Elastic shape memory polymeric materials for comfort fitting footwear

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**NANYANG
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SINGAPORE

**Elastic Shape Memory Polymeric Materials for
Comfort Fitting Footwear**

Wang Taoxi

School of Mechanical and Aerospace Engineering

Nanyang Technological University

2018

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

1 Mar 2019

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Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journals in which I am listed as an author.

1. Chapter 3 is published as T. X. Wang, W. M. Huang, J. E. Aw, L. W. He & M. Vettorello. Comfort fitting using shape memory polymeric foam. *Journal of Testing and Evaluation*, 45(4), 1201-1212 (2016). DOI: 10.1520/JTE20160011.

The contributions of the co-authors are as follows:

- A/Prof Huang provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts.
- I co-designed the study with A/Prof Huang and performed all the laboratory work at School of Mechanical and Aerospace Engineering. I also analyzed the data.
- All experiments, including sample preparation, was conducted by me in the Facility for Analysis, Characterization and Testing.
- Dr. Vettorello assisted in the figure drawing of the concept of shape memory shoes.
- Miss. Aw and Mr. He assisted in the picture collection of the cross-sectional views of foam samples.

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- A/P Huang suggested on the materials selection and edited the manuscript drafts.
- I prepared the drafts of the manuscript.

- I co-designed the study with A/Prof Huang and conducted all the tensile tests at School of Mechanical and Aerospace Engineering. I also collected and analyzed all data, measured dimensions of samples for shape fixity and shape recovery ratios.
 - Mr. Renata prepared dog-bone shaped samples for tensile tests.
 - Dr. Chen assisted in capturing pictures from scanning electron microscopy.
3. Appendix B is published as T. X. Wang, W. M. Huang, H. M. Chen, R. Xiao, H. B. Lu & S. F. Kang. Temperature Memory Effect and Its Stability Revealed via Differential Scanning Calorimetry in Ethylene-Vinyl Acetate Within Glass Transition Range. *Journal of Polymer Science Part B: Polymer Physics*, 54, 1731-1737 (2016). DOI: 10.1002/polb.24076.

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- A/Prof Huang provided the initial project direction and edited the manuscript drafts.
- I prepared and revised the manuscript drafts.
- I co-designed the study with A/Prof Huang and performed all the laboratory work at School of Mechanical and Aerospace Engineering.
- All experiments and data analysis including sample preparation and data plotting were conducted by me in the Facility.
- Dr. Chen and Dr. Xiao advised on the interpretation of the relationship between heating stop temperatures and turning points.
- Dr. Lu and Dr. Kang reviewed the drafts for amendments.

1 Mar 2019

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Abstract

Nowadays consumers demand more and more comfort and functionality from their footwear, making these characteristics very important considerations in footwear design and evaluation. Both are the results between the nature of human body and different elements of the footwear. Although there are quite many different methods or ways to achieve better comfort fitting, for instance, via 3D printing, disadvantages are still quite obvious in available products in the market. Thus, in order to improve comfort fitting and provide a better solution to consumers, shape memory polymers are introduced.

First, a commercially available polymer, namely ethylene-vinyl acetate (EVA) foam is investigated in terms of its shape memory effect (SME). It is concluded that this EVA foam can satisfy some but not all of the requirements for comfort fitting shoes.

Since it is difficult to find an existing shape memory material that meets the requirements for comfort fitting footwear, both thermoset and thermoplastic shape memory hybrids (SMHs) programmable at around human body temperature with tailorable elasticity and stretchability are developed. The fitting time window for the thermoset version is over 10 minutes, while it is less than two minutes for the thermoplastic version. No similar materials have been reported so far.

Additionally, some possible shoe designs are proposed and the enhanced stretchability via local structural design is investigated by finite element method (FEM). Subsequently, a few prototypes are fabricated and the feasibility to actualize comfort

fitting shoes using developed materials is demonstrated. Although the shoe prototypes are only for the purpose of proof-of-concept, the demonstration successfully shows that the prototypes are deformable to fit different sized feet at around human body temperature. Such a kind of comfort fitting approach has yet been achieved using any other existing materials and technologies.

Keywords: Comfort fitting footwear; Shape memory effect; Shape memory hybrid.

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Table of contents

Statement of Originality.....	i
Supervisor Declaration Statement.....	ii
Authorship Attribution Statement.....	iii
Abstract.....	v
Acknowledgement	vii
Table of contents	viii
List of figures.....	x
List of tables.....	xviii
Chapter 1 Introduction.....	1
1.1 Background.....	1
1.2 Objectives	3
1.3 Outline of the report.....	3
Chapter 2 Literature review	5
2.1 Comfort fitting	5
2.2 Methods for comfort fitting	7
2.3 Shape memory materials.....	22
2.3.1 Shape memory alloy	22
2.3.2 Shape memory polymer	24
2.3.3 Shape memory hybrid.....	26
2.3.4 Elastic shape memory polymeric materials	27
2.3.5 Working mechanisms for polymeric materials	29
2.3.6 Elastic foam, memory foam and shape memory foam	33
2.3.7 Characterization of shape memory performance	34
Chapter 3 Comfort fitting using ethylene-vinyl acetate (EVA) foam.....	37
3.1 Introduction.....	37
3.2 Basic concept	37
3.3 Material, thermal analysis and sample preparation.....	41
3.4 Experimental and results.....	43
3.4.1 Uni-axial tensile test	44
3.4.2 Uni-axial compression test.....	48
3.4.3 Shape fixity ratio and shape recovery ratio.....	51
3.4.4 Influence of long-term compression	53
3.4.5 Further discussions.....	58
3.5 Conclusion remarks	60
Chapter 4 Thermoset elastic shape memory hybrids.....	62
4.1 Introduction.....	62
4.2 Material, sample preparation and characterization	62
4.2.1 Material and sample preparation.....	62
4.2.2 Materials characterization.....	65
4.3 Experimental results and analysis.....	68
	viii

4.4	Conclusion remarks	78
Chapter 5	Thermoplastic elastic shape memory hybrids.....	79
5.1	Introduction.....	79
5.2	Material, sample preparation and experimental.....	79
5.3	Experimental results and analysis	85
5.4	Conclusion remarks	91
Chapter 6	Design of shape memory comfort fitting shoes	92
6.1	Introduction.....	92
6.2	Design concepts	92
6.3	Local structural design.....	95
6.4	Design and fabrication of prototypes.....	102
6.4.1	Version I: Sock-EVA foam.....	103
6.4.2	Version II: Modified shoe upper-EVA foam	105
6.4.3	Version III: Modified normal shoe upper-TP6040.....	108
6.5	Demonstration of fitting with Version III	109
6.6	Conclusion remarks	112
Chapter 7	Conclusions and future works.....	113
7.1	Conclusions.....	113
7.2	Future works	116
References		118
Appendix A		127
Appendix B		131
B.1	Introduction.....	131
B.2	Material and experimental	132
B.3	Results analysis and discussion	135
B.3.1	Single-stop test.....	135
B.3.2	Triple-stop test	138
B.3.3	Analysis and further discussion	141
B.4	Conclusion remarks	144
Appendix C		146
C.1	Introduction.....	146
C.2	Material, sample preparation and experimental.....	146
C.3	Experimental results and analysis	150
C.4	Further investigation	154
C.5	Conclusion remarks	164
List of publications		166

List of figures

Figure 2.1 Different toe shapes (a) and arch heights (b) in human foot.	6
Figure 2.2 3D printed shoes and footwear models. (a) Running shoes from New Balance; (b) running shoes from Adidas; (c) fully 3D printed shoes; (d) shoes with 3D printed heel; (e) 3D printed boots; (f) 3D printed high-heel shoes.....	10
Figure 2.3 Typical sock-shoes in the footwear market. (a) Low cut version; (b) high cut version.	11
Figure 2.4 A few types of sock-shoes from Nike for running (a); football (b); basketball (c).	12
Figure 2.5 Vibram Five Fingers with shoelaces (a) and without shoelaces (b).	13
Figure 2.6 Modular shoes. (a) Concept; (b) available shoe uppers and outsoles; (c) zoom-in view of the zip.	14
Figure 2.7 Shimano custom-fit and Atomic memory fit oven to heat cycling shoes (a), insoles (b) and ski boots (c).	16
Figure 2.8 Fondue slippers. (a) Illustration of DIY procedure of Fondue slipper; (b) package including all tools and materials for DIY; (c) dip-coating; (d) produced slippers.....	16
Figure 2.9 Top view (a) and side view (b) of Crocs shoes.....	17
Figure 2.10 Assembly shoes with different bonding solutions. (a) Velcro; (b) wrapping; (c) elastic band; (d) ribbon and (e) shoelaces.	19
Figure 2.11 Shape memory insole made of ethylene-vinyl acetate (EVA) foam (left side one is for reference). (a) After fitting; (b) after heating for shape recovery.	20

Figure 2.12 Shape memory effect (SME) and shape change effect (SCE) (Huang et al., 2012).....	30
Figure 2.13 Basic working mechanisms for the SME in polymeric materials. (I) Dual-state mechanism (DSM); (II) dual-component mechanism (DCM); (III) partial-transition mechanism (PTM). (a) Original sample at room temperature; (b) upon heating and compressing; (c) after cooling and constraint removal; (d) after heating for shape recovery (Huang et al., 2012).....	31
Figure 2.14 Illustration of a full SME cycle.	35
Figure 3.1 Basic concept of comfort fitting shoes (I) and proof-of-concept (II). (Reproduced from (Wang et al., 2016a))	38
Figure 3.2 Cross-section of EVA foam sheet (a) and zoom-in-view under scanning electron microscope (SEM) (b). (Reproduced from (Wang et al., 2016a))	42
Figure 3.3 DSC curve of EVA foam. Inset: zoom-in view of the glass transition range upon heating. (Reproduced from (Wang et al., 2016a)).....	42
Figure 3.4 Dimensions of the sample for uni-axial tensile test (unit: mm). (Reproduced from (Wang et al., 2016a))	43
Figure 3.5 Typical stress vs. strain relationships of uni-axial tension to a maximum strain of 30% at three different temperatures followed by cooling back to room temperature and then unloading. (Reproduced from (Wang et al., 2016a))	45
Figure 3.6 Typical stress vs. strain relationships in uni-axial tension to a maximum strain of 80% at three different temperatures followed by cooling back to room temperature and then unloading. (Reproduced from (Wang et al., 2016a))	46

Figure 3.7 Typical stress vs. strain relationships of cyclic stretching at room temperature in samples with/without pre-stretching. (Reproduced from (Wang et al., 2016a))	47
Figure 3.8 Stress vs. strain relationships in uni-axial compression to a maximum strain of 30% at three different temperatures followed by cooling back to room temperature and then unloading. (Reproduced from (Wang et al., 2016a))	48
Figure 3.9 Stress vs. strain relationships in uni-axial compression to a maximum strain of 80% at three different temperatures followed by cooling back to room temperature and then unloading. (Reproduced from (Wang et al., 2016a))	49
Figure 3.10 Stress vs. strain relationships obtained by cyclic compression tests at room temperature in samples with/without pre-compression. (Reproduced from (Wang et al., 2016a))	50
Figure 3.11 Shape fixity ratio as a function of programming temperature. (Reproduced from (Wang et al., 2016a)).....	51
Figure 3.12 Shape recovery ratio as a function of programming temperature. (Reproduced from (Wang et al., 2016a))	52
Figure 3.13 Shape recovery of EVA foam after clamping at room temperature for different periods of time. (Reproduced from (Wang et al., 2016a)).....	53
Figure 3.14 Influence of programming temperature on long term clamping and shape recovery. (Reproduced from (Wang et al., 2016a)).....	54
Figure 3.15 Stress vs. strain relationships of EVA foam upon compressing to 0.329 MPa/0.1645 MPa and then holding the applied compression stress for 24 hours before unloading (a) and the corresponding strain/stress vs. time relationships (b). (Reproduced from (Wang et al., 2016a))	56

Figure 3.16 Evolution of recovery ratios in samples with different compression stresses of 0.329 MPa and 0.1645 MPa, respectively. (Reproduced from (Wang et al., 2016a))	57
Figure 3.17 SME in EVA foam from Daiso, Japan. (a) After elongation; (b) after heating for recovery.....	60
Figure 4.1 Sample dimensions (unit: mm). The thickness is 6 mm. (Reproduced from (Wang et al., 2017))	65
Figure 4.2 DSC results of PPM003365 at heating/cooling speeds of 10°C/min (black line) and 5°C/min (grey line). (Reproduced from (Wang et al., 2017))	66
Figure 4.3 Typical SEM image of SPPM4. The scale bar is 50 μ m. (Reproduced from (Wang et al., 2017))	67
Figure 4.4 Typical stress vs. strain relationships of SPPM samples under uni-axial tension at room temperature to fracture. (Reproduced from (Wang et al., 2017))	69
Figure 4.5 Typical stress vs. strain relationships under uni-axial cyclic tension at room temperature of all samples (a), and zoom-in view of all samples excluding SPPM2 (b). (Reproduced from (Wang et al., 2017)).....	70
Figure 4.6 Typical stress vs. strain relationships of all samples programmed with 20% strain (a), and 50% strain (b). (Reproduced from (Wang et al., 2017))	70
Figure 4.7 Comparison of the stress vs. strain relationships under uni-axial tension at room temperature and 37°C (to 20% and 50% strains) in SPPM1 (a), SPPM2 (b), SPPM3 (c), SPPM4 (d), and SPPM5 (e). (Reproduced from (Wang et al., 2017))	71

Figure 4.8 Comparison of the corresponding stresses at 20% and 50% strains in loading at room temperature and in programming at 37°C. (Reproduced from (Wang et al., 2017))	72
Figure 4.9 Comparison of SPPM samples after heated at 50°C for five minutes for shape recovery. In each sample, the applied programming strain is indicated above the hybrid type (1 to 5). The rightmost sample is original for comparison. (Reproduced from (Wang et al., 2017))	73
Figure 4.10 Shape fixity ratio and shape recovery ratio of all SPPM samples (black hollow symbols: shape fixity ratio; grey solid symbols: shape recovery ratio). The applied programming strain in each sample is indicated in % in the legend (top). (Reproduced from (Wang et al., 2017))	74
Figure 4.11 Evolution in the stress vs. strain relationship of all SPPM samples under cyclic uni-axial tension during crystallization induced hardening at 37°C (a); and the slope ratios in unloading at 20% strain in the loading process of each cycle as a function of testing time (b) (in which the slope of the stress vs. strain curve at 20% strain of the first cycle of each sample is taken as the reference). (Reproduced from (Wang et al., 2017))	75
Figure 4.12 Typical stress vs. strain relationships under uni-axial cyclic tension at room temperature in all samples programmed with 20% strain (a) and zoom-in view for samples excluding SPPM2 (b); and programmed with 50% strain (c) and zoom-in view for samples excluding SPPM2 (d). (Reproduced from (Wang et al., 2017))	76
Figure 4.13 Shape memory effect of the insole made of SPPM2 with a layer of elastic fabric covered on both surfaces. (a) After elongation; (b) after heating for recovery	77

Figure 5.1 DSC results of PCL at two different heating/cooling rates of 3°C/min (grey line) and 10°C/min (black line). (Reproduced from (Salvekar et al., 2015))	80
Figure 5.2 DSC result of TPR at a heating/cooling rate of 5°C/min.....	82
Figure 5.3 DMA result of TPR at a heating rate of 5°C/min.	83
Figure 5.4 Typical stress vs. strain relationships under uni-axial cyclic stretching at room temperature for TPR.	83
Figure 5.5 Dimensions of the dog-bone shaped 1 mm thick sample. (Unit: mm).....	84
Figure 5.6 Typical stress vs. strain relationships of both TP6040 and TP7030 under uni-axial tension to fracture at room temperature.....	86
Figure 5.7 Typical stress vs. strain relationships of both TP6040 and TP7030 samples programmed to 30% (a) and 100% (b) maximum strains. (“1st” and “2nd” in legend are meant for two repetitions).....	87
Figure 5.8 Shape memory behaviors of TP7030 programmed to 30% (a) and 100% (b) maximum strains and TP6040 programmed to 30%(c) and 100% (d). Top: original sample; middle: programmed sample; bottom: recovered sample. The scale bar is for 10 mm.....	88
Figure 5.9 Shape fixity ratio and shape recovery ratio of TP6040 and TP7030 with 30% and 100% maximum programming strains, respectively. (“1st” and “2nd” in legend are meant for two repetitions)	88
Figure 5.10 Typical stress vs. strain relationships under uni-axial cyclic tension at room temperature for both TP6040 (grey line) and TP7030 (black line) without programming (solid line) and programmed with 30% (dash-dotted line) and 100% (dashed line) strain.....	90

