Thermo-/chemo-responsive shape memory/change effect in hydrogels and their composites

Zhang, Jiliang

2014

Zhang, J. (2014). Thermo-/chemo-responsive shape memory/change effect in hydrogels and their composites. Master's thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/61745>

<https://doi.org/10.32657/10356/61745>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**THERMO-/CHEMO-RESPONSIVE SHAPE
MEMORY/CHANGE EFFECT IN HYDROGELS AND
THEIR COMPOSITES**

**ZHANG JILIANG
SCHOOL OF MECHANICAL AND AEROSPACE
ENGINEERING**

2014

**THERMO-/CHEMO-RESPONSIVE SHAPE
MEMORY/CHANGE EFFECT IN HYDROGELS AND
THEIR COMPOSITES**

ZHANG JILIANG

School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Master of Engineering

2014

Abstract

Shape memory material (SMM) is a type of smart material, which after being severely and quasi-plastically deformed, is able to return its original shape at the presence of the right stimulus. This feature is known as the shape memory effect (SME). Great attention has been attracted on this feature ever since it was discovered. On the other hand, the shape change effect (SCE) is defined as the shape change in a linear or nonlinear fashion with or without hysteresis in response to the applied right stimulus. Many applications of both effects have already been in engineering practice.

In this project, water/moisture-content dependent behaviors in three hydrogels are systematically investigated. It is found that at lower water/moisture contents, all hydrogels have the thermo-responsive and moisture (or water)-induced SME; while at higher water/moisture contents, the hydrogel has the rubber-like mechano-responsive SCE and water-induced SCE. Furthermore, it is shown that on the one hand, programming can be realized by means of distortion at high temperatures (above the glass transition temperature, T_g) of a hydrogel with lower water/moisture content or dehydration after pre-deforming a piece of rubber-like hydrogel (which has higher water/moisture content). Some possible applications utilizing the SME/SCE either individually or combined together are proposed. On the other hand, hydrogel can be used as the elastic matrix in a hybrid for tailored SME.

Keywords: hydrogel; shape memory effect; shape change effect; wetting;
heating; swelling

Acknowledgements

Foremost I would like to express my sincere and warmest thanks to my supervisor, Dr. Huang Wei Min, for his kindness, guidance, keen insight, inspiration and friendship.

Special gratitude must go to Dr. Wang Changchun, Mr. Tang Chen and Mr. Hendra Purnawali for their assistance in the experiments.

Finally, my sincere thanks go to the technicians of Laser Micro-processing Laboratory, the Centre for Mechanics of Micro-Systems and Materials Lab of NTU, for their assistance in various aspects of the operation of the instruments.

The double network nanocomposite hydrogel studied in Chapter 5 was kindly provided by Professor Fu Jun at Ningbo Institute of Material Technology & Engineering, Chinese Academy of Sciences, P. R. China.

Contents

Abstract.....	i
Acknowledgements.....	iii
Contents.....	iv
List of figures	viii
Chapter 1 Introduction	1
1.1 Background	1
1.2 Typical innovative applications of hydrogel	3
1.3 Objectives of this project.....	4
1.4 Outline of the report	4
Chapter 2 Literature review	5
2.1 Polymerization of hydrogels.....	5
2.2 Types of stimulus-responsive hydrogels	7
2.3 Swelling.....	9
2.4 Hydrogel based shape memory hybrid	11
2.5 Thermo-responsive SME in hydrogel	12
2.6 Chemo-responsive SME in hydrogel	13
Chapter 3 Thermo-/chemo-responsive shape memory/change effect in hydrogel	14

3.1 Materials and experiments.....	14
3.1.1 Raw materials	14
3.1.2 Sample preparation	16
3.1.3 Thermal analysis	17
3.1.4 Compression test.....	18
3.1.5 Characterization of SME and SCE	19
3.2 Results and discussion.....	21
3.2.1 Thermal analysis	21
3.2.2 Compression tests	25
3.3.3 Shape change/memory effect.....	27
3.3 Further discussion.....	34
3.4 Conclusions	36
Chapter 4 Characterization of cuboid hydrogel and its potential applications .	
.....	38
4.1 Materials and experiments.....	38
4.1.1 Raw materials	38
4.1.2 Sample preparation	38
4.1.3 Compression tests	40

4.1.4 Thermal analysis	41
4.1.5 Characterization of SME and SCE	41
4.2 Results and discussion.....	43
4.2.1 Compression tests	43
4.2.2 Thermal analysis	45
4.2.3 Thermo-responsive SME	47
4.2.4 Moisture-responsive SME	47
4.2.5 Water-responsive SME/SCE.....	48
4.2.6 Thermo-responsive SME in CHGPH	52
4.2.7 Wrinkling	52
4.3 Further discussion and remarks	55
4.4 Potential applications	55
Chapter 5 Shape memory/change effect in a double network nanocomposite hydrogel	58
5.1 Materials and experiments.....	58
5.1.1 Raw materials	58
5.1.2 Sample preparation	58
5.1.3 Compression tests	59

5.1.4 Thermal analysis	60
5.1.5 Characterization of SME	60
5.2 Results and discussion.....	63
5.2.1 Compression tests	63
5.2.2 Thermal analysis	64
5.5.3 Shape memory effect	65
5.3 Further discussion and remarks	72
Chapter 6 Conclusions and future work	74
6.1 Conclusions	74
6.2 Future work	76
References.....	78
List of publications.....	82

List of figures

Figure 1.1 Illustration of energy barrier between two states (A and B) of a material, where H and H' indicate different levels of energy barrier.....	2
Figure 2.1 Chemical structures of reactants and general pathways to prepare an acrylic network. (a) Cross-linking polymerization by a polyvinyl cross-linker; (b) cross-linking of a water-soluble prepolymer by a polyfunctional cross-linker. R is often CH_2 or from another aliphatic group. M stands for the sodium or potassium cation. X= O, NH.....	8
Figure 2.2 Schematic illustration of cross-linked structure of hydrogel in dehydrate state.	10
Figure 2.3 Water induced SCE in a silicone strip with hydrogel embedded in a part of it. (a) Original straight shape; (b) bending upon immersing into room temperature water; (c) shape recovery after drying. [36].....	12
Figure 2.4 Cooling for shape recovery. [37]	12
Figure 3.1 Wetting of hydrogel ball in water and drying. (a) Original shape; (b-d) upon wetting in water; (e) after drying in air. (b1, c1) are photos taken in water; (b2, c2) are photos taken after being taken out of water for a while.	15
Figure 3.2 Illustration of dimension change in hydrogel ball.	19
Figure 3.3 TGA result of hydrogel.....	21
Figure 3.4 TGA result of PEG.	22

Figure 3.5 (a) DSC results of hydrogels with different R_w ; (b) T_g as a function of R_w	22
Figure 3.6 DSC result of PEG in one thermal cycle.	23
Figure 3.7 Cyclic DSC result of HGPH: (a) In heating; (b) in cooling.	24
Figure 3.8 Evolution of T_m upon thermal cycling.	24
Figure 3.9 Compression load vs. R_c relationship of 10 pieces of HG _{0.05} at 80°C and then cooled to room temperature.	26
Figure 3.10 Evolution of compression load against time in the compression test (refer to Figure 3.9).	26
Figure 3.11 HG _{0.8} in a typical loading-unloading cycle (a) Compression load vs. R_c relationship; (b) Evolution of compression load against time.	27
Figure 3.12 Thermo-responsive SME in HG _{0.05} . (a) Original shape; (b) after pre-compression at 80 °C; (c) after kept in dry cabinet for four days at 30% RH and 25°C; (d) after recovery by heating to 80°C for a few seconds.	27
Figure 3.13 Moisture-responsive SME in HG _{0.05} (right ball without compression is for comparison). (a) Original shape; (b) left ball was compressed at 80°C and kept in dry cabinet for four days at 30% RH and room temperature; (c) after one hour at 100% RH and room temperature.	28
Figure 3.14 Time for <i>apparent</i> full recover vs. RH relationship. Black curve is to show the general trend.	29

Figure 3.15 Evolution of R_w against time at room temperature and different RHs. Grey symbols indicate <i>apparent</i> full shape recovery; and dotted grey line is data-fitting.....	29
Figure 3.16 Rubber-like behavior in HG _{0.8} . Top ball is presented for comparison. (a-c) During compression; (c-f) during release.	30
Figure 3.17 Moisture induced programming and shape recovery in HG _{0.8} . (a) Original shape; (b) after being compressed and kept in oven at 40°C for three hours; (c) after exposing to 100% RH at 25°C for two hour.....	31
Figure 3.18 The SCE in HG _{0.05} . (a) Balls with/without pre-compression; (b1-d1) snapshots during swelling (side-view of pre-compressed ball); (b2-d2) snapshots during swelling (top-view of pre-compressed ball); (e) 60 minutes in water; (f) three days after drying in the air.	31
Figure 3.19 Variation in dimensions during swelling of HG _{0.05} . W and H are for the pre-compressed ball, while D is for the ball without pre-compression.	32
Figure 3.20 Thermo-responsive SME in HGPH (blue one, at right, is for comparison). (a) Original shape; (b) compressed at 70°C; (c1-c3) upon immersing into 70°C silicone oil.	33
Figure 3.21 Moisture/water content dependent response of hydrogel.	35
Figure 4.1 As received Rainbow Clay ($\approx 4 \times 4 \times 4$ mm).....	38

Figure 4.2 Fully wetted hydrogel, from which CHG _a , CHG _b and CHG _c were produced. (a) Original hydrogel; (b) upon wetting in room temperature water; (c) comparison of fully wetted and dry hydrogel.	40
Figure 4.3 CHG _a , CHG _b and CHG _c . Fully wetted (left); dry (right).....	40
Figure 4.4 CHGPH. (a) fully wetted; (b) after dehydration for 17 hours.	40
Figure 4.5 Compression stress vs. compression strain relationship of CHG ₀ in a typical loading-unloading cycle.....	44
Figure 4.6 Dry hydrogel after compression.	44
Figure 4.7 Compression stress vs. compression strain relationship of CHG _{0.21} in three loading-unloading cycles.	45
Figure 4.8 DSC results of CHG ₀ CHG _{0.21}	46
Figure 4.9 DSC result of CHGPH.....	46
Figure 4.10 Thermo-responsive SME in CHG ₀ : (a) Original shape; (b) after bending in silicone oil at 80°C; (b-e) shape recovery upon immersing into 80°C silicone oil.....	47
Figure 4.11 Heating-responsive SME of small sized CHG ₀ . (a) Original shape; (b) after being deformed; (b-e) shape recovery sequence. The ball (top) has a diameter of 1.5 mm and is used as a reference.....	47
Figure 4.12 Moisture-responsive SME in CHG ₀ : (a) Original shape; (b) after being deformed in silicone oil at 80°C; (b-e)sequence of shape recovery.....	48

Figure 4.13 Swelling in distorted hydrogel.....	48
Figure 4.14 Dehydration of hydrogel (Figure 4.13e).....	49
Figure 4.15 Swelling of hydrogel (pre-stretched at high temperatures) upon immersing into room temperature water.	49
Figure 4.16 Dehydration of hydrogel (Figure 4.15c5).....	50
Figure 4.17 Shape recovery induced by water droplet.....	50
Figure 4.18 Shape recovery induced by water droplet.....	51
Figure 4.19 Swelling of CHG _a , CHG _b and CHG _c . (a1), (b1) and (c1) are dry samples, (a1-a6), (b1-b6) and (c1-c6) are in swelling process. The ball has a diameter of 6 mm and is for reference.....	51
Figure 4.20 D/d vs. time relationship in the swelling of CHG _a , CHG _b and CHG _c ..	52
Figure 4.21 Thermo-responsive SME in CHGPH. (a) Original shape; (b) after bending at 70°C; (b-e) upon immersing into 70°C silicone oil. The ball (top) has a diameter of 1.5 mm and is used for reference.	52
Figure 4.22 Evolution of morphology in wetting/drying top surface of a piece of hydrogel. (a) Original shape; (b) after slight wetting; (c) further wetting; (d) upon further wetting; (e) after drying for a while.	53
Figure 4.23 Water droplet on hydrogel. (a) Before wetting; (b) spreading of water droplet; (c-l) after wetting by water droplet. The horizontal size of all images is 1 mm.	54

