 (a) Schematic illustration of the experimental setup, and (b) three-dimensional AFM image of a deformed structure. (Kwon 2006)

Polymeric nanochannel arrays (Figure 2.28) which are separated by a mean distance of 166 nm and have a mean shallow channel height of 3 nm were prepared on glass (Müller – Buschbaum 2006). A highly diluted Polydimethylsiloxane (PDMS) solution is deposited onto a standard microscopy glass slide surface. The deposition was realized by several successive parallel wipings with 100%-cellulose based fuzz-free wipe under a contact pressure of $p = 24 \pm 3 \text{ kPa}$, followed by evaporating the solvent in the polymer solution. The nanostructure initially was induced by the

interplay of orientational deposition and dewetting and freeze by the evaporation.

The spontaneous formation of wrinkle patterns by moduli mismatch can be used to pattern large surfaces (Chan and Crosby 2006). This method is simple and rapid. The surface-relief structures can be varied and controlled into 2D wrinkles, dimple patterns or microlens patterns (e.g. Figure 2.29).

Figure 2.28 Real space structural data of nanochannels. (Müller – Buschbaum 2006)

Figure 2.29 Morphologies of the wrinkled structures using laser and microlens array.
(Chan and Crosby 2006)

Microstructures of arbitrary shapes can be directly patterned on polymer films by a

lithographically induced self-construction method (Figure 2.30). A protruded-patterned mask was placed a distance above a flat polymer film cast on a substrate. The polymer was attracted to the mask protrusions on their own after the polymer was heated to above its T_g and then cooled back to room temperature. The formed microstructure has a lateral dimension identical to that of the mask protrusions and a height equal to the distance between the mask and the substrate with a relatively steep sidewall.

Besides the above mentioned methods, electrical field is widely applied to pattern polymer thin films to form different nano/micro structures. Self-assembled islands (Figure 2.31) were fabricated on a thin polymer film involving use of an in-plane electric field (Salace *et al* 2004). The film was first spin coated onto a glass wafer. Then it was heated to above its glass transition temperature to achieve mobility in the fluid. An in-plane electric field was applied with 10 mm spacing, whereupon the initially flat polymer/air interface lost stability and formed islands.

Figure 2.30 (a) Optical image of protruded pattern of PRINCETON on the mask, and (b) AFM image of the PMMA LISC patterns. (Chou *et al* 1999)

Chiu *et al* (2006) realized self-organization of islands on nano-scale on a

Stranski-Krastanow film-substrate system. The scheme uses an electric field generated by a patterned electric plate and the field has complete control over the sizes, shapes, and sites of the self-organized nanoislands. Voicu *et al* (2006) reached the similar conclusion that the lateral structure of the pattern formed in polymer films can be controlled by introducing an inhomogeneity into the electric field. Furthermore they found that the ratio of the film thickness to the electrode spacing determines the late-stage pattern morphology in homogeneous electric fields and the development of the resulting polymer morphologies is a function of time (Figure 2.32). With increasing time, further columns are nucleated radially outward from the initial columns.

Figure 2.31 The AFM images showing the morphology of the islands, (a) 10 μm by 10 μm area, (b) a closer image of an island and (c) height profile. (Salac *et al* 2004)

A three-dimensional model of electrostatically induced pattern formation in thin polymer films was proposed by Kim and Lu (2006) based on the simulation results, and

they concluded that the relationship between the film thickness and electrode pattern suggest a significant degree of experimental control in directing thin film morphologies. Theoretically, the origin of the film surface instability induced between two electrodes can be explained by the balance of forces that act at the polymer-air interface (Schäffer *et al* 2000). The surface tension minimizes the area of the polymer-air surface and stabilizes the homogeneous polymer film. The electric field, on the other hand, polarizes the dielectric. This results in an effective displacement charge density at the interface, which destabilizes the film. A local perturbation in the film thickness results in a pressure gradient which drives a flow of the dielectric part in the plane of the film.

Figure 2.32 Evolution of nucleated pattern formation in an electric field with time.

(Voicu *et al* 2006)

An electric field has the ability to convert the morphology of a monolayer of spherical domains embedded in the thin film matrix to cylindrical domains that penetrate through

the matrix (Matsen 2006). This is because the applied electric field increases the relative stability of cylindrical domains and simultaneously reduces the energy barrier that impedes the transition to cylinders (Figure 2.33).

When living systems encounter synthetic surfaces, the biological response is affected by the surface topography (Senaratne *et al* 2005). As such, polymer brushes as surface-active materials have attracted consideration attention in biological applications. Ma *et al* (2004) polymerized PEG-containing monomer polymer brush from a SiO_x surface. Another example is nitroxide-mediated CRP of styrene-based PEG-containing monomers from a SiO_x surface (Andruzzi *et al* 2005). Feng *et al* (2004) polymerized a biomimetic monomer from SiO_x surface at room temperature. Copolymer brushes have also been synthesized using electrografting method onto stainless steel (Ignatova *et al* 2004).

Figure 2.33 (a) Spherical nanodomains in a monolayer of copolymer, and (b) transforming the spherical nanodomains into perpendicular cylinders. (Matsen 2006)

2.2.2 Patterning by indentation atop of SMA/SMP

The most popular method to form the surface texture and topography is atop SMAs by indentation, both on nano and micro scales, followed by thermally induced recovery.

Figure 2.34 illustrates the load-depth curve of a typical indentation test. Here, h_{imax} is the prescribed depth in control, h_h is the depth due to holding, h_{max} is the maximum indentation depth, h_{er} is due to the elastic recovery, h_{ir} is the instant recovery depth upon unloading, h_{vr} is the viscous recovery depth due to the viscous property of the material, h_{SME} is the recovery depth due to the SME upon heating.

The spherical sloped microindents atop NiTi SMA can be almost completely recovered by moderate heating (Figure 2.35). Partial recovery was observed for pyramidal indents formed by a Vickers indenter (Ni *et al* 2002). The recovery ratio is independent on the indentation depth. In addition, the microscopic SME of NiTi SMA is also independent upon the depth under Berkovich and Vickers indenters (Ni *et al* 2004).

Temperature-controlled reversible surface protrusions were made on NiTi shape memory alloys as a result of indentation induced two-way shape memory effect (Zhang *et al* 2006). Spherical indents or scratches are made on the surface of a NiTi alloy in its martensite phase. Then the indented or scratched surface is planarized to restore a flat surface. Reversible circular and line protrusions are produced by altering the temperature to drive the martensite to austenite phase transformation (Figure 2.36). Since the reversible strain in SMP is over 100%, while that of SMA is limited to within 10%, we can expect that SMP should be a better alternative for the formation

of micro/nano sized protrusions.

Figure 2.34 Diagrammatic representation of the load-depth curve of a typical indentation test.

Figure 2.35 Spherical indents on a NiTi SMA (a) before and (b) after heating. (Ni *et al* 2004)

SMP is another type of material with SME other than SMA. Nanometer-scale (1-100nm) recovery actuation of SMPs was examined by Nelson *et al* (2005). Indents were made by an atomic force microscope (AFM) tip on a thermoset SMP at both room

temperature and near transition temperature. The recovery was found to be temperature-dependent and relatively independent upon time. Figure 2.37 shows the images of indents at four different experimental temperatures upon heating, namely 25°C, 60°C, 65°C and 70°C. Full recovery occurs at 70°C ($T_g=70^\circ\text{C}$). This experiment demonstrates that SME in SMP can persist at nano-scale, and the molecular chains structure is reversible in nano-sized volumes of thermoset epoxy network.

Nanoindentation has been reported as an excellent tool for characterization of SMP membranes (Poilane *et al* 2000). Recently, the mechanical properties of SMP networks were investigated by instrumental nano-scale indentation (Wornyo *et al* 2007). It was found that the glassy state hardness statistically increases as a function of the crosslinker concentration but the glassy state modulus does not. The free strain recovery temperature is strongly influenced by the crosslinker concentration through changes in glass transition temperature.

Figure 2.36 Three dimensional profiles of reversible surface protrusions. (a) A 3x3 matrix of circular protrusions, and (b) a protruding line on the surface. (Zhang *et al* 2006)

Figure 2.37 Indentation shape recovery at different temperatures. (Nelson *et al* 2005)

2.3 Constitutive modeling of viscoelastic/viscoplastic deformation and SMPs

2.3.1 Introduction

Amorphous thermoplastic polymers are important engineering materials. SMPs as one type of them are widely used in a variety of applications (see 2.1.4). Over the past three decades, considerable effort has been devoted to develop constitutive models to represent the large deformation elastic-viscoplastic behavior of these materials (Parks *et al* 1985, Boyce *et al* 1988, Arruda and Boyce 1993, Wu and Van der Giessen 1993, Govaert *et al* 2000, Anand Gurtin 2003). In their works, although varying in details, three-dimensional representations combining linear elasticity, non-Newtonian viscoplastic flow due to the motion of polymer segments, and stiffening due to the alignment and locking of the long-chain polymer molecules at large strains are established and analysed. These models are primarily used to describe the isothermal

deformation of polymeric materials below the glass transition temperature. However, Arruda *et al* (1995) and Estevez and Basu (2008) and Anand *et al* (2009) have studied the thermo-mechanical coupling effects. They presented thermal-mechanically coupled, large-deformation elasto-viscoplasticity theory to model the strain rate and temperature dependent large-deformation response of amorphous polymeric materials. Other than these works, Simo and his co-workers have studied the continuum formulation of a fully coupled nonlinear thermomechanical constitutive model for highly deformable viscoelastic polymers (Simo 1987, Gerhard A. Holzapfel and Juan C. Simo 1996, Govindjee and Simo 1992, Simo J.C. and Taylor R.L. 1991.). Recently, there are other nice works on thermomechanical modeling of SMPs.

2.3.2 Constitutive modeling for plastic deformation

Under stress states where the maximum principle stress is compressive, amorphous glassy polymers typically show extensive plastic deformation by a “shear yielding” mechanism which involves profuse densely-packed microscopic shear bands; the material shows substantial ductility, and eventual failure occurs at large stretches by chain-scission mechanism. In contrast, under stress states where the maximum principal stress is tensile, glassy polymers may at first show a little (or no) macroscopic inelastic deformation due to shear yielding, but then the mechanism of inelastic deformation switches to “crazing”. An individual craze is a thin plate-like microscopic region in the material with a microstructure distinguished by a dense array of fibrils interspersed with elongated voids which span the boundaries of individual

crazes. The dominant inelastic deformation occurs by craze widening in the local maximum principal stress direction. However, macroscopically, the material shows little ductility, and the nominally brittle fracture occurs by craze breakdown, crack-formation and crack-growth to failure. In most high molecular weight, flexible chain glassy polymers, such as polystyrene (PS) and polymethylmethacrylate (PMMA), fracture under stress states where the maximum principal stress is tensile, is preceded by this craze initiation, widening, and breakdown process (Kambour 1973, Kramer 1983). Therefore, their ductility differs significantly between uniaxial compression and uniaxial tensile.

In all constitutive models, it requires three elements (Boyce *et al* 1988). These are illustrated in Figure 2.38 for a one-dimensional analog to the polymer deformation model. The three elements are: a linear spring used to characterize the initial response as elastic and represented by the Young's modulus E ; a viscous dashpot representing rate- and temperature-dependent yield that monitors an isotropic resistance to chain segment rotation; and a nonlinear rubber elasticity spring element that accounts for an anisotropic resistance to chain alignment. The dashpot and nonlinear spring operate in parallel to deliver the total response of the material, σ , given by $\sigma = \sigma_v + \sigma_b$, where σ_v and σ_b are the stresses on the elements as shown in Figure 2.38.

Figure 2.38 One dimensional analog to the spring and dashpot model of polymer deformation (Boyce *et al*1988).

Figure 2.39 Stress-strain response of glassy PC showing contribution of all model elements to the total deformation response (Boyce *et al* 1988).

The contributions of these individual elements to the glassy polymer responses can be seen from the typical isothermal stress-strain response of glassy polymer sketched in Figure 2.39.

Figure 2.40 Eight-chain model simulations and experimental curves of the uniaxial compression and plane-strain compression responses of PC (a) and PMMA (b) (Arruda and Boyce 1993).

Arruda and Boyce (1993) reported a three-constitutive model to successfully predict the true stress vs. true strain data obtained in isothermal uniaxial compression and plane strain compression experiments on amorphous polycarbonate (PC) and PMMA at moderate strain rate. Figure 2.40 shows the model simulations and experimental curves of the uniaxial compression and plane-strain compression response of PC and PMMA. This model is based on a three-dimensional rubber elasticity spring system which is capable of capturing the state of deformation dependence. An internal state variable model was developed for the evolving polymer response.

2.3.3 Constitutive modeling of viscoelastic deformation

In literature, the continuum approach to a thermodynamic theory of a highly deformable thermo-viscoelastic medium undergoing large thermomechanical changes

is well established (Koh and Eringen 1963, Truesdell and Toupin 1960, Chadwick and Seet 1971). As discussed by the previous authors, there are two basic approaches to the thermodynamics of a continuous medium: rational and irreversible thermodynamics. The second law in the Truesdell-Toupin form of the local Clausius-Dehem inequality (Truesdell and Toupin 1960, eqn (258.3)) serves as a restriction on the constitutive equations for a continuous medium. Basically, the constitutive equations must be such that every thermodynamical process leads to positive entropy production. Dissipative models which satisfy this restriction then satisfy balance laws and the second law of thermodynamics for any arbitrary process in the body. In contrast, in the irreversible thermodynamics theory, the second law serves as a restriction on the processes that can occur in the continuum body.

Within the rational thermodynamics framework, models for fully coupled nonlinear thermoviscoelasticity which are applicable to numerous engineering polymer materials are studied by Simo and his co-workers (Gerhard A. Holzapfel and Juan C. Simo 1996, Govindjee and Simo 1992, Simo J.C. and Taylor R.L. 1991.). They developed a new three-dimensional constitutive model which describes the thermo-viscoelastic response of highly deformable continuous media, which is of special interest within the scope of rubber elasticity. The model is centered around the construction of a Helmholtz free energy function capable of accommodating anisotropic response and representing the coupled thermomechanical properties of polymeric materials in the finite-strain domain and in temperature ranges in which polymers exhibit stress relaxation. The approach employs nonlinear kinematics together with explicit thermodynamical constitutive

laws for dissipative materials based on rational thermodynamics and on the concept of internal state variables. The proposed formulation is valid for all thermoviscoelastic materials in the large strain domain.

2.3.4 Constitutive modeling of SMPs

While the majority of research activities of the last decade on SMPs were focused on the experimental characterization of the SME and its principal physical understanding, there are a few studies concentrated on the development of constitutive theories that describe the thermomechanical properties of SMPs as the macroscopic level. Two different approaches have been intensively explored. The first approach was based on the application of existing linear viscoelastic models consisting of coupled spring, dashpot, and frictional elements (Lin J.R. and Chen L.W. 1999, Khonakdar H.A. *et al* 2005, Abrahamson E.R *et al* 2003, Bhattacharyya A. and Tobushi H. 2000, Li F.K. and Larock R.C. 2002, Lin J.R. and Chen L.W. 1999, Morshedian J. *et al* 2005, Tobushi H. *et al* 1997, Tobushi H. *et al* 2001). Such models were applied to the chemically crosslinked amorphous and semi-crystalline polymer networks and the thermoplastics with crystalline hard and switching domains of SMPs. Models of the second approach considered in detail the specific molecular transition for the chemically crosslinked amorphous and semi-crystalline polymer networks (Liu Y.P. *et al* 2006).

Thermoplastic thermally-induced SMPs consist of at least two phases, the switching domains and the hard domains. The transition temperature of the switching domains is lower than that of the hard domains. Consequently, a viscoelastic model was proposed

by Lin and Chen (1999), consisting of two Maxwell models connected in parallel to describe the strain-controlled shape-memory cycle of some SMPs. In Figure 2.41a, the left side represents the hard domains (subscripts “h”), and the right side is assigned to the reversible switching domains (subscript “s”). The modulus of the spring unit is E and η is the viscosity of the respective dashpot units. The change of the model in a whole strain-controlled shape-memory cycle is shown in Figure 2.41b. At T_{high} , where $T_{\text{high}} > T_{\text{trans}}$, the model at state (1) is stretched to a constant strain ϵ_m and maintained there (state (2)). The time- and temperature-dependency of the modulus E can be expressed as the sum of two contributions from the hard and soft domains. At T_{high} , the viscosity of the switching domain is very low. At constant strain ϵ_m , after a sufficiently long time, the model shifts to a steady state. The strain of the switching domains corresponds nearly entirely to that of the deformed dashpot $\epsilon_s^V \approx \epsilon_m$ and the respective elastic contribution shifts to zero. After cooling down the system at constant strain to $T_{\text{low}} < T_{\text{trans}}$, state (3) is approached. It is assumed that in the considered temperature range $T_{\text{low}} < T < T_{\text{high}}$ the modulus E_b and the viscosity η_b in the hard domains have a constant value. At T_{low} , the stress is released and after a sufficiently long time state (4) is attained. Under the condition of no external force at T_{low} , the viscous contribution of the hard domains will not change any more, and if, furthermore, the viscosity η_h is nearly infinite, the respective strain contribution will be insignificant. Therefore the hard domain contributes practically only with an elastic part to the strain development. This allows calculating the strain rate at T_{low} . If the viscosity of the switching domain is very high, as if the SMP is in a glassy state, then the rigid switching

domains could effectively fix the deformation, and resist the elastic recovery of the hard domains. During heating back to T_{high} the viscosity of the dashpot of the switching domain $\eta_s(T)$ would reduce during the heating process. The temperature-dependency could be approximated in the case of glass transitions by the Williams-Landers-Ferry equation. After reheating to T_{high} the initial state (5) could be obtained.

Figure 2.41 Mechanical-viscoelastic model of Lin and Chen (1999) with two Maxwell models to describe SME in segmented PUs. (a) General model. (b) Change of the model in the shape-memory cycle.

The model of Tobushi *et al* (Bhattacharyya A. and Tobushi H. 2000, Tobushi H. *et al* 1997, Tobushi H. *et al* 2001) takes irreversible deformations into account by adding a “friction slider” into a linear viscoelastic model. The model considers in detail the

change of modulus, viscosity, stress relaxation, and other parameters around $T_{trans} = T_g$.

With a nonlinear version of the model (Tobushi H. *et al* 2001), it was possible to describe well thermomechanical properties and the recovery stress.

Li and Larock (2002) employed a viscoelastic model with three components in a row:

(1) elastic deformation (represented by a spring) caused by the change of length or angles of covalent bonds, (2) viscoelastic deformation represented by a Voigt-Kelvin

element representing micro-Brownian Motion of molecular segments, and (3) plastic

deformation (dashpot) which is caused by the slippage between polymer chains. It is

assumed that the last part cannot be recovered – it remains as residual irreversible

deformation. The model was applied to simulate the creep behaviour of linear polymers.

Similarly, a specific model for thermosetting SMPs was developed by Abrahamson *et al* (2003).

Models of the second approach describes the glass transition as the specific molecular

transition $T_{trans} = T_g$ or $T_{trans} = T_m$. A 3-D thermomechanical model for covalently

crosslinked SMPs was developed by Liu *et al* (2006). The multiphase character of

thermoplastic SMPs was modeled by assuming that, at a certain temperature during the

thermomechanical cycle, the polymer state is a mixture of two phases, an “active” and a

“frozen” phase. These phases are defined on the basis of two kinds of idealized C–C

bonds, “frozen bonds” and “active bonds,” which coexist in the polymer. The frozen

bonds represent the fraction of the C–C bonds that is fully disabled with regard to the

conformational motion in the glassy state at $T < T_g$, while the active bonds represent the

rest of the C–C bonds that can undergo localized free conformational motions in the rubbery state at $T > T_g$.

In the glassy state the major phase of a polymer is the frozen phase composed of frozen bonds, where conformational motions of chain segments are locked. In contrast, the active phase consists of active bonds and the free conformational motion can potentially occur and the polymer exists in the full rubbery state. Figure 2.42 shows a schematic picture of a simplified 3-D SMP model with “frozen phase” (dark shaded region) and “active phase” (light shaded region) and a 1-D simplification to describe uniaxial stretches.

Figure 2.42. Thermomechanical model for covalently crosslinked SMPs. (a) Schematic diagram of the micromechanics foundation of the 3-D SMP constitutive model. (b) 1-D model. (Liu Y. *et al* 2005)

An important innovation of this model is the inclusion of the time-dependency of the shape-memory response, such as the influence of a varied cooling and heating rate on

recovery values.

Other than the two approaches, Diani and Gall (2007) showed the principal approach on atomistic modelling of SMPs.

In conclusion, currently under investigation are models that incorporate the rate dependent and time dependent behaviour of materials. Accurate experiments for large deformations of SMPs are necessary to calibrate and validate respective nonlinear constitutive models.

2.4 Modeling of indentation of polymer

The development of very low-load depth-sensing indentation instruments, over the past twenty years or so, which produce indents as shallow as a few nanometers, make these instruments particularly well-suited for indentation experiments on materials available in small volumes, such as thin coatings (Pethica *et al* 1983; Oliver and Pharr 1992). Since these instruments allow continuous recording of both load, P , down to micro-Newtons, and indentation depths, h , down to nanometers during the indentation cycle, results from such nano/microindentation experiments hold the promise of the in situ estimation of mechanical properties of materials from the measured P - h curves. Giannakopoulos *et al* (1994), Larsson *et al* (1996) and Dao *et al* (2001) have found that the problems of estimating material properties from experimentally-measured P - h curves depends crucially on the availability of a large catalog of numerically calculated P - h curves, the attendant details of the time-varying “true projected contact areas”, “pile-up/sink-in profiles”, and stress and strain distributions in the inhomogeneously

deforming volume of material under the indenter.

Since, in typical ductile metallic materials, the plastic strain levels under sharp indenters exceed ≈ 0.15 in the majority of the plastically deforming volume directly beneath an indenter, and can reach as high as ≈ 1.5 just beneath the indenter tip as shown in Figure 2.43 (Dao *et al* 2001), the numerical simulations of indentation need to be performed with accurate large deformation constitutive models for the material being indented. Most of the recent analyses (Cheng and Cheng 1998 and 1999, Dao *et al* 2001) of indentation on metallic materials were performed using a large deformation version of the classical isotropic, rate-dependent, elasto-plastic flow theory.

Figure 2.43 Contour plot of the equivalent plastic strain (PEEQ) within the aluminum near the tip of the conical indenter (Dao *et al* 2001).

A simple, rate-dependent, power-law strain-hardening Mises type model, as has been used to simulate the indentation response of metallic materials (Cheng and Cheng 1998, Dao *et al* 2001), does not represent the various physical phenomena- strain-softening

and then strain-hardening, Bauschinger effects, strain-rate sensitivity, pressure sensitivity of plastic flow-observed in polymeric materials.

Figure 2.44 One-dimensional spring-dashpot representation of the constitutive model (Anand and Ames, 2006).

Figure 2.45 Comparison of P-h curves from micro-indentation simulations against corresponding experimental results, (a) without dwell and (b) with dwell (Anand and Ames 2006).

Anand and Ames (2006) based on previous authors' work reported a three-dimensional, internal variable, finite deformation model for the elasto-visco-plasticity of amorphous polymers, which phenomenologically capture the important aspects of the complex mechanical response of these materials associated in indentation. This model is based on the generalized Kelvin-Voigt model of classical linear viscoelasticity which consists of several paralleled spring-dashpot elements arranged in series. A simple rheological picture of the physical idea is shown in Figure 2.44. They extended the Kelvin-Voigt model to the nonlinear finite deformation range and also account for the strain hardening due to the alignment of the macromolecular network at large strains in the spirit of Haward and Thackray (1968). Figure 2.45 shows that this constitutive model predicts various important features of experimentally-measured micro-indentation load-versus-depth curves with reasonable accuracy. The testing material used here is PMMA.

Other than the above mentioned works, Lu and his coworker (2008) have also investigated the indentation process on viscoelastic materials. In the study, a flat-tipped indenter was simulated using the finite element method to address the exact characteristics of deformation at large-strain indentation. The specimen was modeled with second order eight-node axisymmetric elements to handle the potential large distortion of the elements occurred during large indentation. The indenter was assumed undeformable and thus modeled with rigid surfaces. The contact between specimen and indenter was treated as frictionless. The base of the specimen was completely constrained while the nodes along the centerline constrained in the horizontal direction.