Figure 5.11 Stress and strain vs. time relationships of TP6040 and TP7030 for ten stretching cycles to 200% maximum strain and then unloading to 0.1 MPa and 0.01 MPa for TP6040 and TP7030, respectively, at a strain rate of $10^{-1}/s$ at $37^{\circ}C$	90
Figure 6.1 Four possible embodiments of shape memory comfort fitting shoes.....	93
Figure 6.2 The sole portion of shape memory shoes.	96
Figure 6.3 Boundary conditions (a) and mesh (b) for FEM (in a representative structural design).....	97
Figure 6.4 Comparison between original structure and deformed structure. Inner: original structure; outer: deformed structure. Arrows indicate the node points used for analysis of displacements in X direction (D_x) and Y direction (D_y).....	98
Figure 6.5 Dimensions of the cavities in each type of structural designs. (a_1), (a_2) and (a_3) represent Design (a); (b_1), (b_2) and (b_3) represent Design (b); (c_1), (c_2) and (c_3) represent Design (c). Unit: mm.....	99
Figure 6.6 The relationship between displacements (a) and nominal strain (b) in X and Y directions for local structural designs with three different sized cavities.	100
Figure 6.7 Visualization of the von Mises stress in each design with different cavity sizes.	101
Figure 6.8 Results of the maximum von Mises stress in MPa.....	101
Figure 6.9 Typical shoe sole (unit: cm).....	103
Figure 6.10 Version I. (i) Top and (ii) back views of Prototype IA, Prototype IB and Prototype IC fabricated using socks and EVA foam.	104
Figure 6.11 Fitting result of Prototype IA.....	105

Figure 6.12 (a) Polyester fabric and TPU layer with pre-punched holes before hot compression; (b) polyester fabric with holes punched and TPU layer attached atop after hot compression; (c) side view of the 3D printed shoe last with 235 mm length; (d) top view of the 3D printed shoe last with 235 mm length.	106
Figure 6.13 Version II. (i) Front and (ii) back views of Prototypes IIA and IIB fabricated using EVA foam as sole material and modified shoe upper. (iii) Side view of Prototype IIA on foot and (iv) side view of bending Prototype IIA on foot.	107
Figure 6.14 (a) The extra insole made of EVA foam for Version III; (b) the insole attached on the shoe last before assembling the shoe; (c) partially assembled; (d) side view of Version III; (e) top view of Version III.....	108
Figure 6.15 Elasticity of Version III.	109
Figure 6.16 Demonstration of the shape fitting and recovery of Version III with a 3D printed shoe last. (a) Comparison between shoe and last after fitting (left: top view; right: side view); (b) comparison between shoe and last after recovery (left: top view; right: side view).	110
Figure 6.17 Shape fitting and recovery of Version III with a real human foot. (a) Comparison between shoe and foot after fitting; (b) comparison between shoe and foot after shape recovery.....	111

List of tables

Table 2.1 Comparison of different footwear comfort fitting technologies.	21
Table 4.1 Components of five SPPM hybrids.....	64
Table 5.1 Components of TP hybrids.....	81
Table 7.1 Comparison of major features in EVA foam, SPPM and TP.....	115

Chapter 1 Introduction

1.1 Background

Nowadays, more and more people are keen to invest in their own personal fitness. Taking the footwear market as an example, consumers want more comfort and functionality from their footwear (Rupérez et al., 2010). Depending on the purposes, shoes may be classified under four major categories, namely leisure shoes, walking shoes, running shoes and athletic shoes. The actual meaning of “comfort” depends on the exact activity that the shoes are used for. Shoes for different purposes have different design requirements. For instance, a natural wearing experience is the major concern for walking shoes, while that is the cushioning effect for running shoes. Even within one piece of shoe upper, different areas require different elasticity and hardness. Thus, material properties, such as elasticity, hardness and etc., should be different for different applications. Mis-fitting between the foot and footwear impairs foot function and may result in undue pressure on the foot from tightly fitting footwear or unwanted friction from loosely fitting footwear (Xiong et al., 2009). For example, CrocsTM is popular in particular among the young generation, mostly because it is soft, comfortable, lightweight and odor-resistant. However, in terms of fitting, it is only limited to within the contact interface between the underneath of foot and top of sole. There is indeed a large empty space between the foot and inner part of the shoes. Hence, the foot inside is prone to moving, which increases the risk of, for instance, foot injury.

Although customized shoes might be fabricated for better fitting via different methods, such as three-step fitting¹, 3D printing and memory foam etc., most of them have some apparent problems. For instance, 3D printing requires a tedious process of foot scanning and printing is still an expensive fabrication process.

As a consequence, a cost-effective approach to realize comfort fitting, not only for shoes, but also for a range of other personal items, is highly in demand at present.

Shape memory materials (SMMs) may provide a possible solution. Basically, SMMs are featured by their unique ability to return their original shapes when the right stimulus, such as heat (thermo-responsive), chemical (chemo-responsive), light (photo-responsive), is applied (Liu et al., 2007, Dietsch and Tong, 2007, Ratna and Karger-Kocsis, 2008, Mather et al., 2009, Lendlein, 2010, Havens et al., 2005, Gunes and Jana, 2008). This phenomenon is known as the shape memory effect (SME). Traditionally, shape memory alloy (SMA) and shape memory polymer (SMP) are two most popular types of SMMs and they have been widely used in a range of engineering applications, such as medical engineering (Baer et al., 2007, Sokolowski et al., 2007, Yakacki et al., 2008, Sun and Huang, 2010a, Wischke and Lendlein, 2010), surface patterning (Hidber et al., 1996, Liu et al., 2008, Liu et al., 2010, Wang et al., 2011b, Zhao et al., 2011), and

¹ <http://strolz.co.uk/aboutus.html> [Accessed on 14 April 2016]

aerospace engineering (Hartl and Lagoudas, 2007, Liu et al., 2014, Yamauchi et al., 2011).

With such a unique feature, shoes made of SMMs are expected to have the capability to be programmed to fit individual's foot and subsequently to hold this shape even after being taken off. Once the stimulus, which most likely is heat in this application, is applied, shape recovery happens. Consequently, the shoes return the original shape and then are ready to be reused again. Hence, the shoes may be designed to have only one single size and even without left/right side difference.

1.2 Objectives

The focus of current study is on developing solid materials only, while shoe design is slightly touched in Chapter 6 to demonstrate the feasibility to tailor the performance of materials via structural design. Foam materials, which are able to provide much better cushioning effect and have been used extensively in shoes, are not explored due to the time and equipment limit. Hence, the objectives of this project are twofold, one is materials development to provide a range of options for selection in future applications and the other is proof-of-concept of shape memory shoes focusing on shape fitting with the focus on shape fitting.

1.3 Outline of the report

The outline of this report is as follows.

Chapter 1 briefly introduces the concept of comfort fitting shoes and its current status, together with the objectives of this project and the outline of this thesis.

Chapter 2 reviews the current state-of-the-art in comfort fitting footwear, the current commercial methods to achieve it, the shape memory effect and shape memory materials.

Chapter 3 presents the feasibility study of using commercial ethylene-vinyl acetate (EVA) foam for comfort fitting and identify the actual problems in implementation.

Chapter 4 introduces the fabrication process of a newly developed type of elastic thermoset shape memory hybrid and characterizes its shape memory effect and feasibility in comfort fitting.

Chapter 5 presents the fabrication process and characterization of an elastic thermoplastic shape memory hybrid for comfort fitting.

Chapter 6 proposes a few possible designs of the comfort fitting shoes and compares three local structures by computational simulation via finite element method (FEM). Shoe prototypes as well as the fitting are demonstrated.

Conclusions and future works are summarized in Chapter 7.

Chapter 2 Literature review

2.1 Comfort fitting

Nowadays, more customers choose garment or footwear that provides better fitting experience as well as fashionable design. More comfort and functionality are in demand from their footwear, making these characteristics important considerations in footwear design and evaluation. Both are the result of a complex interaction between the nature of the human body and the different elements of footwear (Rupérez et al., 2010).

In terms of comfort, fit is a primary reason in the purchase of footwear. In Figure 2.1, different types of human foot shapes are presented for comparison. As we can see, some apparent differences in foot shapes can be found on the toes and the sole arches as the length of five toes, as well as the arch height, varies. In fact, the foot shapes vary from individuals not only in toes and arches, there are numbers of detailed information that need to be considered. Thus, it is obvious that people's requirements for fitting of the shoes are also different. Misfits between the foot and the footwear impair foot function and may result in undue pressure on the foot from tightly fitting footwear or unwanted friction from loosely fitting footwear (Xiong et al., 2009).

Since every consumer has a unique foot shape/configuration and personal preference for shoes, finding a pair of shoes from the market that can comfortably fit an individual's feet become not always an easy matter, especially for those who need foot orthotics.

Figure 2.1 Different toe shapes² (a) and arch heights³ (b) in human foot.

Thus, comfort fitting becomes a popular problem to solve. However currently, footwear industry is still focusing more on aesthetic, and shoe sizing bases only on standard foot length and width. This method may require several rounds of fitting trials before a preferred fitting is achieved (Luximon et al., 2001).

Some ideas have been proposed to quantify fitting between foot and footwear, e.g., based on dimensional differences to quantify footwear fit, including the orientation and alignment of foot and shoe, and shape adjustment to take care of shoe characteristics such as toe-spring and heel height as key elements (Luximon et al., 2003, Luximon et al., 2001). Such a method provides a better way for designers and developers to understand the misfit problems happening on customers. Furthermore, it is suggested in (Wong et al., 2004) that measuring the dynamic pressure distribution may be a way to identify the comfort fitting level of human body through investigating its relationship with the people's physical and psychological responses. Thus, an improved numerical

² <https://diply.com/dip/article/feet-describe-you?config=25> [Accessed on 26 March 2016]

³ <http://www.richardsonpodiatrycenter.com/library/foot-arch-types.cfm> [Accessed on 26 March 2016]

simulation system has been proposed to simulate the pressure distribution between human body and a tight-fit garment. The results reveal great linear relationship with Pearson correlation coefficient of 0.564 between the predicted and experimental comfort rating. Another system for footwear fitting measurement is introduced in (Kos and Duhovnik, 2002), in which the fitting of shoes is measured with a weighting function of several user-defined parameters. No explicit directions are given for the synthesis of such a function, while only some guidelines are provided by experienced manufacturers.

2.2 Methods for comfort fitting

Since the comfort fitting measuring systems have been developed by several researchers in the past few decades, the optimized footwear aiming to achieve better comfort fitting based on these measuring systems started to emerge in the market⁴⁵. Several different techniques have been carried out to achieve better footwear comfort fitting.

In the field of traditional footwear customization, usually three-step fitting method is applied for individual customization (Weerasinghe and Goonetilleke, 2011, Frappier and Swanson, 2001). The first step is foot analysis, in which individual foot information

4 <https://www.abefootwear.com/> [Accessed on 17 February 2019]

5 <https://www.burlingtonorthotics.com/> [Accessed on 17 February 2019]

is scanned and analyzed. The second is footwear creation. Based on the data collected in the first step, a product with unique inner shape for a particular individual is fabricated manually. The last stage is fitting. The customer tries his/her footwear and spot any problems, so that the product can be further modified for better satisfactory.

In (Rupérez et al., 2010), a computational model is proposed to study the shoe upper behavior and to estimate the distribution of pressure on the foot surface. Such a kind of model allows footwear designers to perform virtual evaluations of comfort and functionality of their designs, so that further modification, if required, can be conducted more specifically. Additionally, shoe last customization is also important during the second stage. As a consequence, quite a number of innovated ways for shoe-last customization have been developed to offer better fitting (Cheng and Perng, 2000, Xiong et al., 2010, Leng and Du, 2006, Leng and Du, 2005, Wang et al., 2011a, Zhang et al., 2012b, Chen et al., 2005). For example, in (Luximon and Luximon, 2009), a computational system, which integrates existing shoe-last standards, twenty types of commercially available shoe lasts and the general information of human foot, is created to achieve better shoe-last design for better fitting experience. In such a way, a faster and more accurate shoe-last design progress can be developed by slight automatic variation of parameters. In (Rout et al., 2010), via 3D scanning of customers' feet, more details of the foot shapes can be obtained that allow the designers and developers to understand better the essence of fitting problems, so that design modifications can be processed even without fitting trials.

On the other hand, in footwear design, shoe last is not considered to be compulsory among some researchers. Better fitting, e.g., in personalized insoles, may be achieved by additive manufacturing technology (Salles and Gyi, 2013). Comparing with a generic shape, lower discomfort ratings on the heel is found in wearing of such insoles.

In the past few years, additive manufacturing, also known as 3D printing, has attracted a lot of attention from a number of famous footwear companies. Recently, both New Balance and Adidas have started to market their 3D printed running shoes.

According to the official introduction, such sci-fi looking shoes (refer to Figure 2.2a and b) with unique 3D printed outsoles can be customized to satisfy the needs in cushioning for individuals, thus improving users' sporting performance. Moreover, fully 3D printed shoes with their shapes exactly following customers' feet contour have also been created to provide more comfortable wearing experience.

In recent years, sock-shoes started to become popular especially among female consumers. As shown in Figure 2.3, the design of these sock-shoes is basically a combination of normal shoe outsoles and socks. Instead of conventional shoe uppers that made of fused materials, such as thermoplastic polyurethane (TPU), socks or sock-like woven fabrics are used to create elastic shoe uppers with relatively lighter weight and better breathability. More importantly, with such a design, the sock-shoes provide sock-like wearing feeling, which elevates the comfort to customers.

Figure 2.2 3D printed shoes and footwear models. (a) Running shoes from New Balance⁶; (b) running shoes from Adidas⁷; (c) fully 3D printed shoes⁸; (d) shoes with 3D printed heel⁹; (e) 3D printed boots¹⁰; (f) 3D printed high-heel shoes¹¹.

However, the shortcoming of such sock-like shoes is also apparent, which is the protection to feet. Such thin layer of fabrics for the shoe upper is not able to offer

⁶ <https://www.3ders.org/articles/20151119-new-balances-3d-printed-shoes-to-arrive-by-april-2016.html> [Accessed on 15 April 2016]

⁷ <https://www.digitaltrends.com/cool-tech/adidas-3d-printed-shoes/> [Accessed on 15 April 2016]

⁸ <http://blogs.3ds.com/fashionlab/3d-printed-xyz-shoes-by-earl-stewart/> [Accessed on 15 April 2016]

⁹ <https://www.designboom.com/design/leather-meets-3d-printing-in-the-bits-shoe-by-earl-stewart/> [Accessed on 15 April 2016]

¹⁰ <https://www.3ders.org/articles/20150215-sols-unveils-adaptiv-robotic-3d-printed-shoes-adjusts-pressure-and-shape.html> [Accessed on 15 April 2016]

¹¹ <https://www.gloomy-grim.info/3d-printed-shoes-men/> [Accessed on 15 April 2016]

enough protection for wearers' feet and thus, such shoes are appropriate only for limited occasions. Any defects that happen on the shoe upper may propagate fast and subsequently the shoes lose the function immediately.

Figure 2.3 Typical sock-shoes in the footwear market¹². (a) Low cut version; (b) high cut version.

In another way, Nike developed a kind of sock-shoes with the so-called Flyknit technology, which is also a combination of socks and outsoles (Figure 2.4). As compared with the above mentioned ones, the difference is mainly in the materials used for shoe uppers. As a sports footwear company, Nike has enhanced the material for shoe uppers in strength and density, thus to cater the requirements for footwear in different sports. Such sock-shoes can be divided into three parts, namely outsole, sock-like inner layer and outer supporting layer. The outsole has essentially no difference from normal Nike's sports shoes. However, there is a novel design on the shoe upper, in which a

¹² <https://footwearnews.com/2017/fashion/designers/mens-sock-fit-stretch-sneakers-spring-2017-326118/> [16 April 2016]

skin-friendly textile material is used to imitate the feeling of wearing socks, which can provide better wearing experience to customers. The sock-like inner layer on the shoe upper makes the shoes not only much lighter than conventional sports shoes, but also more breathable and comfortable. Additionally, the elastic inner layer is able to deform passively to adapt the foot shape and thus achieve better supports for customers' ankles to lower the risk of injury. Since the invention of Nike Flyknit, followers, such as Adidas, Puma and Lining, all have developed their own sock-shoes to compete Nike in the market. However, similar to the sock-shoes in Figure 2.3, due to the nature of the woven fabrics, any defect that accidentally happens on the sock-like shoe upper during sports may propagate quickly and thus causes severe damage to the shoes.

Figure 2.4 A few types of sock-shoes from Nike for running¹³ (a); football¹⁴ (b); basketball¹⁵ (c).

¹³ <https://news.nike.com/news/nike-zoom-vaporfly-elite> [Accessed on 16 April 2016]

¹⁴ <https://hypebeast.com/2018/2/nike-mercurial-superfly-vapor-360> [Accessed on 16 April 2016]

¹⁵ <https://www.kicksonfire.com/nike-react-hyperdunk-2017-flyknit-multicolor-release-date/> [Accessed on 16 April 2016]

Vibram (Italy), also known as Vibram Five Fingers, comes up with an idea to make the shape of a shoe exactly follow the general contour of the entire human foot, even for the toes. As shown in Figure 2.5, such shoes provide customers a skin-like wearing experience. High elasticity of the material also offers enough pressure on the foot. However, the shoe upper is too thin to give enough support when doing sports. Thus, the risk of injury may be higher than normal shoes.

Figure 2.5 Vibram Five Fingers¹⁶ with shoelaces (a) and without shoelaces (b).

In the footwear market, there is also a type of modular shoes, which refers to the changeable shoe upper and outsole. Figure 2.6 is an example of these shoes which are actually separated into two independent parts, namely upper and outsole. A zip makes them connectible. Customers are able to change any part according to their preference. Many different types of uppers and outsoles are available to cope with different wearing purposes.