Figure 4.24 Illustration of changes in micro structures in hydrogel in shape switching. (a) Fully swelled; (b) wet shape without apparent swelling; (c) dry shape; (d) deformed temporary shape.	56
Figure 4.25 Accumulated moisture sensor based on hydrogel. (a) Dry hydrogel deformed above T_g ; (b) shape recovery upon absorbing moisture.	56
Figure 4.26 Hydrogel coil for embolization. (a) Fully swelled shape; (b) dry shape; and (c) (dry) gel after stretching at high temperatures.	57
Figure 5.1 Bending rubber like DNHG _{0.3}	62
Figure 5.2 Compression stress vs. compression strain relationship of DNHG ₀ (a); after compression (b).	64
Figure 5.3 (a) Compression stress vs. compression strain relationship of DNHG _{0.3} in three loading-unloading cycles; (b) compression stress vs. compression strain relationship of DNHG _{7.5} in seven loading-unloading cycles.	64
Figure 5.4 DSC results of hydrogels with different R_w	65
Figure 5.5 Thermo-responsive SME in DNHG ₀ . (a) Original shape; (b) after bending at 100°C; (b-e) recovery sequence in 100°C silicone oil.	66
Figure 5.6 Thermo-responsive SME in DNHG _{0.05} . (a) Original shape; (b) after bending at 80°C; (b-f) subsequent of recovery upon immersing into 80°C silicone oil.	66

Figure 5.7 Thermo-responsive SME in DNHG _{0.05} . (a) Original shape; (b) after impression; (c) 3-D scanning image scan; (d) 3-D scanning image three hours after a droplet was applied on the right flower; (e) after immersing into 80°C silicone oil.	67
Figure 5.8 Comparison of surface profiles along line A marked in Figure 5.7 (c) and (d).	67
Figure 5.9 Wetting by one water droplet (vertical size is about 1 mm).	68
Figure 5.10 Low swelling ratio tough hydrogel (DNHG ₀) upon wetting in water and its dehydration. (a) Original shape; (b) deformed at high temperature; (c1- c6) swelling in room temperature water.	69
Figure 5.11 Dehydration of the swelled hydrogel (Figure 5.10c6).	69
Figure 5.12 SME based on swelling. (a) Original shape; (b) bent and dehydrated; (c1-c13) shape recovery upon swelling.	70
Figure 5.13 SME during swelling in water in a pre-stretched sample.	70
Figure 5.14 SME based on wetting in water. (a) Original shape; (b) after being dried in the open air at room temperature; (c) after being straightened in silicone oil at 80°C and cooled; (c-f) shape recovery of the top half upon immersing into room temperature water.	71
Figure 5.15 Thermo-responsive SME based on melting of water in DNHG _{7.5} . (a) Original shape; (b) after being bent and kept at -20°C for one hour; (c-e)	

shape recovery sequence at around 25°C; (f) after being immersed in room temperature water for 30 minutes. 72

Figure 5.16 Moisture/water content dependent response of hydrogel.(a) Fully swelled; (b) wet shape without apparent swelling; (c) dry shape; (d) deformed temporary shape. 73

Chapter 1 Introduction

1.1 Background

Shape change material (SCM) is able to instantly and spontaneously change its shape in a linear or nonlinear fashion with or without hysteresis in response to the applied right stimulus. A typical example of the SCMs is hydrogel, in which swelling and rubber-like elasticity are two types of classic shape change effect (SCE). If a material can be deformed and fixed into a temporary shape, and it has the ability to recover its original shape only upon applying the right external stimulus, which is a phenomenon known as the shape memory effect (SME), this material is called shape memory material (SMM) [1].

Shape memory alloys (SMAs) and shape memory polymers (SMPs) are the most important SMMs, and they have received great attention in the past years among all SMMs. Shape memory hydrogels are relatively new, but have started to show their potential in many engineering, in particular bioengineering, applications.

From the energy point of view, the difference between these two effects, namely SME and SCE, is due to the difference in energy barrier between the permanent and temporary shapes. As illustrated in Figure 1.1, if the energy barrier (H) is high enough to prevent free and reversible transition between the permanent shape and temporary shape, this is the SME. Otherwise, it is the SCE.

Typical stimuli to trigger the SCE and SME in hydrogels include heat, stress/pressure, magnetic field, electrical/voltage, pH-change/solvent/moisture and light, etc [2, 3]. A plenty of applications have been developed based on both interesting phenomena [4, 5].

Figure 1.1 Illustration of energy barrier between two states (A and B) of a material, where H and H' indicate different levels of energy barrier.

The first generation of hydrogel was synthesized by Wichterle and Lim in the late 1950s for biomedical applications based on poly (hydroxyethyl methacrylate) (PHEMA) cross-linked with ethylene dimethacrylate. This marks the beginning of the research of polymer gel [6]. Hydrogels are three-dimensional networks which are able to absorb a large amount of solvent (water/moisture) without dissolving in it themselves, and the absorbed solvent is hardly removable even under pressure [7, 8].

A hydrogel is either physical cross-linked or chemical cross-linked [9]. A physical hydrogels is cross-linked by the junctions (physically connected

aggregates). While in chemical hydrogels, permanent covalent bonds produce a three-dimensional network. Physical or chemical cross-linked hydrogels can undergo controlled and reversible shape changes in response to an applied variable field, such as thermal, electrical, magnetic, pH, UV/visible light, ionic or metallic interactions, etc [8, 10-12].

Shape memory behavior has been observed in a couple of hydrogels [13-15]. These hydrogels are mainly synthesized by copolymerization of n-stearyl acrylate (SA) and acrylic acid (AA) at the presence of a cross-linker. Copolymer of SA and AA can be regarded to consist of a water-soluble poly (AA) as main chain and hydrophobic stearyl (octadecyl), which is attached to SA, as side chains. The mechanism behind the SME in these hydrogels is a reversible order-disorder transition.

1.2 Typical innovative applications of hydrogel

Hydrogel has an enormous capacity to attract and hold water with its imbibing polymeric networks. It has been used in a wide range of medical products, such as drug delivery, tissue replacement, heart surgery, gynaecology, ophthalmology, plastic surgery and orthopaedic surgery, based mainly on the SCE. For example, Hydrogel GelFix Interspinous Spacer, composed of hydrolyzed polyacrylonitrile, is a commercial product of Replication Medical Inc. After Gelfix is delivered into the right place inside body in the collapsed dehydrated state, the spacer expands and swells upon absorbing human body's own fluids, and thus the flexible GelFix distracts the interspinous space to

reduce nerve encroachment and provides viscoelastic resistance to painful extension [16, 17].

1.3 Objectives of this project

In this project, water/moisture-content dependant behavior in three hydrogels is systematically investigated. Some possible applications utilizing the SME/SCE either individually or combined together are proposed. In addition, the feasibility of using hydrogel as the elastic matrix in a hybrid for tailored SME is studied.

1.4 Outline of the report

The outline of this report is as following,

Chapter 2 reviews some fundamental issues, including the polymerization of hydrogels, swelling in hydrogels, and typical mechanisms in previous shape memory hydrogels.

Chapter 3 reports a systematical investigation on the thermo-/chemo-responsive shape memory/ change effect in a commercial hydrogel.

Chapter 4 is about characterization of a cuboid hydrogel and its potential applications.

Chapter 5 presents a study of a double network nanocomposite hydrogel.

Major conclusions together with future work are discussed in Chapter 6.

Chapter 2 Literature review

An extensive literature review is presented in this chapter to introduce some fundamental issues about hydrogels, such as polymerization, swelling, and the mechanisms in previous shape memory hydrogels (SMHs).

2.1 Polymerization of hydrogels

Most hydrogels are synthesized by solution polymerization or inverse polymerization, and the solution method is preferred industrially for economic reasons plus its simplicity [18, 19]. Acrylamide (AM), acrylic acid (AA) and the salts of the acid are common monomers used for the synthesis of hydrogels. Cross-linker and initiator are required during polymerization.

- **Cross-linker**

A relatively small amount of cross-linkers plays an important role in modifying the properties of hydrogels. The existence of cross-linker produces cross-links between chains. It is the presence of the cross-links between these chains, i.e., the formation of a three-dimensional polymer network, that leads to the special characteristics of polymerization [20]. In many occasions, the cross-linker is methylenebisacrylamide (bis, or MBA). Except MBA, piperazine diacrylate (PDA), N, N'-bisacrylylcystamine (BAC), and N, N'-diallyltartardiamide (DATD) are also used as cross-linkers.

- **Initiators**

Polymerization is initiated by free-radicals in the aqueous phase, using thermally redox initiators, decomposable initiators or combinations. Couples of persulfate/bisulfite, persulfate/thiosulfate, persulfate/ascorbate and hydrogen peroxide/ascorbate are typical redox systems used for cross-linking copolymerization, while persulfates, 2, 2'-azobis-(2- amidinopropane)-dihydrochloride, and 2, 2'-azobis (4-cyanopentanoic acid) are some well-known thermal initiators. When polymerization takes place over a broad temperature range, a combination of more than one initiator may be used. Appropriate concentrations of multiple initiators can achieve the desired constant-rate of polymerization [19]. During drying, initiators take action in reducing the level of unreacted monomer [20].

- **Neutralizing agents**

Before or after polymerization, carboxylic acid groups of hydrogel are partially neutralized [21]. Sodium hydroxide and sodium carbonate are usually used as neutralizing agents largely because they are more cost effective. The pH value of the base solution, solubility limits of the base in water and solubility of the monomer salt in water are major factors to be considered in choosing the right neutralizing agent.

- **Polymerization of cross-linked poly(AM-co-AA)-based hydrogel**

AM, a white powder with the chemical formula C_3H_5NO , is toxic before polymerization. Consisting a vinyl group connected directly to a carboxylic acid terminus, AA, an organic compound with the formula $C_3H_4O_2$, is the simplest unsaturated carboxylic acid. This colorless liquid has the typical

characteristics of tart smell. Both AM and AA are miscible in water, alcohols, ethers, and chloroform, etc [22].

To synthesis a cross-linked poly(AM-co-AA)-based hydrogel as illustrated in Figure 2.1, simultaneous polymerization and cross-linking by a polyvinyllic cross-linker, or cross-linking of a water-soluble prepolymer by a polyfunctional cross-linker is commonly applied [21].

2.2 Types of stimulus-responsive hydrogels

According to the type of stimulus, stimulus-responsive hydrogels may be divided into the following groups,

- **pH-sensitive gels**

Polymers containing acidic or alkaline functional groups which can respond to the change in pH value are called pH-sensitive gels. For pH-sensitive hydrogels, the change in solvent's pH value affects the difference in concentration of mobile ions interior the hydrogel and solvent, and hence the change in volume [23]. The degree of swelling in these hydrogels is highly dependent on the degree of ionization of the actual functional groups. Poly(acrylic acid) (PAA) [24] and poly(methacrylic acid) [25] are typical examples of pH-sensitive hydrogels.

Figure 2.1 Chemical structures of reactants and general pathways to prepare an acrylic network.

(a) Cross-linking polymerization by a polyvinyl cross-linker; (b) cross-linking of a water-soluble prepolymer by a polyfunctional cross-linker. R is often CH_2 or from another aliphatic group. M stands for the sodium or potassium cation. $\text{X} = \text{O}, \text{NH}$.

- **Thermo-responsive gels**

It might be reasonable to say that the study of thermo-responsive shape memory gels started in 1978 when Tanaka [10] reported the thermodynamics underlying the collapse of the polymer network in a polyacrylamide gel. In water, poly(*N*-isopropylacrylamide) (poly(NIPAM)) shows remarkable hydration–dehydration in response to the change in temperature. As we know, now temperature is a commonly used triggering signal for modulating drug release [26]. Thermal stimulus is physiologically very relevant. A common example is the elevation

of body temperature under the influence of pyrogens in fever. This is mediated by elevated concentrations of prostaglandin E_2 (PGE_2) within certain areas of the brain altering the firing rate of neurons that control thermo-regulation in the hypothalamus [27].

- **Analyte-sensitive gels**

Most physiological processes are carried out in the form of closed feedback loops to maintain body homeostasis [28]. For example, the release of insulin from β -cells of the pancreas is governed by the physiological levels of blood glucose. Researchers are trying to fabricate such closed-loop platforms in order to mimic these physiological processes, aiming to deliver therapeutics to patients at a rate regulated by feedback modulation, rather than following the hitherto targeted zero order rate kinetics. Due to the promising potential of ionic hydrogels in responding to a range of different stimuli, a number of analyte-sensitive gels have been synthesised. Glucose-sensitive gels [29], glutathione-sensitive gels [30] and antigen-sensitive gels [31] are typical examples among others.

2.3 Swelling

As shown in Figure 2.2, polymer chains are in a collapsed state when hydrogel is in the dehydrated state, leaving almost no room for molecular diffusion [28]. Most hydrogels are hard and brittle in the dehydrated state due to the collapsed network.