A vertical described displacement was applied to the rigid surface through a reference node and the reactant force was calculated. The constitutive behavior of the polymeric material was modeled as a piecewise linear/power-law hardening relation (Equation (2.1)) (Mesarovic S.D. and Fleck N.A. 1987) where σ and ε are the applied stress and strain, σ_y and ε_y are the material yield stress and strain (assuming the material was linear elastic to the yield point), E is Young's modulus, and n is the strain-hardening exponent describing the post-yield material behaviour as a power-law relation. The plasticity was modeled by a standard von Mises (J_2) flow criterion. The arbitrary Lagrangian-Eulerian adaptive meshing technique was used to deal with the severe distortion of elements, which occurred in the large displacement indentation.

$$\sigma = \begin{cases} E\varepsilon & \text{for } \sigma \leq \sigma_y \\ \sigma_y \left(\frac{\varepsilon}{\varepsilon_y} \right)^n & \text{for } \sigma > \sigma_y \end{cases} \quad (2.1)$$

2.5 Remarks

We may conclude that various properties of SMPs can be further improved, in particular for reinforcement and electrical conductivity. On the other hand, utilizing the unique SME, SMPs may be excellent candidate for micro/nano patterning in a more convenient matter. There are plenty of potential applications of SMPs in medical devices. Well-developed finite element constitutive models are available to accurately predict the mechanical response of SMPs.

Chapter 3 Characterization of SMP and indentation test

The SMP used in the current study is a shape memory styrene copolymer thermoset resin system, which is thermo-responsive and was provided by Cornerstone Research Group (CRG), US. The as-received material is in a sheet form with a thickness about 4 mm. The samples were cut from the sheets into two different shapes, namely 10x10 mm square and 100x10 mm rectangular for thermomechanical tests. A WYKO interferometer and a Taylor Hobson (112/054DS) were used to exam the surface morphology of samples.

3.1 Thermal tests

Differential scanning calorimetry (DSC) measures endothermic and exothermic transitions, including T_g , melting and crystallization, as a function of temperature. TGA measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere.

DSC (MDSC 2920) was used to detect the step-increase in heat capacity and determine T_g , which is defined as the median point of the glass transition range in the heating ramp of the styrene SMP. A constant heating/cooling rate of 10°C /min was applied. The specimen (with a weight of 12.51 mg) was cut out from the as-received sample.

Figure 3.1(a) plots the DSC curve of the styrene SMP in a full heating and cooling

cycle and Figure 3.1(b) is the zoom-in view of the area A marked in Figure 3.1(a) in which T_g was determined as 57.63°C. This is slightly lower than the value provided by CRG (62°C).

(a)

(b)

Figure 3.1 DSC result. (a) Overall view, and (b) zoom-in view of A.

Thermogravimetric analysis (TGA) test was applied to investigate the thermal stability of the styrene SMP experimentally. TGA test was carried out with a specimen weighed

around 20 mg at a constant heating rate of 10°C/min purging with air gas on a Perkin-Elmer TGA 7. Figure 3.2 reveals that there are three parts of weight loss upon heating from 30°C to 900°C in this styrene SMP. Before heating to 100°C, there is only negligible weight loss which is largely attributed to the evaporation of moisture in the sample. In the temperature range of 100°C to 300°C, a small portion of weight loses while in the range of 300°C to 500°C, a large weight loss happens and until reaching 650°C, the sample totally vanishes in air. Therefore, 300°C is taken as the decomposition temperature of this styrene SMP and the sample is not suitable to be heated higher than 100°C, although the working temperature suggested by CRG is below 135°C.

In addition, in all subsequent tests, the samples were pre-heated to 100°C in order to stabilize the material.

Figure 3.2 TGA result of the styrene SMP.

A C-MATIC thermal conductive tester was used to determine the thermal conductivity

of the styrene SMP and the results at some different temperatures as shown in Figure 3.3. It decreases with the increase in temperature. The average is about 0.164 W/mK, which is close to the value provided by CRG (0.17 W/mK).

Figure 3.3 Thermal conductivity of styrene SMP.

3.2 Thermalmechanical test

Square and rectangular shaped samples were used to investigate the thermomechanical properties of the styrene SMP at both room temperature (23°C) and high temperature (80°C). According to Figure 3.1, the SMP is in the glass state at room temperature and in the rubber state at 80°C.

Note that unless otherwise stated, all strain and stress are the engineering strain and engineering stress in the course of this study.

3.2.1 Uniaxial compression

Square shaped samples were uniaxially compressed in the thickness direction by an

Instron 5569 with a 50 kN load cell (room temperature test) or a 500 N load cell (high temperature test).

- Room temperature test

Figure 3.4 shows the typical result of a strain vs. stress curve in a loading/unloading cycle with a maximum compressive strain of 60% at a strain rate of $1.6 \times 10^{-3}/s$. The result shows that in the loading process, beyond a small range of almost linear proportional relationship between the strain and stress, the material experiences a distinct upper yield point, followed by an apparent plateau and then hardening. The slope of the unloading curve is steep. The instant recovery is largely attributed to the elastic recovery and a large residual strain is obtained. Full recovery was observed upon heating (indicated by the dashed line).

Figure 3.4 Compression at room temperature.

-High temperature test (80°C)

A series of cyclical loading/unloading compressive test were carried out at a strain rate of $10^{-3}/s$ and 80°C. In these tests, the sample was loaded to different maximum strains and then unloaded at the same strain rate. The maximum strain was set from 10% to 60% with a 10% interval. Figure 3.5 illustrates the relationship of the stress vs. strain in the first two cycles. Significant recovery is observed upon unloading, in which shape memory is involved in addition to the elastic recovery.

Figure 3.5 Result of the cyclical compression test at 80°C.

3.2.2 Uniaxial tension

To investigate the tensile response of the SMP material, rectangular shaped samples were used in uniaxially tensile tests by an Instron 5569 with a 500 N load cell at 80°C. A constant strain rate of $10^{-3}/s$ was applied in both loading and unloading. Before testing, the samples (in a hot chamber) was uniformly heated to 80°C and then loaded

to a prescribed maximum strain, which was also held until the sample was cooled back to room temperature. After cooling, the sample was unloaded. Figure 3.6 shows a typical result of tensile test with the maximum strain of 100%. It was found that the polymer does not break even at pre-tension of 200%.

Figure 3.6 Strain vs. stress relationship in uniaxial tension.

Figure 3.7 Stress vs. strain relationship in cyclical tension.

As we can see, after a small elastic deformation range, the stress vs. strain curve becomes nonlinear. There is no apparent yield point and the stress increases in a gradual and smooth manner. Upon unloading, the slope is steep and the residual strain is about the same as the maximum strain applied. This means that the shape fixity of this SMP in this way is excellent.

Figure 3.8 Residual strain and strain recovery (in %).

The dependency of the stress vs. strain relationship in tension with a pre-strain was studied by a cyclical tensile test at 80°C and at a strain rate of 10^{-3} /s. The maximum pre-strains were from 0% to 140% in a 10% interval (Figure 3.7). As observed, the envelope formed by these cycles shares the similar trend as in the stress vs. strain curve of the single tensile test. In addition, the stress increases steadily with the applied maximum strain. Figure 3.8 shows the residual strain and strain recovery against the maximum strain (in %) in each cycle. The residual strain increases with

the maximum strain applied, while the strain recovery (in %) increases until the maximum strain reaches about 50% and then decreases with further increase in the maximum strain.

3.3 Indentation test

As mentioned in Section 2.2.2, protrusions can be obtained atop SMA by indentation/polishing/heating. As SMP has a much higher recoverable strain as compared with that of SMAs, SMP should be a better choice for nano/micro patterning with even more features. Macro indentation was applied to demonstrate the advantages in using SMP for patterning before nano indentation test was performed.

3.3.1 Macro indentation test

A SHIMADZU-DXT-3 with a steel ball indenter (ball diameter: 1.6 mm) can produce macro sized indents in a second. We used this machine as a quick way to demonstrate some basic concepts. There are four groups of spherical macro-indentation tests. The first group was on the original cylindrical shaped samples (radius=5mm). The second group was on the pre-compressed square shaped samples (compressed in the thickness direction as described in Section 3.2.1) at a strain rate of 10^{-3} /s and the maximum compressive strain 40% at room temperature. The third group was on the pre-stretched rectangular shaped samples. The maximum tensile strain was 50%, the strain rate was 10^{-3} /s (refer to Section 3.2.2 for details of testing). The samples of the above three groups were indented at room temperature with a small pre-load of 29.42 N applied before the final one of 147.1 N. The fourth group was indented at elevated

temperature on the original square shaped samples. The 3-D surface scanning was done by the Taylor Hobson (112/054DS) at a speed of 3000 $\mu\text{m/s}$ with inductive gauge.

The results of these tests will be reported and discussed in Section 4.1.

3.3.2 Nano indentation test

In order to investigate the response of the styrene SMP down to a few microns scale and even nano scale atop the surface, a series of nano-indentation tests were carried out. Both square and rectangular shaped samples were used. Before testing, each sample was well-polished (refer to Section 3.2.3) for the procedure of polishing.

A MST Nano Instrument with a Berkovich indenter was used to make micro sized indents atop the SMP samples. All indentation tests were done at room temperature in depth control mode. The targeted strain rate was 0.05 /s following XP CSM method. After the pre-described maximum depth (thereinafter defined as the nominal maximum depth) was reached, there was a holding time of 10 seconds under the maximum force before unloading at the same speed. The residual depth immediately after unloading is defined as the nominal residual depth. Further recovery is possible as the polymer is a viscous material.

There are three groups of nano-indentation tests. The first group was done on the original square shaped samples. The second group was on the 20% pre-compressed (maximum strain) square shaped samples (refer to Section 3.2.1). The third group was

on the 50% stretched (maximum strain) rectangular shaped samples (refer to Section 3.2.2). After compression/tension, the sample average surface roughness was measured as 35.126 nm (R_a) and 25.182 nm (R_a). The typical results of the force vs. depth curves of these three groups are plotted in Figures 3.9-3.11.

Figure 3.9 Force vs. depth curves of original sample.

Figure 3.10 Force vs. depth curves of 20% pre-compressed sample.

Figure 3.11 Force vs. depth curves of 50% pre-stretched sample.

Figure 3.12 Depth increase due to holding and maximum force vs. normal maximum depth. Dark lines: depth increase due to holding. Gray lines: maximum force. Solid lines: original sample. Dashed lines: 20% pre-compressed sample. Dotted lines: 50% pre-stretched sample.

Figure 3.12 summarizes the relationship between the maximum force vs. the nominal maximum depth, and that of the depth increase due to holding under the maximum force against the nominal maximum depth. As shown in the figure, the maximum force (Grey lines) applied during indenting increases with the nominal maximum depth achieved after indenting in all the samples (original, pre-compressed and pre-stretched). The original and the pre-compressed samples almost are the same trend and it is almost linearly increase in the pre-stretched sample. On the other hand, the depth increment due to holding at the maximum force during indenting in all samples share the same trend until a nominal maximum depth of 20 μm is reached. After this, the depth increment is almost constant and the largest (about 1500 nm) in the pre-stretched

sample and the smallest (about 1150 nm) in the original sample and about 1300 nm in the pre-compressed sample.

Figure 3.13 Nominal residual depth vs. nominal maximum depth. Dark lines: nominal residual depth. Gray lines: nominal residual depth against nominal maximum depth (in %). Solid lines: original sample. Dashed lines: 20% pre-compressed sample.

Dotted lines: 50% pre-stretched sample.

Figure 3.13 reveals that relationship of the nominal residual depth vs. nominal maximum depth and that of the nominal residual depth against the nominal maximum depth (in %) vs. nominal maximum depth of all samples. As a general trend, the nominal residual depth against the nominal maximum depth (in %) decreases slightly with the increase in the nominal maximum depth.

3.4 Remarks

The styrene SMP has a T_g of about 57.53°C. It is stable at below 100°C. The thermal conductivity is about 0.164 W/mK.

The polymer is fully recoverable upon stretching to 100% or compressing to 60%. Deforming at high temperature and then cooling the sample is a more effective way for pre-deformation. Macro and nano indentation tests were carried out. The nominal residual depth against the nominal maximum depth (in %) decreases slightly with the increase in the nominal maximum depth.

Chapter 4 Surface patterning by indentation

A systematic investigation is presented in this chapter to demonstrate the feasibility and advantages of using SMP for patterning on macro to micro and even nano scales. Preliminary results are obtained for realizing protrusive arrays by indentation/polishing

4.1 Macro-Indentation

4.1.1 Original sample

Six indents were made on six different samples at room temperature with the same setup as described in Section 3.3.1. The indents were more or less the same in size and shape. Figure 4.1 shows the 3-D view and cross-section of two typical indents. The indents are piled-up and approximate 250 μm deep.

Figure 4.1 3-D view and cross-section of two indents.

After indentation, each sample was polished for 2 hours by silicon carbide paper of grit 800 and then grit 1200 and finally grit 2400 with ECOMET 6 and water as lubricant. Reasonable smooth surface was obtained (without visible scratch under optical microscope). Six different polishing depths were applied in these six samples. For the samples in which polishing depth was less than 250 μm , the exact depth is the difference between the original indent depth and that after polishing. Figure 4.2 compares the cross-sectional view of the indents before and after polishing ($< 250 \mu\text{m}$). In Figure 4.2, the gray dashed line in the center graph indicates the polishing depth and the black solid line indicates the residual depth.

Figure 4.2 Comparison of indents before and after polishing. (a) A typical indent before polishing; (b) the residual indent after the top most pile-up part removed; (c) and (d) are the residual indents after about 1/3 and 3/4 depth of the indent, respectively, removed.

After polishing, the samples were uniformly heated to 100°C and soaked for 1 minute in the laboratory oven. Various shaped protrusions were resulted. The 3-D and

cross-sectional views of these protrusions are shown in Figure 4.3. In Figure 4.3 (a), the polishing depth is only 20 μm , which is about half of the depth of the pile-up (as shown in Figure 4.2b). Elsewhere, the polishing is practically none. Upon heating the shape recovery is triggered and the indented part protrudes out of the polished surface. Because the polishing depth is small, the protrusion is slight. Hence, virtually a circular trench is resulted. The protrusion looks like a cylinder with a flat top. With the increase in polishing depth, the protrusion becomes more apparent, while the flat top becomes less significant (Figure 4.3 b-e), and eventually a spherical crown like shape is formed (Figure 4.3 f).

Figure 4.3 3-D view and cross-section of protrusions. (a) 20 μm polished (the top pile-up removed); (b) 90 μm polished; (c) 223 μm polished; (d) 250 μm polished (fully polished); (e) slightly over polished; and (f) well over polished.

4.1.2 Pre-deformed sample

Compared with SMA, SMP has a much higher recoverable strain, which enable us to

investigate the protrusion on pre-deformed samples.

As shown in Figure 4.3 (b) and (c), the protrusive shapes formed by partially polishing are similar. Hence, in the subsequent experiments, only one polishing depth within this range was investigated. For the same reason, only fully polishing was investigated, but slightly over polishing was not considered. Three square shaped samples were used for pre-compression to a maximum strain of 40% at room temperature in the thickness direction (as described in Section 3.2.1) and a rectangular shaped one for pre-stretching to a maximum strain of 50% at 80°C (as described in Section 3.2.3). The pre-stretched sample was then cut into four equal sized pieces. After pre-deformation, indentation, polishing and heating were conducted in the exactly same procedure as described in those conducted on the original samples in Section 4.1.1. Typical 3-D view and cross-section of the indents on a pre-compressed sample and a pre-stretched sample right after indentation test are shown in Figure 4.4.

Figure 4.4 3-D view and cross-section of indent before polishing. (a) Pre-compressed sample; (b) pre-stretched sample.

As observed in Figure 4.4, the depth of the indent on the pre-compressed sample is $410\text{ }\mu\text{m}$ and there is no pile-up, while that of the pre-stretched sample is $320\text{ }\mu\text{m}$ with a very small pile-up. After polishing and heating, the obtained protrusive shapes are shown in Figures 4.5 and 4.6.

Figure 4.5 Protrusive shapes formed on pre-compressed samples. (a) $250\text{ }\mu\text{m}$ polished (part of the indent removed); (b) $410\text{ }\mu\text{m}$ polished (the whole indent removed); and (c) well over polished.

In Figure 4.5, the protrusive shapes formed on the pre-compressed samples are similar to those on the original samples, but without trench shape due to no pile-up.

As shown in Figure 4.6, various types of elliptic protrusive shapes are formed. Such elliptic features can not be realized in shape memory alloys due to their limited recoverable strain. Hence, by controlling the amount of pre-stretching and later on polishing, not only elliptic trench but also elliptic crown with a different ovality can

be produced. Even an array of such feature can be realized.

Figure 4.6 Protrusive shapes formed on pre-stretched samples. (a) 10 μm polished (pile-up removed); (b) 140 μm polished (part of the indent removed); (c) 320 μm polished (indent fully removed); and (d) well over polished.

In order to characterize the elliptical protrusions, we define a and b as the major and minor axes of the ellipse and r the radius of the circular indent right after polishing (Figure 4.7). We consider the slightly polished case (only the pile-up part is polished away). As we can see, the ellipticity (a/b) is about 1.75. The extension ratio along the major axis (X-axis as indicated in Figure 4.7b), $(a-r)/r$, is about 0.3 and the contraction ratio along the minor axis (Y-axis), $(r-b)/r$ is 0.26. As such, the extension vs. contraction ratio, $(a-r)/(r-b)$, is 1.14.

Figure 4.7 (a) Indent after polishing (pile up removed), (b) protrusion after heating (pile up removed) and (c) comparison between the indent and the protrusion.

4.1.3 High temperature test

Three square shaped samples were immersed into boiling water for 20 seconds. After which, indents were made by applying an approximately same load (manually controlled) and held until the samples were cooled back to room temperature. Figure 4.8 shows the 3-D view and cross-section of these indents.

As we can see, although the exact temperature during each indentation test may not be

the same, the produced indents are more or less the same in both size and shape and they are all sink-in. After polishing and heating, the resulted protrusive shapes are presented in Figure 4.9. As shown, apart from that no trench can be found as the indents are sink-in, the productions are similar to those of the original samples.

Figure 4.8 3-D view and cross-section of indents produced at high temperature.

Figure 4.9 Protrusive shapes formed at high temperature. (a) 160 μm polished (part of the indent removed); (b) 400 μm polished (fully polished); and (c) well over polished.

4.1.4 Further discussions

The ratio of protrusive height to the polishing depth is defined as $R_{H/P}$ in this study. For the fully polished case, $R_{H/P}$ of the indents on the pre-compressed sample and that of the pre-stretched sample are about 1.22 (as shown in Figure 4.5b) and 1.25 (as shown in Figure 4.6c), respectively, while that of the original sample is about 1 at both room temperature and high temperature (as shown in Figures 4.3d and 4.9b). The difference of about 20% in the pre-compressed sample is due to the around 20% residual strain after 40% maximum compression. For the pre-stretched sample, the higher $R_{H/P}$ is due to the decrease in thickness during stretching.

Figure 4.10 Protrusive height vs. polishing depth/indentation depth. The solid line: original sample; the dotted line: pre-stretched sample; the dashed line: pre-compressed sample; the dashed and dotted line: high temperature sample.

The protrusive height is plotted against the ratio of polishing depth and indentation depth ($R_{P/I}$) for all the samples (original sample, pre-stretched sample, pre-compressed sample and high temperature sample), as shown in Figure 4.10. It demonstrates that for the partially polished indents, the protrusive height increases with the $R_{P/I}$ and the trends of the pre-compressed and the high temperature cases are almost similar. While in the over polished cases, the protrusive height decreases with the $R_{P/I}$. At the $R_{P/I}=1$, the protrusive height reaches the maximum for all the samples.

4.2 Micro-Indentation

The above-study (Section 4.1) demonstrates the feasibility and advantages of using SMP (instead of SMA) to produce various shaped protrusions by indentation. In this section, we further investigate the possibility of forming protrusions down to a few microns in height and even smaller. The protrusive shapes were made by a Berkovich nano indenter (pyramidal shape), instead of a spherical one as in the macro indentation. There were three types of indentation tests (refer to Section 3.3). The 3-D surface was obtained from the WYKO interferometer. Same as before, in order to improve the reflection, a thin layer of gold (about 20 nm) was pre-coated atop the samples before surface scanning.

4.2.1 Sample preparation and testing

Two original square shaped samples were well polished and afterward indented (refer to Section 3.3.2 for procedure). Eight groups of indents (in 2 x 2 matrix) of different depths were obtained on each sample. The depths were 4 μm (I-1), 6 μm (I-2), 7.5 μm

(I-3), 9 μm (I-4), 11 μm (I-5), 15 μm (I-6), 20 μm (I-7), and 25 μm (I-8). Four indents (namely I-2501, I-2502, I-2503 and I-2504) of 25 μm deep were produced at each corner of the sample, which were used to determine the polishing depth. Figure 4.11 illustrates the location of indents atop the surface of a sample after indentation. As both samples were indented under the same setup and conditions, we assume the indents are more or less the same.

Figure 4.11 Illustration of a sample surface after indentation.

Twenty-four hours after indentation, one of the two samples was gold coated for WYKO scanning. Figure 4.12 shows the typical indent of each depth.

The cross-sections (along the direction indicated in the inset figure in Figure 4.13) of typical indents are superimposed and presented in Figure 4.13.

Figure 4.12 2-D view of typical indents on original sample, (a) I-1, (b) I-2, (c) I-3, (d) I-4, (e) I-5, (f) I-6, (g) I-7, and (h) I-8.

Figure 4.13 Cross-sections of typical indents (I-1 to I-8).

Another sample was also coated with the same thickness of gold, but only on the four corner indents, namely, I-2501, I-2502, I-2503 and I-2504. The depths of these four indents were measured as 7.54 μm (I-2501), 7.44 μm (I-2502), 7.61 μm (I-2503) and 7.58 μm (I-2504), respectively, by WYKO. Subsequently, this sample was polished until I-4 nearly disappeared. Hence, the shallower indents were over polished, and the medium ones were about fully polished and the deeper ones were only partially polished.

Pre-compressed and pre-stretched samples were also investigated in the exactly same way as that of the original samples. Pre-compression (20% maximum strain) was carried out in the same way as described in Section 3.2.1, while pre-stretching (50%

maximum strain) was performed following the same procedure as described in Section 3.2.2.

Figure 4.14 2-D view of CI-1 to CI-8. (a) CI-1, (b) CI-2, (c) CI-3, (d) CI-4, (e) CI-5, (f) CI-6, (g) CI-7, and (h) CI-8.

Figure 4.15 2-D view of SI-1 to SI-8. (a) SI-1, (b) SI-2, (c) SI-3, (d) SI-4, (e) SI-5, (f) SI-6, (g) SI-7, and (h) SI-8.

The eight groups of indents atop the pre-compressed samples were named as CI-1 (4 μm), CI-2 (6 μm), CI-3 (7.5 μm), CI-4 (9 μm), CI-5 (11 μm), CI-6 (15 μm), CI-7 (20 μm), and CI-8 (25 μm).

μm) and CI-8 (25 μm). Those of pre-stretched samples were named as SI-1 (4 μm), SI-2 (6 μm), SI-3 (7.5 μm), SI-4 (9 μm), SI-5 (11 μm), SI-6 (15 μm), SI-7 (20 μm) and SI-8 (25 μm). The typical 2-D view and the cross sections of CI-1 to CI-8 and SI-1 to SI-8, are presented in Figures 4.14-4.17.

Figure 4.16 Cross-sections of CI-1 to CI-8.

Figure 4.18 plots the residual depth before polishing determined by WYKO vs. nominal maximum depth in indentation for the three types of samples. Generally speaking, at the same nominal maximum depth, the residual depth of the indents of the pre-compressed sample is the largest, while that of the indents of the pre-stretched sample is the smallest. An interesting point is that the residual depth increases with the nominal maximum depth in almost a linear fashion in the indents on the

pre-stretched sample, which is the same as the relationship of the nominal residual depth vs. nominal maximum depth as shown in Figure 3.13. However, for the indents on other two samples, the relationship between the residual depth vs. nominal maximum depth can be described by two straight lines. The slope in the high nominal maximum depth range is much smaller than that in the low nominal maximum depth range.