¹⁶ <https://www.pinterest.com/micah6967/five-toe-shoes/> [Accessed on 18 April 2016]

Figure 2.6 Modular shoes¹⁷. (a) Concept; (b) available shoe uppers and outsoles; (c) zoom-in view of the zip.

Material instead of the manufacturing technology is also important in comfort fitting. In (Miller et al., 1975), memory foam is used for the inner lining of footwear. In such a way, footwear is able to adjust itself to accommodate different feet shapes and return the original shape after being taken-off due to slow recoverable inner liner made of typical polymeric foam.

¹⁷ <https://www.indiegogo.com/projects/shooz-the-world-s-first-modular-tech-travel-shoe#/> [Accessed on 18 April 2016]

Thermoformable polymeric foam is also applied in comfort fitting (Bordin and Romanato, 2004, Daley, 1999). Customers need to heat up the inner part of such shoes to certain temperature, so that the material can be deformed easily to permanently fit different foot shapes. In fact, products based on this technology have been available in the market of professional sports footwear, e.g., Atomic memory fit and Shimano custom-fit. Such a type of thermoformable material has been applied in cycling shoes and ski boots as well. During the fitting process, an oven is used to heat up the entire footwear or just a few key parts, as shown in Figure 2.7. Taking Atomic memory fit technology (Figure 2.7 b) for instance, after around 10 minutes of heating at 117°C, the shoes are taken out and worn by users. Footwear inner layer softens at high temperatures and thus can be deformed instantly to adapt user's foot contour and this shape maintains after cooling back to room temperature. Hence, a pair of customized individually fitted shoes or boots is created. However, the overall shape of the shoes is not reshapable.

In 2014, Satsuki Ohata, a Japanese designer, came out with the idea of Fondue slipper (Figure 2.8). Polyvinyl chloride (PVC), which is a very commonly used polymeric material and has been used widely in pipes, electric cables, clothing and furniture due to its relatively low cost, biological and chemical resistance and workability, is used as the basic material in such shoes.

Figure 2.7 Shimano custom-fit and Atomic memory fit oven to heat cycling shoes (a), insoles (b) and ski boots (c)¹⁸.

Figure 2.8 Fondue slippers¹⁹. (a) Illustration of DIY procedure of Fondue slipper; (b) package including all tools and materials for DIY; (c) dip-coating; (d) produced slippers.

¹⁸ http://www.shimano-lifestylegear.com/gl/fw/technologies/custom_fit_molding.php [Accessed on 19 April 2016]

¹⁹ <http://satsuki.co/fondueslipper.html> [Accessed on 19 April 2016]

First, PVC is dissolved in a solvent, e.g., aromatic hydrocarbons or ketones. The foot of a customer is dipped into it and then dried in air. After a while, PVC hardens on foot due to the evaporation of the solvent, then a unique slipper that exactly fits a customer's foot is created and as claimed, satisfies the wearing requirements in daily life. However, the designer also indicates that the current material, PVC may not be safe enough for a skin-sensitive use and new materials for Fondue slippers are still under developing. Additionally, unlike normal textile materials, PVC is not able to provide breathable and comfortable wearing experience for human foot²⁰.

Crocs has earned its fame all over the world in the past few years. Crocs shoes (Figure 2.9), which are made of a polymeric material by one-step molding technology, become very popular due to the soft, comfortable, lightweight wearing features.

Figure 2.9 Top view (a) and side view (b) of Crocs shoes²¹.

²⁰ https://en.wikipedia.org/wiki/Polyvinyl_chloride#Vinyl_gloves_in_medicine [Accessed on 17 February 2019]

²¹ <http://www.webmd.com/diabetes/features/crocs-healthy-shoes-just-comfy?page=2> [Accessed on 17 February 2019]

However, it has been reported that permanent plastic deformation is likely to occur after long time wearing, which limits the life span of shoes²². Moreover, odor is another problem that can not be ignored. After long-term use, sweat is very difficult to be removed, even after careful cleaning, which causes the shoes smelly. More importantly, for Crocs shoes, fitting happens only between the underneath of foot and the top of the outsole. There is always a large space between other parts of foot and the inner layer of shoes. Therefore, the foot inside the shoe is very likely to move, which increases the risk of, for instance, foot injury.

Apart from the designs mentioned above, a number of other fancy forms of shoes for improved comfort have been invented. Although they appear to be attractive, practically they are not suitable for wearing in daily life.

A number of typical examples of assembly shoes are presented in Figure 2.10. As shown, basically the common point of such shoes is that only one piece of material is used. The difference is the bonding. Different solutions, such as Velcro, shoelaces, elastic-band and etc., are used. However, these shoes are mostly made of very soft material, so that they can hardly provide enough support or protection to human foot. In most occasions, they are meant for casual and indoor use only.

²² <http://www.slideshare.net/CharmaineLim/crocs-5023628> [Accessed on 20 April 2016]

Figure 2.10 Assembly shoes with different bonding solutions²³. (a) Velcro; (b) wrapping; (c) elastic band; (d) ribbon and (e) shoelaces.

As we can see, there is a need of cost effective personalized footwear to provide comfort, functionality and protection to the entire foot. Shape memory insoles (Figure 2.11) made of shape memory polymeric foam are commercially available in the market. According to (Lo, 2008), a shape memory insole can self-adjust its shape to meet the needs of different foot pressure of individuals due to the shape memory effect (SME).

²³ <http://www.muji.net/award/results/04/result.html?lang=en> [Accessed on 20 April 2019]

Hence, to achieve the idea of fully personalized footwear, it may be possible to utilize shape memory materials to create footwear with excellent reshapeability to adapt different users' foot shapes at a low cost. In comparison with insoles, shoes have more complex requirements on the materials, which vary according to not only the purpose of shoes, but also the area on shoes (outsole, upper and etc.). Therefore, the development of shape memory materials programmable at around or below human body temperature with tailorable material properties, such as elasticity, hardness, stretchability and etc., is the main focus of this current study.

Figure 2.11 Shape memory insole made of ethylene-vinyl acetate (EVA) foam (left side one is for reference). (a) After fitting; (b) after heating for shape recovery.

Table 2.1 Comparison of different footwear comfort fitting technologies.

Methods	Advantages	Disadvantages
Three-step fitting	Firm foundation for human body; improvement in biomechanical alignment; guaranteed comfort level.	Quite complicated system; time-consuming to fabricate; high cost.
3D printing (Figure 2.2)	Improved comfortable level; significant decrease in mean heel pressure; less ankle dorsiflexion at foot strike; lower maximum eversion.	Complex procedure; time-consuming to fabricate; high cost.
Sock shoes (Figure 2.4)	Light weight; comfortable sock-like inner layer.	Lack of protection for ankles; Inner layer absorb sweat.
Vibram Five Fingers (Figure 2.5)	Following human foot contour; close to bare feet feeling; light weight.	Lack of support and protection; single-purpose.
Modular shoes (Figure 2.6)	Fashionable; multipurpose.	Zip connection easy to get spoiled;
Thermoformable material (Figure 2.7)	Instant deforming for fitting; localized pressure distributed.	Forming process lacks of repeatability; time-consuming.
Fondue slippers (Figure 2.8)	Easy to DIY; exactly following the foot shape; light weight.	Material probably not safe; lack of support for entire foot.
Crocs shoes (Figure 2.9)	Soft and comfortable; lightweight.	Permanent deformation after long time wearing; higher risk of foot injury.
Assembly shoes (Figure 2.10)	Material-saving; soft and comfortable.	Bonding easy to get spoiled; single-purpose.

2.3 Shape memory materials

Essentially, shape memory material (SMM), as a member of smart materials, is known by its distinctive property of the shape memory effect (SME), *i.e.*, after being severely and quasi-plastically distorted, the material is able to recover its original shape at the presence of the right stimulus (Otsuka and Wayman, 1999, Huang et al., 2010a, Huang et al., 2012). SMMs provide an alternative approach for many designs that are difficult to achieve by conventional materials/technologies, thus they can reshape design in many ways (Toensmeier, 2005). Traditional SMMs include shape memory alloy (SMA) and shape memory polymer (SMP) (Huang et al., 2010a). The stimulus used for triggering the SME might be heat (thermo-responsive), stress/pressure (mechano-responsive), electrical current/voltage (electro-responsive), magnetic field (magneto-responsive), pH-change/solvent/moisture (chemo-responsive) and light (photo-responsive) (Kumpfer and Rowan, 2011, Huang et al., 2010b, Cuevas et al., 2009). Nowadays, we can find applications of the SME in many different fields, such as aerospace engineering, maritime engineering, bio-medical engineering and clothing (Duerig et al., 2013, Otsuka and Wayman, 1998, Lo, 2008).

2.3.1 Shape memory alloy

According to (Ölander, 1932), the SME was firstly found by A. Ölander in 1932 in a SMA. However, not much attention was attracted until 1971, when large strain recovery was observed in a NiTi alloy at the Naval Ordnance Laboratories, USA (Otsuka and

Wayman, 1998). Since then, more and more different types of SMAs have been invented and extensively investigated by researchers all around the world.

Today, a large number of SMAs have been well developed in different forms, e.g. solid, film or even foam. At present, only three alloy systems, namely NiTi-based (Melton, 1990, Duerig et al., 2013), Cu-based (Tadaki, 1998) and Fe-based (Wuttig et al., 2001), emerge with higher potential for commercial applications. Systematic investigation and comparison of these three types of SMAs can be found in (Huang, 2002). Due to its high performance and good biocompatibility, NiTi is mostly preferred (Otsuka and Ren, 2005). NiTi-based SMAs have been used in stent and guide wire in minimally invasive surgery (Pelton et al., 1997). Cu-based SMAs are featured by its low cost and good workability in processing. Rubber-like behavior induced by martensite aging has been revealed in some of them (Ren and Otsuka, 1997). The SME in Fe-based SMAs is much weaker than the others and they are mainly restricted in one-time type of applications for their extremely low cost (Pelton et al., 1997).

All SMAs that mentioned above are thermo-responsive, which means that heat is the stimulus to trigger shape recovery. On the other hand, ferromagnetic SMAs, which are categorized under magneto-responsive SMMs, have also been developed in recent years (Karaca et al., 2009).

2.3.2 Shape memory polymer

In terms of engineering applications, polymers are much easier to be tailored for the required properties than metals/alloys (Xie and Rousseau, 2009, Yakacki et al., 2008). In the early 1960s, the SME in a radiation-crosslinked polyethylene was reported in (Charlesby, 2013). Since 1990s, the SME has been investigated in various segmented polyurethanes with a wide range of shape recovery temperature (Feng and Xiao, 2002). At present, crosslinked polycaprolactone (Bai et al., 2013, Zotzmann et al., 2010), crosslinked polyethylene (Wang et al., 2013), polyurethane (Chu and Wang, 2011, Xue et al., 2010), liquid crystalline polymers (Lee et al., 2012) are some popular SMPs. In addition to the high recoverable strain and possibility of multiple stimuli for shape recovery, many SMPs are naturally biocompatible and even biodegradable. SMPs are more flexible to be manipulated for different applications (Yang et al., 2006, Huang et al., 2010b).

From an engineering application point of view, instead of developing and introducing a new material to the industry, it is more cost-effective and convenient to use an existing material, which has been used with well characterized performance. Thus, for comfort fitting, finding an existing shape memory polymeric material with an appropriate transition temperature range could be the starting point.

Ether–vinyl acetate copolymer (EVA), as a copolymer of ethylene and vinyl acetate, usually has two segments, elastic and transition segments (Huang et al., 2012), in which

the elastic segment remains highly elastic throughout its entire working temperature range, while the transition segment is able to switch its stiffness reversibly from hard status at low temperatures to very soft and quasi-plastic at high temperatures. Hence, excellent SME is expected in EVA (Wu et al., 2013). Experimental results also reveal significant creeping in EVA. Good biocompatibility of EVA enables it for biomedical applications, such as in drug delivery devices (Matsumura et al., 2000, Arun et al., 2011). Moreover, the foamed EVA has already been applied in the footwear industry as one of the raw materials to fabricate insoles.

Polycaprolactone (PCL), as another polymeric material that has been widely used in footwear fabrication, also performs excellent heat-responsive SME (Salvekar et al., 2015). However, the good SME of it relies on its melting point as the transition temperature and is only applicable for low temperature programming, which is a process to fix the temporary shape. Furthermore, the programming must be completed in less than five minutes, otherwise crystallization takes place, which affects the shape fixity. Relatively high hardness also restricts its value in comfort fitting. All these points indicate that PCL is not ideal for this comfort fitting application that needs material to perform body temperature programming with also a long enough fitting time window.

Therefore, it is necessary to develop new polymeric materials for shape memory comfort fitting, in which a combination of good elasticity, thermo-responsive SME at around human body temperature, long enough fitting time window as well as suitable hardness is required.

2.3.3 Shape memory hybrid

In recent years, the concept of shape memory hybrid (SMH) has been proposed to add in a new dimension in developing new SMMs to meet the needs of particular engineering applications (Huang et al., 2010a). A SMH normally includes at least two components, one is elastic component and the other is the transition component. As explained in (Huang et al., 2012), the elastic component is always highly elastic and stores the elastic energy after programming, while the transition component is able to soften upon heating to above the transition temperature and then largely maintains the deformed shape after cooling for hardening. Upon heating to soften the transition component again, the elastic energy stored in the elastic component is released, which provides the drive force for shape recovery of the hybrid. The particular feature of SMHs is that these two components do not have the SME as an individual under the given working environment.

By carefully selecting those two components and the process to mix them together without inducing any chemical interaction between them (or with minimized interaction), the mechanical properties and commonly observed shape memory features in most of SMAs and SMPs (such as dual-SME, triple-SME, two-way reversible SME, thermo-responsive, moisture-responsive) of the resulted hybrid can be pre-determined (Sun et al., 2012).

In addition, due to the flexibility in selecting the components for SMHs, some special features, such as water-responsive (Fan et al., 2011), cooling-responsive (Wang et al., 2012c) and healing (Wang et al., 2012b), become a matter of convention. Furthermore, if highly elastic silicone is utilized as the elastic component, rubber-like SMHs at both high and low temperatures have been realized in (Wang et al., 2012a).

2.3.4 Elastic shape memory polymeric materials

Except the SME and proper fitting time window, material's elasticity is also an important concern for comfort fitting, as it does affect the customers' wearing experience. Good elasticity ensures wearers' feet to be wrapped up well by the shoes, thus advanced protection is achievable. Reversely, shoes may not be worn tightly enough on the feet, which results in bad coordination between feet and shoes during walking or running.

In 2012, Wang and Huang reported a series of rubber-like shape memory polymeric materials in (Wang et al., 2012a), which are essentially a mixture of silicone and melting glue. Rubber-like elasticity, as well as repeatable SME, is confirmed for such materials. However, because the transition component used in (Wang et al., 2012a) is made of melting glue, in which the melting and crystallization temperatures are 70°C and 55°C, respectively, the programming temperature to fix the temporary shape (e.g., for fitting) is well above 37°C, and the time window for programming is also too short for comfort

fitting applications. Hence to enhance the adaptability for comfort fitting, improved SMH needs to be developed for the intended application of this thesis.

An overview of the elastic shape memory polymeric materials for the applications of comfort fitting is presented in (Sun et al., 2017). Selected polymeric foams such as EVA foam and polyurethane (PU) foam are proved to have the potential in comfort fitting. Good elasticity and excellent shape recovery naturally advance the foams over normal polymeric materials. It has to be pointed out that although properties, like porosity ratio or hardness, can be easily tailored for different requirements, the relatively high transition temperatures in these foams are still a problem to be solved.

Some elastic 3D printing filaments are also potential materials for comfort fitting as the quality of them has been improved recently with the intensive development of fused deposition modeling (FDM) 3D printing technology. However, as revealed in Appendix A, a typical elastic filament bought from Shenzhen Esun Industrial Co., Ltd., PR China is not able to fully recover to the original shape (shape recovery ratio is only 54.2%). Moreover, the temperature required to trigger the SME is also too high for direct contact with human body. The shoe printed with this filament is revealed to be still hard for human foot after long time wearing according to the wearer, which downgrades the comfortable feeling for users.

It should be reasonable to conclude that it is necessary to develop new elastic shape memory polymeric materials for comfort fitting of footwear.

2.3.5 Working mechanisms for polymeric materials

In many occasions in the literature, the SME is discussed together with the shape change effect (SCE). Different from the SME, in which a material is able to actually keep the quasi-plastic deformation permanently, the SCE is featured by an elastic or superelastic behavior in response to the applied stimulus (Lendlein, 2010, Sun et al., 2012). For example, electro-active polymers (EAPs) and polarized piezoelectrical materials are able to change their shape instantly when an electrical voltage is applied and recover their original shape once the voltage is removed. Moreover, the displacement is proportional to the magnitude of the electrical voltage (Aschwanden and Stemmer, 2006, Haertling, 1999). In a similar way, we may consider the elastic deformation in materials is a kind of mechano-responsive SCE.