There are several factors which determine a hydrogel's capability to absorb water. Among others, hydrophilic chains, charge repulsion, osmosis, and cross-links are most important ones. More cross-links in the chains make the hydrogel tougher, while reduce its ability to absorb water [32]. Bounded, semi-bounded and free water exist in swelling hydrogel, and bounded water is tightly attached to hydrogel's polymer chains, while free water can be easily removed [33].

Figure 2.2 Schematic illustration of cross-linked structure of hydrogel in dehydrate state.

Hydrogels are ideal for water absorption related applications, such as disposable diapers, feminine napkins, etc, due to their strong swelling behavior. To quantitatively characterize absorption capability of a hydrogel, several techniques have been developed [19, 34]. The main concerns in real engineering practices are,

- **Free-absorbency capacity**

Free-absorbency capacity is a measure of the ability of a hydrogel to absorb distilled water when it swells. Several methods, such as tea-bag

method, centrifuge method and sieve method are commonly applied to measure this parameter [21, 35].

- **Absorbency under load (AUL)**

AUL is a measure of the ability of a hydrogel to absorb distilled water when it swells under a load.

Figure 2.2 shows a piece of silicone strip with hydrogel embedded in one side (only a part within the whole length of the silicone strip) [36]. The strip is able to bend significantly upon immersing into room temperature water, and then return its original straight shape by drying. According to above definition, this is the water-induced SCE, and the sample is actually a hybrid.

2.4 Hydrogel based shape memory hybrid

The tailored SME may be achieved by means of shape memory hybrid (SMH). Based on the dual-component concept, in which one component is always elastic and the other is able to change its stiffness dramatically when exposed to the right stimulus. As such, one can design a SMH made of two materials without any SME as an individual, and the performance of the resultant SMH can be pretty well predicated, even in the early design stage and hence, significantly shorten the time spending on trial and error.

A hybrid made of polymeric sponge filled with aqueous solution of poloxamer 407 (P407) is prepared according to the working principle of SMH to achieve not only cooling- responsive but also water-responsive SME [37]. Figure 2.4 reveals the cooling induced SME in this hybrid. The unique cooling induced

melting feature of poloxamer 407 gel (which has been approved by US Food and Drug Administration as biocompatible) at around 10°C enables this interesting feature.

Figure 2.3 Water induced SCE in a silicone strip with hydrogel embedded in a part of it. (a) Original straight shape; (b) bending upon immersing into room temperature water; (c) shape recovery after drying. [36]

Figure 2.4 Cooling for shape recovery. [37]

2.5 Thermo-responsive SME in hydrogel

Osada and coworkers reported the shape memory behavior in a hydrogel [14], which is synthesized by copolymerization of n-stearyl acrylate (SA) and AA. The hydrogel has water-soluble poly (AA) as main chains and hydrophobic stearyl (octadecyl) chain as side chains. A reversible order-disorder transition associated with the interactions between the alkyl side chains of the stearyl

acrylate units is the underlying mechanism behind the SME in this poly (SA-co-AA) [38].

Thermo-responsive SME has also been reported in a hydrogel, formed by biodegradable and biocompatible recombinant telechelic polypeptides, with collagen-like end blocks and a random coil-like middle block [15]. The shape memory behavior of the hydrogel arises from the reversible association of the collagen-like end blocks into triple helical nodes.

2.6 Chemo-responsive SME in hydrogel

Chemo-responsive SME has been reported in a hydrogel of poly (vinyl Alcohol) (PVA) [39]. After the formation of physical cross-links through hydrogen bonds and microcrystallites, linear PVA molecules form hydrogel. Subsequently, chemical cross-links are introduced by chemical treatment with glutaraldehyde (GA) at above 80°C. The temporary shape can be fixed by means of immersing the system in methanol, a poor solvent, under elongation. The permanent shape can be recovered by exposing the gel to boiling water when physical cross-links become soluble [39, 40].

Chapter 3 Thermo-/chemo-responsive shape memory/change effect in hydrogel

The purpose of this chapter is to systematically investigate the influence of water/moisture content on the shape memory effect (SME) and shape change effect (SCE) in a commercial hydrogel. In addition, the feasibility to utilize hydrogel as the matrix to produce a hybrid with the tailored SME is explored. The major results of this chapter have been published in [46].

3.1 Materials and experiments

3.1.1 Raw materials

The hydrogel balls (Magic Crystal Jelly) used in this study was obtained from Water Babies (<http://www.mementoenterprise.com>). The diameter of dry balls is 1.8 ± 0.1 mm. The hydrogel balls are able to expand significantly upon immersing into room temperature water (about 25°C). The diameter of the hydrogel ball increases from about 1.8 mm before wetting in water to about 9 mm after fully wetting, which means that the volume of the hydrogel ball expands almost 100 times and its weight increases about 400 times. Fully wetted hydrogel balls are able to completely recover their original shape upon drying in air [41] (Figure 3.1). Such a wetting/drying cycle may be repeated many times without apparent degradation in the hydrogel balls themselves. A close look reveals that upon immersing into water, in the early stage, the hydrogel ball actually expands in an anisotropic manner, so that during expansion, right after being taken out of water, *grain* like feature is observed

(Figure 3.1b,c). After leaving the ball in the air for a while, *grain* like feature disappears and the ball appears rather uniform (Figure 3.1b2,c2). Hence, the grain like feature is most likely due to wrinkling of the significantly swelled outer layer of the hydrogel ball.

The typical molecular structure of this type of hydrogel is illustrated in Figure 2.1, in which the cross-linker is N, N' – methylenebisacrylamide [21].

Figure 3.1 Wetting of hydrogel ball in water and drying. (a) Original shape; (b-d) upon wetting in water; (e) after drying in air. (b1, c1) are photos taken in water; (b2, c2) are photos taken after being taken out of water for a while.

Polyethylene glycol (PEG, $\text{HO-CH}_2\text{-(CH}_2\text{-O-CH}_2\text{)}_n\text{-CH}_2\text{-OH}$) was purchased from Sigma-Aldrich Corporation (<http://www.sigmaaldrich.com>). PEG is a water soluble polyether compound with low toxicity and has a range of applications, from industrial manufacturing to medicine [42, 43]. PEG was used to prepare hydrogel/PEG hybrid (HGPH).

Viscous colorless silicone oil with a formula of $(-\text{Si}(\text{CH}_3)_2\text{O}-)_n$ was also bought from Sigma-Aldrich Corporation and was used as received. According to Sigma-Aldrich, its freezing point is -55°C , boiling point is higher than 140°C and flash point is 316.00°C . Instead of heating HGPH in water, silicone oil was used to avoid interaction between water and PEG.

3.1.2 Sample preparation

Hydrogel balls with different water/moisture contents were prepared. Hereinafter, R_w donates the ratio of the weight of the absorbed water/moisture in a hydrogel ball to that of the dry hydrogel itself, i.e.,

$$R_w = \frac{W - W_0}{W_0} \quad (3.1)$$

where W_0 and W are the measured weight of dry hydrogel ball and that after wetting in water or within high humidity environment, respectively. Dry samples were prepared by keeping the hydrogel balls in an oven at 150°C for two hours for *full* water/moisture evaporation.

After exposing the dry samples in the open air for three days at an relative humidity (RH) of about 50% and room temperature (around 25°C), the measured R_w of the resultant samples was about 0.05. These samples are named $\text{HG}_{0.05}$, hereinafter.

Some dry hydrogel balls were placed inside a humidity/temperature controllable chamber at $\text{RH}=100\%$ and room temperature for two hours. The resultant balls had an R_w about 0.8, so that these samples are called $\text{HG}_{0.8}$.

HG_{0.05} were compressed (refer to Section 2.4 for the detailed experimental procedure of compression) at 80°C and left in the open air for three days. The resultant hydrogel balls had an R_w about 0.15 and hence are named HG_{0.15} hereinafter. HG_{0.3}, HG_{0.65}, and HG_{1.2} were prepared by placing the compressed HG_{0.05} balls inside the humidity/temperature controllable chamber at RH=80%, 90%, 100%, respectively, at room temperature for 4.5 hours.

HGPH balls were also prepared to demonstrate the concept of shape memory hybrid [36]. Some dry hydrogel balls were immersed into water containing 1.0 wt % PEG for one day for fully swelling. Subsequently, they were taken out and exposed in the open air for three days (RH=50%, 25°C) for dehydration to produce *dry* HGPH balls. The HGPH balls had a diameter of about 2.5 mm and the weight percentage of PEG in HGPH was about 40%.

3.1.3 Thermal analysis

Thermogravimetric analysis (TGA) tests were conducted to investigate thermal stability of as-received hydrogel and PEG. The experiments were carried out with a specimen around 10 mg (2 hydrogel balls) at a constant heating rate of 10°C/min on a PerkinElmer TGA 7. The temperature range for hydrogel was from 0°C to 800°C and the temperature range for PEG was from 0°C to 600°C.

A series of differential scanning calorimeter (DSC) test were carried out using a DSC-Q200 differential scanning calorimeter at a heating/cooling rate of 10°C/min. The purpose of these DSC tests was to investigate the glass transition temperature (T_g) of hydrogel under different conditions and to investigate the melting temperature (T_m) and crystallization temperature (T_c) of PEG. In these

tests, the specimens were around 10 mg (2 hydrogel balls). The temperature range for hydrogel was between about 0°C and about 100°C, for PEG that was between about 0°C and around 250°C and for HGPH that was between around 0°C and about 100°C. The DSC test for HGPH was conducted for five continuous cycles in order to investigate the influence of thermal cycle number (N_{cycle}) on its T_m .

3.1.4 Compression test

A number of compression tests were conducted using an Instron 5569 with a temperature controllable chamber to investigate the thermo-mechanical properties of hydrogel balls under different conditions and to pre-compress the hydrogel balls.

Ten pieces of hydrogel balls were used in each test. The compression ratio, R_c , is defined as,

$$R_c = \frac{D - H}{D} \quad (3.2)$$

where D is the diameter of the hydrogel balls, while H is the height after compression (refer to Figure 3.2). Note that as shown in Figure 3.2, W is the diameter in the lateral direction of the compression direction.

Ten pieces of HG_{0.05} were compressed at 80°C and a speed of 2.5 mm/min to a maximum compression of $R_c=0.45$, and then held for six minutes, while in the mean time, the compressed balls were cooled down in the air. After cooling, the balls were taken out and found to be *plastically* compressed.

Figure 3.2 Illustration of dimension change in hydrogel ball.

Ten pieces of $HG_{0.8}$ were compressed at room temperature and a speed of 6 mm/min to a maximum compression of $R_c=0.65$, and then unloaded at the same speed. In the other test, ten pieces of $HG_{0.8}$ were compressed at room temperature and a speed of 6 mm/min to a maximum compression of $R_c=0.65$ and then held for four hours at 40°C to dry them. After the removal of the constraint, the balls were observed to be *plastically* compressed.

3.1.5 Characterization of SME and SCE

A series of experiments were conducted to investigate the SME and SCE in hydrogel balls. Refer to Section 3.1.2 for the detailed procedure of sample preparation.

- The SME in $HG_{0.05}$ and $HG_{0.8}$

Pre-compressed $HG_{0.05}$ balls (refer to Section 3.2.2 for the experimental procedure) were kept inside the humidity/temperature controllable cabinet with a setup of $RH=30\%$ and room temperature for four days.

Subsequently, some balls were heated to 80°C to check their thermo-responsive SME. Other balls were placed inside of the humidity/temperature controllable chamber at room temperature but at different RHs. The weight of individual balls was continuously recorded at a time interval of 30 minutes and R_w was calculated accordingly. DSC test was conducted on some balls to investigate the evolution of T_g .

HG_{0.8} balls which were dried at 40°C for four hours before unloading were kept in the humidity/temperature controllable cabinet with a setup of RH=100% and room temperature to investigate their moisture-responsive behavior.

- **The SCE in HG_{0.8} and HG_{0.05}**

HG_{0.8} balls were compressed by a piece of tweezers to check their pressure-responsive behavior.

After being compressed at 80°C to about $R_c=0.45$ and then cooled back to room temperature, HG_{0.05} balls were kept inside the humidity/temperature controllable cabinet at RH=30% and room temperature for four days. Subsequently, these balls were put into room temperature water for swelling test. Some dry balls were also tested for comparison. Their shape change was recorded at a time interval of 15 minutes until fully swollen.

- **Thermo-responsive SME in HGPH**

A piece of HGPH ball was placed inside 70°C silicone oil for two seconds and then compressed to about $R_c=0.5$ using a piece of tweezers. Subsequently, the silicone oil together with the HGPH ball (with the compressed shape being held)

was gradually cooled down to room temperature in the air. After this, the HGPH ball was put into 70°C silicone oil again to check its thermo-responsive behavior.