Figure 4.17 Cross-sections of SI-1 to SI-8.

The difference between the nominal residual depths determined from the indentation test (Figure 3.13) and the residual depth right before polishing measured by WYKO is due to the slow recovery at room temperature.

Subsequently, all samples were polished.

Figure 4.18 Residual depth vs. nominal maximum depth.

4.2.2 Result and discussion

The residual depths of the four corner indents were determined and then the actual polishing depth of individual indent was estimated for each sample. The average polishing depths were 4.7872 μm, 4.056 μm and 2.7674 μm for the original, pre-compressed and pre-stretched samples, respectively.

The residual depth determined by WYKO before polishing is defined as D_I and the polishing depth as D_P . In each indent, H' and L stand for the height and lateral length of the 2-D in-plane triangle for each indent or protrusion. The ratio of the polishing depth to the residual depth before polishing against the maximum nominal depth is

plotted in Figure 4.19, and thus the over-polished indents, fully polished indents and partially polished indents are identified.

Figure 4.19 D_p/D_l vs. nominal maximum indentation depth.

These samples were then heated to 100 °C and held for 1 minute. The resulted protrusive features were measured by WYKO and their 2-D profiles and cross-sections are presented in Figures 4.20-4.22 and Figures 4.23-4.25 respectively. As we can see, protrusive pyramidal shapes are formed on the sample surfaces.

In Figures 4.20 and 4.21, the protrusive shapes are formed on the original and pre-compressed samples. They are pyramidal and their projections are equilateral triangles. However, the pre-stretched samples projections are no longer equilateral triangles, because of the shape recovery of the sample, i.e. the contraction in the vertical direction (pre-stretching direction), and expansion in the horizontal direction.

Figure 4.20 2-D view of protrusions made of I-1 to I-8. (a) I-1, (b) I-2, (c) I-3, (d) I-4, (e) I-5, (f) I-6, (g) I-7, and (h) I-8.

Figure 4.21 2-D view of the protrusive shapes made of CI-1 to CI-8. (a) CI-1, (b) CI-2, (c) CI-3, (d) CI-4, (e) CI-5, (f) CI-6, (g) CI-7, and (h) CI-8.

Figure 4.22 2-D view of the protrusive shapes made by SI-1 to SI-8. (a) SI-1, (b) SI-2, (c) SI-3, (d) SI-4, (e) SI-5, (f) SI-6, (g) SI-7, and (h) SI-8.

Figure 4.23 Cross-sections of protrusive features made of I-1 to I-8.

Figure 4.24 Cross-sections of the protrusive shapes made of CI-1 to CI-8.

Figure 4.25 Cross-sections of the protrusive shapes made of SI-1 to SI-8.

In Figure 4.23 (original sample), the over polished indents form relatively smaller and sharper protrusive pyramid, while the fully polished and over polished ones are about the same height which is close to the polishing depth. In Figure 4.24 (pre-compressed sample), the protrusive shape of CI-1 has a sharp peak and CI-5 has a clear flat top and the top of CI-5-8 becomes wider. But unlike to those of original samples, all protrusive shapes are more or less same height, around $3.5 \mu\text{m}$, which is lower than the average polishing thickness, $4.056 \mu\text{m}$. In Figure 4.25 (pre-stretched sample), sharp peaks which are observed hardly on original (Figure 4.23) and pre-compressed (Figure 4.24) samples can be observed. From SI-1 to SI-8, their cross-sections tend to be wider and wider, while the deepest indents has a flat top. The difference in height of these indents is more obvious. The highest is about 4.5 , which is much higher than

the average polishing thickness of $2.7674\text{ }\mu\text{m}$. This is because the sample thickness decreases upon stretching. But this is due to a different mechanism as compared with that by direct compression.

The protrusive height is plotted against the residual depth before polishing in Figure 4.26. It shows that for shallow indents, the protrusive height increases with the residual depth and the three types of samples share the same trend. From the residual depth equals about 4 on, the protrusive height increases slightly with the residual depth for the each type of sample and they share a same slope. All the flat top protrusions are resulted at large residual depth and firstly emerge in the pre-compressed samples with increase the residual depth while last in the pre-stretched samples.

Figure 4.26 Protrusive height vs. residual depth before polishing. Black color-filled symbol: flat-top protrusion; Gray color-filled symbol: unclear; hollow symbol: sharp protrusion.

The relationship between the protrusive height and residual depth after polishing is shown in Figure 4.27, in which the over polished, fully polished and partially polished indents are indicated. For the three kinds of samples, the protrusive height of the over polished and fully polished indents is about linearly proportional about the same slope to the residual depth after polishing. For the same residual depth, the height of the original sample is largest, while that of the pre-stretched sample is the smallest. For partially polished indents, the height is about a constant in the original sample, pre-compressed sample and pre-stretched sample (only for high residual depth indents).

Figure 4.27 Protrusive height vs. residual depth after polishing. Black color-filled symbol: flat-top protrusion; Gray color-filled symbol: unclear; hollow symbol: sharp protrusion.

In order to find out a clear relationship in a dimensionless manner, in Figure 4.28, the

protrusive height is normalized by the polishing depth and residual depth after polishing is normalized by that before polishing. As we can see, for pre-stretched sample, the relationship between height/D_P and $(D_I - D_P)/D_P$ is about linear. However, for the original and pre-compressed samples, before $(D_I - D_P)/D_P$ reaches -0.5, the height/D_P vs. $(D_I - D_P)/D_P$ curve is virtually linear and parallel to that of the pre-stretched sample, but a slightly low position. At $(D_I - D_P)/D_P$ above -0.5, height/D_P is about a constant.

Figure 4.28 Height/D_P vs. $(D_I - D_P)/D_P$. Black color-filled symbol: flat-top protrusion; Gray color-filled symbol: unclear; hollow symbol: sharp protrusion.

Figure 4.29 illustrates that mechanism of the formation of the protrusions by over polishing and fully polishing and partially polishing. First, different depths of indents are made on the top surface of a sample (Figure 4.29a). The gray line represents the

region affected by the indentation. In Figure 4.29(b) the sample is polished a thin layer away so that the shallow indent is over polished and the medium size indent is fully polished and the deep one is partially polished (Figure 4.29c).

Figure 4.29 Formation of the protrusions.

Subsequently, the sample is heated and protrusions are resulted (Figure 4.29d). In the partially polished one, the residual indent returns back to its original shape. A flat top is formed and the protrusive height equals to the polishing depth. In the over polished one, the indented sample surface part is polished away, a sharp protrusion is formed and the protrusive height is linearly increasing with the residual depth after polishing. The fully polished one is supposed to be the boundary between flat and sharp protrusions. However, as we can see, the Height/D_P is 0.8, but not 1. So that this boundary is actually at a lower $(D_I - D_P)/D_P$ point (about -0.5), as shown in Figure

4.28. At this point of time, we have not yet found a good explanation to this point.

Figure 4.30 Protrusive height/ H' vs. the residual depth after polishing. Black color-filled symbol: flat-top protrusion; Gray color-filled symbol: unclear; hollow symbol: sharp protrusion.

The protrusions of the three types of samples and their 2-D in-plane projections are investigated and compared. The ratio of protrusive height to the height of the 2-D triangle (H') against the residual depth after polishing is plotted in Figure 4.30. As shown, in the three types of samples, the ratio decreases with the increase of the residual depth after polishing and the slowest is in the pre-stretched sample. The pre-compressed and original samples share the same decreasing slope in the over polishing region, and for the same residual depth after polishing, the ratio of the pre-compressed sample is larger than that of the original one. However, in the

partially polishing region, both have the same slope which is less steep than that of the over polishing region.

For the in-plane triangle of the pre-stretched sample, the ratio of triangular height (H') to lateral (L) after heating is plotted in Figure 4.31. As shown in Figure 4.31, the ratio is more or less a constant, about 0.55, with varying the residual depth after polishing.

Figure 4.31 2-D triangular height (H') over lateral (L) after heating in the pre-stretched sample.

4.2.3 Nano sized protrusions

Apart from these protrusive pyramidal hills, some circular cones with a height down to 94.7 nm were also observed on the surface of the pre-compressed samples, as shown in Figure 4.32. Lubricant was used in order to reduce the friction between SMP sample and an aluminum block with a very smooth surface (to ensure a smooth surface

on SMP sample) during the compression test. It reckons that there are some small particles in the lubricant, so that some small indents were resulted as a by-product of the compression test.

Figure 4.32 Two nano sized protrusive shapes formed on pre-compressed sample.

After polishing, these particles were removed and the underneath indents were also fully or partially polished. After heating, these unexpected circular cones were resulted, which demonstrates the possibility to produce nano sized protrusions of various shapes if different indenters are used.

4.3 Protrusive array

4.3.1 Introduction

Chan and Crosby (2006) introduced an approach for fabricating microlens arrays based on the confinement of surface wrinkles (Figure 4.33). They demonstrated the ability to control the size and the arrangement of the microlenses through clever control of the geometric shape and material properties of the wrinkled regions.

Figure 4.33 Structure of the compound lens. (a) Optical profile of the micro-lens structures on a polydimethylsiloxane (PDMS) hemisphere; (b) Magnified optical profile of microlens surface; (c) surface profile of a single microlens measured using a stylus profiler. (Chan and Crosby 2006)

4.3.2 Results and discussion

In this section, micro sized protrusive bumps and arrays fabricated atop SMP by indentation (using indenter and packed steel balls) are demonstrated. Taylor Hobson and 2-D stylus were used to exam the surface profiles.

As discussed in Section 4.2.1, nano indentation arrays were made on SMP samples. Hence, after polishing and heating (following the same procedure as description in Sections 4.2.1 and 4.2.2), the protrusive arrays were formed (Figure 4.34). The Taylor Hobson was used to scan the protrusions at a speed of 300 $\mu\text{m/s}$. It is rather slow to form the indents one by one. Using well packed hard balls may be a better alternative.

Figure 4.34 Protrusive arrays. (a) Original sample and (b) 50% pre-stretched sample.

Steel balls (diameter: 420 μm to 710 μm) were well packed (in 10x7 array) on a piece of double-side adhesive tape which was stuck to a flat surface of an aluminum block. The aluminum block was then placed on the top of a SMP sample with the well packed steel balls facing the polymer. An Instron 5565 with a 5 kN load cell was used to compress the aluminum block at a speed of 0.0005/s till a maximum compression of 500 μm was reached. Before compression, a thin layer of lubricant was applied between the ball array and SMP surface for easy detachment afterwards. Two SMP samples were compressed. The 3-D view and cross-section of 3x3 arrays are presented in Figure 4.35 (scanned by the Taylor Hobson scanner).

Figure 4.35 3-D view and cross-section of the compressed SMP surface of two samples.

Subsequently one sample was polished to partially remove the indents (Figure 4.36).

The polishing depth was about 100 μm as determined by the Taylor Hobson. For another sample, the polishing depth was about 200 μm , so that all indents were virtually removed.

Figure 4.36 3-D view and cross-section of surface after partially polishing.

After polishing, the two samples were heated in the laboratory oven to 100°C and held for 1 minute. The protrusive arrays were formed atop the sample surface (Figure 4.37).

Figure 4.37 3-D view and cross-section of the surfaces after heating. (a) Partially polished sample, and (b) over polished sample.

Figure 4.37 reveals flat-top-protrusion array is resulted atop the partially polished SMP sample, while spherical top protrusion array is formed atop the over polished SMP sample.

4.4 Remarks

To summarize, a generic approach is demonstrated to realize various sized protrusive shapes using a thermo-responsive SMP. Utilizing the large recoverable strain in this SMP, and depending on the pre-straining in SMP, shape/size of indenter, temperature during indentation and the depth of polishing, it is shown that a variety of features of different sizes can be resulted. Given the much higher recoverable strain, SMPs can overcome the limit in patterning using SMAs. The temperature dependency of indent shape in SMP is similar to that in SMAs, but opposite in terms of temperature condition. Protrusive features at nanometer height are observed. Indentation using packed steel balls is a simple way to produce protrusive arrays atop SMP.

Chapter 5 Theory of protrusion formation

5.1 Introduction

In this chapter, a constitutive model to study the protrusion formation process on top of amorphous styrene SMP through indentation-polishing-heating method is investigated and presented. The model is implemented in the finite-element computer program ABAQUS/Explicit (ABAQUS, Inc., 2002). We assume the SMP is free from any pre-straining. Indentation and polishing are conducted isothermally at temperature below the glass transition temperature and stress states under which the SMP does not exhibit crazing. The detailed procedures are outlined as follows.

5.2 Constitutive model for PS SMP

Micro-indentation of polymeric materials below their glass transition temperature involves large elastic-viscoplastic deformation response. Anand and Gurtin (2002) have generalized the work of previous authors (e.g. Parks et al 1985; Boyce et al 1988; Arruda and Boyce 1993; Wu and Van der Giessen 1993) and developed a continuum frame-indifference theory for this response of amorphous solids, which is capable of capturing the response in a reasonably accurate manner. In their theory, a new mathematical definition of an amorphous material is used to restrict the constitutive assumptions. It is based on the notion that the constitutive relations for such materials

should be invariant under all rotations of the reference configuration and, independently, all rotations of the relaxed configuration. At the same time, the theory explains the dependence of the Helmholtz free energy on the plastic deformation in a thermodynamically consistent manner. It directly results into a backstress in the underlying flow rule. Two internal variables: a variable $s(>0)$ that represents an isotropic intermolecular resistance to plastic flow and an unsigned variable η that represents the local free-volume are added into the standard kinematic and stress variables. The theory is based on the multiplicative decomposition, $\mathbf{F} = \mathbf{F}^e \mathbf{F}^p$ of the deformation gradient $\mathbf{F}$ into elastic and plastic parts, $\mathbf{F}^e$ and $\mathbf{F}^p$ (Kroner, 1960; Lee, 1969). A specialized form of this constitutive model for isotropic metallic materials will be discussed first, and then a more generalized form suitable for amorphous polymeric materials will be presented.

5.2.1 Isotropic metallic materials

For metallic materials, one internal variable $s > 0$ which represents an isotropic resistance to plastic flow is used in the theory. The other variables are

$\mathbf{T}$, $\mathbf{T} = \mathbf{T}^T$, Cauchy stress,

$\mathbf{F}$, $\det \mathbf{F} > 0$, deformation gradient,

$\mathbf{F}^p$, $\det \mathbf{F}^p = 1$, plastic part of the deformation gradient,

The parameters used are defined by

$\mathbf{F}^e = \mathbf{F}\mathbf{F}^{p-1}$, $\det \mathbf{F}^e > 0$, elastic deformation gradient,

$\mathbf{E}^e = \frac{1}{2}(\mathbf{F}^{eT}\mathbf{F}^e - \mathbf{I})$, elastic strain,

$\mathbf{T}^e = \mathbf{R}^{eT}\mathbf{T}\mathbf{R}^e$, stress conjugate to the elastic strain $\mathbf{E}^e$,

$\sigma = \frac{1}{3}tr\mathbf{T}$, mean normal pressure,

$\mathbf{T}_0^e = \mathbf{T}^e - \sigma\mathbf{I}$, deviatoric stress,

$\mathbf{D}^p = sym(\dot{\mathbf{F}}^p\mathbf{F}^{p-1})$, $tr\mathbf{D}^p = 0$, plastic stretching,

Under the usual assumption of small elastic stretches, the constitutive equations are given by

1 Equation for the stress:

$$\mathbf{T}^e = 2G\mathbf{E}_0^e + K(tr\mathbf{E}^e)\mathbf{I}. \quad (5.1)$$

where G and K are the elastic shear and bulk module, respectively.

2 Flow rule:

$$\dot{\mathbf{F}}^p = \mathbf{D}^p\mathbf{F}^p, \quad \mathbf{F}^p(\mathbf{X}, 0) = \mathbf{I}, \quad (5.2)$$

with

$$\mathbf{D}^p = \nu^p \left(\frac{\mathbf{T}_0^e}{2\bar{\tau}} \right), \quad \nu^p = \nu_0 \left(\frac{\bar{\tau}}{s} \right)^{\frac{1}{m}}, \quad 0 < m \leq 1, \quad (5.3)$$

where

$$\bar{\tau} = \frac{1}{\sqrt{2}} |\mathbf{T}_0^e|, \quad \text{and} \quad \nu^p = \sqrt{2} |\mathbf{D}^p|, \quad (5.4)$$

are an equivalent shear stress and equivalent plastic shear-strain rate, respectively. Here, ν^0 is the reference plastic shear-strain rate and m is the strain-rate sensitivity parameter. When $m \rightarrow 0$, Equation (5.3) is rate-independent, and when $m=1$ it is linearly viscous. The equivalent plastic shear strain, γ^p , is defined by $\gamma^p = \int \nu^p dt (> 0)$.

3 Evolution equation for the internal variable s :

The evolution of s is governed by the differential equation

$$\dot{s} = h_0 \left(1 - \frac{s}{s_*}\right)^a \nu^p, \quad s(\mathbf{X}, 0) = s_0, \quad (5.5)$$

where $\{s_0, h_0, s_*, a\}$ are additional material parameters.

For a particular isotropic metal, below are the constitutive parameters needed to be specified to complete the constitutive model.

$$\{G, K, \nu_0, m, s_0, h_0, s_*, a\}$$

5.2.2 Amorphous polymeric materials

For polymeric materials, it is commonly believed that the evolution of the local free-volume is the major reason for the highly non-linear stress-strain behavior of glassy materials which precedes the yield-peak and gives rises to the post-yield strain

softening. Accordingly, in this case the model employs two internal variables: a variable $s(>0)$ that represents an isotropic intermolecular resistance to plastic flow; and an unsigned variable η that represents the local free-volume. The model (Anand and Gurtin 2002) explicitly accounts for the dependence of the free energy on the plastic deformation in a thermodynamically consistent manner. In amorphous polymeric materials, the major part of this dependence arises from an “entropic” contribution due to the stretching of the molecular chains. This dependence leads directly to a back stress in the underlying flow rule, which allows the model to capture the rapid strain-hardening response after the initial yield-drop in monotonic deformations. This theory is adopted to model the micro-indentation response of the SMP used in our work.

The constitutive equations for amorphous polymeric materials are summarized below.

1 Equation for the stress:

$$\mathbf{T}^e = 2G\mathbf{E}_0^e + K(tr\mathbf{E}^e)\mathbf{I}. \quad (5.6)$$

2 Flow rule:

$$\dot{\mathbf{F}}^p = \mathbf{D}^p \mathbf{F}^p, \quad \mathbf{F}^p(\mathbf{X}, 0) = \mathbf{I}, \quad (5.7)$$

with

$$\mathbf{D}^p = \nu^p \left(\frac{\mathbf{T}_0^e - \mathbf{S}_{back}}{2\bar{\tau}} \right), \quad \nu^p = \nu_0 \left(\frac{\bar{\tau}}{s - \alpha\sigma} \right)^{\frac{1}{m}}, \quad 0 < m \leq 1, \quad (5.8)$$

where

$$\bar{\tau} = \frac{1}{\sqrt{2}} |\mathbf{T}_0^e - \mathbf{S}_{back}|, \quad \text{and} \quad \nu^p = \sqrt{2} |\mathbf{D}^p|, \quad (5.9)$$

are an equivalent shear stress and equivalent plastic shear-strain rate, respectively. Here, ν^0 is the reference plastic shear-strain rate, m is a strain-rate sensitivity parameter, and α a pressure sensitivity parameter.

The tensor $\mathbf{S}_{back}$ represents a back stress, which using the definitions

$$\mathbf{B}^p = \mathbf{F}^p \mathbf{F}^{pT}, \quad \text{left Cauchy-Green tensor corresponding to } \mathbf{F}^p,$$

$$\mathbf{B}_0^p = \mathbf{B}^p - \frac{1}{3} (\text{tr} \mathbf{B}^p) \mathbf{I}, \quad \text{deviatoric part of } \mathbf{B}^p,$$

$$\lambda^p = \frac{1}{\sqrt{3}} \sqrt{\text{tr} \mathbf{B}^p}, \quad \text{effective plastic stretch},$$

is given by

$$\mathbf{S}_{back} = \mu \mathbf{B}_0^p, \quad \text{with} \quad (5.10)$$

$$\mu = \mu_R \left(\frac{\lambda_L}{3\lambda^p} \right) L^{-1} \left(\frac{\lambda^p}{\lambda_L} \right), \quad (5.11)$$

where L^{-1} is the inverse of the Langevin function $L(\cdots) = \coth(\cdots) - (\cdots)^{-1}$. The back stress modulus μ involves two material parameters: μ_R , called the rubbery modulus, and λ_L called the network locking stretch; this modulus $\mu \rightarrow \infty$ as $\lambda^p \rightarrow \lambda_L$, since $L^{-1}(z) \rightarrow \infty$ as $z \rightarrow 1$.

3 Evolution equations for the internal variables s and η :

The evolution of s and η is taken to be governed by the coupled differential equations

$$\dot{s} = h_0 \left(1 - \frac{s}{\tilde{s}(\eta)} \right) \nu^p, \quad s(\mathbf{X}, 0) = s_0, \quad (5.12)$$

$$\dot{\eta} = g_0 \left(\frac{s}{s_{cv}} - 1 \right) \nu^p, \quad \mu(\mathbf{X}, 0) = 0, \quad (5.13)$$

with

$$\tilde{s}(\eta) = s_{cv} [1 + b(\eta_{cv} - \eta)], \quad (5.14)$$

where $\{h_0, g_0, s_{cv}, b, \eta_{cv}\}$ are additional material parameters. Here $\tilde{s} = \tilde{s}(\eta)$ is a saturation value of s : $\dot{s}$ is positive for $s < \tilde{s}$ and negative for $s > \tilde{s}$. By definition ν^p is nonnegative. Assuming that $\nu^p > 0$, all solutions to the pair of evolution equations satisfy

$$s \rightarrow s_{cv} \text{ and } \eta \rightarrow \eta_{cv} \text{ as } t \rightarrow \infty.$$

We restrict our attention to the initial conditions $s = s_0$ with

$$s_0 \leq s \leq s_{cv}(1 + b\eta_{cv}).$$

Also, as is tacit from (5.13), the free-volume is measured from the value $\eta = 0$ in the virgin state of the material, and thus η at any other time represents a change in the free-volume from the initial state.

To complete the constitutive model for a particular amorphous polymeric material the constitutive parameters/functions that need to be specified are

$$\{G, K, \nu_0, m, \alpha, \mu_R, \lambda_L, s_0, h_0, s_{cv}, g_0, b, \eta_{cv}\}.$$

We have implemented the constitutive models in the finite-element computer program ABAQUS/Explicit (ABAQUS, 2002), by writing user material subroutines to capture the large elastic visco-plastic behavior of our SMP PS material upon micro indentation.

5.2.3 Material parameter determination for the SMP PS

In this part, the material parameters which need to be specified in the constitutive mode of micro indentation are determined. All SMP PS samples are annealed at 100°C for 30 minutes and then furnace-cooled for 20 hours before compression and indentation experiments in order to ensure the consistent initial sample conditions.

The material parameters that need to be determined are

- 1 The elastic shear and bulk moduli (G, K).
- 2 The reference shear strain rate ν_0 , the strain-rate sensitivity parameter m , and the pressure sensitivity parameter α in the flow equation (5.8).
- 3 The parameters (μ_R, λ_L) for the back stress modulus, (5.11).
- 4 The parameters $\{h_0, g_0, s_{cv}, b, \eta_{cv}, s_0\}$ in the evolution equations for (s, η) , (eqs. 5.12, 5.13, 5.14).

Figure 5.1 Large deformation compression tests at two different strain rates.