From the energy perspective, the SCE and SME are essentially differentiated by the magnitude of the energy barrier between two states, in which one is under the right stimulus, while the other one is not. As shown in Figure 2.12, the SCE refers to the situation, in which the energy barrier between Shape A and Shape B is almost zero. Thus, the material is able to return to its original shape once the applied stimulus is removed. However, if the energy barrier is high (H), the material maintains the deformed shape, unless an additional driving force is applied to overcome the barrier. Another situation, in which the energy barrier is low (H'), the material may return slowly to its original shape, resulting in, for instance, viscoelasticity.

According to the actual situation, a material may have either the SME or the SCE. Therefore, for the classification of materials, a material may belong to both SMM and shape change material (SCM).

Figure 2.12 Shape memory effect (SME) and shape change effect (SCE) (Huang et al., 2012).

Unlike that of SMAs, in which the reversible martensitic transformation is the driven mechanism (Otsuka and Wayman, 1999, Miyazaki et al., 2009, Ge et al., 2006, Huang, 2002), there are a few possible working mechanisms for the SME in polymeric materials. Three basic working mechanisms, namely dual-state mechanism (DSM), dual-component mechanism (DCM) and partial-transition mechanism (PTM) are reported in (Huang et al., 2012) for the heating-responsive SME in polymeric materials.

— *Dual-State Mechanism (DSM)*

In the first category (Figure 2.13I), assume a glassy polymer is heated to above its glass transition temperature (T_g) (a) and then deformed in the rubbery state (b). Subsequently, the constraint is removed after it is cooled back to its glassy state (c). The procedure is normally called “programming” in SMM community. After that, the polymer is reheated to above its glass transition temperature, thus turning to the rubbery state, the SME is observed (d).

Figure 2.13 Basic working mechanisms for the SME in polymeric materials. (I) Dual-state mechanism (DSM); (II) dual-component mechanism (DCM); (III) partial-transition mechanism (PTM). (a) Original sample at room temperature; (b) upon heating and compressing; (c) after cooling and constraint removal; (d) after heating for shape recovery (Huang et al., 2012).

Since there are two phases (glassy and rubbery) in this mechanism, it may be called dual-state mechanism (DSM). The thermally induced SME can be regarded as the intrinsic property in almost all polymers and their composites. Enough cross-linking (either both physically and chemically), which provides the driven force for shape recovery, is needed to store elastic energy after programming (Ratna and Karger-Kocsis, 2008).

— ***Dual-Component Mechanism (DCM)***

A hard/soft segment structure or an inclusion-matrix microstructure exist in quite a number of polymers and polymer blends/hybrids, such as EVA and PU (Lendlein, 2010, Wang et al., 2012a, Weiss et al., 2008, Shi et al., 2013, Dong and Weiss, 2013, Koerner et al., 2013, Lee et al., 2013, Ahn and Kasi, 2011, Zhang et al., 2012a, Gunes and Jana, 2008). As shown in Figure 2.13II, if the soft segment or inclusion is able to change its stiffness significantly once the temperature reaches melting or glass transition, while the hard segment or matrix remains elastic within the entire intended working temperature range, thermo-responsive SME can be achieved.

This category (II) may be called as dual-component mechanism (DCM). Similar to DSM, the elastic matrix/elastic segment can be considered as the elastic component, while the inclusion/soft segment is considered to be the transition component.

— ***Partial-Transition Mechanism (PTM)***

This mechanism (Figure 2.13III), namely partial-transition mechanism, is also applicable to achieve the SME.

Instead of heating for full softening, if heating stops at a certain temperature within the transition range, a part of the material softens, which plays a role as the transition component. This is the partial-transition mechanism (PTM). Upon deforming the polymer (b), the un-softened portion is able to deform in an elastic way. After cooling back and removal of the constraint, the hardened transition component prevents the original shape is to be recovered (c). Once reheating is applied to soften the transition component (d), shape recovery occurs.

Note that in real practice, the three working mechanisms may exist either individually or in combination.

2.3.6 Elastic foam, memory foam and shape memory foam

In many occasions, shape memory polymeric foam, as a kind of SMM, is mentioned together with the other two types of polymeric foams, namely elastic foam and memory foam in comfort fitting. However, in terms of working mechanism, they are different.

Elastic foam, which refers to its good elasticity, is able to respond instantly to the external loading in a linear or non-linear manner with minimal hysteresis. According to Figure 2.12, the energy barrier between the deformed and original shape is almost zero. Thus, the deformed shape is recovered spontaneously without any driving force

required upon removal of the constraint. Such a phenomenon is categorized under the SCE.

On the other hand, memory foam is able to return its original shape in a much slower speed. Such a situation refers to a relatively low energy barrier (H' in Figure 2.12). Therefore, after the removal of the constraint, the material gradually recovers its original shape.

Due to a high energy barrier (H in Figure 2.12) between the original and the deformed shapes, shape memory foam is able to maintain the deformed shape unless an additional driving force is applied to overcome the energy barrier.

Apart from them, thermoformable material (Figure 2.7c) has been used for comfort fitting purpose. Unlike foams, which are mostly based on the glass transition, thermoformable material works based on melting/crystallization. Upon heating to above its melting point, the material melts and thus, plastically flows upon loading. After removal of the constraint and cooling, the material keeps the deformed shape permanently. Thus, the shape change in thermoformable material is irreversible.

2.3.7 Characterization of shape memory performance

A typical thermo-responsive SME cycle includes two processes, namely programming and recovery (Wu et al., 2013), with four major steps (a-d) as shown in Figure 2.14.

Figure 2.14 Illustration of a full SME cycle.

In step (a), after being stretched to a prescribed maximum strain (ε_m) at a given programming temperature, the material is unloaded (step b) at the programming temperature or after cooling back to the room temperature. The resulted residual strain is denoted by ε_1 . This is the first process of programming.

In the following process of recovery, after the applied constraint is removed, the material may recover slightly due to the creeping in the material (step c), and thus the residual strain is reduced to ε_2 . Finally, the material is heated (step d) to induce shape recovery and the remaining strain is denoted by ε_3 .

Refer to (Wu et al., 2013), the instant shape fixity ratio (R_f^i) and the long-term shape fixity ratio (R_f^l) may be defined as,

$$R_f^i = \frac{\varepsilon_1}{\varepsilon_m} \quad (2.1)$$

$$R_f^l = \frac{\varepsilon_2}{\varepsilon_m} \quad (2.2)$$

respectively, and the shape recovery ratio (R_r) may be defined as,

$$R_r = \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2} \quad (2.3)$$

These three ratios are the key parameters for the characterization of shape memory performance of SMM.

Chapter 3 Comfort fitting using ethylene-vinyl acetate (EVA) foam

3.1 Introduction

Light-weight and highly elastic thermo-set polymeric foams, mostly made of ethylene-vinyl acetate (EVA) and polyurethane (PU), have been used extensively in footwear applications. In (Wu et al., 2013), excellent heating-responsive SME in a commercial thermoplastic EVA has been revealed. According to Appendix B, the glass transition temperature of commercial EVA is slightly above our body temperature, so that EVA may be considered for comfort fitting applications. In this chapter, we characterize the heating-responsive shape memory effect (SME) of a commercial EVA foam, which is cross-linked, and investigate its feasibility for comfort fitting.

3.2 Basic concept

Figure 3.1(I) illustrates the concept of comfort fitting shoes utilizing the SME. After heating to slightly above body temperature (e.g., 45°C), the shoe becomes soft and highly elastic. Therefore, we can easily wear it as wearing elastic socks with perfect fitting. After cooling back to body temperature, it turns slightly harder, but still elastic enough for us to walk comfortably around. Furthermore, it can be taken-off and worn-on again and again whenever wanted. Every time if refitting is needed due to, for

instance, slight shape difference in our feet between in early morning and in later afternoon, the shoe can be reheated to 45°C for reuse/refitting.

Figure 3.1 Basic concept of comfort fitting shoes (I) and proof-of-concept (II).
(Reproduced from (Wang et al., 2016a))

For such a concept, comfort is meant for both during and after fitting, i.e., for not only comfort in the fitting process, but also comfort wearing after fitting. Comfort wearing after fitting requires shape/size fitting, good elasticity, and proper hardness (e.g., Shore Hardness A 30 for insoles and Shore Hardness A 50 for soles); while comfort during fitting requires a long enough time window for fitting at around or below body temperature, easy to wear (i.e., good stretchability).

Figure 3.1(II) is the proof-of-concept of above idea of comfort fitting shoes. In Figure 3.1(IIa), the sock on top is modified by coating it with a layer of thermo-plastic

polyurethane (TPU) (Sun et al., 2014a), while the bottom one is the original sock for comparison. After heating to 60°C, the TPU, which is a kind of vitrimer-like material according to Appendix C, becomes soft, and so is the piece of modified sock. When the modified sock is cooled to slightly above our body temperature, the thermo-plastic polyurethane is still easy to deform. Therefore, the modified sock can be conveniently worn just like without the layer of TPU. Subsequently, after a few minutes, the TPU becomes fully crystallized, and hence the sock turns to be harder, but is still flexible enough for us to walk around with it (Figure 3.1IIb). The sock is able to maintain the new shape even after being taken-off (Figure 3.1IIc). Only after reheating to soften the TPU, the sock returns its original shape and subsequently, it is ready to be reused again. Since such shoes do not have a particular size and even there is no difference between the right-side and left-side ones, from manufacturing and logistics points of view, the investment and efforts in fabrication and storage are significantly reduced. On the other hand, from the customers' point of view, instead of trying hard to find a right pair of shoes, now each piece of shoe is guaranteed to fit any individual feet. Hence, the only concern for a customer is to ensure to buy/order two pieces of such shoes for him/her.

Technically speaking, the shape recovery phenomenon discussed in Figure 3.1(II) is the SME (Huang et al., 2010a, Otsuka and Wayman, 1999) in which the original sock serves as the elastic component and the TPU functions as the transition component (Huang et al., 2012). The process to fix the temporary shape is traditionally called programming

as mentioned in Chapter 2, while the process of heating to return the original shape is called shape recovery.

Among some different types of materials with the SME (Sun et al., 2014b, Huang et al., 2010b, Huang et al., 2013, Huang, 2002, Sun et al., 2012), because of their high recoverable strain, suitable heating for shape fix/recovery temperature range, high flexibility, lightweight and low cost (in term of both material itself and processing), shape memory polymers (SMPs) and their composites appear as the possible candidates for comfort fitting applications. Another important advantage of SMPs, in particular for comfort fitting applications, is that SMP foams can be easily produced with the required porosity ratio, and thus their density can be reduced remarkably, while the flexibility/elasticity can be significantly enhanced (Tey et al., 2001, Metcalfe et al., 2003, Tobushi et al., 2004, Sauter et al., 2012, Huang et al., 2006).

As discussed in Section 2.3.6, shape memory foam is different from memory foam, which has been commercially available in the market for some years and also has been used for insole. Memory foam is essentially a kind of viscous-elastic foam at ambient temperature. It is able to slowly recover its original shape and hence memory foam does not have the capability to maintain the temporary shape (thus, no SME). Furthermore, it also lacks enough stiffness for supporting foot.

This chapter aims to investigate the feasibility of using a commercial thermoset EVA foam as the material for comfort fitting shoes. EVA foam, as well as some other

polymeric foams, such as polyurethane foam, have been used extensively as low-cost engineering polymeric foams for many engineering applications, including insoles, cushions and pads.

For the purpose of comfort fitting shoes as illustrated in Figure 3.1, among others, the basic requirements of a polymeric foam are: 1) flexible/elastic at both low and high temperatures; 2) able to maintain the temporary shape; 3) good shape recovery capability; and 4) heating temperature for activation, in particular during programming, should be only slightly above our body temperature. In this chapter, these requirements will be systematically examined to simulate the real wearing situation and thus evaluate the feasibility of EVA foam for such an application.

3.3 Material, thermal analysis and sample preparation

The material investigated in this study is a commercial thermoset EVA foam sheet about 5.6 mm in thickness with a porosity ratio around 15%. Figure 3.2 reveals the cross-section of this foam sheet under an optical microscope and a zoom-in-view under scanning electron microscope (SEM) captured by a field emission scanning electron microscope (FESEM), JOEL 7600F. The samples for thermo-mechanical tests were cut out of the EVA foam sheet.

Figure 3.2 Cross-section of EVA foam sheet (a) and zoom-in-view under scanning electron microscope (SEM) (b). (Reproduced from (Wang et al., 2016a))

Figure 3.3 DSC curve of EVA foam. Inset: zoom-in view of the glass transition range upon heating. (Reproduced from (Wang et al., 2016a))

Differential scanning calorimeter (DSC) test was conducted using a TA Instruments (New Castle, DE, USA) Q200 DSC between 0°C and 100°C at a heating/cooling rate of 5°C/min (under nitrogen atmosphere). As revealed in Figure 3.3, there are two

transitions in this EVA. The glass transition occurs at around 55°C, while melting and crystallization are at 80°C and 65°C upon heating and cooling, respectively. In applications, such as comfort fitting shoes, the glass transition between about 50°C and 60°C (inset of Figure 3.3) is almost right, and this transition was used in the course of this study.

Following ASTM D638 standard (type IV), dumbbell-shaped samples (as shown in Figure 3.4) and small rectangular samples (25×20 mm) were cut out of the EVA foam for uni-axial tensile test and compression test, respectively. Unless otherwise stated, the stress and strain used in this study are meant for engineering stress and engineering strain, respectively.

Figure 3.4 Dimensions of the sample for uni-axial tensile test (unit: mm). (Reproduced from (Wang et al., 2016a))

3.4 Experimental and results

In order to determine if a material could be used for comfort fitting, uni-axial tension and uni-axial compression at different programming temperatures were conducted.

Furthermore, room temperature cyclic tests were carried out to reveal whether a material still has excellent elasticity for high comfort with/without programming.

3.4.1 Uni-axial tensile test

An Intron (Norwood, MA, USA) 5565 testing system with an integrated temperature-controllable chamber was used for uni-axial tensile tests. A constant strain rate of $10^{-3}/\text{s}$ was applied in both loading and unloading in all tests.

Note that remarkable creep in this EVA foam was only observed in samples deformed at room temperature (about 23°C) to high strains. Thus, unless programming was carried out at room temperature, for other programming temperatures, $\varepsilon_2 \cong \varepsilon_l$, i.e., step c in Figure 2.14 is ignored.

Figure 3.5 shows three typical stress vs. strain relationships of EVA samples, which were pre-stretched to a maximum programming strain of 30% at three different temperatures, namely 50°C , 55°C and 60°C . It can be seen that the residual strain of the sample pre-stretched at the lowest temperature (50°C , dashed line) is the lowest (22.6%). The largest residual strain of about 27.4% is found in the sample pre-stretched at the highest temperature of 60°C (grey line).

In the subsequent recovery process, the samples were heated to less than 5°C above their respective pre-stretching temperatures for five minutes. It was found that all samples were able to fully recover their original shape, which proved that the shape

recovery temperature for such EVA foam is not necessarily the same as the transition temperature.

Figure 3.5 Typical stress vs. strain relationships of uni-axial tension to a maximum strain of 30% at three different temperatures followed by cooling back to room temperature and then unloading. (Reproduced from (Wang et al., 2016a))

Figure 3.6 presents three typical stress vs. strain curves upon stretching to a maximum strain of 80% at 50°C, 55°C and 60°C, respectively. Same trend as revealed in Figure 3.5 is observed, but the residual strains are much higher (around 70%).

After heating to less than 5°C above their respective pre-stretching temperatures for five minutes, all samples were able to almost fully recover their original shape.

The shape fixity ratio and shape recovery ratio of the samples in both uni-axial tension and uni-axial compression (Section 3.4.2) in one single SME cycle are discussed in detail in Section 3.4.3.

Figure 3.6 Typical stress vs. strain relationships in uni-axial tension to a maximum strain of 80% at three different temperatures followed by cooling back to room temperature and then unloading. (Reproduced from (Wang et al., 2016a))

Figure 3.7 shows the stress vs. strain relationships in cyclic uni-axial stretching at room temperature in the samples with/without pre-stretching. Pre-stretching was conducted at 60°C to 30% maximum strain or 80% maximum strain. Note that for simplicity, herein, the calculation of engineering strain is based on the gauge length in each individual test. Five cycles to maximum programming strains of 10%, 20%, 30%, 40% and 50% (in an increment order) were carried out. Note that in the last cycle of all samples, there was a five minutes of holding period before unloading.

The stress vs. strain curves of the samples with 30% and 80% pre-stretching show that the residual strain after unloading in each cycle is almost the same as that of the sample without pre-stretching. On the other hand, it is observed that the difference between 30% pre-stretched sample and original sample is small. A close-look reveals some noticeable

residual strain after unloading in each cycle. Furthermore, with the increase of the maximum strain in loading, the corresponding residual strain increases. However, it was observed that 10 minutes after unloading, the residual strain could be largely removed. Therefore, it is concluded that at room temperature, the foams with/without pre-stretching may be considered as largely elastic with limited elastic-viscosity.

Figure 3.7 Typical stress vs. strain relationships of cyclic stretching at room temperature in samples with/without pre-stretching. (Reproduced from (Wang et al., 2016a))

It should be pointed out that as expected, while the stress vs. strain curve of the sample with 30% pre-stretching is only slightly higher than that of the sample without pre-stretching, the sample with 80% pre-stretching appears to be much harder. In addition, a larger hysteresis in the sample with higher pre-stretching indicates a higher energy dissipation in a loading/unloading cycle. We may conclude that the influence of pre-tensile strain (at least up to 30%) does not have significant effect on the mechanical response of the foam.