3.2 Results and discussion

3.2.1 Thermal analysis

Figure 3.3 presents the TGA result of hydrogel, which reveals that upon heating from room temperature, the weight of the hydrogel decreases all the way monotonically. When being heated to 200°C, the weight lost is about 16%. Upon further heating to about 500°C, the remaining weight is only around 40%.

Figure 3.3 TGA result of hydrogel.

TGA result of PEG is revealed in Figure 3.4. As we can see, PEG starts to decompose at about 200°C.

Figure 3.4 TGA result of PEG.

Figure 3.5(a) plots the DSC results of hydrogels with different R_w . Note that due to the non-uniformity nature of moisture absorption in hydrogel balls, R_w determined here is essentially nominal. As we can see, dry sample (HG_0) and $HG_{1,2}$ do not show apparent T_g within the temperature range of 0~100°C. On the other hand, for other tested samples, with the increase in R_w , T_g , which is defined as the median point as marked in Figure 3.5(a), decreases.

Figure 3.5 (a) DSC results of hydrogels with different R_w ; (b) T_g as a function of R_w .

Based on the results in Figure 3.5(a), we plot the evolution of T_g as a function of R_w in Figure 3.5(b). We can see that T_g drops from about 58°C to around 37.5°C, when R_w increases from 0.05 to 0.65. Apparently, T_g drops dramatically when R_w changes from 0.05 to 0.09. After that, the change becomes gradual. It is noticed that while the onset point decreases with the increases of R_w , the end point does not change much, which partially confirms the non-uniformity of moisture within the hydrogel ball.

Figure 3.6 reveals the DSC result of PEG, in which T_m and T_c are found to be about 67°C and 42°C, respectively. A hysteresis of about 25°C between melting and crystallization is observed.

Figure 3.6 DSC result of PEG in one thermal cycle.

DSC result of five continuous heating/cooling cycles of HGPH is presented in Figure 3.7. As revealed, in the 1st cycle, the T_m of HGPH is about 60.5°C, while the T_c of HGPH is around 51°C. Both are different from those of the pure PEG. The interaction of PEG with hydrogel should be the reason for the difference.

During thermal cycling, T_m increases from originally 60.5°C to 62.7°C in the 5th cycle, largely due to the loss of water. However, this is still lower than the T_m of pure PEG by about 5°C. The relationship between T_m and N_{cycle} is plotted in Figure 3.8 (together with data-fitting to show the trend).

Figure 3.7 Cyclic DSC result of HGPH: (a) In heating; (b) in cooling.

Figure 3.8 Evolution of T_m upon thermal cycling.

On the other hand, T_c is always around 49°C even after five thermal cycles. i.e., it is always about 7°C higher than that of the pure PEG.

It might be possible to conclude that the hysteresis in HGPH is narrower than that of pure PEG, and 70°C is above the melting transition temperature range of HGPH.

3.2.2 Compression tests

Figure 3.9 plots the experimental result of HG_{0.05} upon compression at 80°C, which is above its T_g , and then cooled back to room temperature. Figure 3.10 presents the evolution of the corresponding compression load against time in the whole compression and the cooling processing. As shown, there is a sudden drop in the compression load at 8 s, which corresponds to an R_c of 0.18. After that the compression force increases continuously as before. According to [36], it should be reasonable to say that this sudden drop indicates the turning point from elastic deformation to *quasi-plastic* deformation. Upon cooling, the compression load decreases sharply at the beginning of cooling process and then gradually until reaches 0. Essentially, there are two major players which contribute to the decrease in the compression load, one is shape fixing during cooling and other is thermal contraction. While both are in active in the early cooling process, the latter should be the key reason for zero compression force after cooling back to room temperature.

Figure 3.11(a) shows the compression result of 10 pieces of HG_{0.8} in a typical loading-unloading cycle at room temperature. Low hysteresis in the cycle indicates good elasticity of HG_{0.8}. As compared with the compression force in Figure 3.9 for HG_{0.05}, which is at 100s N level, HG_{0.8} is much softer (a couple of N only, even at 65% compression). In addition, Figure 3.11(b) plots the

evolution of compression load against time in this cycle, which is within 24 s for a complete cycle, and thus confirms the rubber-like nature of HG_{0.8}.

Figure 3.9 Compression load vs. R_c relationship of 10 pieces of HG_{0.05} at 80°C and then cooled to room temperature.

Figure 3.10 Evolution of compression load against time in the compression test (refer to Figure 3.9).

Figure 3.11 HG_{0.8} in a typical loading-unloading cycle (a) Compression load vs. R_c relationship; (b) Evolution of compression load against time.

3.3.3 Shape change/memory effect

- Thermo-responsive SME in HG_{0.05}

Figure 3.12(a) and (b) present two pieces of typical HG_{0.05} balls, before and after pre-compression at 80°C, respectively. The compressed balls were kept in the dry cabinet for four days at 30% RH and 25°C. There is not any apparent shape change in both of them (Figure 3.12c). HG_{0.05} is able to virtually fully recover its original shape within a few seconds upon heating to 80°C (Figure 3.12d).

Figure 3.12 Thermo-responsive SME in HG_{0.05}. (a) Original shape; (b) after pre-compression at 80 °C; (c) after kept in dry cabinet for four days at 30% RH and 25°C; (d) after recovery by heating to 80°C for a few seconds. The left one is for reference.

- **Moisture-responsive SME in HG_{0.05}**

In Figure 3.13, after being compressed at 80°C and kept at room temperature and RH=30% for four days, the ball (HG_{0.05}) was still distorted (Figure 3.13b). After exposing to an environment of RH=100% and room temperature for one hour, full shape recovery was observed in Figure 3.13(c).

Figure 3.14 plots the relationship between RH and the required time for *apparent* full shape recovery, while Figure 3.15 presents the evolution of R_w at different RHs. As we can see, *apparent* full shape recovery time is dramatically shortened when RH is increased from 50% to 80%. On the other hand, based on the trend, it is possible to conclude that at RH=30%, the required time for full shape recovery is almost infinite. The corresponding R_w at *apparent* full shape recovery for different situations is marked in grey in Figure 3.15. Apparently, at a higher RH, it takes shorter time for full shape recovery, while the corresponding R_w is higher, which attributes to the non-uniformity nature of moisture penetration. RH=50% and $R_w=0.15$ is about the minimal requirement for moisture induced full shape recovery for this hydrogel.

Figure 3.13 Moisture-responsive SME in HG_{0.05} (right ball without compression is for comparison). (a) Original shape; (b) left ball was compressed at 80°C and kept in dry cabinet for four days at 30% RH and room temperature; (c) after one hour at 100% RH and room temperature.

Figure 3.14 Time for *apparent* full recover vs. RH relationship. Black curve is to show the general trend.

Figure 3.15 Evolution of R_w against time at room temperature and different RHs. Grey symbols indicate *apparent* full shape recovery; and dotted grey line is data-fitting.

- Rubber-like behavior in $HG_{0.8}$

Figure 3.16 presents the snapshot of $HG_{0.8}$ in compression using a pair of tweezers at room temperature. Given that the whole compression/release

operation was done within 8 seconds in total (4 s for compression and 4 s for release), and remarkable shape change was fully recovered, the features of high elasticity and rubber-like behavior of $\text{HG}_{0.8}$ observed in Figure 3.11 are reconfirmed.

Instead of compression at high temperatures, Figure 3.17 reveals another approach to fix the temporary shape (programming). Since $\text{HG}_{0.8}$ is rubber-like, it is able to be easily compressed at room temperature. After dehydration at 40°C for three hour with the distorted shape being held, $\text{HG}_{0.8}$ was able to maintain the compressed shape at room temperature and $\text{RH}=30\%$ (Figure 3.17b). Full shape recovery was achieved after it was placed in the cabinet at 100% RH for two hours at room temperature (Figure 3.17c).

Figure 3.16 Rubber-like behavior in $\text{HG}_{0.8}$. Top ball is presented for comparison. (a-c) During compression; (c-f) during release.

Figure 3.17 Moisture induced programming and shape recovery in $HG_{0.8}$. (a) Original shape; (b) after being compressed and kept in oven at 40°C for three hours; (c) after exposing to 100% RH at 25°C for two hour.

Figure 3.18 The SCE in $HG_{0.05}$. (a) Balls with/without pre-compression; (b1-d1) snapshots during swelling (side-view of pre-compressed ball); (b2-d2) snapshots during swelling (top-view of pre-compressed ball); (e) 60 minutes in water; (f) three days after drying in the air.

- SCE in $HG_{0.05}$

Two pieces of $HG_{0.05}$ balls were tested for the water-induced SCE (Figure 3.18(a)). One was pre-compressed (refer to Section 3.2.4 for the experimental procedure), while the other was without pre-compression (for comparison). They were put into room temperature water at the same time and their recover

process was monitored. Snapshots of the swelling process for both of them are presented in Figure 3.18(b-e) with the immersing time indicated.

Variation in dimensions (i.e., D , W and H , refer to Figure 3.2) during wetting in room temperature water is estimated and plotted in Figure 3.19. We can clearly see that,

- Grain-like feature observed in both samples with/without pre-compression reveals the non-uniformity in swelling in the early wetting stage (at least till 45 minutes in water).
- More importantly, while the ball without pre-compression expanded in a quasi-isotropic fashion, the other ball with pre-compression swelled in a rather anisotropically manner.
- The pre-compressed ball maintained its disk shape in the early swelling stage (till at least 45 minutes in water) and then became spherical (similar, if not identical, to that without pre-compression).

Figure 3.19 Variation in dimensions during swelling of $HG_{0.05}$. W and H are for the pre-compressed ball, while D is for the ball without pre-compression.

After wetting in water for 60 minutes, grain-like features disappeared in both balls (Figure 3.18e). After dehydration in open air for three days, both balls returned their original shape (Figure 3.18f).

- **Thermo-responsive SME in HGPH**

The ability to swell or shrink in response to the presence or removal of the right external stimulus enables hydrogels for many applications, such as in biomedical devices and drug delivery [28, 44, 45]. Furthermore, hydrogels can be used as the skeleton/matrix in the design of shape memory hybrids with tailored features [36]. The PEG we used here is very brittle and fragile at room temperature, which prevents it having good SME.

In Figure 3.20(a), HGPH prepared according to the procedure presented in Section 3.1.2 was immersed into 70°C silicone oil (which is above the melting temperature of PEG) for two seconds and then compressed using a piece of tweezers (Figure 3.20(b)). After cooling the silicone oil (together with the compressed HGPH ball) back to room temperature, the distorted shape of the compressed HGPH was largely maintained. Upon immersing into 70°C silicone oil again, HGPH fully recovered its original shape within nine seconds.

Figure 3.20 Thermo-responsive SME in HGPH (blue one, at right, is for comparison). (a) Original shape; (b) compressed at 70°C; (c1-c3) upon immersing into 70°C silicone oil.

3.3 Further discussion

Unlike that in most of the previous studies on hydrogels, in which the heating-/moisture-responsive SME and SCE are investigated separately[6-8, 19], the results of above systematical investigation reveal some interesting features of this hydrogel, and these features may be used in a combined manner for novel applications, which cannot be easily achieved by utilizing only one feature.

Due to the high non-uniformity nature of water/moisture penetration in the hydrogel, it is difficult to work out quantitative expressions for the relationships among $R_w/T_g/RH$ /wetting time. However, based on the results of above experiments the thermo-/chemo- (water/moisture) response of the hydrogel can be qualitatively summarized as shown in Figure 3.21. It should be pointed out that for this hydrogel, the cross-linker N, N' – methylenebisacrylamide serves as the elastic network, which stores elastic energy for shape recovery.

A is fully dried hydrogel, which is hard and brittle, and has no apparent transition within the tested temperature range (refer to Figure 3.5). B has around 5wt% of water and C has about 80wt% of water content. B and C are obtained upon exposing into high humidity environment. Despite of the difference in water/moisture content, A, B and C are about the same size.

Wetting A or B in water, water penetrates into them from the out surface inward (C'') and finally reaches D, which has 40000wt% of water. C is able to swell in water as A and B as well. Dried in air, D shrinks back to C, and upon further dehydration, back to B and finally to A. Between D and C, it is a reversible process of swelling and deswelling (shrink) (the water induced SCE).

Figure 3.21 Moisture/water content dependent response of hydrogel.

A is fully dried hydrogel, which is hard and brittle, and has no apparent transition within the tested temperature range (refer to Figure 3.5a). B has around 5wt% of water and C has about 80wt% of water content. B and C are obtained upon exposing into high humidity environment. Despite of the difference in water/moisture content, A, B and C are about the same size.

Wetting A or B in water, water penetrates into them from the out surface inward (C'') and finally reaches D, which has 40000wt% of water. C is able to swell in water as A and B as well. Dried in air, D shrinks back to C, and upon further dehydration, back to B and finally to A. Between D and C, it is a reversible process of swelling and deswelling (shrink) (the water induced SCE).