The values of (G, K) are determined by measuring the Young's modulus ($E = 755 \text{ MPa}$) of the SMP PS from a room-temperature compression test (Figure 3.4) and assuming a Poisson's ratio of $\nu = 0.33$. The standard conversion relations of isotropic elasticity formula are used to obtain the elastic shear and bulk moduli. We choose a reference strain rate of $\nu_0 = 1 \times 10^{-3} s^{-1}$. Stress-strain curves from large deformation compression tests at two different strain rates, $\dot{\epsilon}_1 = 1 \times 10^{-3} s^{-1}$ and $\dot{\epsilon}_2 = 1.6 \times 10^{-3} s^{-1}$, are shown in Figure 5.1. The lower yield points corresponding to these two strain rates are $\sigma_{1yp,1} = 47 \text{ MPa}$ and $\sigma_{1yp,2} = 51 \text{ MPa}$. These values give us an estimate for the strain rate sensitivity parameter

$$m \approx \frac{\ln(\sigma_{1yp,2} / \sigma_{1yp,1})}{\ln(\dot{\epsilon}_2 / \dot{\epsilon}_1)} \approx 0.1736 \quad (5.15)$$

The pressure sensitivity parameter $\alpha = 0.1$ was estimated from the data reported by Anand and Gearing (2002). The parameters $\{h_0, g_0, s_{cv}, b, \eta_{cv}, s_0\}$ and (μ_R, λ_L) are estimated by fitting a stress-strain curve in compression to large strains. The fit is performed by adjusting the values of these parameters in finite element simulations of a simple compression experiment using a single ABAQUS/CPE4R element. After a few attempts, a reasonable fit is obtained and shown in Figure 5.2. The parameters used and obtained from this calibration procedure are listed in table 5.1.

$G = 746.2687 MPa$	$K = 2083.3 MPa$	$\mu_R = 15 MPa$	$\lambda_L = 1.7$
$\nu_0 = 1 \times 10^{-3} s^{-1}$	$m = 0.1736$	$\alpha = 0.1$	
$s_0 = 45 MPa$	$s_{cv} = 36 MPa$	$h_0 = 4 GPa$	
$b = 850$	$g_0 = 1.2 \times 10^{-2}$	$\eta_{cv} = 0.001.$	

Table 5.1 Parameters obtained from the calibration procedure

Figure 5.2 Fit of the constitutive model to the simple compression at room temperature.

5.3 Modeling of polishing

After indentation, the indented SMP surfaces are polished to different depths. This process is modeled as deactivation of a layer of elements of corresponding polishing depths from the model after indenting, as shown in Figure 5.3. So these deactivated elements are not involved in the following heating process as they are removed from the sample. Consequently, a new surface constituted by the elements just under the deactivated elements is formed. All the nodes forming the new surface are recorded. From Figure 5.3, it can be seen that the new surface consists of two parts. The first (Part ONE) is the bottom of the indent which comes from the original surface of the SMP PS sample before indenting and is directly below the indenter through the

indenting process. The other part (Part TWO) is the surface around the bottom of the indent which is originally below the untouched sample surface before indenting and is exposed due to polishing. With increasing polishing depth, the area of Part ONE decreases until zero when the indent is fully and over polished, and that of Part TWO increases to the maximum.

Figure 5.3 Illustration of modeling of polishing process.

5.4 Modeling of heating

After polishing, the SMP PS samples are heated up to 100°C and the SME is triggered. Experiments are conducted to test the shape memory ability of the SMP PS material upon micro indenting. A 10x10x4 mm PS sample is first indented by a spherical indenter at room temperature. Then, the sample is gradually heated up to 70°C, 80°C, 90°C and 100°C and soaked at each temperature for 5 minutes. The sample surface is viewed by optical microscope at every step and the results are shown in Figure 5.4.

Figure 5.4 Recovery of the indented SMP PS sample at different temperatures.

From figure 5.4, it is clear that the indent gradually becomes shallow with increasing temperature and finally is flat and visibly the same as the original surface after heating up to 100°C. The surface roughness examined by Tylorscan is 496.648 nm and 537.493 nm for the original surface before indenting and for the surface after heating up to 100°C respectively. We conclude that the PS samples almost fully recover at 100°C. Therefore, in modeling, all the recorded nodes of the new surface go back to their original positions after the heating process. The original position of a node is its position at the original surface before the indentation. So the Part ONE forms the original surface of the SMP PS sample before indenting and polishing and has the same height as the original sample since this area is not affected by the polishing process, while the Part TWO forms the surface which is originally below the sample surface before indenting, because the layer of material above is removed in the polishing

process. Consequently, its height is less than the original sample height and the Part One height. By this way, after heating, the Part ONE area protrudes out of the new surface and protrusions are formed.

5.5 Remarks

A systemical model is presented and explained in this chapter on numerically simulating the protrusion formation process through indentation-polishing-heating. The next chapter discusses the modeling aspects and the simulated results.

Chapter 6 Modeling the formation of the protrusions on top of PS SMP surface

In this chapter, indentation on SMP PS is studied by modeling based on the theory outlined in the previous chapter. Emphasis is given on comparing the experimentally measured profile of the protrusion formed on top of SMP PS surface with FEM result. As discussed in Chapter 4, this protrusion formation method is through indentation-polishing-heating process. The protrusions investigated and modeled in this chapter are made by micro indentations and on top of the original sample without pre-straining (refer to section 4.1.1).

ABAQUS is a suite of software applications for finite element analysis (FEA) and computer-aided engineering. It was initially designed to address non-linear physical behavior; as a result, the package has an extensive range of material models and can be customized to analyze and solve the problem at hand (writing user material subroutines). Taking into consideration the success of ABAQUS in modeling the mechanical properties of materials with good accuracy as evidenced from the literature, ABAQUS is used to simulate the indentation study and to analyze the protrusion features. More details about FEA approach and ABAQUS can be found in ABAQUS documentation. The experimental details and the theoretical aspects can be found in chapter 4 and chapter 5 of this thesis, respectively.

6.1 Modeling results and discussion

6.1.1 Outline of the model structure and mesh

The dimension of the SMP PS original sample is cylindrical with 5mm in radius and 4mm in height. The indent is made around the center of the sample. Owing to the inherent symmetry of the experimental setup and to reduce the computation cost, the model can be simplified into a 2-D structure. It is to be noted that the results obtained will be the same if we consider a 3-D structure and the full surface.

Figure 6.1 The layout of the model using axisymmetry.

We take the right half side of the out of plane cross section of the experimental setup through the center of the sample surface and parallel to the sample radius to be the symmetric representation of the whole setup and build the model, as shown in Figure

6.1. In the model, the SMP PS substrate is cylindrical with radius as 5mm and 4mm in height and the indenter is at the top left corner of the substrate. The radius of the spherical indenter defined in the simulation is 800 μm (same value as used in the experiment of section 4.1.1). Because the model is an axisymmetric represent of the experimental 3-D structure, boundary conditions have to be set. The bottom of the substrate is restricted to be only movable along the X-axis and the left side of the substrate is only movable along the Y-axis. The indenter can only move along Y-axis.

The mesh consists of 24713 ABAQUS/CPE4R elements. CPE4R, a four node plane strain reduced integration element type is used for meshing because this modeling involves large deformation in Y-axis and contact mechanism. The region of the substrate close to the indenter is meshed with a higher density. It is to be noted that finer the meshing, the longer the computation time. Depending on the simulation, a trade-off should be made on the mesh density taking into consideration the accuracy needed. This procedure of dense meshing in the region close to the indenter is due to the following reasons;

- At the very beginning of the indenting process, the indenter comes in contact with many substrate elements so that the risk of the substrate penetrating into the indenter is minimized.
- The region close to the indenter deforms most severely upon indenting compared to the region away from the indenter and the corresponding high density mesh helps in increasing the accuracy of the simulated result. This is

important especially in simulations that study the nodal displacement.

- The small variations in the morphology that occur in the surface after indentation can be observed only if the mesh is fine enough (denser the mesh, better the morphology details). This results in the surface profile to be smooth and continuous.
- The deactivated elements can be precisely determined in the polishing simulation (Finer the mesh, better the accuracy in length).

Figure 6.2 Close up view of the region near the indenter

Figure 6.2 shows the close up view of the region in direct contact with the indenter. The mesh details are clearer.

6.2 Indentation simulation results and discussion

The indentation simulation was carried out taking into consideration the contact nature

of indentation (indentation is a contact process). In the experiment, the indenter first touches the substrate surface and then is forced to move down towards the substrate when the indenting force increases and always keeps contact with the surface of the substrate. When the indenting force is reduced, the indenter starts to move up and keeps contact with the substrate surface until the force becomes zero. The indenting force is loaded to maximum 147.1 N and immediately released within a short time.

In the simulation, the outside rim of the ball shape indenter and the top surface of the substrate are defined as a contact pair. The rim of the indenter is the master surface and the substrate surface is the slave surface. The contact is modeled as frictionless. It is to be mentioned that the ball shape indenter is modeled as a rigid body which is assumed undeformable at any time during the whole simulation. The indenting force is applied on the reference point of the indenter and in the negative Y-axis direction. The position of the reference point is demonstrated in Figure 6.2 as the cross in yellow color. The indenting force is assumed to increase to the maximum value in 5 seconds and another 5 seconds to reduce to zero and without holding at the maximum value. Figure 6.3 shows the indenting force vs. time plot. In the loading process, the force is determined to increase fast in the first second to 90 N and then at a slower rate in the following 4 seconds. The reason is when the indenting force is less than 90 N, the SMP PS largely experience simple elastic deformation and while this force exceeds 90 N, the nonlinear visco plastic flow starts in the SMP PS in which any step with big force increment causes un-convergence in the simulation result. The same force increment is adopted in the unloading process.

Figure 6.3 The plot of the indenting force vs. time applied to the simulation.

Figure 6.4 shows the contour plot of the nodal displacement in Y-axis with the application of the indenting force. It is clear that an indent results at the top left surface of the substrate. The maximum indentation depth is around $230\text{ }\mu\text{m}$. For the nodes which are directly under the indenter and near to the edge, the nodal displacements are negative. The nodal displacements of the between nodes are positive and a pile-up is formed around the edge of the indent. The elements in the dark blue color which are near to the bottom of the indent are displaced the most severely in the Y-axis. This is also where first contact is made with the indenter during the loading process. In the area around the axis of the symmetry of the substrate and with the width of the radius of the indent, there are several half-U shape front lines. The lines illustrate the distribution of

the Y-axis displacement resulted by the indentation process. Each line stands for a level of displacement corresponding to the legend. The further away from the indenter, the less the displacement is.

Figure 6.4 Contour plot of the nodal displacement in Y-axis after indentation.

Figure 6.5 shows the contour plot of the nodal displacement in the X-axis after the indentation. There are V shape front wave lines starting from near to the curvature of the indent towards the bottom of the substrate. The more to the bottom the wider is the V shape. All the nodal displacements are in the positive X-axis direction. The elements in the blue area which are directly under the indenter are not displaced in the X-axis which means this area is only compressed during the indenting. The top elements which are near to the bottom of the indent are compressed the most severely. Therefore, the elements near to the bottom of the indent are originally of the flat substrate surface which was directly under the indenter before indenting. The blue area becomes wider with the depth into the SMP PS substrate. The most severe X-axis stretching occurs in

the red area which is near to the curvature of the indent because this place experiences the indenting force from the direction diverted from the Y-axis direction which is along the radial direction of the indenter. The maximum X-axis displacement reaches around 100 μm .

Figure 6.5 Contour plot of the nodal displacement in X-axis after indentation.

The series of plot of the nodal displacement flow directions during the indentation are demonstrated in Figure 6.6. The red arrowed lines indicate the direction in the XY space at the different indenting depths.

Figure 6.6 The nodal displacement flow direction during the indentation.

In Figure 6.6(a), when the indenter just touches the substrate surface, although the magnitude of the flow is very small, the influence can reach as far as $180\mu\text{m}$ horizontally and as deep as around $180\mu\text{m}$ vertically. Both the Y-axis and X-axis flow

occur at the beginning of the indenting. For the elements which are under the indenter and are near to the substrate surface, the flow direction is almost vertical. For the elements between, the small counter-clockwise diversion from Y-axis happens. With the indenting (Figure 6.6(b) to 6.6(c)), the flow displacement increases and the elements under the indenter keep flowing vertically while the flow direction turns counter-clockwise largely for all the other elements. Figure 6.6(d) shows the final nodal flow direction after unloading. As can be seen, the elements under the indenter flow vertically. The substrate surface elements move up against the indenting direction and the displacement decreases as further away from the indenter which results in the pile-up phenomena observed in polymeric materials upon indentation. Between these two areas, the elements flow almost horizontally towards the negative X-axis direction.

The numerically predicted and the experimentally measured cross section of the indent right after indentation are compared in Figure 6.7. The original substrate surface before indenting is shown by the grey line. The height of the original sample is 4000 μm and it is assumed not compressed by the indentation.

The experimental data is plotted in the solid black line. As can be seen, the maximum height of the pile-up is around 40 μm and gradually flattens to the surface. So the indent depth calculated from the substrate surface is around 230 μm . The indent is as wide as around 600 μm . The dashed black line shows the simulation data. The simulation can predict the indent depth accurately and the curvature of the indent and the pile-up feature closely. It is noted that the bottom of the indent is partially flat instead of curved

as the spherical indenter. This is coherent with the experimental data. The flat part is about 200 μm horizontally.

Figure 6.7 The comparison of the numerically-predicted and the experimentally-measured cross-section view of the surface morphology after indenting.

6.3 Protrusion simulation results and discussion

The protrusions compared and discussed here are demonstrated experimentally and numerically in Figures 6.8 to 6.13 and named respectively as CaseA, CaseB, CaseC, CaseD, CaseE and CaseF.

Figure 6.8 The comparison of the numerically-predicted and the experimentally-measured cross-section view of the protrusion of CaseA.

The numerically predicted protrusive profile of the CaseA is compared with the experimental data and shown in Figure 6.8. In CaseA, the polishing depth is about 20 μm so that only the pile-up feature is removed partially and the substrate surface height is not changed. Therefore, the new sample surface should be 4000 μm (as indicated by the grey line). In Figure 6.8, both the experimental and simulation data show a flat-top protrusion with the height around 20 μm and width around 600 μm . The flat top nearly covers the whole protrusive width. This is same as the width of the indent right after indentation. It is clear that the flat top reaches the original substrate surface height of 4000 μm and the simulation prediction of the shape of the groove formed around the

flat-top protrusion is within an acceptable accuracy. So the model can be applied to decide the protrusive shape in the very shallow polished cases, such as pile-up removal case.

Figure 6.9 The comparison of the numerically-predicted and the experimentally-measured cross-section view of the protrusion of CaseB.

Figure 6.9 shows the comparison of CaseB. In CaseB, the polishing depth is $90\text{ }\mu\text{m}$ and the $40\text{ }\mu\text{m}$ pile-up is fully removed and a thin layer of the substrate is also removed. Therefore, calculating from the substrate surface, the actual polishing depth is $50\text{ }\mu\text{m}$ and the new sample surface should be around $3950\text{ }\mu\text{m}$. As shown, both the experimental and simulation data show a flat-top protrusion with the height around $50\text{ }\mu\text{m}$ and width near to $600\text{ }\mu\text{m}$. The protrusive flat-top is almost same as that of CaseA

but the groove around the protrusion disappears. Instead, a sharp slope down to the new substrate surface from the flat-top and a slow slope from the root of the protrusion towards the surface are shown as well as captured by the simulation.

Figure 6.10 The comparison of the numerically-predicted and the experimentally-measured cross-section view of the protrusion of CaseC.

The polishing depth increases to $223\text{ }\mu\text{m}$ in CaseC. The comparison is shown in Figure 6.10. Now, the new surface is at around $3810\text{ }\mu\text{m}$. From the figure, it is obvious that the protrusive height increases and the flat top width decreases dramatically. The numerical model precisely predicts the increment as well as the width of the flat-top. Very small difference from the experimental data exists at the protrusive curvature towards to its root and the curvature from the root to the new substrate surface. With increasing the

polishing depth, the model successfully predicts the changes to the curvatures from the slopes and the profile of the curvature from the root to the surface.

In CaseB and CaseC, the indent is partially polished and around 1/5 and 3/4 of the residual indent depth after indentation, respectively. For both cases, the model is accurate in the prediction of the protrusive height and the flat top width and is able to capture the changes from the slopes to the curvatures of the protrusive shape and its connection with the new substrate surface. It predicts the curvatures in CaseC with acceptable small diversion.

Figure 6.11 The comparison of the numerically-predicted and the experimentally-measured cross-section view of the protrusion of CaseD.

In CaseD, the indent is fully polished and the protrusion has a flat top and its height is

around 230 μm . The width of the flat top further decreases to around 200 μm . The comparison of the numerically predicted and the experimentally measured data is demonstrated in Figure 6.11. Now, the new sample surface after polishing is at around 3770 μm . It is noted that the two results are coherent with each other. The protrusive height and the flat top width are precisely given by the model. It is noted that the curvature connecting the protrusive root to the new substrate surface become shallow and flattened and the protrusive curvature is more round. The simulation data reflects the changes and meets the experimental data with good accuracy.

Another nearly fully polished case is CaseE (the indent of 230 μm is polished around 260 μm). The protrusive height decreases together with an increase in the polishing depth. The flat top width is almost not affected and is near to 200 μm . These are successfully captured by the simulation model, as shown in Figure 6.12. The curvature of the protrusion is predicted accurately and the difference that occurs at the protrusive root is almost overcome.

In CaseD and CaseE, the polishing depth increases and the residual indents after indentation are almost fully removed. The protrusive height, curvature and the flat top width also change accordingly. The presented model shows very good ability to capture these changes.

Figure 6.12 The comparison of the numerically-predicted and the experimentally-measured cross-section view of the protrusion of CaseE.

The CaseF is the well over polished case in which the sample after indentation is polished off around 340 μm. The comparison result is shown in Figure 6.13. Now the protrusive height is about 165 μm and instead of the flat top, the protrusion shows a sharp top. These are accurately demonstrated by the numerically predicted data. Furthermore, the numerical result follows perfectly together with the experimental data.

Figure 6.13 The comparison of the numerically-predicted and the experimentally-measured cross-section view of the protrusion of CaseF.

6.4 Remarks

The theory presented in Chapter 5 is used to model the protrusive shape formed by the macro indentation which was investigated experimentally in Chapter 4.1. The numerically predicted and the experimentally measured protrusive shape are compared and analyzed. It shows that the model can be applied to decide the protrusive shape in the very shallow polished cases, such as pile-up removal case. For the indent in partially polished cases, the model is accurate in the prediction of the protrusive height and the flat top width and is able to capture the changes from the slopes to the curvatures of the protrusive shape and its connection with the new substrate surface. It

predicts the curvatures in relatively large polishing depth with acceptable small diversion. With further increasing the polishing depth so that the residual indents are almost fully removed, the presented model shows very good ability to capture the resulted changes in the protrusive height, curvature and the flat top width. The last case is to well-over polish the indent. The profile of the sharp top protrusion is accurately predicted by the numerical model.

Chapter 7 Conclusions and future work

7.1 Conclusions

After an extensive literature review on SMPs, their current applications and potential ones in other close related fields, a few promising directions for future applications of SMPs were identified.

The thermomechanical properties of styrene SMP was characterized by means of DSC, TGA, and uniaxial tension/compression test. In addition to T_g , the thermal conductivity of SMP is obtained. It is found that the polymer is fully recoverable upon stretching to 100% or compressing to 60%. Deforming at a high temperature and then cooling the sample is a more effective way for pre-deformation. Macro and nano indentation tests were carried out. The nominal residual depth against the nominal maximum depth (in %) decreases slightly with the increase in the nominal maximum depth.

A generic approach is demonstrated to realize various sized protrusive shapes using a thermo-responsive SMP. Utilizing the large recoverable strain in this SMP, and depending on the pre-straining in SMP, shape/size of indenter, temperature during indentation and the depth of polishing, it is shown that a variety of features of different sizes can be resulted.

The pre-stretched and original and pre-compressed SMP samples were tested to

produce protrusive features through macro and nano indentation/polishing.

In the macro indentation at room temperature, for the original sample, when the polishing depth is small, the protrusion is slight and a circular trench is resulted. The protrusion looks like a cylinder with a flat top. With the increase in polishing depth, the protrusion becomes more apparent, while the flat top becomes less significant, and eventually a spherical crown like shape is formed. The protrusive shapes formed on the pre-compressed samples are similar to those on the original samples, but without trench shape due to no pile-up. Various types of elliptic protrusive shapes are formed by the pre-stretched samples. Such elliptic features can not be realized in shape memory alloys due to their limited recoverable strain. By controlling the amount of pre-stretching and later on polishing, not only elliptic trench but also elliptic crown with a different ovality can be produced. For the indenting at high temperature, apart from the observation that no trench can be found as the indents are sink-in, the productions are similar to those of the original samples. For the fully polished case, $R_{H/P}$ of the indents on the pre-compressed sample and that of the pre-stretched sample are about 1.22 and 1.25, respectively, while that of the original sample is about 1 at both room temperature and high temperature. The difference of about 20% in the pre-compressed sample is due to the 20% residual strain after 40% maximum compression. For the pre-stretched sample, the higher $R_{H/P}$ is due to the decrease in thickness during stretching.

In the nano indentation, it is found that for partially polished indents, the protrusive height increases with the residual depth after indentation and the three types of samples

share the same trend. The protrusive height increases slightly with the residual depth for each type of sample and they share a same slope for the fully and over polished indents. All the flat top protrusions are resulted at the partially polished indents and first emerge in the pre-compressed samples with increase in the residual depth after indentation while in the end in the pre-stretched samples. For the three kinds of samples, the protrusive height of the over polished and fully polished indents is about linearly proportional about the same slope to the residual depth after polishing. For the same residual depth after polishing, the height of the original sample is largest, while that of the pre-stretched sample is the smallest. For partially polished indents, the height is about a constant in the original sample, pre-compressed sample and pre-stretched sample. In the three types of samples, the ratio of protrusive height to the height of the 2-D triangle (H') against the residual depth after polishing decreases with the increase of the residual depth after polishing and the slowest is in the pre-stretched sample. The pre-compressed and original samples share the same decreasing slope in the over polishing region, and for the same residual depth after polishing, the ratio of the pre-compressed sample is larger than that of the original one. However, in the partially polishing region, both have the same slope which is less steep than that of the over polished region.

Given the much higher recoverable strain, SMPs can overcome the limit in patterning using SMAs. The temperature dependency of indent shape in SMP is similar to that in SMAs, but opposite in terms of temperature condition. Protrusive features at nanometer height are observed. Preliminary results are obtained for realizing protrusive arrays by

indentation/polishing.

With the well developed theory of indentation, a general quantitative model is proposed for the single protrusive patterning on top of the original styrene SMP by macro indentation/polishing at room temperature. The theory accurately captures the depth and curvature of the indent directly after indentation but the sink-in feature is found instead of the pile-up feature. The proposed model is well accurate in predicting the protrusive height and the flat-top width. For the partially polished indents, the prediction to the protrusive curvature is less accurate and is mainly due to the pile-up feature. The model shows a good coherence with the experimental data for the fully polished and well over polished indents.

7.2 Future works

In terms of future works, there are three directions to follow.

Further fabrication and/or characterization of SMP and SMP composites will be carried out. Reversible micro/nano brush can be resulted from self-assembly of long SMP/Ni column. A theoretical model will be developed for controlling the dimension and stiffness of the brush. Reversible micro/nano brush will be produced, characterized and compared with the prediction.

The second one is to modify the technique of patterning atop SMP using different sized and shaped micro/nano indenters. A variety of micro/nano indenters will be used for producing different shapes of features on different scales.

The last is to propose and demonstrate SMP based devices, in particular, for medical applications. The conductive SMP and water quick reaction SMP thin films/wires developed in the course of this study will be applied in, for instance, minimally invasive surgery. Reversible micro/nano brush and various sided/shaped patterns can be used for surface modification of biomaterials.

Appendix A

This appendix presents some preliminary results of protrusive arrays produced by laser. In addition, a study on attapulgite reinforced SMP is carried out. The focus is on the influence of moisture and attapulgite on T_g at present. The chapter also contains the results of the studies on the thermomechanical properties of SMP filled with different amount of nickel powder.