3.4.2 Uni-axial compression test

Rectangular-shaped samples with thickness of 6 mm were used for a series of single and cyclic uni-axial compression tests. Same testing machine and parameters as those in above mentioned uni-axial tensile tests were used.

Three samples were compressed by 30% at three different temperatures, namely 50°C, 55°C and 60°C, and then held for cooling back to room temperature and finally unloaded. Figure 3.8 presents the stress vs. strain relationships of these three samples in the programming process. As we can see, same as that in uni-axial tension, the sample tested at the highest temperature of 60°C has the largest residual strain of about 30%, while the sample tested at the lowest temperature of 50°C has the least residual strain of about 25%.

Figure 3.8 Stress vs. strain relationships in uni-axial compression to a maximum strain of 30% at three different temperatures followed by cooling back to room temperature and then unloading. (Reproduced from (Wang et al., 2016a))

80% pre-compression tests were also carried out. Their stress vs. strain relationships are plotted in Figure 3.9. In general, the residual strains are around to be 75% and follows the same tendency as reported above, i.e., a higher programming temperature results in a larger residual strain.

Figure 3.9 Stress vs. strain relationships in uni-axial compression to a maximum strain of 80% at three different temperatures followed by cooling back to room temperature and then unloading. (Reproduced from (Wang et al., 2016a))

After programming by means of compression to 80%, as before, the samples were heated to slightly above their respective programming temperature for five minutes. After that, the thickness of all samples was measured. The remaining strain in all samples was found to be around 40%.

Figure 3.10 presents the stress vs. strain relationships in three cyclic compression tests at room temperature in samples with/without pre-compression. As before, pre-compression with a maximum programming strain of 30% or 80% was produced at

60°C. Three maximum programming strains of 15%, 30% and 45% (in increment order) were applied in all samples in cycling. No remarkable residual strain was observed in all samples at the end of each cycle, which indicates excellent elastic response in both pre-compressed samples and original sample.

Figure 3.10 Stress vs. strain relationships obtained by cyclic compression tests at room temperature in samples with/without pre-compression. (Reproduced from (Wang et al., 2016a))

Similar to that in uni-axial tension in Figure 3.7, Figure 3.10 reveals that while the stress vs. strain curve of 30% pre-compressed sample is very close to that of the sample without pre-compression (same as that in uni-axial tension), 80% pre-compressed sample is apparently much stiffer after being compressed to above 20% strain.

3.4.3 Shape fixity ratio and shape recovery ratio

While the shape fixity ratio is a measure of how a piece of comfort fitting shoe can fit the profile of a particular foot, the shape recovery ratio reveals the capability of a piece of comfort fitting shoe to recover its original size for the next round of comfort fitting.

The shape fixity ratios as a function of programming temperature in both uni-axial tension and uni-axial compression to two different strains of 30% and 80% are plotted in Figure 3.11.

Figure 3.11 Shape fixity ratio as a function of programming temperature. (Reproduced from (Wang et al., 2016a))

As we can see, in all tests, the shape fixity ratio is over 75%. As general trends,

- A higher programming temperature always results in a higher shape fixity ratio;
- The shape fixity ratio in compression is normally higher than that in tension;

- A higher maximum programming strain is more effective to increase the shape fixity ratio, but this is not applicable at higher programming temperatures.

Figure 3.12 reveals the shape recovery ratio as a function of programming temperature in both uni-axial tension and uni-axial compression to 30% and 80% maximum programming strains.

Figure 3.12 Shape recovery ratio as a function of programming temperature.

(Reproduced from (Wang et al., 2016a))

It is clear that while poor shape recovery (only between 40% to 55%) is observed in all samples programmed via compressing to a maximum programming strain of 80%, all rest samples have a very high shape recovery ratio. In particular, the shape recovery ratio in all 30% stretched samples is 100%. Hence, it may be concluded that,

- The shape recovery ratio is more or less programming temperature independent;

- A higher shape recovery ratio is resulted in samples with a lower programming strain;
- Shape recovery is bad only in samples programmed by over-compression.

3.4.4 Influence of long-term compression

As shoes, unavoidably body weight may be applied continuously over hours in most occasions. As shown in Figure 3.13(a), a piece of EVA foam was compressed at room temperature using two clips (Figure 3.13b). After 80 minutes, one clip was removed (Figure 3.13c1), while the other clip was applied for 115 hours (Figure 3.13d1). The indent made by 80 hours of clamping mostly recovered after 40 hours (Figure 3.13c2), while the indent made by 115 hours of clamping was still visible even after 23 days (Figure 3.13d4), which only disappears instantly in about two minutes upon heating in boiling water (Figure 3.13e) .

Figure 3.13 Shape recovery of EVA foam after clamping at room temperature for different periods of time. (Reproduced from (Wang et al., 2016a))

In Figure 3.14, we compare the influence of programming temperature. There are three pieces of samples in Figure 3.14(a). The middle and right pieces were compressed using a clip for 11 months. While the right piece was compressed at room temperature, the middle one was preheated before compressing. The left piece is for reference.

Figure 3.14 Influence of programming temperature on long term clamping and shape recovery. (Reproduced from (Wang et al., 2016a))

As we can see, after the clips were removed, shape recovery happened in all samples. However, significant residual deformation was still observed in all of them even after 27 days. Upon heating to 130°C, the middle and right pieces became almost flat, while the left one maintained the shape as it was not heated. Hence, we may conclude that the

actual programming temperature on shape recovery, known as the TME (Xiao, 2016, Xiao et al., 2015a, Xiao et al., 2015b, Sun and Huang, 2010b), in this EVA foam can be ignored.

In order for accurate characterization, we took a relatively extreme scenario for investigation, in which a small piece of EVA foam was firstly compressed to a maximum stress of 0.329 MPa, which is supposed to be about the maximum foot pressure of normal young adults as reported in (Hessert et al., 2005), and then this pressure was maintained for 24 hours, before being removed.

Figure 3.15(a) (black line) plots the stress vs. strain relationship of the sample during the whole test. As we can see, a compression strain of around 64% is recorded upon loading to 0.329 MPa. In the subsequent 24 hours, the compression strain gradually increases to 80%. After unloading, the residual strain is 74%.

For comparison, in another test, the applied maximum compression stress was reduced by half to 0.1645 MPa. The resulted stress vs. strain curve is plotted in grey color in Figure 3.15(a). As we can see, although the applied stress is halved, more creeping induced strain (about 10% more) is observed, while more strain recovery (about 4%) is found after unloading.

The evolution of the strain and stress in the whole loading/unloading process is plotted against time in Figure 3.15(b). It appears that within the loading holding period the strain increase gradually becomes less and less. After about 15 hours (for 0.329 MPa)

or 18.5 hours (for 0.1645 MPa) virtually there is no more strain increase. As expected, a higher applied stress requires less time for the stabilization of strain.

Figure 3.15 Stress vs. strain relationships of EVA foam upon compressing to 0.329 MPa/0.1645 MPa and then holding the applied compression stress for 24 hours before unloading (a) and the corresponding strain/stress vs. time relationships (b). (Reproduced from (Wang et al., 2016a))

In the next step, both samples were left in air at room temperature for 120 hours with their thickness recorded in every 24 hours. Finally, the samples were heated to 60°C for 10 minutes. The corresponding shape recovery ratios are calculated and plotted in Figure 3.16. As we can see, the shape recovery ratio vs. time curves of both samples are about the same. The speed of shape recovery gradually decreases over time. After 120 hours in air at room temperature, around 85% recovery is observed in both of them. Further heating to 60°C for 10 minutes results in full shape recovery in 0.1645 MPa compressed sample and over 97% recovery in 0.329 MPa compressed sample.

Figure 3.16 Evolution of recovery ratios in samples with different compression stresses of 0.329 MPa and 0.1645 MPa, respectively. (Reproduced from (Wang et al., 2016a))

Hence, it should be reasonable to conclude that this EVA foam is suitable for reasonable long-time wearing. After long-time wearing at room temperature, its excellent heating-responsive SME is not compromised.

3.4.5 Further discussions

Although still preliminary and not exhausted to cover all kinds of real scenarios, above systematical investigation on a particular EVA foam does reveal the feasibility of using shape memory polymeric foam for comfort fitting shoes.

According to Figure 3.5, Figure 3.6, Figure 3.8 and Figure 3.9, at high temperatures this foam is soft and can be stretched or compressed by 30% or more. Thus, shoes made of this foam should be easy to wear, while comfort fitting is also ensured.

As reported in Figure 3.11, the corresponding shape fixity ratios in both uni-axial tensile and compression are high, so that the foam is able to largely maintain the programmed shape. Consequently, the temporary shape of the shoes made of this foam is able to largely keep the personalized shape after “programming”.

Even after being programmed to 80% strain in either uni-axial tension or uni-axial compression, the foam is still highly elastic at room temperature, as evidenced by Figure 3.7 and Figure 3.10, which indicate that the personalized shoes are still elastic even being stretched to 50% or compressed by 45%. Therefore, a personalized shoe made of it is not only easy to take off and wear, but also comfortable to walk around with it.

High elasticity at room temperature also means that even after programming the shoes are able to mostly keep the personalized shape in the cases of short to medium term of

loading. As for long time loading, creeping does happen in this foam (Figure 3.13 and Figure 3.15), but most of the deformation due to creeping of the material can be recovered automatically even without heating (Figure 3.16). Heating to 60°C may be applied to induce almost full shape recovery.

Excellent heating induced shape recovery is observed in Figure 3.12, except in the 80% compressed foam. This is a major potential problem spotted in this study. The possible reason behind the difficulty for shape recovery should be that the foam is over compressed at high temperatures (Huang et al., 2012). A possible way to eliminate this problem is to reduce the deformation in the EVA foam. Theoretically, for the same compression load, with the increase in the stiffness of a material, the corresponding deformation decreases accordingly. As for this EVA foam, its stiffness can be easily increased by means of reducing its porosity ratio.

On the other hand, according to (Allwood and Burry, 1954), if the contact temperature is higher than 45°C, human foot may start to feel uncomfortable. According to Figure 3.11, the best result of shape fixity ratio in all tests is always obtained at a programming temperature of 60°C, which is 15°C above the comfortable temperature. Thus, the glass transition temperature of this EVA should be lowered down slightly.

An insole with a thickness of around 2 mm made of an EVA foam bought from Daiso, Japan was fabricated and its shape memory effect is illustrated in Figure 3.17. The insole was firstly heated at around 60°C for five minutes and then stretched by hand.

According to Figure 3.17(a), the insole is elongated to around 250 mm (US 7 in men's size) as the circular holes are apparently deformed to elliptical shape. Comparing with the insole after recovery by reheating to 60°C in Figure 3.17(b), an elongation of more than 15 mm is obtained, so that at least a fitting range from US 5.5 to US 7 (in men's size) is capable for this insole. In addition, good shape recovery is observed and evidenced by the circular holes as previously punched. This experiment demonstrates the possibility of using EVA foam in comfort fitting footwear.

Figure 3.17 SME in EVA foam from Daiso, Japan. (a) After elongation; (b) after heating for recovery.

3.5 Conclusion remarks

The results of a series of experiments on a commercial thermoset EVA foam reveal that this foam is able to meet most of the requirements for comfort fitting, in particular for shoes. It is highly elastic at both high and low temperatures and able to largely maintain the customized shape after programming. Unless being over-compressed at high

temperatures, it normally has excellent SME for shape recovery and subsequently for reuse.

However, poor shape recovery in over-compressed foam at high temperatures is observed. To solve such a problem, reduction in the porosity ratio of the foam is necessary to raise the overall stiffness of the foam.

In addition, as human body may not be able to bear the required high fitting temperature of the EVA foam, decreasing about 15°C of the glass transition temperature of this form is required. However, it may not be easy in real practice. Another challenge is to ensure that there is enough time e.g., at least 2-3 minutes, for fitting.

Chapter 4 Thermoset elastic shape memory hybrids

4.1 Introduction

Through a systematic investigation in Chapter 3, we conclude that the commercial ethylene-vinyl acetate (EVA) foam is not a quite right candidate for comfort fitting applications. To achieve comfort fitting during the programming (fitting) process, it becomes necessary to develop a new shape memory material that can be programmed at around or below body temperature with a long enough programming time window (maybe around five minutes) for fitting. The concept of shape memory hybrid (SMH) may provide a just right solution. As reported in (Wang et al., 2012a), the SMHs based on silicone and melting glue are always highly elastic either at room temperature or during programming. However, since the solidification temperature of melting glue is about 60°C, it cannot be programmed at around body temperature. For the purpose of comfort fitting, such a problem must be eliminated. Thus, in this chapter, an improved series of SMH are developed and then characterized.

4.2 Material, sample preparation and characterization

4.2.1 Material and sample preparation

Same as the elastic SMH reported in (Wang et al., 2012b, Wang et al., 2012a), which is not programmable at body temperature, polydimethylsiloxane (PDMS or SYLGARD® 184) from Dow Corning Corporation (Midland, Mi, USA) was selected to be the elastic

component due to its high compatibility with many materials and excellent elasticity that can be well maintained through a relatively wide temperature range from -50°C to 200°C.

Same as most types of silicone rubbers, two liquid parts, namely the base material (resin monomer) and curing agent are included in a SYLGARD® 184 silicone elastomer kit. The recommended volume ratio of 10 (base material) to 1 (curing agent) by the manufacturer was utilized for mixing and curing can be done at either room temperature (about 23°C) or high temperatures.

Five different transition components were used in the course of this study instead of using melting glue as in (Wang et al., 2012b, Wang et al., 2012a). Based on the datasheet provided by the supplier, Nanjing Licong New Materials Ltd. (Nanjing, Jiangsu, China), the so called PPM series of thermoplastic pellets are majorly composed of polyurethane (PU) and ethylene-vinyl acetate (EVA). Refer to Table 4.1 for the wt% of PU in each PPM model. It was found that PPMs are very similar to polycaprolactone (PCL) and can be crystallized at human body temperature or below.

During fabrication, a particular PPM and base material of the silicone elastomer were put into a beaker together according to the specified weight ratio. Subsequently, at least 15 minutes of heating at 130°C in an oven was necessary to fully melt the PPM pellets. The following was five minutes of high speed stirring to disperse the molten PPM evenly in the silicone matrix. To prevent the PPM from aggregating, the stirring process

must be continued during cooling until PPM completely solidified. After cooling down to around room temperature, curing agent was added in and mixed uniformly at room temperature again. During this step, a lot of air bubbles may be generated inside the mixture itself. Hence, a vacuum de-airing process by means of placing the mixture in a vacuum chamber for 10 minutes with a pressure of 8 mbar at room temperature and then in air for another two minutes was applied. Due to the high viscosity nature of the mixture, the process must be repeated for several times to ensure a perfect mixing. In the last step, the mixture was poured into a polytetrafluoroethylene (PTFE) mold with the specified dimensions to produce dumbbell-shaped samples (as shown in Figure 4.1) following ASTM D638 standard (type IV) for uni-axial tensile test. After 24 hours, the curing completed, thus the samples could be removed from the mold and ready to use. Five different types of samples/hybrids, named SPPM_x (x=1 to 5), were produced. Refer to Table 4.1 for their actual compositions.

Table 4.1 Components of five SPPM hybrids.

Sample/hybrid	wt% of silicone	Model of PPM (according to the supplier)
SPPM1	60	PPM005048 (wt% of PU: 50)
SPPM2	60	PPM000098 (wt% of PU: 0)
SPPM3	55	PPM007820 (wt% of PU: 78)
SPPM4	40	PPM003365 (wt% of PU: 33)
SPPM5	50	PPM0060438 (wt% of PU: 60)

Figure 4.2 DSC results of PPM003365 at heating/cooling speeds of 10°C/min (black line) and 5°C/min (grey line). (Reproduced from (Wang et al., 2017))

DSC results of other PPMs are similar to Figure 4.2. As we have observed, given enough time (e.g., 30 minutes), all PPMs were actually able to fully crystallize at 37°C (around human body temperature) and 50°C is high enough to activate shape recovery for SPPM samples.

Figure 4.3 is the scanning electron microscope (SEM) image of SPPM4 captured by a field emission scanning electron microscope (FESEM), JOEL 7600F. Similar to that reported in (Wang et al., 2012a), spherical balls with a diameter from around 5 μm to 40 μm corresponding to the PPM inclusions are found to be dispersed rather evenly without apparent aggregation within the silicone matrix.

For comfort fitting applications, the characterization of a shape memory material (SMM) requires to test not only the shape memory response, but also its mechanical behavior during and after programming.

Figure 4.3 Typical SEM image of SPPM4. The scale bar is 50 μm . (Reproduced from (Wang et al., 2017))

Intron (Norwood, MA, USA) 5565 tensile testing machine (with a thermal chamber for temperature control) was used to stretch the SPPM samples at a strain rate of $10^{-2}/\text{s}$ till fracture at room temperature to find their maximum strain in uni-axial tension.

Note that unless otherwise stated, in this study, engineering strain and stress are used to represent strain and stress.