B can be programmed (compression) at high temperatures ($> T_g$). The distorted shape (B') can be eliminated upon heating to above its T_g again (back to B, the thermally induced SME) or upon exposing into a high humidity environment (to C, the moisture induced SME).

C has higher water content than B, and behaves in a rubber-like manner when distorted (C'), since its T_g is around or lower than room temperature. Programming (to B') can be realized by means of holding the distorted shape (C') and then drying. The change in shape between B' and C' is small, if not nil.

Upon wetting B' in water, it expands in all directions (B''), in elliptical shape) before turns to be a spherical shape (D).

B-B'-C is a triangle for the SME (lower water/moisture-content), while C-C'-D is a triangle for the SCE (higher water/moisture-content).

As pointed out in [36], depending on the actual working environment, a material may have the SME or SCE. For this hydrogel, the actual amount of moisture content determines whether it has the SME or SCE. This phenomenon is similar to the influence of moisture on polyurethane, although the actual volume expansion in polyurethane is very small [1]. Absorbed water serves as plasticizer to reduce T_g , which is the underlying mechanism for both polyurethane and hydrogel.

This moisture dependent phenomenon is generic and should be applicable in many hydrogels.

3.4 Conclusions

Water/moisture-content dependant behavior in a commercial hydrogel is systematically investigated in this chapter. At lower water/moisture contents, the hydrogel shows the thermo-responsive SME and moisture-induced SME; while at higher water/moisture contents, the hydrogel has the rubber-like SCE and water-induced SCE. Due to the high non-uniformity nature of water/moisture penetration in the hydrogel, the relationships among $R_w/T_g/RH$ /wetting time are only qualitatively established. Furthermore, it is revealed that on the one hand, programming can be realized by means of deforming at high temperatures (above T_g) or dehydration after pre-deforming rubber-like hydrogel; on the other hand, hydrogel can be used as the elastic matrix in a hybrid for tailored SME.

Chapter 4 Characterization of cuboid hydrogel and its potential applications

As revealed in Chapter 3, it is difficult to precisely characterize the shape memory effect (SME) and shape change effect (SCE) in a ball shaped hydrogel. The purpose of this chapter is to systematically investigate the SME/SCE in another commercial hydrogel which is in cuboid shape.

4.1 Materials and experiments

4.1.1 Raw materials

The hydrogel (Figure 4.1) (Rainbow Clay) used in this study was obtained from Water Babies (<http://www.mementoenterprise.com>). Different from the hydrogel investigated in Chapter 3, as received cuboid hydrogel is rubber-like at room temperature (about 25°C). The hydrogel is able to expand significantly upon immersing into room temperature water.

Figure 4.1 As received Rainbow Clay ($\approx 4 \times 4 \times 4$ mm).

4.1.2 Sample preparation

Dry samples (CHG_0) were prepared via keeping inside a dry cabinet for seven days at 20%RH and room temperature.

If leaving the dry samples in the open air for two days, the hydrogels became rubber-like again. The measured R_w of these samples is about 0.21 and these samples are named $\text{CHG}_{0.21}$, hereinafter.

Refer to Figure 4.2 and Figure 4.3. Straw A (outer diameter $D=3.2$ mm and thickness $t=0.3$ mm), straw B ($D=6$ mm and $t=0.1$ mm) and straw C ($D=11.6$ mm and $t=0.45$ mm), were used to cut a fully wetted hydrogel. CHG_a (rod) was cut from fully wetted hydrogel using straw A. CHG_b (tube) was cut from fully wetted hydrogel using straw A and straw B. CHG_c (tube) was cut from fully wetted hydrogel using straw B and straw C. The samples were dried in an oven at 50°C . After being dried, CHG_a had a diameter of 0.47 mm in the middle section. CHG_b had an outer diameter of 0.96 mm and inner diameter of 0.47 mm. CHG_c had an outer diameter of 1.82 mm and inner diameter of 0.96 mm.

Hydrogel/ polyethylene glycol (PEG) hybrid (CHGPH) based on this hydrogel was also fabricated (Figure 4.4). The following procedure was applied. A dry hydrogel is immersed into water containing 1.6 wt % of PEG for one day for fully swelling. Subsequently, it is taken out and exposed in the open air for five weeks (RH=50%, 25°C) for dehydration to produce *dry* CHGPH. The resulted dry CHGPH has 35% of PEG in weight.

Figure 4.2 Fully wetted hydrogel, from which CHG_a , CHG_b and CHG_c were produced. (a) Original hydrogel; (b1-b4) upon wetting in room temperature water; (c) comparison of fully wetted and dry hydrogel.

Figure 4.3 CHG_a , CHG_b and CHG_c . Fully wetted (left); dry (right).

Figure 4.4 CHGPH. (a) fully wetted; (b) after dehydration for 17 hours.

4.1.3 Compression tests

One piece of dry hydrogel with a length of 4 cm, width 4 cm and height 3.8 cm was compressed at room temperature and a constant strain rate of 2.6%/s to a maximum compression of 3 mm, and then unloaded at the same speed to investigate its mechanical performance.

Another piece of hydrogel (with a length of 6 cm, width 5 cm and height 6.5 cm), which was rubber like, was compressed at room temperature and a strain rate of 1.5%/s to a maximum compression of 3 mm, and then unloaded at the same speed. The test was continuously repeated for three times on the same sample.

4.1.4 Thermal analysis

A series of differential scanning calorimeter (DSC) tests were carried out using a DSC-Q200 differential scanning calorimeter at a heating/cooling rate of 10°C/min on CHG₀, and CHG_{0.21} to investigate the glass transition temperature (T_g) in hydrogel under different conditions and to find the transition temperature(s) of CHGPH. In these tests, the specimens were around 10 mg and the temperature range was normally between about -40°C and about 100°C.

4.1.5 Characterization of SME and SCE

- Thermo-responsive SME/SCE

A piece of CHG₀ was bent using a pair of tweezers in 80°C silicone oil. When the sample together with the silicone oil cooled down (with the temporary shape being held), the temporary shape was fixed. After this, the hydrogel was put into 80°C silicone oil again to check its thermo-responsive behavior.

- **Moisture-responsive SME**

A piece of CHG_0 was bent side in 80°C silicone oil using a pair of tweezers. When the sample together with the silicone oil cooled down (with the temporary shape being held), the temporary shape was fixed. After this, the hydrogel was kept in a chamber with 100% RH at room temperature to check its moisture-responsive behavior.

- **Water-responsive SME**

A piece of CHG_0 was bent using a pair of tweezers at high temperatures as mentioned above. When the sample cooled down (with the temporary shape being shape held), the temporary shape was fixed. After this, the hydrogel was immersed into room temperature water to swell and then dehydrated in the open air (50% RH and about 25°C) to check its moisture-responsive behavior.

A piece of CHG_0 was stretched at high temperatures and cooled down to room temperature (with the stretched shape being fixed). Then the temporary shape was fixed. After that the sample was immersed into room temperature water to fully swell and then taken out of water to dehydrate. Meanwhile, another piece of dry hydrogel, which was not stretched, was immersing into room temperature water to observe its behavior for comparison.

A piece of CHG_0 was indented on its surface at high temperatures. After cooled down to room temperature (with the indenter being maintained), the temporary shape was produced. Subsequently, a water droplet was dropped on the indented area to check its response.

A small piece of CHG_0 was bent at high temperatures and then cooled down to room temperature. The temporary shape was obtained. A water droplet was dropped on one end of the bent hydrogel to check its reaction.

CHG_a , CHG_b and CHG_c were immersed into room temperature water to investigate its swelling behavior. Hereinafter D is the diameter of the hydrogel after swelling and d in the original diameter of the hydrogel before swelling.

- **Thermo-responsive SME in CHGPH**

A piece of CHGPH was placed inside 70°C silicone oil for two seconds and then bent using a piece of tweezers. Subsequently, the silicone oil together with the CHGPH (with the bent shape being held) was gradually cooled down to room temperature in the air. After this, the CHGPH was put into 70°C silicone oil again to check its thermo-responsive behavior.

- **Wrinkling**

The top surface of a piece of CHG_0 was wetted slightly using a few water droplets. Further wetting was done by dropping more water droplets on the surface. The wetting process was recorded.

Another piece of CHG_0 was wetted by one water droplet on its top surface. The evolution of the surface morphology was monitored under an optical microscope and recorded in real time.

4.2 Results and discussion

4.2.1 Compression tests

Figure 4.5 plots the experimental result of CHG_0 upon compression to a maximum strain of 78.9%. As we can see, during compression, the stress increases continuously and there is not any sudden drop even the sample cracks (Figure 4.6). After unloading, the residual strain is about 66.9%.

Figure 4.5 Compression stress vs. compression strain relationship of CHG_0 in a typical loading-unloading cycle.

Figure 4.6 Dry hydrogel after compression.

Figure 4.7 shows the compression result of one piece of $\text{CHG}_{0.21}$ in three continuous loading-unloading cycles at room temperature. Low hysteresis during cycling indicates good elasticity of this hydrogel. As compared with the

compression stress of CHG_0 in Figure 4.5, which is at 100s MPa level, rubber like hydrogel is much softer.

Figure 4.7 Compression stress vs. compression strain relationship of $\text{CHG}_{0.21}$ in three loading-unloading cycles.

4.2.2 Thermal analysis

Figure 4.8 presents the DSC results of hydrogels with different R_w . Note that due to the non-uniformity nature of moisture absorption in hydrogel, R_w determined here is essentially nominal. As we can see, there is obvious difference in T_g between CHG_0 and $\text{CHG}_{0.21}$.

Figure 4.8 DSC results of CHG_0 $\text{CHG}_{0.21}$.

DSC result of CHGPH in one thermal cycle is presented in Figure 4.9. As revealed, the melting temperature (T_m) of CHGPH is about 60 $^{\circ}\text{C}$, while its crystallization (T_c) is around 43 $^{\circ}\text{C}$, which is different from pure PEG and HGPH reported in section 3.2.1.

Figure 4.9 DSC result of CHGPH.

4.2.3 Thermo-responsive SME

A piece of CHG_0 ($\approx 4 \times 4 \times 6$ mm) was pre-bent using a pair of tweezers in 80°C silicone oil. When the sample together with the silicone oil cooled down (with the temporary shape being held), the temporary shape was fixed. The sample is able to recover its original shape in 20 seconds upon immersing into 80°C silicone oil again (Figure 4.10).

Figure 4.10 Thermo-responsive SME in CHG_0 : (a) Original shape; (b) after bending in silicone oil at 80°C ; (b-e) shape recovery upon immersing into 80°C silicone oil.

Refer to Figure 4.11. A small piece of CHG_0 ($\approx 0.7 \times 0.7 \times 7$ mm) was pre-bent in 80°C silicone oil using a pair of tweezers. With the temporary shape being fixed, the sample together with the silicone oil was cooled down and the temporary shape was resulted (Figure 4.11a-b). the deformed sample recovered its original shape in 9 seconds upon immersing into 80°C silicone oil again (Figure 4.11b-e).

Figure 4.11 Heating-responsive SME of small sized CHG_0 . (a) Original shape; (b) after being deformed; (b-e) shape recovery sequence. The ball (top) has a diameter of 1.5 mm and is used as a reference.

4.2.4 Moisture-responsive SME

As shown in Figure 4.12, a piece of CHG_0 ($\approx 4 \times 4 \times 6$ mm) was pre-bent using a pair of tweezers in 80°C silicone oil. When the sample together with the silicone oil was cooled down (with the temporary shape being fixed) to room temperature, the temporary shape was obtained (Figure 4.12b). The sample recovered its original shape in 110 minutes after being kept in a circumstance with 100% RH at room temperature to absorb moisture (Figure 4.12b-e).

Figure 4.12 Moisture-responsive SME in CHG_0 : (a) Original shape; (b) after being deformed in silicone oil at 80°C ; (b-e) sequence of shape recovery.

4.2.5 Water-responsive SME/SCE

As revealed in Figure 4.13 and Figure 4.14, a piece of CHG_0 ($\approx 5 \times 5 \times 7$ mm) was pre-bent using a pair of tweezers at high temperatures. After the sample was cooled down (with the temporary shape being fixed), the temporary shape was resulted (Figure 4.13b). The sample recovered its original shape upon swelling and then dehydration for two days (Figure 4.14).

Figure 4.13 Swelling in distorted hydrogel.

Figure 4.14 Dehydration of hydrogel (Figure 4.13e).