A.1 Protrusive arrays

A.1.1 Laser microlens

The square shaped SMP samples were used and manually polished by sandpaper of grit 4000, slurries of 6 μm , 3 μm , 1 μm and polishing liquid. These samples were then uniaxially compressed in the thickness direction at room temperature by an Instron 5569.

- Single bump

The applied maximum compression strain was 50% and the loading speed was 10 mm/min. Subsequently, the samples were point heated by a green laser with different pulse energy and 1/30 s shutter exposure. Bumps were resulted (Figure A.1), due to the local recovery atop surface of SMP.

Figure A.1 Optical profile and 2-D cross-section of two bumps. (a) 14.0 μJ pulse energy and (b) 7.3 μJ pulse energy.

- Protrusive arrays

Protrusive arrays can be realized in a similar way using a microlens array. The maximum compressive strains were 20% and 30% and the loading speed was 10 mm/min. In order to achieve a better heating result, a thin layer (about 10 nm) of gold was coated on the sample surface and subsequently exposed to the green laser at different pulse energy through a microlens array (pitch: 250 μm and focus: 795.5 μm). Figure A.2 shows the green laser setup with a microlens. The shutter exposure time was 1 s.

Figure A.2 Laser setup.

Figure A.3 Protrusive array on 20% pre-compressed sample at pulse energy 2.28 mJ (optical microscopy profile).

The resulted typical protrusive arrays examined by the optical microscopy and Taylor

Hobson are presented in Figures A.3 and A.4, respectively.

Figure A.4 Protrusive array on 30% pre-compressed sample at pulse energy 68 μJ
(Taylor Hobson profile).

A.2 SMP reinforced by attapulgite

Attapulgite (AT) is a kind of crystalline hydrated magnesium-aluminum silicate mineral, which can expand dramatically upon wetting [chemical composition: $(\text{Mg}, \text{Al})_2\text{Si}_4\text{O}_{10}(\text{OH})_4(\text{H}_2\text{O})$] (Frost *et al* 2001) . It is largely biocompatible and exists microscopically in the form of nano tube (10 to 25 nm in diameter, up to 1000 nm long). PU SMP (5520) pellets used are from Mitsubishi Heavy Industries (MHI), Japan with a nominal T_g of 55°C as provided. In this section, the T_g of a PU SMP reinforced by

treated/non-treated AT in wet and dry conditions is investigated.

A.2.1 Sample preparation and testing

The original AT clay has a molecular weight of 411.35 gm. The original clay is called non-treated clay (NTC) hereinafter, while the treated clay (TC) refers to the same type of AT clay after heat-treated in an oven at 850°C for two hours. Figure A.5 is the X-ray diffraction (XRD) results of NTC and TC. The specific density of PU SMP is 1.25 g/cm³, while those of TC and NTC are 2.1459 g/cm³, and 1.5861 g/cm³, respectively.

Figure A.5 XRD results of NTC and TC.

The SMP pellets were melted at 200°C in a Haake Rheocord 90 Torque Mixer and then well-mixed with four different volume percentages (namely, 0%, 10%, 20% and 30%) of TC and NTC. Subsequently, the cooled mixtures were shredded into small pieces and hot-pressed into sheets about 1 mm thick at 200°C. The resulting composites are named as TCx or NTCx, where x indicates the volume percentage of clay; while PU

stands for the pure SMP sample. Small sized samples were cut out of the sheets and stored under wet and dry conditions. Under the wet condition, the samples were immersed into room temperature water (about 22°C) for more than two weeks. Under the dry condition, the samples were stored in an air-tightened container.

The glass transition of SMP/AT composites (hereinafter, named as PU/AT. Similarly PU/NTC and PU/TC stand for PU SMP mixed with NTC and TC, respectively) can be investigated by the DSC. In a full thermal cycle, the sample was heated from -50°C to 150°C, and then cooled to -50°C at a heating/cooling rate of 10°C/minute. Same sample was continuously tested for three full thermal cycles. The DSC results of the same sample in the last two cycles are virtually identical, and could be remarkably different from that of the first cycle, which indicates the influence of moisture (Yang *et al* 2004). According to the previous study (Yang *et al* 2006), upon heating to 150°C, most of the bounded water in this PU SMP, which affects T_g strongly, could be removed. Hence, the DSC curves of the subsequent two cycles are almost identical for both PU and PU/AT. For dry PU/NTC samples, one more thermal cycle was conducted with the highest temperature set as 180°C instead of 150°C in order to investigate an interesting phenomenon we found in the course of this study.

A series of TGA tests were carried out to quantitatively determine the weight fraction of moisture in AT for both PU/NTC and PU/TC. In these tests, the samples were ramped at 10°C/minute from room temperature to 700°C.

A.2.2 Results and discussions

It should be pointed out that

- The DSC result of the third cycle of a PU/AT is not presented, since it is normally very close to that of the second cycle. Only part of the heating curve is plotted.
- T_g (listed in Table A1) is determined by the three tangent method using the attached software to this DSC equipment.
- In order to focus on T_g , we ignore some minor peaks/troughs which might appear elsewhere in the cycling curves.

Table A1 T_g (°C) obtained from DSC tests

Sample		1 st cycle	2 nd cycle
Dry	PU	22.93	40.61
	TC10	32.15	41.84
	TC20	33.83	42.58
	TC30	18.9	42.13
	NTC10	14.47	29.28
	NTC20	-8.92	14.47
	NTC30	-13.9	8.82
	PU	18.98	42.5

Wet	TC10	18.51	41.92
	TC20	N/A	43.95
	TC30		39.79
	NTC10		41.85
	NTC20		27.12
	NTC30		25.23

Figure A.6 DSC results of dry PU/NTC.

Figure A.6 shows the DSC results of dry PU and PU/NTC samples upon heating in the first two thermal cycles. We can see a remarkable increase of T_g in the second thermal cycle in all samples. For PU sample, T_g increases by about 17.5°C, from 22.93°C in the first cycle to 40.61°C in the second cycle. The T_g of NTC10 is 14.47°C in the first cycle, while that of the second is 29.28°C, i.e., a 15°C increase is observed. However, for NTC20 and NTC30, the T_g of them in the first cycle is below 0°C (-8.92°C and

-13.90°C, respectively). After one cycle, the T_g of NTC20 is 14.47°C (increased by 23.5°C), while that of NTC30 is 8.82°C (the increment is around 22.5°C). It reveals that

- The samples were not exactly dry. The moisture absorbed in the dry samples might be from the air inside the container (the humidity is very high in Singapore).
- NTC has great influence on the T_g of PU/NTC composite. The more NTC in the composite, the lower the T_g is.

Figure A.7 DSC results of dry PU/TC.

Figure A.7 plots the DSC results of dry PU/TC upon heating in the first two cycles. The results of PU are also plotted as a reference for comparison. Referring to Table A1, T_g of all composites in the first cycle is low. But after one cycle, they are about the same as that of PU. A lower T_g in the first cycle should be largely due to the influence of moisture. However, the finding that after one cycle, T_g becomes very close to that of PU

indicates the negligible influence of TC on the T_g of PU/TC.

Figure A.8 presents the DSC results of wet PU/NTC. As compared with Figure A.6, we can see noticeable difference in all PU/NTC in the first cycle, i.e., there are two apparent troughs. The first trough at around 0°C should be the result of the phase transformation from ice to water, while the second one looks a bit abnormal, i.e. 1) the bottom of the second trough is located at somewhere well above T_g of even dry PU; 2) the trough is over a very wide temperature range. We have not found either a good explanation to such an appearance of the second trough or a way to derive T_g out of it. Nevertheless, the results of the second cycle seemingly back to normal. However, a closer-look (referring to Table A1) reveals that the T_g is much higher than that of dry PU/NTC in the second cycle, in particular NTC10 has about the same T_g as that of PU. This is very hard to image, since our above-study on dry PU/NTC concludes that NTC should have a strong influence on the T_g of PU/NTC composites. To double check if these dry PU/NTCs were really dry after three cycles, the forth thermal cycle was conducted on the dry PU/NTCs with the highest temperature set as 180°C instead of 150°C as previously done. However, we can hardly see any significant variation in T_g in this cycle, which proves that the influence of moisture is not the reason. We leave this issue at the time being and will get back to it a while later.

Figure A.8 DSC results of wet PU/NTC.

Figure A.9 DSC results of wet PU/TC.

Wet PU/TCs have the same two-trough phenomenon (Figure A.9) as in wet PU/NTCs. However, after one cycle, all samples have the virtually same T_g as that of PU. This confirms that TC itself has no influence on the T_g of composites.

Figures A.10 and A.11 plot the TGA results of both dry and wet PU/NTC and PU/TC,

respectively. They confirm that the dry samples were not exactly water free, but with much less moisture as compared with the wet ones. It proves that PU/AT has good capability in moisture absorption. Thus, PU/AT may be used for quick water actuated recovery (Huang *et al* 2005).

Since the wet samples had been immersed in water for a very long period, we may consider them as saturated. Similar to that in (Yang *et al* 2005), we may take 240°C as the temperature that PU is moisture-free. Subsequently, from the TGA result of wet PU, we can find that the weight percentage of the maximum moisture absorption in PU is 3.51%. As a first order approximation, we may assume this value as a constant in both saturated PU and saturated PU/AT. Consequently, the moisture absorption ratio in NTC of wet PU/NTC can be quantitatively determined as around 35% (in weight percentage) and that in TC of wet PU/TC only 5%.

Figure A.10 TGA results of PU/NTC.

Figure A.11 TGA results of PU/TC.

On the other hand, as a rough estimation, we may take the moisture absorption ratio of dry PU as a reference to investigate the moisture absorption in NTC or TC of dry PU/AT. The moisture absorption ratio in NTC of dry PU/NTC is found to be about 15%, while that in TC of PU/TC is around 2%.

A.2.3 Conclusions

In addition to confirm the strong influence of moisture on the T_g of PU/AT composites, we find that

- TC itself has not much influence on the T_g of PU/TC composites. As such, after one thermal cycle (i.e. drying upon heating to over 150°C), PU/TC has about the same T_g as that of PU.
- NTC itself can significantly decrease the T_g of PU/NTC. The more NTC in the composite, the lower the T_g is.

- However, drying of saturated PU/NTC results in a much high T_g as compared with that in slightly wetted ones. This is most likely due to the shrinkage of NTC upon drying, which causes the partial detachment of NTC from PU.

A.3 SMP brushes with shape memory effect

The surface pattern of SMP brushes possessing shape memory effect is produced and investigated in this section.

A.3.1 Sample preparation and experiments

The polyurethane SMP solution from Diaplex Co.Ltd (MS-5510) was used in this study. It consists of 30 wt% of SMP and 70 wt% of DMF. Nickel powder, which is ferromagnetic and electronically conductive, with an average size from 3 to 7 μm and purity of 99.8% were bought from Goodfellow.

Two types of SMP thin films mixed with different volume fractions of Ni powders were prepared.

Figure A.12 Illustration of setup for sample preparation.

SMP with vertical Ni chains was fabricated by applying magnetic field in the following procedure: First, Ni powders were mixed with the SMP/DMF solution and stirred for uniform dispersion. After that, the highly viscous mixture was poured into a 4 mm diameter petri dish (the final height is about 1.5 to 2.0 mm). Two magnets were placed in a way as shown in Figure A.12 with a gap of 30 mm in between. The petri dish was placed between the two magnets. The whole setup (including the petri dish) was placed in an air-tightened box and kept in an oven for 48 hours at a constant temperature of 80°C for drying. After the volatilization of DMF, the samples with vertical Ni chains were fabricated. This group of samples were named chained samples. Another group of samples was prepared without applying the magnetic field, so that Ni particles were randomly distributed within the SMP matrix. This group of samples were named random sample.

A.3.2 Results and discussions

A. Vertical protrusive chain and its shape recovery effect

We study the variation of surface pattern of protrusive arrays which possess shape memory effect. The magnetic static field in the SMP matrix results in the formation of vertical chain along the direction of magnetic field. Figure A.13 shows the distribution of vertical chains with different contents of Ni powder.

Figure A.13 Distributions of vertical protrusive chains (Ni powder contents: a, 0.5%; b, 1%; c, 2%; d, 3%; e, 5%).

Figure A.14 Top-view of vertical protrusive chains (2%).

Figure A.14 reveals that the vertical chains distribute randomly in the SMP matrix. The

distance between adjacent chains decreases with increasing Ni powder fraction. The height and diameter of vertical chain increase with increasing the content of Ni powder filler (Figure A.15).

Figure A.15 Dimensions of vertical chains.

Figure A.16 Shape recovery sequence of vertical chains.

Figure A.16 shows the thermomechanical cycle of chained sample.

The procedure of the experiment performed is as follows: 1. Heat the SMP with vertical chains above T_g (original shape); 2. Compress the chained sample at 130°C (above T_g) by a piece of aluminium plate and cool well below T_g keeping the external constraint to freeze the bent configuration(150-180°) of Ni chains (pre-deformation); 3. Remove the constraint, the Ni vertical chains will not start to recover, thereby obtaining the bent configuration (storage); 4. Heat the deformed SMP to 80°C, then the bent chains recover to the vertically straight shape(0-45°).

B. Thermomechanical properties of random samples

The moisture content in PU-based SMP matrix can influence the thermomechanical properties of SMP significantly. In order to evaluate the concentration of moisture in SMP, TGA was conducted on pure SMP and Figure A.17 shows the result.

In Figure A.17 (a), the curves, especially for a short time of drying, drop gradually till 230°C. Then, the curves remain horizontal in the range from 230°C to 270°C where the weight of SMP is constant (the moisture is completely removed). Finally, all the curves drop sharply at about 270°C where the composite begin to decompose. Thus, we employ the weight loss at 230°C to define the weight fraction of moisture in SMP, shown in figure A.17 (b). The moisture content decreased significantly as the drying time progressed. At about 8 hours of drying, the moisture content in SMP was completely removed. Therefore, the random and chained samples used for other experiments were dried for 8 hours.

(a)

(b)

Figure A.17 TGA results of pure SMP (a) weight versus temperature; (b) weight versus time of drying.

Figure A.18 (a) plots the DSC results of random samples. It is obvious that the normalized amount of endotherm decreases with increasing the concentration of Ni powders in SMP matrix. It also shows a slight trend in the shift of transition range to a lower temperature with the increase of Ni content. The glass transition occurs between 35°C and 55°C . The glass transition in polymers is within a temperature

range. There are many ways to define T_g . In order to avoid any confusion, we define T_g as the peak point after differentiating either a DSC or DMA curve against temperature. From Figure A.18 (b), the T_g is relatively stable within this amount of incorporated Ni powder.

(a)

(b)

Figure A.18 DSC results of random samples.

Figure A.19 (a) shows the storage modulus vs. temperature curves of random samples from DMA test. The range of glass transition is about 30-50°C, which coincides well

with the results from DSC. The storage modulus in rubbery state is lower than that in glassy state by an order of 100. Furthermore, it is obvious that the storage modulus at 0°C increase with increasing the concentration of Ni powder, corresponding to a reinforcement of the nickel powder filler. From Figure A.19 (b), it is observed that T_g decrease slightly by increasing the Ni powder content.

(a)

(b)

Figure A.19 Storage modulus versus temperature in DMA test.

A.3.3 Remarks

We characterize the thermomechanical properties of SMP filled with different amount of nickel powders. With an increase in Ni contents, the modulus of polymer increases, while the glass transition temperature (T_g) drops. Furthermore, we successfully fabricated the SMP with Ni powder chains by applying vertical magnetic field. The vertical protrusive chains show favorable shape recovery performances under special thermomechanical cycles.

APPENDIX B

B.1 Subroutine for defining the material properties of PSSMP

```
subroutine vumat(  
C read only -  
  1 nblock, ndir, nshr, nstatev, nfieldv, nprops, lanneal,  
  2 stepTime, totalTime, dt, cmname, coordMp, charLength,  
  3 props, density, strainInc, relspinInc,  
  4 tempOld, stretchOld, defgradOld, fieldOld,  
  5 stressOld, stateOld, enerInternOld, enerInelasOld,  
  6 tempNew, stretchNew, defgradNew, fieldNew,  
C Write only -  
  7 stressNew, stateNew, enerInternNew, enerInelasNew)  
C include 'vaba_param.inc'  
C  
C Define state variables and set N=3 alpha=N+1  
C The state variables are stored as:  
C   STATE(*,1)=phi  
C   STATE(*,2)=mu(up0)  
C   STATE(*,3)=mu(up1)  
C   STATE(*,4)=mu(up2)  
C   STATE(*,5)=mu(up3)  
C   STATE(*,6)=s(up0)  
C   STATE(*,7)=s(up1)  
C   STATE(*,8)=s(up2)  
C   STATE(*,9)=s(up3)  
C   STATE(*,10)=A(up0_component 11)  
C   STATE(*,11)=A(up0_component 22)  
C   STATE(*,12)=A(up0_component 33)  
C   STATE(*,13)=A(up0_component 12)  
C   STATE(*,14)=A(up0_component 23)  
C   STATE(*,15)=A(up0_component 31)  
C   STATE(*,16)=A(up0_component 21)  
C   STATE(*,17)=A(up0_component 32)  
C   STATE(*,18)=A(up0_component 13)  
C  
C   STATE(*,19)=A(up1_component 11)
```

```

C    STATE(*,20)=A(up1_component 22)
C    STATE(*,21)=A(up1_component 33)
C    STATE(*,22)=A(up1_component 12)
C    STATE(*,23)=A(up1_component 23)
C    STATE(*,24)=A(up1_component 31)
C    STATE(*,25)=A(up0_component 21)
C    STATE(*,26)=A(up0_component 32)
C    STATE(*,27)=A(up0_component 13)
C
C    STATE(*,28)=A(up2_component 11)
C    STATE(*,29)=A(up2_component 22)
C    STATE(*,30)=A(up2_component 33)
C    STATE(*,31)=A(up2_component 12)
C    STATE(*,32)=A(up2_component 23)
C    STATE(*,33)=A(up2_component 31)
C    STATE(*,34)=A(up0_component 21)
C    STATE(*,35)=A(up0_component 32)
C    STATE(*,36)=A(up0_component 13)
C
C    STATE(*,37)=A(up3_component 11)
C    STATE(*,38)=A(up3_component 22)
C    STATE(*,39)=A(up3_component 33)
C    STATE(*,40)=A(up3_component 12)
C    STATE(*,41)=A(up3_component 23)
C    STATE(*,42)=A(up3_component 31)
C    STATE(*,43)=A(up0_component 21)
C    STATE(*,44)=A(up0_component 32)
C    STATE(*,45)=A(up0_component 13)
C
C    STATE(*,46)=Fp(component 11)
C    STATE(*,47)=Fp(component 22)
C    STATE(*,48)=Fp(component 33)
C    STATE(*,49)=Fp(component 12)
C    STATE(*,50)=Fp(component 23)
C    STATE(*,51)=Fp(component 31)
C    STATE(*,52)=Fp(component 21)
C    STATE(*,53)=Fp(component 32)
C    STATE(*,54)=Fp(component 13)
C
dimension props(nprops), density(nblock),
1 coordMp(nblock,*),
2 charLength(nblock), strainInc (nblock, ndir+nshr),
3 relSpinInc(nblock,nshr), tempOld(nblock),
4 stretchOld(nblock,ndir+nshr),

```

```

5 defgradOld(nblock,ndir+nshr+nshr),
6 fieldOld(nblock,nfieldv), stressOld(nblock, ndir+nshr),
7 stateOld(nblock,nstatev), enerInternOld(nblock),
8 enerInelasOld(nblock), tempNew(nblock),
9 stretchNew(nblock, ndir+nshr),
1 defgradNew(nblock, ndir+nshr+nshr),
2 fieldNew(nblock,nfieldv),
3 stressNew(nblock,ndir+nshr), stateNew(nblock,nstatev),
4 enerInternNew(nblock),enerInelasNew(nblock)

```

C

```
character*80 cmname
```

C

C Defination

```

real :: S_B(9)=0
real :: F(9)=0
real :: C(9)=0
real :: EigenC(3)=0
real :: EigenU(3)=0
real :: EigenE(3)=0
real :: FT(9)=0
real :: E(9)=0
real :: Fstar(9)=0
real :: FstarT(9)=0
real :: Cstar(9)=0
real :: Bstar(9)=0
real :: Bstar0(9)=0
real :: Fp(9)=0
real :: Fp_Inv(9)=0
real :: Fe(9)=0
real :: FeT(9)=0
real :: Ce(9)=0
real :: EigenCe(3)=0
real :: Ue_arg(9)=0
real :: Ue_argInv(9)=0
real :: Ue(9)=0
real :: EigenUe(3)=0
real :: EigenEe(3)=0
real :: Ee(9)=0
real :: Ee0(9)=0
real :: S_Ae(9)=0
real :: S_Ae0(9)=0
real :: Sback(4,9)=0
real :: Sback0(4,9)=0

```

```

real :: sigmaeff(4,9)=0
real :: sigmaeff_det(4)=0
real :: tao(4)=0
real :: nu(4)=0
real :: Dp_arg(4,9)=0
real :: Dp(9)=0
real :: Fp_dot(9)=0
real :: Fp_next(9)=0
real :: phi=0
real :: phi_dot=0
real :: phi_next=0
real :: mu(4)=0
real :: mu_dot(4)=0
real :: mu_next(4)=0
real :: s(4)=0
real :: s_sat=0
real :: s0_arg=0
real :: s0_dot=0
real :: A(4,9)=0
real :: A_dot(4,9)=0
real :: A_dot1(9)=0
real :: A_dot2(9)=0
real :: A_next(4,9)=0
real :: Re(9)=0
real :: ReT(9)=0
real :: T_Aarg1(9)=0
real :: T_Aarg2(9)=0
real :: T_A(9)=0
real :: T_B(9)=0
real :: T(9)=0
real :: T_4(4)=0
real :: sigma_org(1,9)=0
real :: sigma(1,6)=0
real :: Ubar,Cstartrace,arg,arg_abs,Invlang,mu_lang
real :: Eetrace,pai,i,j,si_0,arg_sign,Jacob,s_next
real :: Matrix_unit(9)=0
real :: lambda_l,G,K,mu_r,s_cv,h_0,phi_i,phi_cv,g_0
real :: b,s0_1,s0_2,s0_3,s0_4,mu0_1,mu0_2,mu0_3,mu0_4
real :: mu_sat1,mu_sat2,mu_sat3,mu_sat4,c1,c2,c3,c4
real :: nu0_1,nu0_2,nu0_3,nu0_4,m1,m2,m3,m4,alpa_p
real :: trace
real :: strain(9)=0
real :: strain_abs(9)=0
real :: stress_abs(9)=0

```

```

real :: alpha=4.0,one=1.0,two=2.0,three=3.0,third=0, Nthird=0
real :: defgradNew_det=0
real :: h=0,nu_try(4)=0,z=0,z1=0
C
C
C end of defination
C parameter(alpha=4.,one=1.,two=2.,three=3.,third=one/three,
C 1 Nthird=(-1.0)*third)
C Below defining the props in the input file given in *USER
MATERIAL,CONSTANTS=35
C comma and 8 in a line
G          =props(1)
K          =props(2)
mu_r       =props(3)
lambda_1   =props(4)
s_cv       =props(5)
h_0        =props(6)
phi_i      =props(7)
phi_cv     =props(8)
g_0        =props(9)
b          =props(10)
s0_1       =props(11)
s0_2       =props(12)
s0_3       =props(13)
s0_4       =props(14)
mu0_1      =props(15)
mu0_2      =props(16)
mu0_3      =props(17)
mu0_4      =props(18)
mu_sat1    =props(19)
mu_sat2    =props(20)
mu_sat3    =props(21)
mu_sat4    =props(22)
c1         =props(23)
c2         =props(24)
c3         =props(25)
c4         =props(26)
nu0_1      =props(27)
nu0_2      =props(28)
nu0_3      =props(29)
nu0_4      =props(30)
m1         =props(31)
m2         =props(32)
m3         =props(33)