Subsequently, the elastic response of SPPM samples at room temperature was investigated by uni-axially cyclic stretching to 10%, 30% and 60% strain (ascending order with three cycles at each strain). A strain rate of $10^{-2}/\text{s}$ was applied for both loading and unloading.

The shape memory response of SPPM samples was revealed by means of the standard thermo-responsive SME cycle, which contains two processes, namely programming and recovery, and three steps (Wu et al., 2013) as illustrated in Figure 2.14.

The first step was to pre-heat the chamber to 80°C to fully soften the sample. Subsequently, the sample was uni-axially stretched to a prescribed maximum programming strain (ϵ_m) right after the sample was cooled to 37°C. This temperature was then maintained for 30 minutes to ensure full crystallization. Secondly, the sample was unloaded and the residual strain after unloading was denoted by ϵ_1 . This indicated the end of programming process. Lastly, the sample was heated to 50°C in an oven for five minutes. ϵ_2 represented the remaining strain. This was the end of the recovery process.

In this test, two maximum programming strains of 20% and 50% were applied. A lower strain rate of $10^{-3}/s$ was applied as there was only one cycle in these tests.

The estimation of the time required for complete crystallization at 37°C was done by a set of cyclic tests. Three cycles to 20% strain in each test were applied with eight minutes of holding in between each two consecutive cycles. A strain rate of $1.67 \times 10^{-3}/s$ was applied in these tests for time efficiency.

The elasticity of SPPM samples after programming was also examined. The 20% and 50% pre-stretched samples were cyclically stretched to 10% and 30% at room temperature at a strain rate of $10^{-2}/s$.

4.3 Experimental results and analysis

Most of the tests were repeated three times. Only the typical ones are presented herein.

Figure 4.4 presents typical stress vs. strain relationships of all SPPM samples in uni-axial tension till fracture. Clearly, SPPM2 is outstanding as it is much harder than the rest of the samples with a fracture strain less than 50%, while all other four samples are able to stretch over 100% without fracture. Thus, we may claim that all samples except SPPM2 are soft and highly stretchable.

Typical stress vs. strain relationships of all samples in cyclic tension at room temperature are plotted together in Figure 4.5 for comparison. The applied cyclic strains of SPPM2 are 10% and 30%, since its fracture strain is less than 50% (as revealed in Figure 4.4).

Figure 4.4 Typical stress vs. strain relationships of SPPM samples under uni-axial tension at room temperature to fracture. (Reproduced from (Wang et al., 2017))

As we can see, highly elastic with only small amount of residual strain is concluded for all SPPMs in cyclic stretching at room temperature. In Figure 4.5(b), the de-bonding effect as reported in (Wang et al., 2012a) is revealed as the stress in the first cycle upon

reaching the prescribed maximum strain is larger than that in the subsequent cycles to the same strain.

Figure 4.5 Typical stress vs. strain relationships under uni-axial cyclic tension at room temperature of all samples (a), and zoom-in view of all samples excluding SPPM2 (b). (Reproduced from (Wang et al., 2017))

Figure 4.6 presents the stress vs. strain relationships of all samples during programming.

Figure 4.7 is the comparison with each individual sample as summarized in Figure 4.5.

Figure 4.6 Typical stress vs. strain relationships of all samples programmed with 20% strain (a), and 50% strain (b). (Reproduced from (Wang et al., 2017))

Figure 4.7 Comparison of the stress vs. strain relationships under uni-axial tension at room temperature and 37°C (to 20% and 50% strains) in SPPM1 (a), SPPM2 (b), SPPM3 (c), SPPM4 (d), and SPPM5 (e). (Reproduced from (Wang et al., 2017))

According to the experimental results shown in Figure 4.6 and Figure 4.7, Figure 4.8 compares the stress of all samples to reach 20% and 50% strains during loading. Note that for SPPM2, maximum strain of only 30% is applied in room-temperature stretching (refer to Figure 4.7b), thus there is no result of 50% strain for this sample.

It can be seen in Figure 4.8 that while in SPPM3, the difference is almost negligible, so that the material is always soft, the other materials become significantly harder, in particular for SPPM2, in which after hardening, the stress increases by three times from 0.3 to 1.2 MPa at 20% strain. The stresses for SPPM4 and SPPM5 at 20% and 50% are all about doubled after programming.

After programming, all samples were heated at 50°C for five minutes to induce the shape recovery. As shown in Figure 4.9, nearly full shape recovery is found in all tested samples.

Figure 4.8 Comparison of the corresponding stresses at 20% and 50% strains in loading at room temperature and in programming at 37°C. (Reproduced from (Wang et al., 2017))

Figure 4.9 Comparison of SPPM samples after heated at 50°C for five minutes for shape recovery. In each sample, the applied programming strain is indicated above the hybrid type (1 to 5). The rightmost sample is original for comparison. (Reproduced from (Wang et al., 2017))

Figure 4.10 summarizes the shape fixity ratio and shape recovery ratio of all tests repeated for three times. It is clear that both the type of sample and the applied programming strain have significant impact on the shape fixity ratio, while it is always 100% for the shape recovery ratio in all samples. In general, SPPM2 and SPPM4 show the highest shape fixity ratio (both around 70%) for both 20% and 50% programming strains, while the rest are around or below 50%. For SPPM3, which shows only slight difference in the stress vs. strain curves during programming at 37°C and at room temperature after programming (refer to Figure 4.7c), it still can partially maintain the programmed shape with a shape fixity ratio above 30%.

Figure 4.10 Shape fixity ratio and shape recovery ratio of all SPPM samples (black hollow symbols: shape fixity ratio; grey solid symbols: shape recovery ratio). The applied programming strain in each sample is indicated in % in the legend (top). (Reproduced from (Wang et al., 2017))

Figure 4.11(a) shows the evolution in the mechanical response under uni-axial cyclic tension in all samples during crystallization after being cooled down to 37°C. The constant testing temperature was controlled at 37°C. SPPM2 is much stiffer than others, thus it is difficult to monitor their results in Figure 4.11(a). Nevertheless, we can still clearly see that SPPM2 turns stiffer gradually during cycling. As a simple approach, it may be possible to estimate the process of crystallization induced hardening based on the slope in the stress vs. strain curve at 20% strain upon loading in each cycle. We may take the slope of the first cycle at 20% strain in loading as the reference and define the

slope ratio in loading, which is the ratio (in %) of the slope at 20% strain in a cycle to that of the first cycle.

Figure 4.11 Evolution in the stress vs. strain relationship of all SPPM samples under cyclic uni-axial tension during crystallization induced hardening at 37°C (a); and the slope ratios in unloading at 20% strain in the loading process of each cycle as a function of testing time (b) (in which the slope of the stress vs. strain curve at 20% strain of the first cycle of each sample is taken as the reference). (Reproduced from (Wang et al., 2017))

The slope ratios in loading against testing time for all samples is plotted in Figure 4.11(b). The slope ratio of SPPM2 grows approximate linearly against time, which reveals that the hardening process is still ongoing even when it reaches the end of the loading process in the last cycle, while it shows a moderate (e.g., in SPPM3 and SPPM4) or slight (e.g., in SPPM1 and SPPM5) increase in the last two cycles for the rest of samples. Therefore, SPPM1 and SPPM5 can be concluded to be able to fully crystallize in about 12.5 minutes, while SPPM3 and SPPM4 need slightly more than half an hour

to harden. However, SPPM2 requires more than half an hour for crystallization at 37°C.

The real working temperature is normally less than 37°C, thus a shorter hardening time can be expected in real situations.

Uni-axial cyclic tensile tests with 10% maximum strain in the first cycle and 30% in the second cycle were done to reveal the elasticity of the programmed samples (with both 20% and 50% programming strains) at room temperature. The results are plotted in Figure 4.12.

Figure 4.12 Typical stress vs. strain relationships under uni-axial cyclic tension at room temperature in all samples programmed with 20% strain (a) and zoom-in view for samples excluding SPPM2 (b); and programmed with 50% strain (c) and zoom-in view for samples excluding SPPM2 (d). (Reproduced from (Wang et al., 2017))

Good elasticity is confirmed in all samples. Note that as mentioned above, the tiny residual strains observed in Figure 4.12 are mainly due to the uneven deformation around the clamping area, which is mostly recoverable once the samples are released from the clamps and then heated for shape recovery.

Same as that in Chapter 3, an insole made of SPPM2 is demonstrated in Figure 4.13. A layer of elastic fabric is covered on both front and back surfaces for comfort purpose. The thickness of the insole is around 3 mm. Local circular holes in the middle part of the insole is for the purpose of improving stretchability.

Figure 4.13 Shape memory effect of the insole made of SPPM2 with a layer of elastic fabric covered on both surfaces. (a) After elongation; (b) after heating for recovery.

The fitting was conducted after cooling down to around human body temperature from pre-heating to 80°C. Reheating to 80°C is applied to trigger the shape recovery. The insole is elongated to around 175 mm (US 8.5 in kids' size) and the circular holes are

observed to be distorted to elliptical shape. It is found that the length of the insole is approximately 170 mm (US 8 in kids' size) and the holes restore the original circular shape upon reheating to 80°C for around three minutes.

4.4 Conclusion remarks

A series of silicone-based thermoset elastic SMHs were fabricated. Their shape memory performance and elasticity at room temperature with/without programming were systematically investigated. Additionally, the stress vs. strain relationships of these SMHs during fitting at 37°C were characterized.

High elasticity is confirmed in all samples both during fitting and after programming/fitting and tailoring of elasticity is possible for such elastic hybrids by using different models of PPM via varying the composition.

On the other hand, the required time for hardening during programming at 37°C is always over 10 minutes, which is considered to be a bit too long for actual fitting process. Five minutes is probably ideal for wearers to complete their fitting.

Furthermore, SPPM2 and SPPM4 are identified to be more capable to maintain the programmed shape as their shape fixity ratios are higher.

Chapter 5 Thermoplastic elastic shape memory hybrids

5.1 Introduction

In Chapter 4, a thermoset version of silicone based shape memory hybrid (SMH) is developed for comfort fitting applications. However, from material processing and fabrication point of view, thermoplastic materials are technically more convenient for mass-fabrication in a cost-effective manner. In this chapter, a thermoplastic rubber (TPR), which is commercially available and used by footwear industry for shoe sole fabrication, is hybridized with un-crosslinked polycaprolactone (PCL) to develop thermoplastic SMHs. Their SME and thermo-mechanical response relevant to comfort fitting are characterized.

5.2 Material, sample preparation and experimental

The TPR used in this study is a styrene-butadiene block copolymer (grade 1475) from LCY Chemical Corporation, Taiwan. As received, material is in pellet form. Such a material provides excellent wear resistance and traction to the ground as well as high elasticity, thus is normally molded or shaped to fabricate footwear outsole, especially for sports shoes.

As reported in (Salvekar et al., 2015), even without cross-linking, PCL has excellent heating-responsive SME if programming is carried out at low temperatures. The

underlying mechanism is also revealed. The same PCL as used in (Salvekar et al., 2015) with a melting temperature range between 50°C to 60°C was used in this study and the differential scanning calorimeter (DSC) results of this PCL at two different heating/cooling rate of 3°C/min and 5°C/min are presented in Figure 5.1. As we can see, the crystallization temperature range is quite sensitive to the cooling rate, while no significant variation in terms of melting temperature range is found in heating. It is also observed that the PCL is able to fully crystallize at room temperature (around 23°C), if enough time is given.

Figure 5.1 DSC results of PCL at two different heating/cooling rates of 3°C/min (grey line) and 10°C/min (black line). (Reproduced from (Salvekar et al., 2015))

According to the material data sheet obtained from the manufacturer, the TPR has a melting flow index of 5 g/min at 190°C, which is much higher than the melting point of PCL. Thus, the mixing of TPR and PCL should be conducted at around 190°C to

ensure that both TPR and PCL are processable. Due to the equipment limitation, a hot-compression machine was used for mixing of materials in the following steps.

Firstly, TPR and PCL pellets were weighted according to the desired weight ratio and mixed together at room temperature (about 23°C). In the hot-compression machine, the pellets were heated to 190°C and then compressed into a flat piece with around 1 mm thickness. After cooling down to room temperature, the mixed piece was taken out from the machine and then manually cut into small squared pieces with around 10 mm width. Subsequently, the small pieces were mixed together and then hot-compressed again as before. Such a process was repeated around ten times until no apparent interface between TPR and PCL could be observed. The produced final sample was about 1 mm thick.

Two different weight ratios between TPR and PCL were selected in fabrication and the mixed material was named TP. Table 5.1 lists the actual components of these two types of hybrids. As the matrix for the hybridization, TPR contains 60% and 70% of weight ratio, while PCL inclusion occupies the rest. Samples, namely TP6040 and TP7030, respectively, were produced accordingly for further experiments.

Table 5.1 Components of TP hybrids.

Sample/hybrid	wt% of TPR	wt% of PCL
TP6040	60%	40%
TP7030	70%	30%

Figure 5.2 presents the DSC result of TPR upon thermal cycling between 20°C and 200°C at 5°C/min using the same DSC machine mentioned in Chapter 3 and Chapter 4. Clearly, a glass transition is observable between 60°C and 80°C upon heating while it is not apparent during cooling. Similar conclusion is obtained from the result of dynamic mechanical analysis (DMA) test presented in Figure 5.3 using the same heating rate as that in DSC test. It can be seen that Tan Delta reaches its first peak at around 80°C, which represents the glass transition.

Figure 5.2 DSC result of TPR at a heating/cooling rate of 5°C/min.

The elasticity of TPR is revealed in Figure 5.4. A Shimadzu (Tokyo, Japan) AG-10NX to 10kNXplus tensile tester with a 1 kN load cell was used to conduct the cyclic tension. Five cycles were included with maximum strain of 40%, 80%, 120%, 160% and 200% in each cycle. A strain rate of 10^{-2} /s was applied throughout the entire test. Residual strain of less than 20% with small hysteresis in cycling is observed, which proves

excellent elasticity of this TPR. Furthermore, the residual strain was found to be fully recovered after removing the sample from clamps.

Figure 5.3 DMA result of TPR at a heating rate of 5°C/min.

Figure 5.4 Typical stress vs. strain relationships under uni-axial cyclic stretching at room temperature for TPR.

Dog-bone shaped samples were cut from the TP pieces for a series of uni-axial tensile tests in the following steps. The dimensions of the dog-bone shaped samples follow ASTM D638 standards (type IV) as shown in Figure 5.5.

Figure 5.5 Dimensions of the dog-bone shaped 1 mm thick sample. (Unit: mm)

Note that herein unless otherwise stated, engineering strain and stress are used for strain and stress, respectively.

The same machine as that for Figure 5.4 was used to conduct the uni-axial tensile fracture tests for the TP samples at a strain rate of $10^{-2}/s$ at room temperature to reveal their actual stretching limit.

Same as in Chapter 4, the standard thermo-responsive SME cycle with two processes (programming and recovery) and three steps was utilized to determine the shape memory behavior of TP samples. A thermal chamber was used to provide temperature control. The programming of the samples was conducted after cooling back to $37^{\circ}C$ from pre-heating to $80^{\circ}C$, which took around 20 seconds. The pre-heating process ensured that PCL was fully melted and TPR was also softened. Two maximum strains of 30% and 100% at a strain rate of $10^{-2}/s$ were used to represent small and large

deformation in real situations. Five-minute holding and then unloading followed to complete the tests.

In the next step, the programmed samples were heated to 80°C again to induce the shape recovery. The remaining strains were recorded. This marks the end of the recovery process.

The elastic performance of TP samples at room temperature was determined by uni-axial cyclic stretching to strains of 40%, 80%, 120%, 160% and 200% in ascend order. Same as that in the fracture test, a strain rate of $10^{-2}/s$ was applied in both loading and unloading. Samples without programming were also tested for comparison.

Cyclic tests at 37°C with ten cycles to 200% strain was applied at a strain rate of $10^{-1}/s$ to investigate the actual time needed for the completion of crystallization for the TP, and thus to find the time window for fitting.

5.3 Experimental results and analysis

Figure 5.6 shows the stress vs. strain relationships under uni-axial stretching to fracture at room temperature for both types of TPs. As we can see, TP7030 has a much higher stretching limit (fracture strain around 560%), while that of TP6040 is only 330%, which is slightly more than half of that of TP7030. Stretching to 300% strain should be mostly sufficient for the targeted application of comfort fitting. Besides, the fracture

stress of both types of TP is more than 3.5 MPa, which is higher than that of SPPM in Chapter 4. Hence, TP is able to provide better support.

Figure 5.6 Typical stress vs. strain relationships of both TP6040 and TP7030 under uniaxial tension to fracture at room temperature.

The stress vs. strain relationships of TP6040 and 7030 programmed to 30% and 100% maximum strains are presented in Figure 5.7. Each test was repeated twice. As we can see, the results are very close. During programming, the samples are much softer since the stress level is always below 0.4 MPa. It appears that TP7030 sample is harder than TP6040 during programming, which is opposite to the result of fracture test in Figure 5.6. Such an inconsistency is resulted from the softening of PCL when programming, and thus TP7030, which has a higher weight ratio of TPR, become harder.