In Figure 4.15, shape change in a piece of CHG_0 ($\approx 4 \times 6 \times 9$ mm) pre-stretched at high temperatures upon immersing into room temperature water is revealed. We can see flower shaped features at the beginning of wetting. After prolonged immersion, the sample fully swells and becomes featureless. In Figure 4.2(c), fully swelled hydrogel is compared with the dry hydrogel to reveal remarkable volume expansion in this hydrogel after fully wetted in water. It is noticed in Figure 4.15 that upon wetting in water, the pre-stretched gel does not seemingly shrink at all but expanding all the way (same as a pre-compressed hydrogel ball reported in section 3.3.3 [46], although they are different hydrogel). This is because the magnitude of volume expansion due to swelling is far greater than that in water/moisture-induced shape recovery in these two hydrogels. The fully swelled hydrogel took 14 days to be fully dried (Figure 4.16). And after dehydration the hydrogel recovered its original shape.

Figure 4.15 Swelling of hydrogel (pre-stretched at high temperatures) upon immersing into room temperature water.

Figure 4.16 Dehydration of hydrogel (Figure 4.15c5).

As we can see in Figure 4.17, the indent on the top surface of CHG_0 ($\approx 4 \times 5 \times 6$ mm) recovered its original shape after being wetted by a water droplet.

Figure 4.17 Shape recovery induced by water droplet.

In Figure 4.18, the small piece of CHG_0 ($\approx 1 \times 1 \times 8$ mm) was pre-bent at high temperatures. After the sample was cooled (with the temporary shape being fixed), the temporary shape was produced. One water droplet was dropped on the bottom end of the hydrogel. In a few minutes, the bottom part swelled and recovered its original shape, while the top end maintained their dried size and distorted shape.

Figure 4.18 Shape recovery induced by water droplet

CHG_a, CHG_b and CHG_c were immersed into room temperature water. Figure 4.19 shows their swelling process. Figure 4.20 plots the relationship of D/d against time. It is easy to see that CHG_a and CHG_c swell faster than CHG_b.

Figure 4.19 Swelling of CHG_a, CHG_b and CHG_c. (a1), (b1) and (c1) are dry samples, (a1-a6), (b1-b6) and (c1-c6) are in swelling process. The ball has a diameter of 6 mm and is for reference.

Figure 4.20 D/d vs. time relationship in the swelling of CHG_a, CHG_b and CHG_c.

4.2.6 Thermo-responsive SME in CHGPH

In Figure 4.21, a piece of CHGPH ($\approx 2.5 \times 2.5 \times 7$ mm) was pre-bent in 70°C silicone oil (which is above its melting temperature). With the temporary shape being fixed, the CHGPH together with the silicone oil was cooled down and the temporary shape was achieved. Upon immersing into 70°C silicone oil again, CHGPH fully recovered its original shape within three minutes.

Figure 4.21 Thermo-responsive SME in CHGPH. (a) Original shape; (b) after bending at 70°C; (b-e) upon immersing into 70°C silicone oil. The ball (top) has a diameter of 1.5 mm and is used for reference.

4.2.7 Wrinkling

In Figure 4.15, flower shaped feature is observed in the early wetting stage. Furthermore, it seems that the size of the features seemingly starts from small, then becomes bigger and finally disappears. Two simple wetting tests were conducted to monitor the evolution of surface morphology.

In one test, the top surface of a piece of CHG_0 ($\approx 5 \times 5 \times 4$ mm) (Figure 4.22a) was wetted slightly. Small sized wrinkles were observed on its top surface (Figure 4.22b). Further wetting using more water resulted in larger sized wrinkles on the surface (Figure 4.22c). Upon wetting by more water, eventually the whole top surface swelled but became smooth (Figure 4.22d). After stopping wetting the mushroom like sample for a while, the top part of the sample shrank (Figure 4.22e).

Figure 4.22 Evolution of morphology in wetting/drying top surface of a piece of hydrogel. (a) Original shape; (b) after slight wetting; (c) further wetting; (d) upon further wetting; (e) after drying for a while.

In the other test, a piece of dry hydrogel cuboid was wetted by a water droplet on its top surface. The evolution of the surface morphology was observed under an optical microscope and recorded in real time. Snapshot is presented in Figure

4.23. As we can see, after wetting by water droplet, small *protrusions* emerged at about 55 second and then grew. From about 80 second small *protrusions* merged together to form bigger ones. From 115 second, *protrusions* started to disappear. At 300 second, the surface virtually returned the original morphology.

Above two experiments provide all necessary information to explain the mechanism behind the evolution of morphology in water wetting hydrogel presented in Figure 4.15.

Figure 4.23 Water droplet on hydrogel. (a) Before wetting; (b) spreading of water droplet; (c-l) after wetting by water droplet. The horizontal size of all images is 1 mm.

In the early stage of wetting by water, the surface layer of the hydrogel is wetted and softened. Swelling of the thin softened layer results in small sized wrinkles (Figure 4.22b). Upon further wetting, water penetrates deeper (Figure 4.22c), and thus the wavelength of wrinkles becomes larger, and eventually wrinkles totally disappear while the top part of the hydrogel expands into a mushroom like shape (Figure 4.22d). After stopping wetting by water, water spreads within the hydrogel to move deeper, so that the water content at the top part is reduced.

Consequently, the top part shrinks a bit (Figure 4.22e). Essentially, the experimental observation shown in Figure 4.23 can be explained in a similar way.

4.3 Further discussion and remarks

The change in microstructures in hydrogel is schematically illustrated in Figure 4.24. Let us start from (a), which is fully swelled gel. Upon drying [(1)], it shrinks to (b). Further drying [(3)] to (c), the volume change is relatively ignorable. Upon wetting in high humidity environment [(4)], i.e., (c) to (b), there is no significant volume change, but the gel changes from hard to viscous elastic or rubber-like (depending on the actual amount of water content), i.e., the mechano-responsive SCE. Further wetting in water [(2)], the gel swells remarkably. A combination of steps (1) and (2) is the water-responsive SCE. (d) may be reaches from (a), (b) or (c). But the latter two are practically more accessible. We may either stretch (b) and then dry it [(5)], or heat (a) and then stretch it to produce (d) [(7)]. Heating (d) results in (c) [(8), heating-responsive SME] and wetting (d) in high humidity environment produces (b) [(6), moisture-responsive SME]. Wetting (d) in water produces (a).

4.4 Potential applications

In addition to utilizing only individual phenomenon as in many previous research works (e.g., in [44, 45]), water/moisture content dependent SCE/SME in one hydrogel may be combined together for novel applications.

A moisture accumulation sensor may be fabricated based on the thermo-responsive and moisture-responsive SMEs in such a hydrogel. At above the T_g , one can easily deform a piece of dry hydrogel into the temporary shape (Figure 4.25a). In the later stage, upon absorbing an enough amount of water, due to the moisture-responsive SME, the hydrogel is able to return its original shape. By means of monitoring the shape recovery progress, one can determine the amount of accumulated water in the hydrogel.

Figure 4.24 Illustration of changes in micro structures in hydrogel in shape switching. (a) Fully swelled; (b) wet shape without apparent swelling; (c) dry shape; (d) deformed temporary shape.

Figure 4.25 Accumulated moisture sensor based on hydrogel. (a) Dry hydrogel deformed above T_g ; (b) shape recovery upon absorbing moisture.

Figure 4.26(a) illustrates the fully wetted hydrogel, which is in a coiled shape with both ends expanded to essentially serve as stoppers to prevent migrating after being fully deployed. After drying, it shrinks remarkably (water-responsive SCE) as shown in Figure 4.26(b). Utilizing the thermo-responsive SME, the dry hydrogel coil can be heated and straightened into a straight wire shape (Figure 4.26c). Since the dry hydrogel is hard at room temperature and thin, the straightened hydrogel can be inserted into a syringe and directly injected into the desired position. Upon wetting, the straightened hydrogel swells and recovers its original shape (as shown in Figure 4.26a), and thus to effectively block the vessel. Here, a combination of swelling and forming structure enables better occlusion than previous devices, such as Gelform[®] and Surgiform[®].

Figure 4.26 Hydrogel coil for embolization. (a) Fully swelled shape; (b) dry shape; and (c) (dry) gel after stretching at high temperatures. [46]

Chapter 5 Shape memory/change effect in a double network nanocomposite hydrogel

The hydrogels investigated in Chapter 3 and Chapter 4 are brittle after being fully wetted. In this chapter the SME in a double network nanocomposite hydrogel (DNHG) which is tougher even after full swelling is studied.

5.1 Materials and experiments

5.1.1 Raw materials

The double network nanocomposite hydrogel (PAMPS/PAAm) is provided by professor Jun Fu and is synthesized following the procedure reported in [47]. In this hydrogel, silica nanoparticles grafted with vinyl end groups are used as macro-crosslinkers to copolymerize with AMPS, yielding a nanocomposite first network, and subsequent introduction of a secondary PAAm network resulted in super-tough double-network (DN) composite hydrogels, which do not fracture upon stretching up to 73 MPa and a strain above 98%. As received hydrogel was about 6.8 cm thick (fully wetted).

5.1.2 Sample preparation

Dry samples were prepared by keeping the hydrogel in an oven at 70°C for 1 hour for *full* water/moisture evaporation. The R_w of the resultant samples was set as 0. These samples are named DNHG₀, hereinafter.

Fully wetted samples were prepared by immersing the DNHG_0 into room temperature water for one day until the water content was stable. The measured R_w of the resultant samples was about 7.5. These samples are named $\text{DNHG}_{7.5}$.

After exposing $\text{DNHG}_{7.5}$ in the open air for one day at a relative humidity (RH) of about 50% and room temperature (around 25°C) to lose water and the measured R_w of the resultant samples was about 0.3 and these were in the rubber like state. These samples are named $\text{DNHG}_{0.3}$.

After exposing $\text{DNHG}_{7.5}$ in the open air for three days at a relative humidity (RH) of about 50% and room temperature (around 25°C) to lose water and the measured R_w of the resultant samples was about 0.05. These samples are named $\text{DNHG}_{0.05}$.

Using two pieces of aluminum strips which were bent into an “S” shape, a piece of “S” shaped fully wetted hydrogel was cut from a big piece of hydrogel. An “S” shape $\text{DNHG}_{0.05}$ (about 3 mm thick) was obtained after drying in the open air at room temperature for three days.

5.1.3 Compression tests

One piece of DNHG_0 ($\approx 3 \times 3 \times 2.4$ cm) was compressed at room temperature and a strain rate of 4.2%/s to a maximum compression of 1.2 mm to study its mechanical behavior.

One piece of $\text{DNHG}_{0.3}$ ($\approx 4 \times 4 \times 3.2$ cm), which was in the rubber like state, was compressed at room temperature and a strain rate of 3.1%/s to a maximum

compression of 2.5 mm, and then unloaded at the same speed. The test was continuously repeated for three times.

Another piece of DNHG_{7.5} ($\approx 8 \times 6.3 \times 6.8$ cm) was compressed at room temperature and a strain rate of 1.5%/s to a maximum compression of 4 mm, and then unloaded at the same speed. The test was finished after seven continuous cycles.

5.1.4 Thermal analysis

A series of differential scanning calorimeter (DSC) tests were carried out using a DSC-Q200 differential scanning calorimeter at a heating/cooling rate of 10°C/min for DNHG₀, DNGH_{0.05}, DNGH_{0.3} and DNHG_{7.5}. The purpose of these DSC tests was to investigate the glass transition temperature (T_g) of hydrogel with different conditions. In these tests, the specimens were around 10 mg. The temperature range was normally between about -40°C and about 100°C for all samples.

5.1.5 Characterization of SME

A series of experiments were conducted to investigate the SME in the double network nonocomposite hydrogel. Refer to Section 5.1.2 for the detailed procedure of sample preparation.

- The SME in DNHG₀

A piece of DNHG₀ was placed inside 100°C silicone oil for 30 seconds and then deformed using a piece of tweezers. Subsequently, the silicone oil together with

the DNHG_0 (with the temporary shape being held) was gradually cooled down to room temperature in the air. After this, DNHG_0 was put into 100°C silicone oil again to investigate its thermo-responsive behavior.

- **The SME in $\text{DNHG}_{0.05}$**

A piece of $\text{DNHG}_{0.05}$ was placed inside 80°C silicone oil for 30 seconds and then bent using a piece of tweezers. Subsequently, the silicone oil together with the $\text{DNHG}_{0.05}$ (with the temporary shape being held) was gradually cooled down to room temperature in the air. After this, $\text{DNHG}_{0.05}$ was put into 80°C silicone oil again to check its thermo-responsive behavior.