```

```

        m4          =props(34)
        alpa_p      =props(35)
C
C Initialization
C Given in the job-1 input file before step
C *initial conditions, type=solution, comma, 8 in a line
C Initialize Fp(X,0)=1
C     STATE(1,46)=1
C     STATE(1,47)=1
C     STATE(1,48)=1
C     STATE(1,49)=0
C     STATE(1,50)=0
C     STATE(1,51)=0
C     STATE(1,52)=0
C     STATE(1,53)=0
C     STATE(1,54)=0
C
C Initialize phi
C     STATE(1,1)=0
C
C Initialize s(1,:)=s0
C     STATE(1,6)=28.5
C     STATE(1,7)=8.66
C     STATE(1,8)=11.55
C     STATE(1,9)=14.43
C Initialize mu(1,:)=mu0
C     STATE(1,2)=1
C     STATE(1,3)=2000
C     STATE(1,4)=2000
C     STATE(1,5)=2000
C Initialize A(X,0)=1
C     STATE(1,10)=1
C     STATE(1,11)=1
C     STATE(1,12)=1
C     STATE(1,13)=0
C     STATE(1,14)=0
C     STATE(1,15)=0
C     STATE(1,16)=0
C     STATE(1,17)=0
C     STATE(1,18)=0
C
C     STATE(1,19)=1
C     STATE(1,20)=1
C     STATE(1,21)=1

```

```

C    STATE(1,22)=0
C    STATE(1,23)=0
C    STATE(1,24)=0
C    STATE(1,25)=0
C    STATE(1,26)=0
C    STATE(1,27)=0
C
C    STATE(1,28)=1
C    STATE(1,29)=1
C    STATE(1,30)=1
C    STATE(1,31)=0
C    STATE(1,32)=0
C    STATE(1,33)=0
C    STATE(1,34)=0
C    STATE(1,35)=0
C    STATE(1,36)=0
C
C    STATE(1,37)=1
C    STATE(1,38)=1
C    STATE(1,39)=1
C    STATE(1,40)=0
C    STATE(1,41)=0
C    STATE(1,42)=0
C    STATE(1,43)=0
C    STATE(1,44)=0
C    STATE(1,45)=0
C end of initialization
C Dp plastic stretches from every micro-mechanism
C
C Begin Computation
C
C    Matrix_unit(1)=1
C    Matrix_unit(2)=1
C    Matrix_unit(3)=1
C    Matrix_unit(4)=0
C    Matrix_unit(5)=0
C    Matrix_unit(6)=0
C    Matrix_unit(7)=0
C    Matrix_unit(8)=0
C    Matrix_unit(9)=0
C    open(unit=150,file='C:\SIMULIA\ABAQUS work\Aems1\output.dat',
C        1 access='append')
C
C    write(150,*)"nblock=",nblock

```



```

third=1.0/3.0
Nthird=(-1)*third
if ( stepTime .eq. zero ) then
    do k = 1, nblock
*      Trial stress
        trace = strainInc(k,1) + strainInc(k,2) + strainInc(k,3)
        stressNew(k,1) = stressOld(k,1)
*          + 2*G * strainInc(k,1) + K * trace
        stressNew(k,2) = stressOld(k,2)
*          + 2*G * strainInc(k,2) + K * trace
        stressNew(k,3) = stressOld(k,3)
*          + 2*G * strainInc(k,3) + K * trace
        stressNew(k,4)=stressOld(k,4) + 2*G * strainInc(k,4)
    end do
    else
    do 100 i=1,nblock
    h=h+1
C   write(150,*)"counting=",h
    strain(1:4)=strain(1:4)+strainInc(i,:)
C   write(150,*)"strain",strain
    strain_abs=abs(strain)
C   write(150,*)strain_abs(2)
C   write(150,*)"strainInc(i,:)",strainInc(i,:)
C   write(150,*)"defgradNew(i,:)",defgradNew(i,:)
    call Det(defgradNew(i,:),defgradNew_det)
C   write(150,*)"defgradNew_det",defgradNew_det
C   write(150,*)stretchNew(i,:)
C   write(150,*)"dt",dt
C calculate the stress due to B system
    F(1:5)=defgradOld(i,:)
C   write(150,*)defgradOld(i,:)
C   write(150,*)"defgradOld(i,:)",defgradOld(i,:)
C   write(150,*)"F",F(:)
C   write(150,*)F(1:3)
    call Array_Transpose(F,FT)
    call Multiply(FT,F,C)
C   write(150,*)"C",C(:)
    call Eigen(C,EigenC)
C   write(150,*)"EigenC",EigenC
    EigenU=sqrt(EigenC)
C   write(150,*)"EigenU",EigenU
    EigenE=log(EigenU)
    call Eigentomatrix(EigenE,E)
C   write(150,*)"E",E

```

```

C  write(150,*)E(2)
   call Det(F,Jacob)
C  write(150,*)"Jacob",Jacob
   if (Jacob <=0.0) then
C      write (150,*)"WRONG Jacob<=0, i=",i
   end if
C  write(150,*)"Nthird",Nthird
   z=Jacob**Nthird
C  write(150,*)"z",z
   Fstar=z*F
C  write(150,*)"Fstar",Fstar
   call Array_Transpose(Fstar,FstarT)
C  write(150,*)"FstarT",FstarT
   call Multiply(FstarT,Fstar,Cstar)
C  write(150,*)"Cstar",Cstar
   call Multiply(Fstar,FstarT,Bstar)
C  write(150,*)"Bstar",Bstar
   Cstartrace=Cstar(1)+Cstar(2)+Cstar(3)
C  write(150,*)"Cstartrace",Cstartrace
   Ubar=SQRT(Cstartrace)/SQRT(three)
C  write(150,*)"Ubar",Ubar
C  write(150,*)Ubar
   arg=Ubar/lambda_1
C  write(150,*)"arg",arg
   arg_abs=ABS(arg)
C  write(150,*)"arg_abs",arg_abs
   if(arg_abs>0.AND.arg_abs<0.84136) then
       Invlang=1.31446*TAN(1.58986*arg)+0.91209*arg
   elseif(arg_abs<1) then
       call Sign(arg,arg_sign)
       Invlang=one/(arg_sign-arg)
   else
C       write(150,*) "error in inverse langevin argument i=", i
   end if
C  write(150,*)"Invlang",Invlang
C  write(150,*)Invlang
   mu_lang=mu_r*(lambda_1/(three*Ubar))*Invlang
C  write(150,*)"mu_B",mu_lang
   call Deviatoric(Bstar,Bstar0)
C  write(150,*)"Bstar0",Bstar0
   S_B=(1/Jacob)*mu_lang*Bstar0
   z1=1/Jacob
   z2=z1*mu_lang
C  write(150,*)"z1",z1

```

```

C  write(150,*)"z2",z2
C  write(150,*)"T_B",T_B
  T_B=S_B
C  write(150,*)T_B(2)
C calculate the plastic stretching due to the A system
  mu(1)=stateOld(i,2)
  mu(2)=stateOld(i,3)
  mu(3)=stateOld(i,4)
  mu(4)=stateOld(i,5)
C  write(150,*)"mu",mu
  A(1,:)=stateOld(i,10:18)
  A(2,:)=stateOld(i,19:27)
  A(3,:)=stateOld(i,28:36)
  A(4,:)=stateOld(i,37:45)
C  write(150,*)"A(1,:) ",A(1,:)
C  write(150,*)A(1,2)
C  write(150,*)"A(2,:) ",A(2,:)
C  write(150,*)"A(3,:) ",A(3,:)
C  write(150,*)"A(4,:) ",A(4,:)
  Sback(1,:)=mu(1)*A(1,:)
  Sback(2,:)=mu(2)*A(2,:)
  Sback(3,:)=mu(3)*A(3,:)
  Sback(4,:)=mu(4)*A(4,:)
C  write(150,*)"Sback(1,:) ",Sback(1,:)
C  write(150,*)Sback(1,1:3)
C  write(150,*)"Sback(2,:) ",Sback(2,:)
C  write(150,*)"Sback(3,:) ",Sback(3,:)
C  write(150,*)"Sback(4,:) ",Sback(4,:)
C
  Fp=StateOld(i,46:54)
C  write(150,*)"Fp",Fp
C  write(150,*)Fp(1:3)
  call Inverse(Fp,Fp_Inv)
C  write(150,*)"Fp_Inv",Fp_Inv
  call Multiply(F,Fp_Inv,Fe)
C  write(150,*)"Fe",Fe
C  write(150,*)Fe(2)
  call Array_Transpose(Fe,FeT)
  call Multiply(FeT,Fe,Ce)
C  write(150,*)"Ce",Ce
  call Eigen(Ce,EigenCe)
C  write(150,*)"EigenCe",EigenCe
  EigenUe=sqrt(EigenCe)
  call Eigentomatrix(EigenUe,Ue_arg)

```

```

C  write(150,*)"EigenUe",EigenUe
   EigenEe=log(EigenUe)
C  write(150,*)"EigenEe",EigenEe
   call Eigentomatrix(EigenEe,Ee)
C  write(150,*)"Ee",Ee
C  write(150,*)Ee(1:3)
   call Deviatoric(Ee,Ee0)
C  write(150,*)"Ee0",Ee0
   Eetrace=Ee(1)+Ee(2)+Ee(3)
C  write(150,*)"Eetrace",Eetrace
   S_Ae=2*G*Ee0+K*Eetrace*Matrix_unit
C  write(150,*)"S_Ae",S_Ae
C  write(150,*)S_Ae(1:3)
   S_Aetrace=S_Ae(1)+S_Ae(2)+S_Ae(3)
C  write(150,*)"S_Aetrace",S_Aetrace
   call Deviatoric(S_Ae,S_Ae0)
C  write(150,*)"S_Ae0",S_Ae0
   call Deviatoric(Sback(1,:),Sback0(1,:))
   call Deviatoric(Sback(2,:),Sback0(2,:))
   call Deviatoric(Sback(3,:),Sback0(3,:))
   call Deviatoric(Sback(4,:),Sback0(4,:))
C  write(150,*)"Sback0(1,:) ",Sback0(1,:)
C  write(150,*)"Sback0(2,:) ",Sback0(2,:)
C  write(150,*)"Sback0(3,:) ",Sback0(3,:)
C  write(150,*)"Sback0(4,:) ",Sback0(4,:)
   sigmaeff(1,:)=S_Ae0-Sback0(1,:)
   sigmaeff(2,:)=S_Ae0-Sback0(2,:)
   sigmaeff(3,:)=S_Ae0-Sback0(3,:)
   sigmaeff(4,:)=S_Ae0-Sback0(4,:)
C  write(150,*)"sigmaeff(1,:) ",sigmaeff(1,:)
C  write(150,*)"sigmaeff(2,:) ",sigmaeff(2,:)
C  write(150,*)"sigmaeff(3,:) ",sigmaeff(3,:)
C  write(150,*)"sigmaeff(4,:) ",sigmaeff(4,:)
   call Det(sigmaeff(1,:),sigmaeff_det(1))
   call Det(sigmaeff(2,:),sigmaeff_det(2))
   call Det(sigmaeff(3,:),sigmaeff_det(3))
   call Det(sigmaeff(4,:),sigmaeff_det(4))
C  write(150,*)"sigmaeff_det",sigmaeff_det
   tao=sqrt(0.5)*abs(sigmaeff_det)
C  write(150,*)"tao",tao
C  write(150,*)tao
   pai=(-1.0/3.0)*S_Aetrace
C  write(150,*)"pai",pai
   s(1)=stateOld(i,6)

```

```

s(2)=stateOld(i,7)
s(3)=stateOld(i,8)
s(4)=stateOld(i,9)
C write(150,*)"s",s
C write(150,*)s(1)
nu_try(1)=tao(1)/(s(1)+alpa_p*pai)
nu_try(4)=tao(4)/(s(4)+alpa_p*pai)
nu(1)=nu0_1*((tao(1)/(s(1)+alpa_p*pai))**(1.0/m1))
nu(2)=nu0_2*((tao(2)/(s(2)+alpa_p*pai))**(1.0/m2))
nu(3)=nu0_3*((tao(3)/(s(3)+alpa_p*pai))**(1.0/m3))
nu(4)=nu0_4*((tao(4)/(s(4)+alpa_p*pai))**(1.0/m4))
C write(150,*)"nu_try",nu_try
C write(150,*)"alpa_p",alpa_p
C write(150,*)"m",m1,m2,m3,m4
C write(150,*)"nu0",nu0_1,nu0_2,nu0_3,nu0_4
C write(150,*)"nu",nu
C write(150,*)nu(1)
Dp_arg(1,:)=nu(1)*(sigmaeff(1,:)/(2*tao(1)))
Dp_arg(2,:)=nu(2)*(sigmaeff(2,:)/(2*tao(2)))
Dp_arg(3,:)=nu(3)*(sigmaeff(3,:)/(2*tao(3)))
Dp_arg(4,:)=nu(4)*(sigmaeff(4,:)/(2*tao(4)))
C write(150,*)"Dp_arg(1,:) ",Dp_arg(1,:)
C write(150,*)Dp_arg(1,2)
C write(150,*)"Dp_arg(2,:) ",Dp_arg(2,:)
C write(150,*)"Dp_arg(3,:) ",Dp_arg(3,:)
C write(150,*)"Dp_arg(4,:) ",Dp_arg(4,:)
do j=1,9,1
    Dp(j)=sum(Dp_arg(:,j))
end do
C write(150,*)"Dp",Dp
C write(150,*)Dp(2)
C
C
C Update Up
C
    call Multiply(Dp,Fp,Fp_dot)
C write(150,*)"Fp_dot",Fp_dot
C write(150,*)"dt",dt
Fp_next=Fp+dt*Fp_dot
C write(150,*)"Fp_next",Fp_next
stateNew(i,46:54)=Fp_next
C write(150,*)"stateNew(i,46:54)",stateNew(i,46:54)
C
C Update free volume phi

```

```

C
  phi=stateOld(i,1)
C  write(150,*)"phi",phi
C  write(150,*)phi
C  write(150,*)"phi_cv",phi_cv
C  write(150,*)"s_cv",s_cv
C  write(150,*)"g_0",g_0
  if (phi<=phi_cv) then
    phi_dot=g_0*((s(1)/s_cv)-1)*nu(1)
  else
    phi_dot=0
  end if
C  write(150,*)phi_dot
C  write(150,*)"phi_dot",phi_dot
  phi_next=phi+phi_dot*dt
C  write(150,*)"phi_next",phi_next
  stateNew(i,1)=phi_next
C  write(150,*)"stateNew(i,1)",stateNew(i,1)
C
C Update mu's
C
  mu_dot(1)=c1*(1-(mu(1)/mu_sat1))*phi_dot
  mu_dot(2)=c2*(1-(mu(2)/mu_sat2))*phi_dot
  mu_dot(3)=c3*(1-(mu(3)/mu_sat3))*phi_dot
  mu_dot(4)=c4*(1-(mu(4)/mu_sat4))*phi_dot
  mu_next=mu+mu_dot*dt
  stateNew(i,2)=mu_next(1)
  stateNew(i,3)=mu_next(2)
  stateNew(i,4)=mu_next(3)
  stateNew(i,5)=mu_next(4)
C  write(150,*)"cs",c1,c2,c3,c4
C  write(150,*)"mu_sats",mu_sat1,mu_sat2,mu_sat3,mu_sat4
C  write(150,*)"mu_dot",mu_dot
C  write(150,*)"dt",dt
C  write(150,*)"mu_next",mu_next
C  write(150,*)"stateNew(i,2:5)",stateNew(i,2:5)
C Update the s's
  s_sat=s_cv*(1+b*(phi_cv-phi))
  s0_arg=1-s(1)/s_sat
  s0_dot=h_0*s0_arg*nu(1)
  s_next=s(1)+s0_dot*dt
  stateNew(i,6)=s_next
  stateNew(i,7)=s(2)
  stateNew(i,8)=s(3)

```

```

stateNew(i,9)=s(4)
C write(150,*)"b",b
C write(150,*)"s_sat",s_sat
C write(150,*)"s0_arg",s0_arg
C write(150,*)"h_0",h_0
C write(150,*)"s0_dot",s0_dot
C write(150,*)"s_next",s_next
C write(150,*)"stateNew(i,6:9)",stateNew(i,6:9)
C Update the A
call Multiply(Dp_arg(1,:),A(1,:),A_dot1)
call Multiply(A(1,:),Dp_arg(1,:),A_dot2)
A_dot(1,:)=A_dot1+A_dot2
C
call Multiply(Dp_arg(2,:),A(2,:),A_dot1)
call Multiply(A(2,:),Dp_arg(2,:),A_dot2)
A_dot(2,:)=A_dot1+A_dot2
C
call Multiply(Dp_arg(3,:),A(3,:),A_dot1)
call Multiply(A(3,:),Dp_arg(3,:),A_dot2)
A_dot(3,:)=A_dot1+A_dot2
C
call Multiply(Dp_arg(4,:),A(4,:),A_dot1)
call Multiply(A(4,:),Dp_arg(4,:),A_dot2)
A_dot(4,:)=A_dot1+A_dot2
C write(150,*)"A_dot(1:)",A_dot(1,:)
C write(150,*)"A_dot(2:)",A_dot(2,:)
C write(150,*)"A_dot(3:)",A_dot(3,:)
C write(150,*)"A_dot(4:)",A_dot(4,:)
A_next=A+A_dot*dt
C write(150,*)"A_next(1:)",A_next(1,:)
C write(150,*)"A_next(2:)",A_next(2,:)
C write(150,*)"A_next(3:)",A_next(3,:)
C write(150,*)"A_next(4:)",A_next(4,:)
stateNew(i,10:18)=A_next(1,:)
stateNew(i,19:27)=A_next(2,:)
stateNew(i,28:36)=A_next(3,:)
stateNew(i,37:45)=A_next(4,:)
C write(150,*)"stateNew(i,10:45)",stateNew(i,10:45)
C Update stress/strain
C write(150,*)"Ue_argInv"
call Inverse(Ue_arg,Ue_argInv)
call Multiply(Fe,Ue_argInv,Re)
call Array_Transpose(Re,ReT)
call Multiply(Re,S_Ae,T_Aarg1)

```

```

    call Multiply(T_Aarg1,ReT,T_Aarg2)
    T_A=(1/Jacob)*T_Aarg2
    T=T_B+T_A
    call From9to4(T,T_4)
    stressNew(i,:)=T_4
    stress_abs=abs(T)
C   write(150,*)stress_abs(2)
C   write(150,*)"Ue_arg",Ue_arg
C   write(150,*)"Ue_argInv",Ue_argInv
C   write(150,*)"Re",Re
C   write(150,*)"ReT",ReT
C   write(150,*)"T_Aarg1",T_Aarg1
C   write(150,*)"T_Aarg2",T_Aarg2
C   write(150,*)"T_A",T_A
C   write(150,*)T_A(2)
C   write(150,*)"T_B",T_B
C   write(150,*)"T",T
C   write(150,*)T(2)
C   write(150,*)"T_4",T_4
C   write(150,*)"stressNew(i,:)",stressNew(i,:)
C   write(150,*)"defgradOld(i,:)",defgradOld(i,:)
100 continue
    end if
    return
end
C
C
C
    subroutine Array_Transpose(X,R)
    implicit none
    real :: X(9)
    real :: R(9)
    R(1)=X(1)
    R(4)=X(7)
    R(9)=X(6)
    R(7)=X(4)
    R(2)=X(2)
    R(5)=X(8)
    R(6)=X(9)
    R(8)=X(5)
    R(3)=X(3)
    return
end subroutine Array_Transpose
C

```


C

```
subroutine Det(X,R)
implicit none
real :: X(9)
real :: R
R=X(1)*X(2)*X(3)+X(4)*X(5)*X(6)+X(9)*X(7)*X(8)-
1 X(1)*X(5)*X(8)-X(4)*X(7)*X(3)-X(9)*X(2)*X(6)
return
end subroutine Det
```

C

C

```
subroutine Multiply (X1,X2,R)
implicit none
real :: X1(9),X2(9)
real :: R(9)
R(1)=X1(1)*X2(1)+X1(4)*X2(7)+X1(9)*X2(6)
R(4)=X1(1)*X2(4)+X1(4)*X2(2)+X1(9)*X2(8)
R(9)=X1(1)*X2(9)+X1(4)*X2(5)+X1(9)*X2(3)
R(7)=X1(7)*X2(1)+X1(2)*X2(7)+X1(5)*X2(6)
R(2)=X1(7)*X2(4)+X1(2)*X2(2)+X1(5)*X2(8)
R(5)=X1(7)*X2(9)+X1(2)*X2(5)+X1(5)*X2(3)
R(6)=X1(6)*X2(1)+X1(8)*X2(7)+X1(3)*X2(6)
R(8)=X1(6)*X2(4)+X1(8)*X2(2)+X1(3)*X2(8)
R(3)=X1(6)*X2(9)+X1(8)*X2(5)+X1(3)*X2(3)
return
end subroutine Multiply
```

C

C

```
subroutine Inverse (X1,R)
implicit none
real :: X1(9),det,d,b
real :: R(9)
det=X1(1)*X1(2)*X1(3)+X1(4)*X1(5)*X1(6)+X1(9)*X1(7)*X1(8)-
1 X1(1)*X1(5)*X1(8)-X1(4)*X1(7)*X1(3)-X1(9)*X1(2)*X1(6)
if (det==0) then
C write (150,*)"0 det found in function Inverse"
end if
d=1.0/det
b=-1.0/det
R(1)=d*(X1(2)*X1(3)-X1(8)*X1(5))
R(4)=b*(X1(4)*X1(3)-X1(8)*X1(9))
R(9)=d*(X1(4)*X1(5)-X1(2)*X1(9))
R(7)=b*(X1(7)*X1(3)-X1(6)*X1(5))
R(2)=d*(X1(1)*X1(3)-X1(6)*X1(9))
```

```

R(5)=b*(X1(1)*X1(5)-X1(7)*X1(9))
R(6)=d*(X1(7)*X1(8)-X1(2)*X1(6))
R(8)=b*(X1(1)*X1(8)-X1(6)*X1(4))
R(3)=d*(X1(2)*X1(1)-X1(7)*X1(4))
return
end subroutine Inverse

```

C

C

```

subroutine Sign (x,r)
implicit none
real :: x,r
if (x<0) then
  r=-1
else if (x>0) then
  r=1
else
  r=0
end if
return
end subroutine Sign

```

C

C

```

subroutine Deviatoric (X,R)
implicit none
real :: X(9),R(9)
real :: mean
mean=(X(1)+X(2)+X(3))/3.0
R(1)=X(1)-mean
R(4)=X(4)
R(9)=X(9)
R(7)=X(7)
R(2)=X(2)-mean
R(5)=X(5)
R(6)=X(6)
R(8)=X(8)
R(3)=X(3)-mean
return
end subroutine Deviatoric

```

C

C

```

subroutine Eigen(X,R)
implicit none
real :: X(9),R(3),n
complex :: a2,a1,a0,p,q,m

```

```

complex :: s1,s2,z1,z2,z3,i1,i,x1
m=sqrt(3.0)/2.0
i1=-1
i=sqrt(i1)
a2=(-1)*(X(1)+X(2)+X(3))
a1=(-1)*(X(5)*X(8)-X(1)*X(2)-X(1)*X(3)-X(2)*X(3)
  1 +X(4)*X(7)+X(9)*X(6))
a0=(-1)*(X(1)*X(2)*X(3)-X(1)*X(5)*X(8)+X(4)*X(5)*X(6)
  1 -X(7)*X(4)*X(3)+X(9)*X(7)*X(8)-X(9)*X(2)*X(6))
p=((a1*a2)-(3*a0))/6-(a2**3)/27
q=a1/3.0-(a2**2)/9.0
x1=q**3+p**2
s1=(p+((x1)**(1.0/2.0)))*(1.0/3.0)
s2=(p-((x1)**(1.0/2.0)))*(1.0/3.0)
z1=a2/(-3.0)+(s1+s2)
z2=(a2/(-3.0))-((s1+s2)/2.0)+i*m*(s1-s2)
z3=(a2/(-3.0))-((s1+s2)/2.0)-i*m*(s1-s2)
R(1)=z1
R(2)=z2
R(3)=z3
return
end subroutine Eigen

```

C
C

```

subroutine Eigentomatrix(X,R)
implicit none
real::X(3),R(9)
R(1)=X(1)
R(4)=0
R(9)=0
R(7)=0
R(2)=X(2)
R(5)=0
R(6)=0
R(8)=0
R(3)=X(3)
return
end subroutine Eigentomatrix

```

C
C

```

subroutine From9to4(X,R)
implicit none
real :: X(9),R(4)
R=X(1:4)

```

```

    return
end subroutine From9to4
C

SUBROUTINE WFILEIN(HAT,NROW,NCOL,NUNIT)

IMPLICIT DOUBLE PRECISION (A-H,O-Z)
INTEGER I,J,NROW,NCOL,NUNIT
DIMENSION HAT(NROW,NCOL)
CHARACTER(LEN=100) FNAME
C  NFILEUNIT=17
C  CLOSE(NFILEUNIT)
C  OPEN(NFILEUNIT,FILE=FNAME,
C    &    ACCESS='APPEND')

C  WRITE(FILEUNIT,*)"ENTER INTO"
C  WRITE(FILEUNIT,*)NROW
C  WRITE(FILEUNIT,*)NCOL
C  WRITE(FILEUNIT,*)FNAME
C  WRITE(NUNIT,"(/)")
C  DO I=1,NROW
C    DO J=1,NCOL
C      WRITE(NUNIT,"(<NCOL>E20.12)")HAT(I,:)
C    END DO
  END DO
  RETURN
end

```

B.2 Flowchart describing the subroutine

Figure B.1 Flowchart describing the subroutine

Appendix C

C.1 Butterfly shaped features

Some rectangular shaped samples were polished to an average surface roughness of 25.796 nm (R_a). This was achieved by polishing using Mecaprex diamond compound (3 μm and then 1 μm) with lubricant by ECOMET 6. A surface scanning by a WYKO interferometer on 50% stretched (at 80°C) pre-polished sample reveals that there are many micro butterflies on the surface (Figure C.1). Note that, in order to enhance the reflection, a thin layer of gold (around 20 nm) was pre-coated atop the sample surface. The body of the butterflies is parallel to the direction of stretching. Further observation reveals that the body is apparently split into two parts, which suggests that something underneath is broken, so that a sharp valley is formed.