Shape fixity ratio of over 90% is found in all samples. Small fluctuation in the stress vs. strain curve is observed in all samples in Figure 5.7. Such a kind of fluctuation disappears if the strain is over 40%.

Figure 5.7 Typical stress vs. strain relationships of both TP6040 and TP7030 samples programmed to 30% (a) and 100% (b) maximum strains. (“1st” and “2nd” in legend are meant for two repetitions)

The original (top piece), programmed (middle piece) and recovered samples (bottom piece) of TP7030 and TP6040 are compared in Figure 5.8.

The shape fixity ratio and shape recovery ratio of all tested samples in Figure 5.7 are summarized in Figure 5.9. As we can see, R_f of all samples is always over 94%, which ensures good fitting, while slight elastic recovery after programming is ideal to provide better wrapping to wearers’ feet. Excellent shape recovery is also concluded for both TP7030 and TP6040 as R_r of over 94% is confirmed in all samples.

Figure 5.8 Shape memory behaviors of TP7030 programmed to 30% (a) and 100% (b) maximum strains and TP6040 programmed to 30%(c) and 100% (d). Top: original sample; middle: programmed sample; bottom: recovered sample. The scale bar is for 10 mm.

Figure 5.9 Shape fixity ratio and shape recovery ratio of TP6040 and TP7030 with 30% and 100% maximum programming strains, respectively. (“1st” and “2nd” in legend are meant for two repetitions)

The elasticity of TP6040 and 7030 hybrids was examined via uni-axial cyclic tension to a maximum strain of 200% with 40% interval between two consecutive cycles at room temperature for both 30% and 100% pre-stretched samples. Results are presented in Figure 5.10. The original sample (without pre-strain) was also included for comparison. The results show that hardening is slight in the 30% pre-stretched samples (dash-dotted lines) for both TP6040 and 7030. Especially for TP6040, no apparent difference is found after being pre-stretched to 30% strain. However, the 100% pre-stretched samples (dashed lines) are apparently much harder during cyclic stretching. The residual strain in both types of hybrids is almost the same for all samples as observed. Note that the residual strain in cyclic stretching is mainly due to the deformation around the clamping area, which can be largely eliminated right after releasing the samples from the clamps and can be fully removed upon reheating.

Figure 5.11 reveals the actual time window for TP to complete crystallization at 37°C after being pre-heated to 80°C for full melting of PCL. Ten uni-axial tensile cycles to 200% maximum strain was applied at a strain rate of $10^{-1}/s$. The unloading was then conducted to 0.1 MPa stress for TP6040, while it is 0.01 MPa for TP7030. As shown, solid lines and dotted lines represent TP6040 and 7030, respectively (black for stress and grey for strain). With a fixed maximum strain of 200%, the residual strain keeps almost the same from the second cycle onwards for TP7030, while it becomes stable after five cycles for TP6040. In terms of stress, the peak stress is almost a constant in each cycle for TP7030 from the second cycle onwards, while it keeps increasing in the

first five cycles for TP6040. Hence, it may be concluded that the time window for shape fixing at 37°C for TP6040 is around 80 seconds, while that for TP7030 is 50 seconds.

Figure 5.10 Typical stress vs. strain relationships under uni-axial cyclic tension at room temperature for both TP6040 (grey line) and TP7030 (black line) without programming (solid line) and programmed with 30% (dash-dotted line) and 100% (dashed line) strain.

Figure 5.11 Stress and strain vs. time relationships of TP6040 and TP7030 for ten stretching cycles to 200% maximum strain and then unloading to 0.1 MPa and 0.01 MPa for TP6040 and TP7030, respectively, at a strain rate of $10^{-1}/s$ at 37°C.

5.4 Conclusion remarks

Thermoplastic TPR and PCL were heated and mixed together using two specific weight ratios to produce a thermoplastic version of elastic SMH. The shape memory behaviors of the materials were investigated for the actual practice in fitting. The elasticity of samples with/without pre-programming was also examined at room temperature. The results reveal good elasticity for both TP6040 and 7030 before and after programming. Over 94% of both shape fixity ratio and shape recovery ratio is confirmed for both TP6040 and 7030, which ensures not only excellent fitting, but also good recovery. A small amount of elastic recovery upon unloading is ideal to provide good wrapping. Furthermore, the time window for shape fixing at 37°C for these SMHs is much shorter than the silicone based SMH reported in Chapter 4. TP6040 with 80 seconds of fitting time at 37°C is seemingly a good candidate for the shape memory comfort fitting shoes.

Chapter 6 Design of shape memory comfort fitting shoes

6.1 Introduction

Both thermoset and thermoplastic versions of shape memory hybrids (SMHs) have been developed in Chapters 4 and 5, and the characterization results reveal them to be suitable to be selected for comfort fitting. Although materials development is the main focus of this project, shoe design and local structural design are only briefly explored in this chapter. Prototypes are produced to demonstrate the feasibility to realize comfort fitting shoes using the developed materials.

As mentioned in Chapter 1 and Chapter 2, depending on the purposes, shoes may be classified under four major categories, namely leisure shoes, walking shoes, running shoes and athletic shoes. Different design requirements are considered for different categories. Even within one piece of shoe upper, the elasticity and hardness vary according to the area. Indeed, the branded shoes are integrated with many high-technologies, which are actually resulted by years of R&D. As the proof-of-concept, we only focus on shape fitting at this stage.

6.2 Design concepts

Figure 6.1 illustrates four possible embodiments of such shape memory comfort fitting shoes.

In the first embodiment (Figure 6.1a), the shoe is designed to be very thin (from about 1 to 3 mm). In order to attain the perfect fit, the shoe is first heated using warm water, a heater or a hot blower making the shoe moldable, then the user inserts his/her foot (1) into the shoe or shoe insert (2) which will deform to accommodate the shape of user's foot. As shown, the moldable shoe or shoe insert covers the entire surface of the foot, right up to the talus of the user, providing stability for the entire foot. After cooling down, the deformed shape is retained with proper stiffness and flexibility. The user obtains a comfort fitting shoe with an internal shape profile custom molded to the shape of his/her foot.

Figure 6.1 Four possible embodiments of shape memory comfort fitting shoes.

Unlike, for instance, Crocs shoes, there is no extra gap between foot and shoe making it more comfortable and thus decreasing injury risk caused by foot slip. There is no

extra inner space and improper pressure between foot and shoe, thus the potential risk of injury can be minimized.

In addition, the shoe can be made very thin and allow, if required for instance, walking on rough ground, the user to further protect their feet by using the product as a shoe insert to a normal shoe (3) (i.e., removable inner lining, in order to eliminate possible uncomfortable feelings resulting from the rough ground (e.g., thick rocks)) or hard/stiffer shoes. In this way, the comfort fitting can be preserved although the user is wearing a normal shoe. When subjected to a second-time heating, such moldable shoe or shoe insert can deform back to its original shape. With such a material, fitting processes are repeatable and instant whereby comfort fitting can be easily achieved.

In the second embodiment (Figure 6.1b), the moldable shoe insert (2) is pre-fixed to the inner surface of a normal shoe (3), playing the role of a non-removable inner lining of a normal shoe. This can be achieved through the use of a known adhesive product used in shoe manufacture. All the shaping processes are the same as those mentioned for the first embodiment. Excellent fitting performance still can be achieved in such an embodiment.

In the third embodiment (Figure 6.1c), the moldable shoe made of shape memory polymeric material is thicker from about 2 to 15 mm than the shoe in the first embodiment in order to give better protection for the user.

In the fourth embodiment (Figure 6.1d), a thick outer sole (4) may be added underneath the moldable shoe (2). With this additional bottom layer, this shoe is able to deal with rougher ground conditions without compromising on comfort fitting performance. The bottom layer or outer sole material could be made of a much harder and wear resistant material with/without the SME. Multiple layers can also be incorporated in selected areas on the surface with impact absorbing material to cater to sports activities, such as jogging.

In still a further embodiment, thermoplastic polyurethane (TPU) can be attached on both inner and outer layers of such shoes in order to provide certain degree of breathability and prevent the shoes (in particular those made of foam) from smelling foul based on perspiration. Ventilation holes/slots at strategic areas can also be incorporated to further minimise fouling.

6.3 Local structural design

Based on above four embodiments, local structures need to be incorporated to improve the stretchability of the shoe.

As Figure 6.2 shows, a shoe sole design is provided with numbers of through/non-through holes and slots/grooves in the middle part. In Figure 6.2 (a), referring to the normal outsole made of the shape memory material, (b) and (c) are the extra rubbery pieces in the front and rear part of the shoe to provide extra protection and traction for

the shoe. Besides, local structure (d) is cut in the middle part of the outsole to improve the stretchability and lower down the local stress concentration at the same time.

Figure 6.2 The sole portion of shape memory shoes.

Some local structural designs have been created by SOLIDWORKS and subsequently a single unit of each design is extracted from the entire structure and simulated using a commercial software, ABAQUS 6.13, for the comparison of stretchability and local stress via finite element method (FEM). In Figure 6.3, one standard unit of local structural designs is taken as an example to show the boundary conditions and mesh.

As shown in Figure 6.3(a), with a constant thickness of 2 mm in all designs, the displacement in X and Z directions on the left side of the structure is controlled to be 0, while the rotational movement is not restricted. Similarly, the displacement in Y and Z directions on the bottom of the structure is 0 and no restriction is set for rotational movement. As the purpose is only to compare stretchability and local stress in different local structural designs, a linear elastic model is used for simplicity. The applied total force is 100 N, which is considered to be achievable by a normal adult and

is assumed to be distributed evenly within the whole cross-sectional area along the X axis on the right side of the surface of the structure. In this study, the shape memory hybrid TP7030 in Chapter 5 is chosen to be the material for simulation. According to Figure 5.7, the Young's modulus of the TP7030 during programming is about 3.5 MPa and the Poisson's ratio is about 0.35 (He et al., 2017). 20-noded hexahedral (brick) element without reduced integration (C3D20) is applied to mesh the structure for FEM.

Figure 6.3 Boundary conditions (a) and mesh (b) for FEM (in a representative structural design).

Three different designs are presented in Figure 6.4, together with the simulated deformation (using a linear analysis). The original (inner) and deformed (outer)

structures are overlapped together for easy comparison. Design (a) basically contains rectangular shaped holes (smoothed corners) interlaced together both horizontally and vertically. Small circular holes are added beside the rectangular shaped holes in Design (b) to reduce stress concentration, while there are only circular shaped holes in Design (c). The lengths (L_x) and widths (L_y) for these three structures are all around 40 (± 5) mm and 27.5 (± 0.5) mm, respectively.

Figure 6.4 Comparison between original structure and deformed structure. Inner: original structure; outer: deformed structure. Arrows indicate the node points used for analysis of displacements in X direction (D_x) and Y direction (D_y).

As shown in Figure 6.5, three different cavity sizes for each design are actually used to reveal the effect of hole size.

Figure 6.5 Dimensions of the cavities in each type of structural designs. (a₁), (a₂) and (a₃) represent Design (a); (b₁), (b₂) and (b₃) represent Design (b); (c₁), (c₂) and (c₃) represent Design (c). Unit: mm.

The displacements and nominal strains of the corresponding node points (refer to arrows in Figure 6.4 for their exact locations) in X and Y directions are plotted in Figure 6.6(a) and (b), respectively. Note that herein, the nominal strain is defined to be the value of displacement in X or Y direction (D_x or D_y) to the overall length or width (L_x or L_y) of the structure in percentage. Obviously, displacement and strain increases in

both X and Y directions with the cavity size increases. For Design (c), the nominal strain in Y direction is negative, which indicates a positive Poisson's ratio for this structure, while it is negative for Design (a) or (b). On the other hand, Design (b) is found to have the largest displacement in both X and Y direction comparing with the other two designs and Design (c) seems to have the smallest displacement in X direction among all designs.

Figure 6.6 The relationship between displacements (a) and nominal strain (b) in X and Y directions for local structural designs with three different sized cavities.

Figure 6.7 visualizes the von Mises stress on the deformed mesh of all three designs with three different cavity sizes. The maximum value of von Mises stress in each mesh is plotted in Figure 6.8 for comparison. Normally, larger sized cavity results in less cross-sectional area in the structure to sustain the load. Thus, the maximum von Mises stress increases with the increase of cavity size as shown in Figure 6.8. On the other side, Design (a) has the highest maximum von Mises stress among all three designs, while Design (c) shows the least, which is always less than half of that in Design (a).

Hence, we may conclude that Design (c), if is used in shoe design, can remarkably reduce the risk of local fracture.

Figure 6.7 Visualization of the von Mises stress in each design with different cavity sizes.

Figure 6.8 Results of the maximum von Mises stress in MPa.

Although Design (a) and (b) have larger deformation with also a negative Poisson's ratio, which is ideal for this application, from a more practical point of view, local fracture is least likely to happen in Design (c) due to its lowest stress level and the circular holes in Design (c) are much easier to be realized at this stage in fabrication. Therefore, Design (c) is used in the prototypes.

6.4 Design and fabrication of prototypes

As Figure 3.1 shows, the concept of the shape memory shoes is to utilize the SME to achieve the idea of “shoes fit feet” instead of traditional approach of “feet fit shoes”. In current design, the shoe is roughly separated into two major parts, namely the sole and the upper. Insole may be added. Thus, for shape memory shoes, the sole must be made of a shape memory material with reshapability. Local structure as discussed in Section 6.2 located in the middle part of the sole is also necessary to improve the stretchability. For the upper, which is responsible for shape fitting of the general contour of the foot, we expect it to have not only SME, but also good elasticity both before and after fitting for comfort wearing feeling. In the early stage of the prototype fabrication, normal socks were used as uppers for demonstration purpose. Final prototype was made of almost all shape memory materials.

A typical design of the sole for comfort fitting footwear is presented in Figure 6.9. The local structural Design (c) was applied for the middle part. The side flaps on the front and rear part of the sole are able to be folded up onto the shoe upper to realize a 3D

shape. In such a way, if the wearer's foot is wider than the shoe, the folded side flaps can be extended to create extra space along the width direction, so that wearer's foot width is fitted with good protection. The extra flaps on the heel and toe can also be folded up for not only local shape fitting, but also support to the heel. Note that the actual shape and size of the flaps can be altered to create different appearances of the shoe.

Figure 6.9 Typical shoe sole (unit: cm).

Three versions of prototypes have been fabricated.

6.4.1 Version I: Sock-EVA foam

Three prototypes were fabricated using normal sock as the upper and EVA foam for the sole. The EVA foam and sock were bonded together using Selleys® Kwik Grip contact adhesive. Figure 6.10 shows the top and back views of fabricated prototypes. As we can see clearly, the flaps in three prototypes are different. Prototype IB has flaps of the same shape as in Prototype IC, but the size is smaller. Prototype IA has relatively more

blunt shaped flaps as compared with those in Prototype IB and Prototype IC. Additionally, for the purpose of easy folding, IA and IB have the heel flap cut into two pieces, while a single huge piece is utilized in IC.

Figure 6.10 Version I. (i) Top and (ii) back views of Prototype IA, Prototype IB and Prototype IC fabricated using socks and EVA foam.

Figure 6.11 shows the fitting of Prototype IA on a 3D printed foot model. The shoe matches the foot model well in shape, as the flaps of the shoe manage to wrap up and cover the sides of the foot model. Therefore, we may say that the contour of the foot model is successfully fitted.

Figure 6.11 Fitting result of Prototype IA.

6.4.2 Version II: Modified shoe upper-EVA foam

Commercial polyester fabric in black colour provided by Fujian Putian Huafeng Industry and Trade Co., Ltd (Putian, Fujian, China), which is used in footwear industry as a slightly stretchable shoe upper material for sport shoes, was used to replace the socks in Version I. Furthermore, elastic thermoplastic polyurethane (TPU) film around 0.1 mm thick (Figure 6.12a), which is similar to the 3D printing filament discussed in Appendix A, was pre-punched with holes of 8 mm diameter and then attached firmly on the polyester fabric by hot compression at 133°C for 15 minutes. In such a way, fitting via SME can be realized for the shoe upper. In order to enhance the stretchability, circular holes of the same diameter were produced as well on selected area of the polyester fabric after hot compression (Figure 6.12b). As Figure 6.12(c) and (d) show, a 235 mm long 3D printed shoe last (US5.5 in men's size) without left/right difference was used for the shoe upper to wrapped atop to form the 3D shape. Then a shoe sole of

around 2 mm thickness (refer to Figure 6.9 for the profile) was bonded on the bottom of the shoe upper using the same adhesive as mentioned in Section 6.3.1.

Figure 6.12 (a) Polyester fabric and TPU layer with pre-punched holes before hot compression; (b) polyester fabric with holes punched and TPU layer attached atop after hot compression; (c) side view of the 3D printed shoe last with 235 mm length; (d) top view of the 3D printed shoe last with 235 mm length.

Two prototypes of Version II were fabricated and the top view and back view of them are presented in Figure 6.13(i) and (ii). The shoe uppers of IIA and IIB are also cut with

holes to improve the stretchability of upper. Prototype IIB has holes cut through both TPU film and fabric positioned on the top of the upper, while others cut through the TPU film only. In Prototype IIA, holes cut through both TPU film and fabric are located not only on the top of the upper, but also extended to the side to line up with the same sized holes in the EVA sole for better stretchability and breathability. Figure 6.13(iii) and (iv) show the elastic fitting of a real human foot of US 5 in men's size into prototype IIA. Shoe upper is able to reshape to match the foot and the sole made of EVA foam is able to reshape to the actual foot length.