A piece of $\text{DNHG}_{0.05}$ was placed inside 80°C silicone oil for 30 seconds and then compressed using a one dollar Singapore coin. Subsequently, the silicone oil together with the $\text{DNHG}_{0.05}$ and the coin (with the temporary shape being held) was gradually cooled down to room temperature in the air. After this, one water droplet was dropped on the surface. Finally the piece of $\text{DNHG}_{0.05}$ was put into 80°C silicone oil again to study its thermo-responsive behavior.

A piece of $\text{DNHG}_{0.05}$ was placed inside 80°C silicone oil for 30 seconds and then bent using a piece of tweezers. Subsequently, the silicone oil together with the $\text{DNHG}_{0.05}$ (with the temporary shape being held) was gradually cooled down to room temperature in the air. After this, $\text{DNHG}_{0.05}$ was put into 80°C silicone oil again to reveal its response.

- **SME based on swelling**

Another piece of DNHG_0 was wetted by a water droplet on its top surface. The evolution of the surface morphology was observed under an optical microscope and recorded in real time.

A piece of DNHG_0 was bent at high temperatures, and then cooled down with the temporary shape fixed. After that the distorted shape was largely maintained. Then the sample was immersing into room temperature water for full swelling, and then dehydrated in the air.

$\text{DNHG}_{0.3}$ is highly elastic and one piece of it was bent and held in the open air for 1 day for dehydration. After that, the temporary shape was maintained (Figure 5.1).

Figure 5.1 Bending rubber like $\text{DNHG}_{0.3}$.

Another piece of $\text{DNHG}_{0.3}$ was dried while being stretched. After that, the sample was immersed into room temperature water to check its behavior.

The “S” shape $\text{DNHG}_{0.05}$ was placed inside 80°C silicone oil for 30 seconds and then straightened using a pair of tweezers. Subsequently, the silicone oil together with the $\text{DNHG}_{0.05}$ (with the temporary shape being held) was

gradually cooled down to room temperature in the air. After this, half of the DNHG_{0.05} was put into room temperature water to check its reaction.

- **Thermo-responsive SME in DNHG_{7.5} based on melting of water**

A piece of DNHG_{7.5} was pre-bent and then kept in a refrigerator under -20°C for one hour. After this, DNHG_{7.5} was taken out and put in the open air at 25°C to see its response.

5.2 Results and discussion

5.2.1 Compression tests

As shown in Figure 5.2(a), during compression the DNHG₀ cracked continuously, evidenced by many suddenly drops in stress. Eventually as shown in Figure 5.2b, DNHG₀ was split into small pieces.

Figure 5.3(a) shows the result of compression DNHG_{0.3} in three loading-unloading cycles at room temperature. Virtually we cannot see any difference in the resulted curves in three cycles. Figure 5.3(b) shows the result of compression DNHG_{7.5} in seven loading-unloading cycles at room temperature. It is easy to see the difference after one cycle. In the subsequent six cycles, it becomes nonlinear elastic without any hysteresis (Figure 5.3b). It was noticed that probably some water was pressed out of the hydrogel during the compression. As compared with the level of compression stress in Figure 5.2, in Figure 5.3 (a) and (b), the compression stress of DNHG_{0.3} and DNHG_{7.5} is about the same level, and much lower than that in DNHG₀.

Figure 5.2 Compression stress vs. compression strain relationship of DNHG₀ (a); after compression (b).

Figure 5.3 (a) Compression stress vs. compression strain relationship of DNHG_{0.3} in three loading-unloading cycles; (b) compression stress vs. compression strain relationship of DNHG_{7.5} in seven loading-unloading cycles.

5.2.2 Thermal analysis

Figure 5.4 plots the DSC results of hydrogels with different R_w . Note that due to the non-uniformity nature of moisture distribution within the double network nanocomposite hydrogel, R_w determined here is essentially nominal.

As it is shown, the DNHG_{7.5} melts at around 5°C and freezes at -18°C around. During freezing the peak is very much unstable, as the sample releases energy very fast.

Figure 5.4 DSC results of hydrogels with different R_w .

5.5.3 Shape memory effect

- Thermo-responsive SME in DNHG₀

In Figure 5.5, DNHG₀ ($\approx 3 \times 3 \times 9$ mm) was immersed into 100°C silicone oil for 30 seconds and then bent using a piece of tweezers. After the sample together with the silicone oil was cooled down to room temperature (with the temporary shape being fixed), the temporary shape was resulted. Upon immersing into 100°C silicone oil again, DNHG₀ recovered its original shape within 60 seconds.

Figure 5.5 Thermo-responsive SME in DNHG₀. (a) Original shape; (b) after bending at 100°C; (b-e) recovery sequence in 100°C silicone oil.

- Thermo-responsive SME in DNHG_{0.05}

In Figure 5.6, DNHG_{0.05} ($\approx 3 \times 3 \times 8$ mm) was immersed into 80°C silicone oil for 30 seconds and then bent using a piece of tweezers. The temporary shape was resulted after the sample together with the silicone oil was cooled down to room temperature (with the temporary shape being fixed). DNHG_{0.05} recovered its original shape within four minutes upon immersing into 80°C silicone oil again.

Figure 5.6 Thermo-responsive SME in DNHG_{0.05}. (a) Original shape; (b) after bending at 80°C; (b-f) subsequent of recovery upon immersing into 80°C silicone oil.

Another piece of DNHG_{0.05} was placed inside 80°C silicone oil for 30 seconds and then compressed using a one dollar Singapore coin. After that the sample and coin together with the silicone oil were cooled down to room temperature (with the temporary shape being held), the impression of the coin was on the hydrogel (Figure 5.7b and c). A water droplet was dropped on the right flower marked as A in Figure 5.7c. Three hours later the flower shape disappeared (Figure 5.7d). The surface of the hydrogel became flat again within a few

seconds upon immersing into silicone oil again (Figure 5.7e). The surface profiles along the marked line A (Figure 5.7c and d) were compared in Figure 5.8.

Figure 5.7 Thermo-responsive SME in DNHG_{0.05}. (a) Original shape; (b) after impression; (c) 3-D scanning image scan; (d) 3-D scanning image three hours after a droplet was applied on the right flower; (e) after immersing into 80°C silicone oil.

Figure 5.8 Comparison of surface profiles along line A marked in Figure 5.7 (c) and (d).

- SME based on swelling

A piece of DNHG₀ was wetted by a water droplet on its top surface. The evolution of the surface morphology was observed under an optical microscope and recorded in real time. Snapshot is presented in Figure 4.15. As we can see, after wetting by water droplet, small *protrusions* emerged at about 15 second and then grew. And then small *protrusions* merged together to form bigger ones. After that, *protrusions* disappeared. At 942 second, the surface morphology virtually returned the original one.

Figure 5.9 Wetting by one water droplet (vertical size is about 1 mm)

In this type of hydrogel, which is tough and has limited swelling effect [47], shape recovery can be observed upon wetting in water only. As shown in Figure 5.10, after being immersed into room temperature water, the pre-bent DNHG₀ ($\approx 1 \times 4 \times 10$ mm) swelled and in the mean time returned its original shape (Figure 5.10c). After dehydration in a dry cabinet (35% RH, 25°C), the hydrogel recovered its original shape and size (Figure 5.11).

As compared with the hydrogels investigated in Chapter 3 and Chapter 4, now we may conclude that depending on the actual swelling ratio and swelling speed in a particular hydrogel, wetting by moisture (without significant swelling) or water (remarkable swelling) may result in remarkably different response.

Figure 5.10 Low swelling ratio tough hydrogel (DNHG₀) upon wetting in water and its dehydration. (a) Original shape; (b) deformed at high temperature; (c1- c6) swelling in room temperature water.

Figure 5.11 Dehydration of the swelled hydrogel (Figure 5.10c6)

Based on its high elasticity of DNHG_{0.3}, another experiment was carried out to show its SME based on swelling (Figure 5.12). After distorted and dehydrated, the temporary shape of DNHG_{0.3} ($\approx 1 \times 4 \times 10$ mm) was maintained (Figure 5.12b). 209 minutes after being immersed into room temperature water for swelling, the distorted shape of this piece of hydrogel disappear (Figure 5.12c1-c13).

Figure 5.12 SME based on swelling. (a) Original shape; (b) bent and dehydrated; (c1-c13) shape recovery upon swelling.

Another piece of $\text{DNHG}_{0.3}$ ($\approx 1 \times 3 \times 11$ mm) was stretched and then dehydrated to fix the temporary shape. After being immersed into room temperature water, we can see the sample started to absorb water and swell (from 3 minute to 7 minute in Figure 5.13). Then the sample started to contract upon further wetting (from 13 minute to 29 minute in Figure 5.13). From 29 minute to 116 minute in Figure 5.13, the sample continuously expanded until fully wetted. After dehydrated in the air for 16 hours later, the sample recovered its original shape again.

Figure 5.13 The SME during swelling in water in a pre-stretched sample.

The “S” shape DNHG_{0.05} was placed inside 80°C silicone oil for 30 seconds and then straightened using a pair of tweezers. The temporary shape was fixed after the silicone oil together with the DNHG_{0.05} was gradually cooled down to room temperature in the air (Figure 5.14c). After this, half of the “S” shape DNHG_{0.05} was put into room temperature water, so that this part gradually recovered its original shape upon wetting (Figure 5.14d-f), while the other half maintained its temporary shape.

Figure 5.14 SME based on wetting in water. (a) Original shape; (b) after being dried in the open air at room temperature; (c) after being straightened in silicone oil at 80°C and cooled; (c-f) shape recovery of the top half upon immersing into room temperature water.

- **Thermo-responsive SME in DNHG_{7.5} based on melting of water**

As shown in Figure 5.15, a piece of DNHG_{7.5} ($\approx 6 \times 6 \times 50$ mm) was bent and kept at -20°C for one hour, the temporary shape of was fixed (Figure 5.15(b)). After exposing to an environment (around 25°C) for ten minutes, the free water in the hydrogel melt, and shape recovery of was largely achieved (Figure 5.15e). However obvious shape difference is still observable, because of water lost in

compression side in the bending area (refer to the discussion in section 5.2.1). Only after being immersed into room temperature water for 30 minutes, the hydrogel almost fully recovered its original shape (Figure 5.15f).

Figure 5.15 Thermo-responsive SME based on melting of water in DNHG_{7.5}. (a) Original shape; (b) after being bent and kept at -20°C for one hour; (c-e) shape recovery sequence at around 25°C; (f) after being immersed in room temperature water for 30 minutes.

5.3 Further discussion and remarks

The change in microstructures in this hydrogel is schematically illustrated in Figure 5.16. Let us start from (a), which is fully swelled gel. Upon drying [(1)], it shrinks to (b). Further drying [(3)] to (c), the volume change is relatively ignorable. Upon partially wetted in water [(4)], i.e., (c) to (b), there is no significant volume change, but the gel changes from hard to viscous elastic or rubber-like (depending on the actual amount of water content), i.e., the mechano-responsive SCE. Further wetting in water [(2)], the gel swells remarkably. A combination of steps (1) and (2) is the water-responsive SCE. (d) may be reached from (a), (b) or (c). But the latter two are practically more

accessible. We may either stretch (b) and then dry it [(5)], or heat (a) and then stretch it to produce (d) [(7)]. Heating (d) results in (c) [(8), heating-responsive SME]. Wetting (d) in water produces (a).

Figure 5.16 Moisture/water content dependent response of hydrogel.(a) Fully swelled; (b) wet shape without apparent swelling; (c) dry shape; (d) deformed temporary shape.

Chapter 6 Conclusions and future work

6.1 Conclusions

This study systematically reveals the water/moisture-dependent response in three different types of hydrogels and their composite. A series of experiments were carried out to demonstrate various shape memory/change effects in individual types of hydrogel. Bases on the results of these experiments, the internal relationships among these effects, which are seemingly rather generic and might be applicable to a range of hydrogels, are sketched.

Main conclusions out of this study are summarized as following,

- Dependent on the actual amount of water/moisture content, a hydrogel can be either the shape change material (SCM) or shape memory material (SMM), i.e., it may have the shape change effect (SCE) or the shape memory effect (SME).
- The SME may be induced either by wetting (by moisture or water) or by heating. Dependent on the actual water/moisture level, a hydrogel exhibits either thermo-responsive SME or chemo-responsive SME. If the hydrogel absorbs moisture and the weight percentage of moisture is below a certain level, it has thermo-responsive and moisture-responsive SME, while if the water percentage is higher, it only has moisture-responsive SME.