Figure C.1 A typical butterfly (after tension).

Figure C.2 A typical micro butterfly. (a) 2-D view; (b) 3-D view.

Figure C.3 A typical *garden* of micro butterfly of various sizes (from about 6 to 90 μm). Black parts (wings of big butterflies) are areas that the WYKO machine failed to collect data on this scanning scale.

Subsequently, the sample was slightly polished and then heated to 100 $^{\circ}\text{C}$ (held for 1 minute) in a laboratory oven (GRIEVE). New butterfly-shaped features as shown in Figure C.2 emerged everywhere, like a garden of micro butterfly with butterfly sizes ranging from about 6 to 90 μm (Figure C.3). The body of the butterfly (in red) is

protrusion (peak), while the two wings (in blue) are troughs. A closer-look reveals that the bodies of butterflies are more or less perpendicular to the direction of pre-stretching.

Figure C.4 Size of butterfly vs. vertical height.

Figure C.4 shows the approximate relationship of butterfly size against total height of butterfly (height of peak + depth of trough). It is clear that with an increase in butterfly size (measured with WYKO), the total height increases in an almost linear fashion. Figure C.5 shows the formation of butterfly feature and switching process.

Figure C.5 Formation of butterfly and switching.

Appendix D

Publication List

- 1)* **Liu, N.**, Xie, Q., Huang, W.M., Phee, S.J. and Guo, N.Q., Formation of micro protrusion array atop shape memory polymer, *Journal of Micromechanics and Microengineering*, Vol. 18, 2008, 027001
- 2)* **Liu, N.**, Huang, W.M. and Phee, S.J., A secret garden of micro butterflies: phenomenon and mechanism, *Surface Review and Letters*, Vol. 14, No. 6, 2007, pp1187-1190
- 3)* **Liu, N.**, W.M. Huang, Phee, S.J. and Tong, T.H., Formation of micro protrusions atop thermo-responsive shape memory polymer, *Smart Materials and Structures*
- 4)* **Liu, N.**, Huang, W.M., Phee, S.J., Fan, H. and Chew, K.L., A generic approach for producing various protrusive shapes on different size scales using shape-memory polymer, *Smart Materials and Structures*, Vol. 16, 2007, ppN47-N50
- 5) **Liu, N.** and Huang, W.M., Comments on "incomplete transformation induced multiple-step transformation in TiNi shape memory alloys"[Scripta Mater 2005; 53:335], *Scripta Materialia*, Vol.55, 2006, pp493-495
- 6) **Liu, N.** and Huang, W.M., DSC study on temperature memory effect of NiTi shape memory alloy, *Transactions of Nonferrous Metals Society of China*, Vol.16, 2006,

7)* Leng, J.S., Lan, X., Liu, Y.J., Du, S.Y., Huang, W.M., **Liu, N.**, Phee, S.J. and Yuan, Q., Electrical conductivity of thermo-responsive shape-memory polymer with embedded micron sized Ni powder chains, *Applied Physics Letters*, Vol. 92, 2008, 014104

8) Pan, GH, Huang, WM, Ng, ZC, **Liu, N.** and Phee, SJ, Glass transition temperature of polyurethane shape memory polymer reinforced with treated/non-treated attapulgite (playgorskite) clay in dry and wet conditions, *Smart Materials and Structures*, Vol. 17, 2008, 045007

9) Lan, X., Huang, W.M., Leng, J.S., **Liu, N.**, Phee, S.J. and Yuan, Q., Electrically conductive shape-memory polymer with anisotropic electro-thermo-mechanical properties, *GAK Gummi Fasern Kunststoffe*

Selected publications* are attached as follows.

TECHNICAL NOTE

The formation of micro-protrusions atop a thermo-responsive shape memory polymer

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Abstract

We present an experimental investigation on a novel approach to produce micro-sized protrusive features atop a thermo-responsive shape memory polymer (SMP). This approach includes three steps, namely, indenting atop an SMP sample (using a Berkovich indenter in this study), polishing and then heating it for full shape recovery. Apart from ordinary samples, some SMP samples are pre-stretched in the in-plane direction or pre-compressed in the out-of-plane direction.

The relationships between the height/shape of protrusion and the depth of indent are obtained for all indents in samples with/without pre-straining. Intrinsic relationships among the indentation depth, polishing depth and height/shape of protrusion are further revealed quantitatively in a dimensionless manner. The influence of pre-straining is discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The morphology of a polymer surface is of fundamental importance to many applications, for instance, in the fabrication of polymer electronic and optoelectronic devices, fluidic channels, sensor coatings and biotechnology engineering [1–4]. On the other hand, bio-inspired surface structures can offer significant commercial potential in antireflective, self-cleaning or drag-reducing surfaces, and adhesive systems [5]. However, to realize these surface structures by a cost-effective technology is still a big challenge for the scientific and engineering community. Various approaches for patterning atop a polymer surface have been proposed by means of thermal- or electric-field-induced self-organization, moduli mismatch, etc [2, 6–8].

Recently, we have demonstrated a convenient approach to produce different protrusive patterns atop a thermo-responsive shape memory polymer (SMP) at different scales (from millimeter to nanometer) [9, 10]. It was found that, depending

on the pre-strain, type of indent, indentation depth and polishing depth, different sized and shaped protrusions (e.g. flat-top or sharp-top, spherical or pyramidal, isotropic or anisotropic) can be conveniently obtained. In this paper, we present an experimental investigation into the relationships among the pre-strain, indentation/polishing depth, and the size/shape of protrusion. A Berkovich indenter was used to make indents in the course of this study.

2. Sample preparation

A thermo-responsive shape memory styrene copolymer from CRG, USA was used in the current study. The thermally responsive thermosetting styrene SMP was obtained by bulk random copolymerization of monomers. Figure 1 depicts the scanning electron microscopy (SEM) pictures of the fracture surface at different scales for the cryogenically fractured samples of such an SMP. As we can see, the material has the characteristic of a homogeneous polymer matrix with no phase separation. The dynamic mechanical analysis (DMA) results

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Figure 1. SEM picture of cryogenically fractured styrene SMP at different scales.

(figure 2) also confirmed the presence of only a single sharp glass transition temperature, T_g , at about 65.5°C, as evident from the storage modulus curve. A small shoulder on the loss modulus at -33°C representing the β transition is also shown.

The as-received material was in sheet form with a thickness of about 4 mm. Small samples were cut out of the sheets into 10 × 10 mm² squares or 100 × 10 mm² rectangles, and then heated to 100°C in order to release any possible internal pre-stress and/or pre-deformation during processing and fabrication. Subsequently, the samples were polished using the Mecaprex diamond compound (3 μm and then 1 μm)

Figure 2. DMA graph of styrene SMP.

with ECOMET 6 as lubricant. After polishing, no apparent scratches could be found under a microscope and the average surface roughness (R_a) was measured as about 26 nm.

Some of the polished samples were pre-strained. Pre-straining was done by means of stretching along the length direction of rectangular samples or compression in the thickness direction of square samples. It was found that pre-straining at 80°C (which is well above T_g) is an effective way for good shape fixture, i.e. less shape recovery after unloading, and no necking-induced non-uniformity in deformation and no cracking. Hence, pre-straining was carried out using an Instron 5569 with a 500 N load cell at a constant strain rate of 10⁻³ s⁻¹ in a hot chamber at 80°C. The maximum tensile strain was 50%, while the maximum compressive strain was 20%. The maximum strain was held until the sample was cooled back to room temperature (about 23°C) before unloading at the same strain rate. An aluminum block with a well-polished surface was placed atop the SMP sample in order to obtain a smooth SMP surface after pre-compression. Figures 3 and 4 present typical stress versus strain curves in compression and stretching tests, respectively. Note that, in figure 3, a typical stress versus strain curve in compression at room temperature is also presented for comparison, which reveals that pre-deformation at high temperature (well above T_g) is highly efficient for good shape fixture, since the recovery after cooling and then unloading is significantly reduced. The observed overshoot in compression at 23°C is a kind of Lüder-band phenomenon, which has also been observed in shape memory alloys [11].

Samples without pre-straining are named as the original sample hereinafter, while those with compression/stretching are named as the pre-compressed/pre-stretched sample hereinafter.

3. Experiment

A MST NanoInstrument with a Berkovich indenter was used to make micro-sized indents atop the original, pre-compressed and pre-stretched samples. All indentation tests were carried out at room temperature (23°C) in depth control mode. The targeted strain rate was 0.05 s⁻¹ following the XP CSM

Figure 3. Stress versus strain relationships in compression (out-of-plane) at two different temperatures and subsequently unloading at room temperature (23 °C).

Figure 4. Stress versus strain relationship in uniaxial stretching (in-plane) at 80 °C and unloading after cooling back to room temperature (23 °C).

method (selected from an option provided by the machine). After the prescribed maximum depth (i.e. nominal maximum indentation depth) was reached, there was a holding time of 10 s under maximum force before unloading at the same speed. Eight indents with different depths were obtained in each sample. Figure 5 presents a typical WYKO interferometer image of an indent right after indentation. Figure 6 shows the typical force versus indentation depth curves of the original sample.

Twenty-four hours after indentation, the samples were scanned by the WYKO interferometer. The exact depths (D_1) of all indents were obtained. It was found that the measured depths of indents were slightly less than the ones right after indentation, which is largely due to the relaxation of the polymer, together with a possible slight shape recovery at room temperature.

Subsequently, the samples were polished until the indents of medium depth disappeared or nearly disappeared. Hence,

Figure 5. Typical Wyko image of an indent right after indentation. (a) 3D view; (b) top view; (c) cross-sectional view (refer to the white line in (b) for the section).

Figure 6. Typical force versus depth curves in indentation (original sample).

the shallower indents were over-polished, the medium ones were about fully polished and the deeper ones were only partially polished.

After polishing, the indents were scanned by WYKO again, and the actual polishing depth (D_p) and residual depth ($D_1 - D_p$) of the individual indents were determined. Subsequently, the samples were heated to 100 °C for one minute for shape recovery. The resulting protrusive features were measured again by WYKO. Typical protrusions are presented in figure 7.

Figure 7. Typical protrusions. (a) Sharp-top protrusion (3D view, original sample); (b) flat-top protrusion; (c) 50% pre-stretched sample (top view, the direction of pre-straining is vertical; in the horizontal direction, the sample expanded by 8.1% during shape recovery upon heating).

4. Results and discussions

As shown in figure 7, pyramidal-shaped protrusions are obtained atop the SMP. It is noticed that, unlike the protrusions atop the original sample, the protrusions atop the pre-stretched sample are no longer an equilateral triangle. This is due to the

Figure 8. Protrusive height (H) versus indentation depth (D_1). Black filled symbol: flat-top protrusion; gray filled symbol: unclear; hollow symbol: sharp protrusion.

shape recovery after pre-stretching, i.e. contraction in the pre-stretching direction and expansion in the transverse direction (perpendicular to the pre-stretching direction).

On the other hand, it is found that, in the original samples after shape recovery upon heating, the over-polished indents result in relatively smaller but sharp-topped protrusive pyramids, while the height of protrusions (H) resulting from the partially or fully polished indents is about the same as the polishing depth (D_p).

For a quantitative analysis, the measured height of protrusions (H) is plotted against indentation depth (D_1) in figure 8, which reveals that

- (1) For shallow indents (i.e. D_1 is less than around $3 \mu\text{m}$), H increases with the increase of D_1 following a more or less similar linear function for all types of samples.
- (2) For indents with D_1 greater than about $3 \mu\text{m}$, H still increases but gradually with D_1 in all samples. Each sample follows a different line, which is roughly parallel to each other. While the H versus D_1 curve of the pre-stretched sample is at the top, the H versus D_1 curve of the pre-compressed sample is at the lowest position.
- (3) Sharp protrusions are associated with the original shallow indents. On the other hand, deep indents correspond to flat-top protrusions.

It is apparent that not only the indentation depth (D_1), but also the exact polishing depth (D_p) have strong influence on the shape and height of a protrusion. Thus, $(D_1 - D_p)$, which is the residual depth of the indent after polishing, is a more meaningful parameter. In order to find out a clear intrinsic relationship in a dimensionless manner, in figure 9, the protrusive height (H) is normalized by the polishing depth (D_p) and the indent depth after polishing ($D_1 - D_p$) is normalized by that before polishing (D_1). As we can see, for the pre-stretched sample, the relationship between H/D_p and $(D_1 - D_p)/D_1$ is about a linear function. However, for the

Figure 9. Relationship of H/D_p versus $(D_1 - D_p)/D_1$. Black filled symbol: flat-top protrusion; gray filled symbol: unclear; hollow symbol: sharp protrusion.

original and pre-compressed samples, before $(D_1 - D_p)/D_1$ reaches about -0.5 , the H/D_p versus $(D_1 - D_p)/D_1$ curve is virtually linear and parallel to that of the pre-stretched sample, but at a slightly lower position. At $(D_1 - D_p)/D_1$ above -0.5 , H/D_p is about a constant (around 0.8).

Figure 10 illustrates the mechanisms of forming different shaped/sized protrusions by means of over-polishing, fully polishing and partially polishing. First, indents of different depths are made atop an SMP sample surface (figure 10(a)). The dotted gray line represents the region affected by the indentation (i.e. *plastically compressed*). In figure 10(b), a thin layer is polished away so that the shallow indent is over-polished, the medium-sized indent is fully polished and the deep one is partially polished (figure 10(c)). Subsequently, the sample is heated and protrusions result (figure 10(d)). In the partially polished one, a flat-top is formed and the height of the protrusion is the same as the polishing depth. In the over-polished one, the indent is polished away and a sharp protrusion is formed. Here, the protrusion is a result of the shape recovery of the compressed material right underneath the indent. Hence, with the increase in polishing depth, the height of the protrusion decreases until all pre-compressed material is polished away so that no more protrusion can be formed. The fully polished one is supposed to be the boundary between the flat and sharp protrusions. However, as shown in figure 9, H/D_p is 0.8 as revealed by our experiments, but not 1 as expected. Hence, this boundary is actually at a lower $(D_1 - D_p)/D_1$ value (about -0.5). The reason for this is that, during polishing, a thin layer at the bottom of the indent might be polished away as well. This explanation can be largely supported by the observation that, for the original sample, the boundary between the flat-top and sharp-top protrusions is at $(D_1 - D_p)/D_1 \approx 0$ (i.e. fully polishing), as shown in figure 9.

Pre-stretching helps to push the boundary between the flat-top and sharp-top protrusions to a higher $(D_1 - D_p)/D_1$

Figure 10. Formation of different sized and shaped protrusions.

value, which is somewhere between 0.1 – 0.5 in our 50% pre-stretched sample. This is mainly caused by the additional shape recovery (i.e. further increase in H) from pre-stretching. Pre-compression should have a similar effect. However, since we only pre-compressed the sample by 20% , the influence of pre-compression in the thickness direction is not significant in figure 9.

5. Conclusions

We present a systematic investigation on the formation of micro-protrusions atop a thermo-responsive SMP. We show that, depending on the pre-strain, indentation depth and polishing depth, different sized and shaped protrusions can be obtained. If the indent is partially polished, the resulting protrusion is flat-top. On the other hand, if the indent is fully or over-polished, the protrusion is with a sharp-top. The relationships between the height/shape of protrusion and indent depth are obtained for all indents in samples with/without pre-straining. Intrinsic relationships among the indentation depth, polishing depth and height/shape of the protrusion are further revealed quantitatively in a dimensionless manner. The influence of pre-straining is discussed.

Although we used a Berkovich indenter in this study, the conclusions should be largely applicable to other types of indenters.

Acknowledgments

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A SECRET GARDEN OF MICRO BUTTERFLIES: PHENOMENON AND MECHANISM

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Butterfly-shaped features (with sizes from about 6 to 90 μm) were found on the surface of a shape-memory polymer (SMP) after a process of 50% stretching, slightly polishing, and then heating for shape recovery. We identified the underline mechanism, which is evidenced by the switching of butterflies by 90° from the previous direction after stretching. The case discussed here demonstrates the feasibility of using SMPs for patterning up to nanoscale for different shapes.

Keywords: Shape memory polymer; shape recovery; patterning.

Shape-memory polymers (SMPs) and their composites have the capability to recovery a prestrain of a few hundred percents by external stimuli, such as heat, light, moisture, pH change, etc.^{1–9} They have found many applications from stent to microelectromechanical system (e.g., Refs. 10–13). The origin of shape-memory phenomenon in most SMPs is from a kind of hard-segment/soft-segment system. In the case of thermo-responsive SMPs, at a temperature above the glass transition temperature (T_g), the soft-segment is easy for deforming and the hard-segment is much stiffer, while at well-below T_g , the soft-segment can be frozen. As such, one can reshape a piece of SMP easily at above T_g , and then cools it for the new shape reserved. The original shape can be recovered upon heating to above T_g , which is driven by the returning of the hard-segment to the original shape. As the recoverable strain can be a few hundreds percent, SMPs are far better than many other shape memory materials.¹ Recently, it has been demonstrated that shape-memory phenomenon occurs even on 10 nm scale.¹⁴ In this paper, we

report a study of the micro butterfly phenomenon on the surface of a SMP.

The SMP used in this study is styrene copolymer bought from CRG, USA with a T_g about 63°C. The as-received SMP is about 5 mm thick sheets. We cut a small strip out of the sheet, well-polished the strip and then stretched the strip to 50% at 80°C. After cooling back to room temperature (about 22°C), the strip was carefully polished again and then heated to 80°C for shape recovery. Subsequently, we coated the polished surface with a very thin layer of gold (about 10 nm) and then placed the strip under a WYKO interferometer for three-dimensional surface scanning.

The butterfly-shaped feature as shown in Fig. 1 was observed on the surface. Such feature can be found everywhere, like a garden of micro butterflies with sizes ranging from about 6 to 90 μm (Fig. 2). The body of butterfly (in red) is protrusion (peak), while the two wings (in blue) are troughs. A closer-look reveals that the bodies of butterflies are more or less perpendicular to the direction of pre-stretching.

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Fig. 1. A typical micro butterfly. (a) 2D view; (b) 3D view.

Fig. 2. A typical garden of micro butterflies of various sizes (from about 6 to 90 μm). Black parts (wings of big butterflies) are areas that the WYKO machine failed to collect data on this scanning scale.

Figure 3 shows (estimation only) the relationship of butterfly size against total height of butterfly (height of peak + depth of trough). It is clear that with an increase in butterfly size, the

total height increases as well in an about linear fashion.

A study on the surface of just-stretched strip reveals that there are many micro butterflies on the

Fig. 3. Size of butterfly versus vertical height.

surface as well (Fig. 4(d)). However, the body of them is parallel to the direction of stretching. Further observation reveals that the body is apparently split into two parts, which suggests that something underneath is broken, so that a sharp valley is resulted.

Based on the above-observations, we proposed a mechanism for the butterfly phenomenon as follows. Upon stretching at above T_g , the soft-segment can easily manage to accommodate the extension, and a large hard-segment is gradually straightened from the original curve-shape (Figs. 4(a) and 4(b)). After stretched to a certain amount, a weak point in the

big hard-segment (marked point in Fig. 4(b)) may break. Consequently, the stress in the surrounding area is released and recovery occurs in both the hard-segment and the surround soft-segment since the temperature is high (80°C). At the broken-point, the newly generated hard-segment end retreats back from straight shape to become curved slightly, which results in two peaks (corresponding to the newly generated end in hard-segment) and a trough (the gap due to the break of hard-segment) (Fig. 4(c)). It is obvious that the body of butterfly should be more or less parallel to the stretching direction, as this is the direction of the maximum stretching and thus the easiest to break. After cooling back to room temperature, these features should be largely reserved. Figure 4(d) shows a typical butterfly after stretching and cooling, which reveals the exact same morphology as we expect. The subsequent polishing process smooths the sample surface, so that the peaks will be removed and troughs will become shallow or even be fully removed (Fig. 4(e)). After heating to above T_g for one more time, the strip largely recovers its original shape. However, as the material at the previous peak positions has been removed, a two-bottom-trough is formed, while at the previous trough position, peak(s) can be found due to less-polishing. As such, we can see a new butterfly with its body parallel to the stretching direction, i.e., a 90° switch from the previous direction. This is exactly what has happened.

Fig. 4. Mechanism for the formation of butterfly and switching.

To summarize, the break of hard-segment results in the surface uneven, i.e., the original butterfly. After polishing and subsequently heating, the under-polished area (previously a trough) recovers more and turns to be a peak, while the over-polished area (a peak) recovers less, which results in a trough. Hence, the butterfly switches by 90° .

Previous studies of indentation on shape-memory alloys reveal the possibility of achieving very high storage density¹⁵ and micron-sized protrusions (through subsequently polishing and heating for shape recovery).¹⁶ As the recoverable strain in SMPs is normally an order more than that in shape-memory alloys, SMPs should be a more convenient material for patterning of different shapes up to nanoscale. What demonstrated here, i.e., the butterflies, is one of the patterns.

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NOTE

Formation of micro protrusion arrays atop shape memory polymer

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Abstract

Utilizing the significant shape recovery ability (in the order of 100% strain) in shape memory polymers (SMPs), we propose two simple approaches, namely laser heating and indentation, to produce micro-sized protrusion arrays. In the former, after local laser heating a pre-compressed SMP, protrusive bumps can be produced. In the latter, through an indentation-polishing-heating process, various shaped protrusive bumps can be produced. It is to demonstrate that indentation is a more convenient and powerful approach than laser heating, since well controlled, different shaped protrusion arrays can be realized.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Periodic micro/nano-sized arrays are of great interest in many areas [1–3]. For instance, a patterned surface can have a significant influence on the wetting property of materials [4], arrays of magnetic indents are useful as a magnetic storage medium [5] and microlens arrays are required for the fabrication of a variety of functional devices, such as optical refractive elements or smart surfaces that mimic the patterned surfaces in biological systems used to control solids and liquid adhesion [1]. There are a few techniques developed for producing various sized and shaped patterns [6–8]. Apart from the traditional approaches based on electrostatically induced pattern formation [6] and self-assembly [7], laser induced buckling became a rapid and cost-effective approach recently [2]. Despite of these efforts, a cheaper and more convenient approach suitable for mass fabrication is always highly in demand.