- With the decrease of water/moisture content, hydrogel changes from SCM to SMM. However, fully dried hydrogel more likely does not have either the SCE or SME.
- The underlying mechanism for the SME either induced by heating or induced by wetting is to change the relationship between the T_g of the hydrogel and the environmental temperature. In order to activate the SME, we may either heating the hydrogel to bring the environmental temperature above T_g or to wet the hydrogel to lower its T_g below the ambient temperature.
- For some hydrogels, which are sensitive to moisture, chemo-responsive SME without significant swelling effect may be induced by moisture. For some hydrogels, which are not so sensitive to moisture, chemo-responsive SME with certain swelling effect may be induced by wetting in water. Bear in mind that upon wetting in water, there is a competition between the water induced shape recovery and water induced swelling. For hydrogels with a high swelling ratio, the SCE (i.e., swelling) is dominant. Only in hydrogels with a relatively lower swelling ratio, the water-induced SME may be observed.
- In addition to heating to above the T_g and then deform for programming, which is the first step for the SME in a hydrogel with a relatively lower water/moisture content, programming can be carried out on a piece of rubber-like hydrogel (i.e., with a relatively higher water/moisture content) via deforming and then drying to fix the temporary shape.

- Due to high non-uniformity nature upon wetting, wrinkling may be induced as a result of water induced softening and swelling. With the distribution of water within a piece of hydrogel gradually approaches uniform, wavelength of wrinkles increases continuously and eventually wrinkles disappear .
- Hydrogel may be used as the elastic matrix in a shape memory hybrid. The shape memory performance of such a hybrid may be tailored by means of selecting the right type of filler/inclusion. As demonstrated here, even water itself absorbed by the hydrogel may be considered as a kind of inclusion.
- The thermo-/chemo-responsive SCE and SME of hydrogels may be utilized in a combined manner to achieve complicate shape reconfiguration in novel engineering applications, in particular in biomedical engineering.

6.2 Future work

Due to time limit, current study is only focused on qualitatively investigation to reveal the fundamentals and influential factors. In terms of future work, the following issues may be explored,

- A quantitative investigation to reveal the actual relationships among water/moisture content and the corresponding SCE/SME. From the application point of view, shape memory performance and shape change behavior of a particular hydrogel must be characterized and well documented.

- The competition between swelling (SCE) and shape recovery (SME) in tough hydrogels with limited volume expansion should be further investigated.
- It seems that the water/moisture absorbed may be split into two parts, in which one can be removed upon compression. It is necessary to identify the actual role of each part.
- Shape memory hybrid based on hydrogel is a relative new topic. Is it possible to achieve cooling-responsive SME or other new features based on this concept?

References

1. Sun, L., et al., Stimulus-responsive shape memory materials: a review. *Materials & Design*, 2012. 33: p. 577-640.
2. Huang, W.M., et al., Shape memory materials. *Materials Today*, 2010. 13(7-8): p. 54-61.
3. Sun, L. and W.M. Huang, Mechanisms of the multi-shape memory effect and temperature memory effect in shape memory polymers. *Soft Matter*, 2010. 6(18): p. 4403-4406.
4. Lendlein, A., *Shape-memory Polymers* 2010: Springer-Verlag Berlin Heidelberg.
5. Otsuka, K. and C.M. Wayman, eds. *Shape Memory Materials*. 1998, Cambridge University Press.
6. Wichterle, O. and D. Lim, Hydrophilic Gels for Biological Use. *Nature*, 1960. 185(4706): p. 117-118.
7. Raju, M.P. and K.M. Raju, Synthesis and Water Absorbency of Superabsorbent Copolymers. *International Journal of Polymer Analysis and Characterization*, 2003. 8(4): p. 245-253.
8. Ahn, S.-k., et al., Stimuli-responsive polymer gels. *Soft Matter*, 2008. 4(6): p. 1151-1157.
9. Li, L. and Y. Aoki, Rheological Images of Poly(vinyl chloride) Gels. 1. The Dependence of Sol–Gel Transition on Concentration. *Macromolecules*, 1997. 30(25): p. 7835-7841.
10. Tanaka, T., Collapse of Gels and the Critical Endpoint. *Physical Review Letters*, 1978. 40(12): p. 820-823.
11. Ashley, S., Artificial Muscles. *Scientific American*, 2003. 289(4): p. 53-60.
12. Peteu, S.F., Responsive Materials Configured for Micro- and Nanoactuation. *Journal of Intelligent Material Systems and Structures*, 2007. 18(2): p. 147-152.
13. Mitsumata, T., J.P. Gong, and Y. Osada, Shape memory functions and motility of amphiphilic polymer gels. *Polymers for Advanced Technologies*, 2001. 12(1-2): p. 136-150.
14. Osada, Y. and A. Matsuda, Shape memory in hydrogels. *Nature*, 1995. 376(6537): p. 219.

15. Skrzyszewska, P.J., et al., Shape-Memory Effects in Biopolymer Networks with Collagen-Like Transient Nodes. *Biomacromolecules*, 2011. 12(6): p. 2285-2292.
16. Yue, J.J., et al., Shape Memory Hydrogels—A Novel Material for Treating Age-related Degenerative Conditions of the Spine. *European Musculoskeletal Review*, 2011. 6(3): p. 184-188.
17. Lauryssen, C., et al., Novel application of biomedical hydrogels for treating degenerative conditions of the spine. *European Musculoskeletal Review*, 2010. 5(2): p. 36-38.
18. Omidian, H. and M.J. Zohuriaan-Mehr, DSC studies on synthesis of superabsorbent hydrogels. *Polymer*, 2002. 43(2): p. 269-277.
19. Tomar, R.S., et al., Synthesis of poly(acrylamide-co-acrylic acid)-based super-absorbent hydrogels by gamma radiation: study of swelling behaviour and network parameters. *Designed Monomers & Polymers*, 2007. 10(1): p. 49-66.
20. Buchholz, F.L. and N.A. Peppas, Superabsorbent polymers : science and technology / Fredric L. Buchholz, editor, Nicholas A. Peppas, editor. ACS symposium series: 5731994: Washington, DC : American Chemical Society, 1994.
21. Zohuriaan-Mehr, M.J. and K. Kabiri, Superabsorbent Polymer Materials: A Review. *Iranian Polymer Journal*, 2008. 17(6): p. 451-477.
22. Ohara, T., et al., Acrylic Acid and Derivatives, in *Ullmann's Encyclopedia of Industrial Chemistry* 2000, Wiley-VCH Verlag GmbH & Co. KGaA.
23. Ricka, J. and T. Tanaka, Swelling of ionic gels: quantitative performance of the Donnan theory. *Macromolecules*, 1984. 17(12): p. 2916-2921.
24. Lee, J.W., et al., Synthesis and characteristics of interpenetrating polymer network hydrogel composed of chitosan and poly(acrylic acid). *Journal of Applied Polymer Science*, 1999. 73(1): p. 113-120.
25. Zhang, J. and N.A. Peppas, Synthesis and Characterization of pH- and Temperature-Sensitive Poly(methacrylic acid)/Poly(N-isopropylacrylamide) Interpenetrating Polymeric Networks. *Macromolecules*, 1999. 33(1): p. 102-107.
26. Qiu, Y. and K. Park, Environment-sensitive hydrogels for drug delivery. *Advanced Drug Delivery Reviews*, 2001. 53(3): p. 321-339.
27. Aronoff, D.M. and E.G. Neilson, Antipyretics: mechanisms of action and clinical use in fever suppression. *The American Journal of Medicine*, 2001. 111(4): p. 304-315.

28. Chaterji, S., I.K. Kwon, and K. Park, Smart polymeric gels: Redefining the limits of biomedical devices. *Progress in Polymer Science*, 2007. 32(8–9): p. 1083-1122.
29. Ghanem, A. and A. Ghaly, Immobilization of glucose oxidase in chitosan gel beads. *Journal of Applied Polymer Science*, 2004. 91(2): p. 861-866.
30. El-Sayed, M.E.H., A.S. Hoffman, and P.S. Stayton, Rational design of composition and activity correlations for pH-responsive and glutathione-reactive polymer therapeutics. *Journal of Controlled Release*, 2005. 104(2): p. 417-427.
31. Miyata, T., N. Asami, and T. Uragami, Preparation of an Antigen-Sensitive Hydrogel Using Antigen–Antibody Bindings. *Macromolecules*, 1999. 32(6): p. 2082-2084.
32. Kabiri, K., S. Faraji-Dana, and M.J. Zohuriaan-Mehr, Novel sulfobetaine-sulfonic acid-contained superswelling hydrogels. *Polymers for Advanced Technologies*, 2005. 16(9): p. 659-666.
33. Omidian, H., J. Rocca, and K. Park, Advances in superporous hydrogels. *Journal of Controlled Release*, 2005. 102(1): p. 3-12.
34. Ramazani-Harandi, M.J., et al., Rheological determination of the swollen gel strength of superabsorbent polymer hydrogels. *Polymer Testing*, 2006. 25(4): p. 470-474.
35. Zohuriaan-Mehr, M.J., et al., Gum arabic–acrylic superabsorbing hydrogel hybrids: Studies on swelling rate and environmental responsiveness. *Journal of Applied Polymer Science*, 2006. 102(6): p. 5667-5674.
36. Huang, W.M., et al., Thermo/chemo-responsive shape memory effect in polymers: a sketch of working mechanisms, fundamentals and optimization. *Journal of Polymer Research*, 2012. 19(9): p. 9952.
37. Wang, C.C., et al., Cooling-/water-responsive shape memory hybrids. *Composites Science and Technology*, 2012. 72(10): p. 1178-1182.
38. Osada, Y. and J.P. Gong, *Soft and Wet Materials: Polymer Gels*. *Advanced Materials*, 1998. 10: p. 827-837.
39. Hirai, T., et al., Effect of chemical cross-linking under elongation on shape restoring of poly(vinyl alcohol) hydrogel. *Journal of Applied Polymer Science*, 1992. 46(8): p. 1449-1451.
40. Lendlein, A. and S. Kelch, *Shape-Memory Polymers*. *Angewandte Chemie International Edition*, 2002. 41(12): p. 2034-2057.

41. Sun, L. and W.M. Huang, Wet to Shrink: an Approach to Realize Negative Expansion upon Wetting. *Advanced Composite Materials*, 2009. 18(2): p. 95-103.
42. Krause, T.L. and G.D. Bittner, Rapid morphological fusion of severed myelinated axons by polyethylene glycol. *Proceedings of the National Academy of Sciences*, 1990. 87(4): p. 1471-1475.
43. Borgens, R.B. and D. Bohnert, Rapid recovery from spinal cord injury after subcutaneously administered polyethylene glycol. *Journal of Neuroscience Research*, 2001. 66(6): p. 1179-1186.
44. Jagur-Grodzinski, J., Polymeric gels and hydrogels for biomedical and pharmaceutical applications. *Polymers for Advanced Technologies*, 2010. 21(1): p. 27-47.
45. Zhao, C.S., et al., Polymeric pH-sensitive membranes - A review. *Progress in Polymer Science*, 2011. 36(11): p. 1499-1520.
46. Zhang, J.L., et al., Thermo-/chemo-responsive shape memory/change effect in a hydrogel and its composites. *Materials & Design*, 2014. 53: p. 1077-1088.
47. Wang, Q., et al., Super-tough double-network hydrogels reinforced by covalently compositing with silica-nanoparticles. *Soft Matter*, 2012. 8(22): p. 6048-6056.

List of publications

- 1 Huang WM, Lu HB, Zhao Y, Ding Z, Wang CC, Zhang JL, Sun L, Fu J, and Gao XY, Instability/collapse of polymeric materials and their structures in stimulus-induced shape/surface morphology switching, *Materials and Design*, Vol. 59, 2014, 176-192.
- 2 Zhang JL, Huang WM, Lu HB, Sun L, Thermo-/chemo-responsive shape memory/change effect in a hydrogel and its composites, *Materials and Design*, Vol. 53, 2014, 1077-1088.
- 3 Huang WM, Song CL, Fu YQ, Wang CC, Zhao Y, Purnawali H, Lu HB, Tang C, Ding Z. Zhang JL, Shaping tissue with shape memory materials, *Advanced Drug Delivery Reviews*, Vol. 65, 2013, 515-535.
- 4 Sun L, Huang WM, Lu HB, Wang CC, Tang C, Zhang JL, Shape memory technology for active assembly/disassembly: fundamentals, techniques and example applications, *Assembly Automation*, Vol. 34, 2014, 78-93.
- 5 Huang WM, Zhao Y, Wang CC, Ding Z, Purnawali H, Tang C, Zhang JL, Thermo/chemo-responsive shape memory effect in polymers: a sketch of working mechanisms, fundamentals and optimization, *Journal of Polymer Research*, Vol. 19, No. 9, 2012, 9952.
- 6 Wu X, Huang WM, Zhao Y, Ding Z, Tang C, Zhang J, Mechanisms of the shape memory effect in polymeric materials, *Polymers*, Vol. 5, No. 4, 2013, 1169-1202.