The laser is a powerful tool, which can focus high energy into a small area for local heating or machining. A CO₂ laser has been demonstrated as an excellent tool for local annealing NiTi thin films for their crystallization and hence, inducing shape memory behavior [9]. Shape memory alloys (SMAs) have been used to produce protrusive dots and lines after an

Figure 1. Illustration of forming a protrusive bump atop a SMP using a laser. (a) Original sample; (b) pre-compressed; (c) after laser heating, a bump is formed.

indentation-polishing-heating process [10]. Utilizing the far higher shape recovery capability in shape memory polymers (SMPs) (in the order of 100% [11] against about 7% at the most in SMAs [12]) and full shape recovery even in nanometer scale [13], SMPs have been demonstrated as an excellent material for producing various sized and shaped protrusions [14]. The shape memory phenomenon in SMPs is due to their soft/hard segment structure and that the polymer chains being able to undergo micro-Brownian motion at above the glass transition temperature.

The purpose of this paper is to demonstrate two novel approaches for micro patterning, i.e., protrusion arrays, using SMPs.

Figure 2. Setup for laser heating (with microlens array).

2. Material and sample preparation

The SMP used in this study is a thermo-responsive polystyrene SMP from CRG, USA, in sheet form (3.0 mm thick). The glass transition temperature, T_g , is about 62 °C. Square-shaped SMP samples ($10 \times 10 \times 3 \text{ mm}^3$) were cut out of the sheet for the

experiment. In order to achieve a smooth and flat surface, they were manually polished in a step-by-step manner by sandpaper of grit 4000, slurries of 6 μm , 3 μm , 1 μm with polishing liquid, until no obvious defect (including scratches) can be observed under an optical microscope.

3. Laser heating

The working principle of forming a protrusive bump atop SMP by laser heating is illustrated in figure 1. First, a polished SMP sample is pre-compressed. After that a laser beam shines atop its surface. If the laser power is well controlled, so that the temperature is not too high to cause surface melting but enough to trigger the shape recovery, a bump results due to the localized shape recovery in the heated area. Of course, the exact shape and size of the bump depend on not only the many parameters in the laser heating process (e.g., type of laser, spot size of laser beam, pulse energy and exposure time, etc), but also the amount of pre-compression and the thermo-mechanical properties of the exact SMP.

Figure 3. Optical profile and cross-section of a bump.

Figure 4. Protrusion array atop a 20% pre-compressed sample at pulse energy of 2.28 mJ and shutter exposure time of 1 s. The focus of the microlens array (right top) is 795 μm . Top: optical microscopy profile. Bottom: Taylor Hobson profile (3D and cross-section).

On the other hand, if the laser beam moves following a prescribed path, protrusive lines/dots atop the sample can be obtained. This is a promising research direction, but out of the scope of our current study.

In our experiments, well-polished SMP samples were uniaxially compressed in the thickness direction by an Instron 5569 at a loading speed of 10 mm min^{-1} . The setup for subsequent laser heating is illustrated in figure 2.

Figure 3 presents a typical bump (without microlens array in laser heating) atop a SMP sample, which was pre-compressed to a maximum strain of 50%. The point-laser heating was done using a Lightwave SHG Nd:YAG laser (532 nm) with a pulse energy of $14.0 \mu\text{J}$, 10 kHz frequency, $1/30 \text{ s}$ shutter exposure time, $20\times$ objective lens, 310° HWP angle. As we can see, the resulting bump is about $140 \mu\text{m}$ in diameter and $16 \mu\text{m}$ high.

It is not convenient to obtain an array of such bumps by laser heating in a point-by-point manner. Instead, a microlens array can be used, so that after passing through it, the laser beam heats an array of points atop the sample. Consequently, an array of bumps can result simultaneously by one single laser exposure.

Figure 4 reveals an array of protrusive bumps atop a 20% pre-compressed sample. The pulse energy was 2.28 mJ and shutter exposure time was 1 s. Details of two typical bumps (3D and cross-section) were obtained using a Taylor Hobson (112/054DS) at a scanning speed of $300 \mu\text{m s}^{-1}$. The details of two adjacent micro bumps reveal that the height of both bumps is about $8 \mu\text{m}$, but the size of one is about 0.20 mm in diameter, while the other is 0.12 mm only. It is apparent that an array of bumps is achieved, but the size and shape of these bumps are not so uniform. This might be the result of non-uniformity in the properties of SMP and/or the laser beam.

4. Indentation

Our previous work has demonstrated that different sized and shaped protrusions can be produced atop a thermo-responsive SMP by indentation followed by polishing and heating [14]. A schematic illustration of the working principle is presented in figure 5. First, three hard balls are placed atop a well-polished SMP sample and then compressed into the SMP to three different depths. After the removal of these balls, indents of different depths are obtained. It should be pointed out that according to [15], (1) there is a *plastic zone* surrounding each indent; (2) underneath each indent while within the *plastic zone*, the significant deformation is non-elastic and compressive. Subsequently, the sample is slightly polished, so that the middle and right indents disappear, while the left one remains but becomes smaller and shallower. After polishing, the sample is heated to above its T_g , which results in three different shaped and sized protrusions. The left one is with a flat top as it is less polished. The middle one, which is just polished, should be more or less spherical and has approximately the same height as the left one. The right one, which is over polished, is spherical in shape but the smallest in size among these three protrusions.

Figure 5. Illustration of forming a protrusive bump atop SMP by indentation. (a) Original SMP; (b) indented to different depths using hard balls; (c) after indentation; (d) after polishing; (e) after heating, different shaped bumps (left: flat top; middle and right: round top) are formed.

Figure 6. 3D scanning (Taylor Hobson profile) of protrusive arrays (using a Vickers indenter).

An array of indents can be produced using a conventional indentation machine. Thus, after polishing and heating, an array of protrusions can result as shown in figure 6. As a Vickers indenter was used here instead of a spherical ball, the resultant protrusion is pyramid. It is obvious that such a process for making indents is rather time consuming and highly inefficient for mass fabrication.

Figure 7. Taylor Hobson 3D view and cross-section of the surfaces after indenting using steel balls, polishing and then heating. (a) Less-polished sample and (b) over-polished sample.

Figure 8. 3D view of a protrusion array (measured by Nikon ECLIPSE L150). Inset: SEM image.

An alternative is to pack a layer of hard balls atop a SMP and then compress these balls to produce an array of indents simultaneously. Figure 7 reveals two typical results, in which 1 mm diameter hard steel balls were used for making the indents. As the indentation/polishing depths were different, the protrusions in figure 7(a) (less polished) are flat-top, while those in figure 7(b) (over polished) are more or less spherical.

In order to demonstrate the feasibility of utilizing this technique for micro patterning in a cost-efficient manner for mass fabrication, in the next experiment, 0.1 mm diameter soda lime glass balls (Duke Scientific Corporation, USA) were used. Figure 8 shows the resulting typical 3D image of a uniform spherical protrusion array. The distance between the centers of two spherical protrusions is 0.1 mm. The height of these protrusions is about $6.5 \mu\text{m}$ and the size is around $30 \mu\text{m}$ in diameter. Using smaller hard balls, even smaller protrusion has been achieved.

5. Conclusions

Two novel approaches to produce micro-sized protrusion arrays are proposed and demonstrated in this paper.

As compared with the indentation approach, the quality of the protrusion array produced by laser heating using microlens

array is more difficult to control, although it is more suitable for mass fabrication. Indentation approach also has the advantage for producing various shaped bumps. In addition, as revealed in [14], if a pre-stretched SMP (in plane) is used, an elliptical-shaped protrusion array, i.e., anisotropic pattern, can result. Hence, indentation is a more generic approach for different sized and shaped protrusive patterns.

Instead of heating for shape recovery in thermo-responsive SMPs, the formation of protrusive pattern can be realized by absorbing moisture (e.g., immersing into water) if a moisture-responsive SMP [16] is used.

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TECHNICAL NOTE

A generic approach for producing various protrusive shapes on different size scales using shape-memory polymer

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Online at stacks.iop.org/SMS/16/N47**Abstract**

We demonstrate a generic approach for producing different shaped and sized protrusive features using shape-memory polymer (SMP). Utilizing the large recoverable strain in the SMP, and depending on the pre-straining of the SMP, shape of the indenter, temperature during indenting and the depth of polishing, we show that a variety of features of different sizes can be easily obtained.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The recoverable strain in shape-memory polymers (SMPs) is of the order of 100%, which is far larger than for many other shape-memory materials [1]. The shape recovery in SMPs can be triggered by various external stimuli, such as heat, light, moisture and pH change [1–9]. Among these SMPs, the thermo-responsive SMPs are the most popular ones and many applications, such as in stents, sutures and microelectromechanical devices, have been proposed based on them [10–13]. The shape-memory phenomenon in most SMPs results from the hard/soft segment system. In thermo-responsive SMPs, at above the glass transition temperature (T_g), the soft segment is very flexible and easily accommodates a significant deformation, while the hard segment is much stiffer. On the other hand, at below T_g , the soft segment becomes stiff and can be *frozen*. Consequently, a piece of SMP can be easily re-shaped at above T_g , and then cooled to below T_g with the new shape preserved. Subsequently, the original shape can be recovered by heating the SMP to above T_g . The driving force behind the shape recovery is the returning of the hard segment to its original shape. It has been reported that the shape-memory behavior of SMPs is not only a

macroscopic phenomenon, but also occurs even on the 10 nm scale [14]. The latter finding sheds light on using SMPs for micropatterning and even nanopatterning. This provides the motivation behind this paper.

2. Sample preparation

A styrene copolymer SMP from CRG, USA, with a T_g of about 63 °C was used in the course of this study. The as-received SMP is in sheet form (about 4 mm thick). Small samples were cut out of the sheet and then heated to 100 °C in order to release any possible internal pre-stress and/or pre-deformation during material processing and fabrication. Subsequently, the samples were well polished using Mecaprex diamond compound (3 μ m and then 1 μ m) with ECOMET as lubricant so that no apparent scratch can be found under a microscope.

3. Experiment using macroindentation

In order to verify some basic concepts, we carried out a series of macroindentation tests first. A SHIMADZU-DXT-3 with a steel ball indenter (ball diameter: 1.5875 mm) was used to make indents on top of the SMP samples at room temperature (about 22 °C). In each indentation test, according to the testing

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Figure 1. Various protrusive shapes realized by indenting at room temperature (with a macrospherical indenter). (a) After indentation. The indent piles up. (b) Final shapes after polishing and heating. The polishing depth increases from (1) to (5) as indicated.

Figure 2. Elliptical protrusive (a) cylinder and (b) crown.

procedure, a small pre-load of 29.42 N was applied before the final load of 147.1 N. Figure 1(a) shows the 3D view of a typical indent and its cross-section. The 3D surface scanning was done with a Taylor-Hobson 112/054DS at a speed of 3 mm s^{-1} . We noticed that all resulting indents were more or less the same in both shape and size, and they all pile up. This is opposite to what was reported for a NiTi shape-memory alloy, for which the indent piles up for the high temperature austenite phase and sinks in for the low temperature martensite phase [15].

The samples were then gently polished (following the same procedure mentioned in section 2) to different depths and finally heated to 100°C . Figure 1(b) reveals the typical resulting protrusive shapes (3D and cross-section) at different polishing depths (as indicated). The polishing depth was determined from the difference between the indent depths before and after polishing. In figure 1(b1), the polishing depth is only $20 \mu\text{m}$. Referring to the cross-sectional view of the indent in figure 1(a), the top part of the pile-up is polished away, but elsewhere, the polishing is very small. Hence, upon heating, the indented area protrudes out of the sample surface (only slightly as the polishing depth is small) due to the shape recovery, while the polished pile-up part results in a virtually circular trench. The *protrusion* looks like a cylinder

with a flat top. With the increase in polishing depth, the protrusion becomes more apparent, but the flat top becomes less significant (figure 1(b2)–(b4)), and eventually a spherical crown-like shape results (figure 1(b5); overpolished case). The last case (figure 1(b5)) is very similar to what has been reported for a NiTi shape-memory alloy following the same approach [16]. However, it is not easy to realize other shapes in shape-memory alloys due to their limited recoverable strain ($<10\%$).

Instead of indenting at room temperature, we have carried out indentation at 70°C . The resulting indents sink in, since at 70°C , which is above T_g , the SMP is soft. This is similar to the case for shape-memory alloys for the low temperature martensite phase. Therefore, no trench can be found after polishing and heating.

In the third set of macroindentation tests, we uniaxially pre-stretched the samples by 50% (in-plane) before indentation at room temperature. Thus, after indentation and polishing, the recovery upon heating occurred in the individual indents accompanied by a macroscale overall shape recovery in the sample. Figure 2 shows two typical protrusive shapes, cylinder and crown, which are all elliptic. Such elliptic features cannot be realized in shape-memory alloys due to their limited recoverable strain.

Figure 3. Micron sized features realized using a Berkovich nanoindenter ((a), (b)) and small particles ((c), (d)).

Figure 4. Butterfly-shaped microfeatures. (a) 2D view; (b) 3D view; (c) a small 'butterfly'.

It is apparent that by pre-stretching the SMP, one can produce not only circular trenches (as in figure 1(b1)), but also elliptic trenches. An array of crowns can be easily produced in a similar way. Hence, this provides an alternative approach for producing microlens arrays [17].

4. Experiment using nanoindentation

In the second step, a MST Nano instrument with a Berkovich indenter was used to make microindents on the SMP samples. Depth control was applied during indentation. The targeted strain rate was 0.051 s^{-1} following XP CSM method. After the prescribed maximum depth was reached, there was a holding time of 10 s before unloading at the same speed. The 3D surface was obtained using a WYKO interferometer. To improve the reflection, a thin layer of gold (a few nanometers) was coated atop the SMP samples. The equilateral triangle (the in-plane height is about 25 μm) shown in figure 3(a) is 2.11 μm high in the out-of-plane direction. A non-equilateral triangle was realized with a pre-stretching of 50% in one direction (figure 3(b); pre-stretching in the vertical direction). We found that if we pre-compress the whole SMP sample in the thickness direction at room temperature, make an indent of the same depth, and then produce the same polishing depth, after

heating the height of protrusion increases. This is obviously due to the shape recovery in the thickness direction.

5. Further discussion

We also observed some circular cones with a height down to 94.7 nm on the surface of these pre-compressed samples (figures 3(c) and (d)). We used lubricant in order to reduce the friction between the SMP sample and a very smooth aluminum block (to ensure a smooth surface on the SMP sample) during the compression test. We believe that there are some small particles in the lubricant, so that some small indents were resulting as a by-product of the compression test. After polishing, these particles were removed and the indents underneath were also fully or partially polished. After heating, these unexpected circular cones resulted, which demonstrates the possibility of producing nanosized protrusions of various shapes if different indenters are used.

We have uniaxially stretched some SMP samples to 50% at 80°C and then cooled them to ambient temperature with the length fixed. After slightly polishing them and heating them to 80°C , we found many microsized 'butterflies' (figure 4). We have worked out the mechanism behind this interesting phenomenon [18].

6. Conclusions

To summarize, we demonstrated a generic approach for realizing various sized and shaped protrusive shapes using a thermo-responsive SMP. Utilizing the large recoverable strain in this SMP, we show that a variety of features of different sizes can be obtained, depending on the pre-straining in the SMP, shape/size of the indenter, temperature during indentation and depth of polishing. Given the much higher recoverable strain, SMPs can overcome the limit in patterning using shape-memory alloys [19].

The temperature dependence of the indent shape in SMPs is similar to that for shape-memory alloys, but opposite in terms of temperature condition.

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Electrical conductivity of thermoresponsive shape-memory polymer with embedded micron sized Ni powder chains

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The electrical resistivity of a thermoresponsive polyurethane shape-memory polymer (SMP) filled with micron sized Ni powders is investigated in this letter. We show that, by forming conductive Ni chains under a weak static magnetic field (0.03 T), the electrical conductivity of the SMP composite in the chain direction can be improved significantly, which makes it more suitable for Joule heat induced shape recovery. In addition, Ni chains reinforce the SMP significantly but their influence on the glass transition temperature is about the same as that of the randomly distributed Ni powders.

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While shape-memory polymers (SMPs) can be actuated by various stimuli (e.g., light¹ and water²), an external heater is normally required for the shape recovery in thermoresponsive SMPs. In order to get rid of external heaters, SMP composites with different types of fillers have been developed,³ so that they can be actuated by means of Joule heat (i.e., by passing an electrical current,^{4–6} just like that of NiTi shape memory alloys⁷) or induction heat (e.g., by applying an alternating magnetic field to induce heat through hysteresis in magnetic particles^{8–10}). While the latter approach has the advantage for wireless/remote operation, the former might be more of the interest in many engineering applications in which a bulk system to generate magnetic field is not appreciated.

Electrically conductive powders, fibers, and even nanowires/nanotubes have been utilized as the fillers to improve the electrical conductivity of polymers.^{11–13} Although conductive fiber and nanowire/nanotube can significantly enhance the stiffness and strength of polymers,¹⁴ their deformable strain is limited to within a few percent (at the most).^{15,16} Since the recoverable strain in SMPs is normally on the order of hundred percent, there is a potential problem of deformation compatibility. As such, electrically conductive powders, such as, carbon black and Ni powder, should be better choice.

Previously, we have developed thin film SMPs with embedded magnetic powder (Fe_3O_4) chains inside. This work inspired us to use some other powders, which are both magnetic and electronically conductive, to form conductive chains for enhanced electrical conductivity. The purpose of this letter is twofold. One is to fabricate SMP thin films with embedded conductive powder chains and the other is to investigate their electrothermomechanical properties and compare them with those with randomly distributed powders.

The thermoresponsive polyurethane SMP solution from Diaplex Co. Ltd. (MS-5510) was used in this study. It consists of 30 wt % of SMP (glass transition temperature, T_g : about 40 °C) and 70 wt % of dimethylformamide (DMF). Its

molecule chain consists of alternating sequences of soft segment with low molecular weight and hard segment built from diisocyanates and extenders to form the points for physical linking.¹⁷ Ni powders, which are magnetic and electronically conductive, with an average size from 3 to 7 μm and a purity of 99.8%, were bought from Goodfellow, UK.

SMP thin films filled with different volume fractions of Ni powders were prepared in the following steps. First, Ni powders were mixed with the SMP/DMF solution and well stirred for a uniform dispersion. After that, the highly viscous mixture was poured into a 40 mm diameter Petri dish (to reach a final height about 1.5–2.0 mm) (Fig. 1). Two magnets and a Petri dish were placed in a way, as illustrated in Fig. 1. The whole setup was kept in an oven for 24 h at a constant temperature of 80 °C. After curing, a SMP thin film with Ni chains inside was obtained. The resulted thin film (about 0.5–0.7 mm thick) was kept in an oven at 160 °C for more than 8 h to fully remove any moisture absorbed during processing.¹⁸ Various sized samples were cut out of the thin film for testing. This group of samples is named chained samples hereinafter. Another group of thin films was prepared in the same way but without applying the magnetic field. Hence, Ni particles were randomly distributed within the SMP matrix. This group is named random sample hereinafter.

Optical microscopic observation revealed the formation of clear chain structure in chained samples, in particular, at a small Ni content. A scanning electron microscopy (SEM) (JEOL 5600LV) was used to observe the details of Ni chains

FIG. 1. Illustration of setup for sample preparation. The strength of magnetic field was measured as 0.03 ± 0.003 T in the area underneath the Petri dish.

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FIG. 2. Typical SEM images before (left column) and after (right column) five stretching (at 50% strain)-shape recovery cycles.

before and after five stretching (50% strain)-shape recovery cycles. The volumetric electrical resistance of random and chained samples was measured by a multimeter (IDM91E). An infrared video camera (AGEMA, Thermovision 900) was used to monitor the temperature distribution in samples upon Joule heating. Differential scanning calorimetry (DSC) (modulated DSC, DSC-2920), and dynamic mechanical analysis (DMA) (DMA 2980 TA Instrument) were used to determine the thermomechanical properties of chained and random samples.

SEM images reveal that single chains start to be formed at 1% volume fraction of Ni. With the increase of Ni content, multichains (bundles) are resulted, and eventually no clear

FIG. 3. (Color online) Electrical resistivity vs volume fraction of Ni powder. Right inset: illustration of setup for the resistivity measurement along the chain direction. Bottom-left inset: infrared image of temperature distribution in chained sample (10% Ni, 6 V).

FIG. 4. (Color online) Shape recovery sequence in a chained sample ($30 \times 7 \times 1 \text{ mm}^3$, 10% Ni, 20 V).

Ni chain can be recognized (Fig. 2, left column). In addition, after five stretching-shape recovery cycles, the Ni chains still exist (Fig. 2, right column), which indicates the possibility of using chained SMPs for cyclic actuation.

Figure 3 plots the electrical resistivity of the random and chained samples against the volume fraction of Ni powders. The volumetric electrical resistivity ρ is calculated by

$$\rho = \frac{RA}{L}, \quad (1)$$

where R is the measured resistant, A is the cross-sectional area of sample, L is the length between two aluminum electrodes (refer to the right inset in Fig. 3 for the setup of the resistivity measurement). Although limited by the measuring range of the multimeter, as we expected, ρ of the chained sample in the transverse direction (i.e., perpendicular to the chain direction) is the highest, while ρ of random samples is lower. ρ of chained samples in the chain direction is always the lowest. For example, at 10% volume fraction of Ni powder, ρ of random sample is $2.36 \times 10^4 \Omega \text{ cm}$; while in the chained sample, it is $2.93 \times 10^6 \Omega \text{ cm}$ in the transverse direction, and only $12.18 \Omega \text{ cm}$ in the chain direction. However, at a high Ni content, ρ of all types of samples is close. This is due to that the Ni chains become unrecognizable at a high Ni content, as revealed in Fig. 2. At 10% volume fraction of Ni, the chained sample (with a dimension of $16 \times 0.6 \times 5 \text{ mm}^3$) can be heated from room temperature (20°C) to 55°C by applying a voltage of 6 V (refer to infrared image in Fig. 3, bottom-left inset), which is enough to trigger the shape recovery. However, for the same setup and configuration, it is only about 26°C in the random sample. No shape recovery can be actuated, as it is far below the actuation temperature. The recovery sequence of a chained sample upon Joule heating is shown in Fig. 4. According to the DSC results in Fig. 5, with the increase of Ni

FIG. 5. DSC results of random samples.

FIG. 6. Typical storage modulus vs temperature curves obtained from DMA test.

content, the glass transition shifts a little bit toward a low temperature range, which indicates the slight chemical interaction between Ni powders and SMP.

From the measured storage modulus versus temperature curves of random and chained samples (Fig. 6), we plot the storage modulus (at 0 °C) against the volume fraction of Ni for both random samples and chained samples (chain direction only) in Fig. 7. At around 10% volume fraction of Ni content, the composite is already significantly strengthened. For the same amount of Ni content, the storage modulus of chained samples in the chain direction is always much higher than that of random sample. This indicates that the reinforcement is more effective by forming Ni powder chains.

T_g is one of the major characteristics of SMPs. Traditionally, T_g can be defined in various ways. Here, we differential the storage modulus curve with regard to temperature, and then define the peak temperature as T_g . Figure 8 plots T_g against the volume fraction of Ni powders for both random samples and chained samples (chain direction only). As we can see, with the increase of Ni content, T_g decreases in a more or less same linear fashion in both types of samples. At 20% Ni content (this is extremely high), T_g drops by about 15 °C, to 35 °C only, which confirms the slight chemical interaction between SMP and Ni powders.

In conclusion, we demonstrate a simple way to produce SMPs with embedded micron sized Ni powder chains by application of relatively weak magnetic field. Due to these

FIG. 7. Storage modulus vs volume fraction of Ni at 0 °C.

FIG. 8. T_g of chained and random samples.

conductive Ni chains, the electrical resistivity of SMP composite is greatly reduced in the chain direction, so that Joule heating is possible at a low electrical voltage. In addition, the alignment of Ni powder chains efficiently reinforces the SMP. The slight chemical interaction between Ni powder and SMP results in a lower T_g . This approach, i.e., to form conductive particle chains in SMPs for enhanced electrical conductivity, is easy for implementation. It should be applicable to other types of polymers. Multilayered electrically conductive polymer composites can also be realized by, for instance, bonding a few such layers together.

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