Figure 6.13 Version II. (i) Front and (ii) back views of Prototypes IIA and IIB fabricated using EVA foam as sole material and modified shoe upper. (iii) Side view of Prototype IIA on foot and (iv) side view of bending Prototype IIA on foot.

6.4.3 Version III: Modified normal shoe upper-TP6040

TP6040, which was developed in Chapter 5, was used as the sole with a thickness of around 2 mm. The top view and side view of Prototype III with sole made of TP6040 are shown in Figure 6.14(d) and (e). Note that an insole made of EVA foam (Figure 6.14a) was attached on the bottom of the shoe last before assembling the shoe (Figure 6.14b). Refer to Figure 6.14(c), the shoe upper was then wrapped on the shoe last and insole. Subsequently, the sole was attached on the shoe upper using the same adhesive as mentioned in Section 6.3.1. More holes were cut through both TPU film and fabric for better breathability. Elastic fitting of Version III is revealed in Figure 6.15.

Figure 6.14 (a) The extra insole made of EVA foam for Version III; (b) the insole attached on the shoe last before assembling the shoe; (c) partially assembled; (d) side view of Version III; (e) top view of Version III.

Figure 6.15 Elasticity of Version III.

6.5 Demonstration of fitting with Version III

The fitting and recovery of shape memory shoes were demonstrated using the prototype of Version III. A piece of standard 3D printed shoe last of US 5.5 in men's size for right side was used.

At first, the prototype was heated in an oven at 80°C for 10 minutes to soften the shoe. The shoe last was then slipped into the shoe, when the shoe was cooled to around 40°C in air, which took less than 20 seconds. The top view and side view of Version III after fitting and recovery are presented in Figure 6.16(a) and (b). As shown by the marked white curves, after fitting, the contours of the collar, side and top of the shoe match the shoe last very well and after reheating to 80°C in the oven for 10 minutes for shape recovery, the above mentioned contours return back to the original shapes as the curves

do not match each other any more. Therefore, we can conclude that the profile of the foot is likely to be well fitted using this prototype and good shape recovery can also be achieved.

Figure 6.16 Demonstration of the shape fitting and recovery of Version III with a 3D printed shoe last. (a) Comparison between shoe and last after fitting (left: top view; right: side view); (b) comparison between shoe and last after recovery (left: top view; right: side view).

Although fitting results for the prototype is tested using a 3D printed standard shoe last (right side) of US 5.5 in men's size, the fitting performance in length is not able to be revealed as the this shoe last is about the same length as the one used for fabrication of prototype (refer to Figure 6.12c and d). Therefore to test the fitting and recovery in the length direction, a human foot of US 8.5 in men's size, which is much longer than the

prototype (US 5.5 in men's size), was applied for demonstration of fitting and the results are presented in Figure 6.17. Same fitting and recovery processes as discussed in Figure 6.16 were followed.

We can see from Figure 6.17(a), the length of the shoe fits that of the foot after fitting as marked by white line. After shape recovery, the shoe shrinks to around 238 mm long (US 5.5 in men's size) and is much shorter than the foot, which indicates a good shape recovery performance of the shoe.

Figure 6.17 Shape fitting and recovery of Version III with a real human foot. (a) Comparison between shoe and foot after fitting; (b) comparison between shoe and foot after shape recovery.

Hence, apart from the profile fitting, it seems that the shoe is also able to fit the length of the foot very well.

6.6 Conclusion remarks

In this chapter, three versions of shape memory shoes are presented. Prototypes were fabricated and tested. Different types of local structures were simulated via FEM.

Demonstration of fitting was conducted on Version III. Excellent fitting and recovery results were obtained using a 3D printed standard foot model and then an actual human foot.

Chapter 7 Conclusions and future works

7.1 Conclusions

An extensive literature review on the current state-of-the-art in comfort fitting footwear is presented and the current commercially available methods to achieve better fitting is also compared. It is concluded that although there are plenty of ways to improve the fitting, disadvantages can still be found in each of them. For instance, foot scanning procedure is always compulsory to obtain the foot contour for 3D printed shoes. Once the shoes are printed, their shapes can no longer be altered. Given the interesting phenomenon of the shape memory effect (SME), shape memory material (SMM), in particular polymeric SMM, may provide a new approach for comfort fitting footwear.

The main conclusions out of this study are summarized as following.

A series of tests are carried on a typical commercial elastic EVA foam (for insole) to characterize its thermo-mechanical properties, including the shape memory features (stress vs. strain relationship during programming and after programming to low and high programming strains, shape fixity/recovery ratios, transition temperature, etc), to simulate the actual wearing situations. Although the EVA foam is found to be able to meet most of the requirements for comfort fitting footwear, as the required programming temperature is well above our body-temperature, it is hard to be used in real practice without modification.

As it is difficult to find any existing materials that meet the requirements for comfort fitting, to develop a new material becomes necessary in order to achieve comfort fitting during the programming (fitting) process. Consequently, both thermoset and thermoplastic versions of SMH, namely SPPM and TP, respectively, are developed using commercially available raw materials. The resulted materials are characterized systematically for their thermo-mechanical properties, including the SME (in particular the shape fixity ratio and shape recovery ratio), elasticity at room temperature with/without programming, and their stress vs. strain relationships during fitting at 37°C. The results confirm them to be programmable at around or below human body temperature and have excellent elasticity and stretchability for comfort fitting.

Foam materials usually are able to provide better cushioning effect with extra light-weight, thus have been widely used in footwear for developing outsoles. However, foamed version of SPPM or TP is not fabricated and characterized in this course of study due to the limitation in time and equipment.

The major features of the EVA foam, SPPM and TP are compared in Table 7.1 with the important properties in comfort fitting applications highlighted in grey background. As we can see, the thermoplastic SMH achieves excellence in all aspects, while both the EVA foam and thermoset SMH have some deficiencies.

With the developed materials, preliminary design concepts of shape memory shoes are discussed. Four basic embodiments are proposed to meet different wearing

requirements. Local structural design with different through-hole patterns is investigated via finite element analysis for enhanced performance, in terms of stretchability, stress concentration and positive/negative Poisson's ratio, in the middle part of the sole and shoe upper.

Table 7.1 Comparison of major features in EVA foam, SPPM and TP.

	EVA foam	SPPM	TP
Elasticity	high	high	high
Hardness	low	tunable	tunable
Shape fixity ratio	medium	low	high
Shape recovery ratio	high	high	high
Programming temperature	too high	around 37°C	around 37°C
Fitting time window	short	too long	a bit too short
Cost	low	high	low
Fabrication/processing	complicate [#]	very complicate	simple

[#] Already commercially well established at low cost.

The feasibility to actualize comfort fitting shoes using such materials is demonstrated. As SPPM, which is silicone based, has problem to bond with other materials, only EVA foam and TP are used to fabricate the prototypes. Three versions of prototypes are fabricated and the comfort fitting feature of them is demonstrated. Although the produced shoe prototypes are only for the purpose of proof-of-concept, the

demonstration successfully shows that they are deformable to fit different sized feet at around human body temperature, which is not achievable by any of the existing technologies.

7.2 Future works

In terms of future work, the focus will be on the optimization of materials, fabrication process and shoe design.

- 1) Shape memory materials need to be further optimized to achieve a fitting time window to be around five minutes. For the EVA foam, the programming temperature should be lowered down for around 15°C. Since different parts of the shoes (e.g., sole and upper) require different properties, such as, hardness, elasticity and compressibility during and after programming, material optimization is required for each of these parts.
- 2) Twin screw extruder should be used for mass fabrication of TP, as the current way of fabrication is too time-consuming, and the resulted material is of low quality. On the other hand, the TP and SPPM that have been developed so far are solid and thus, not applicable for high level of compression. Since light-weight and good cushioning are required for the outsole, it is necessary to develop foam version of them for outsole.
- 3) Although the influence of local structures has been revealed via FEM simulation, limited by the available fabrication techniques during the course of this project, the simplest circular-hole pattern is applied in all current shoe design. In future, non-linear

viscoelastic models could also be adopted to develop optimized local structural designs in order to achieve a seamless combination of high stretchability (in particular, during programming) within the required areas, good protection and gradient elasticity after programming.

References

- AHN, S. K. & KASI, R. M. 2011. Exploiting Microphase - Separated Morphologies of Side - Chain Liquid Crystalline Polymer Networks for Triple Shape Memory Properties. *Advanced Functional Materials*, 21, 4543-4549.
- ALLWOOD, M. & BURRY, H. 1954. The effect of local temperature on blood flow in the human foot. *The Journal of Physiology*, 124, 345-357.
- ARUN, M., SILJA, P. & MOHANAN, P. 2011. Evaluation of hydroxyapatite–bioglass and hydroxyapatite–ethyl vinyl acetate composite extracts on antioxidant defense mechanism and genotoxicity: An in vitro study. *Toxicology Mechanisms and Methods*, 21, 561-566.
- ASCHWANDEN, M. & STEMMER, A. 2006. Polymeric, electrically tunable diffraction grating based on artificial muscles. *Optics Letters*, 31, 2610-2612.
- BAER, G., WILSON, T., MATTHEWS, D. & MAITLAND, D. 2007. Shape - memory behavior of thermally stimulated polyurethane for medical applications. *Journal of Applied Polymer Science*, 103, 3882-3892.
- BAI, Y., JIANG, C., WANG, Q. & WANG, T. 2013. A novel high mechanical strength shape memory polymer based on ethyl cellulose and polycaprolactone. *Carbohydrate Polymers*, 96, 522-527.
- BORDIN, M. & ROMANATO, M. 2004. Comfort upper for footwear. US Patent 6,732,455 B2.
- BOTHE, M., EMMERLING, F. & PRETSCH, T. 2013. Poly (ester urethane) with Varying Polyester Chain Length: Polymorphism and Shape - Memory Behavior. *Macromolecular Chemistry and Physics*, 214, 2683-2693.
- CHARLESBY, A. 2013. *Atomic Radiation and Polymers: International Series of Monographs on Radiation Effects in Materials*, Pergamon Press, London.
- CHEN, J., GONG, Y., JIN, T. & TONG, S. Development of an integrated CAD/CAM system for shoe last. Mechatronics and Automation, 2005 IEEE International Conference, 2005. 1107-1111.
- CHENG, F.-T. & PERNG, D.-B. 2000. A systematic approach for developing a foot size information system for shoe last design. *International Journal of Industrial Ergonomics*, 25, 171-185.
- CHU, L. & WANG, J. 2011. Comparison of polyurethane foam and biodegradable polymer as carriers in moving bed biofilm reactor for treating wastewater with a low C/N ratio. *Chemosphere*, 83, 63-68.
- CUEVAS, J., ALONSO, J., GERMAN, L., ITURRONDOBEITIA, M., LAZA, J., VILAS, J. & LEON, L. 2009. Magneto-active shape memory composites by incorporating ferromagnetic microparticles in a thermo-responsive polyalkenamer. *Smart Materials and Structures*, 18, 075003.
- DALEY, P. 1999. Method and apparatus for heating thermoformable material in footwear. U.S. Patent No. 5,885,622.

- DIETSCH, B. & TONG, T. 2007. A review:-: Features and benefits of shape memory polymers (smgs). *Journal of Advanced Materials*, 39, 3-12.
- DONG, J. & WEISS, R. 2013. Effect of Crosslinking on Shape - Memory Behavior of Zinc Stearate/Ionomer Compounds. *Macromolecular Chemistry and Physics*, 214, 1238-1246.
- DUERIG, T. W., MELTON, K. & STÖCKEL, D. 2013. *Engineering aspects of shape memory alloys*, Butterworth-Heinemann, London.
- FAN, K., HUANG, W., WANG, C., DING, Z., ZHAO, Y., PURNAWALI, H., LIEW, K. & ZHENG, L. 2011. Water-responsive shape memory hybrid: Design concept and demonstration. *Express Polymer Letters*, 5, 409-416.
- FENG, Y. & XIAO, C. 2002. Research progress on shape memory polyurethane. *Chemical Industry and Engineering Progress*, 21, 106-108.
- FRAPPIER, J. P. & SWANSON, S. C. 2001. Footwear customization system and process. U.S. Patent No. 6,170,177.
- GE, Y., HECZKO, O., SÖDERBERG, O. & HANNULA, S.-P. 2006. Magnetic domain evolution with applied field in a Ni-Mn-Ga magnetic shape memory alloy. *Scripta Materialia*, 54, 2155-2160.
- GUNES, I. S. & JANA, S. C. 2008. Shape memory polymers and their nanocomposites: a review of science and technology of new multifunctional materials. *Journal of Nanoscience and Nanotechnology*, 8, 1616-1637.
- HAERTLING, G. H. 1999. Ferroelectric ceramics: history and technology. *Journal of the American Ceramic Society*, 82, 797-818.
- HARTL, D. J. & LAGOUDAS, D. C. 2007. Aerospace applications of shape memory alloys. *Proceedings of the Institution of Mechanical Engineers, Part G: Journal of Aerospace Engineering*, 221, 535-552.
- HAVENS, E., SNYDER, E. A. & TONG, T. H. 2005. Light-activated shape memory polymers and associated applications. *Smart Structures and Materials*. International Society for Optics and Photonics.
- HE, L., YANG, J., LI, J., NG, Y. & HUANG, W. 2017. 4D Printing with Sequentially Controlled Morphing. *JOJ Material Science*, 3, 555602.
- HESSERT, M. J., VYAS, M., LEACH, J., HU, K., LIPSITZ, L. A. & NOVAK, V. 2005. Foot pressure distribution during walking in young and old adults. *BMC Geriatrics*, 5, 8.
- HIDBER, P. C., NEALEY, P. F., HELBIG, W. & WHITESIDES, G. M. 1996. New strategy for controlling the size and shape of metallic features formed by electroless deposition of copper: microcontact printing of catalysts on oriented polymers, followed by thermal shrinkage. *Langmuir*, 12, 5209-5215.
- HUANG, W. 2002. On the selection of shape memory alloys for actuators. *Materials & Design*, 23, 11-19.
- HUANG, W., DING, Z., WANG, C., WEI, J., ZHAO, Y. & PURNAWALI, H. 2010a. Shape memory materials. *Materials Today*, 13, 54-61.

- HUANG, W., LEE, C. & TEO, H. 2006. Thermomechanical behavior of a polyurethane shape memory polymer foam. *Journal of Intelligent Material Systems and Structures*, 17, 753-760.
- HUANG, W., SONG, C., FU, Y., WANG, C., ZHAO, Y., PURNAWALI, H., LU, H., TANG, C., DING, Z. & ZHANG, J. 2013. Shaping tissue with shape memory materials. *Advanced Drug Delivery Reviews*, 65, 515-535.
- HUANG, W., YANG, B., ZHAO, Y. & DING, Z. 2010b. Thermo-moisture responsive polyurethane shape-memory polymer and composites: a review. *Journal of Materials Chemistry*, 20, 3367-3381.
- HUANG, W. M., ZHAO, Y., WANG, C. C., DING, Z., PURNAWALI, H., TANG, C. & ZHANG, J. 2012. Thermo/chemo-responsive shape memory effect in polymers: a sketch of working mechanisms, fundamentals and optimization. *Journal of Polymer Research*, 19, 9952.
- HUSSEIN, H. & HARRISON, D. 2008. New technologies for active disassembly: using the shape memory effect in engineering polymers. *International Journal of Product Development*, 6, 431-449.
- JUROWSKA, A. & JUROWSKI, K. 2015. Vitrimers: the miracle polymer materials combining the properties of glass and plastic? *Chemik*, 69, 389-394.
- KARACA, H. E., KARAMAN, I., BASARAN, B., REN, Y., CHUMLYAKOV, Y. I. & MAIER, H. J. 2009. Magnetic Field - Induced Phase Transformation in NiMnCoIn Magnetic Shape - Memory Alloys—A New Actuation Mechanism with Large Work Output. *Advanced Functional Materials*, 19, 983-998.
- KOERNER, H., STRONG, R. J., SMITH, M. L., WANG, D. H., TAN, L.-S., LEE, K. M., WHITE, T. J. & VAIA, R. A. 2013. Polymer design for high temperature shape memory: Low crosslink density polyimides. *Polymer*, 54, 391-402.
- KOS, L. & DUHOVNIK, J. 2002. A system for footwear fitting analysis. *the 7th International Design Conference*.
- KUMPFER, J. R. & ROWAN, S. J. 2011. Thermo-, photo-, and chemo-responsive shape-memory properties from photo-cross-linked metallo-supramolecular polymers. *Journal of the American Chemical Society*, 133, 12866-12874.
- LEE, K. M., BUNNING, T. J. & WHITE, T. J. 2012. Autonomous, Hands - Free Shape Memory in Glassy, Liquid Crystalline Polymer Networks. *Advanced Materials*, 24, 2839-2843.
- LEE, K. M., WANG, D. H., KOERNER, H., VAIA, R. A., TAN, L. S. & WHITE, T. J. 2013. Photomechanical Response of Pre - strained Azobenzene - Functionalized Polyimide Materials. *Macromolecular Chemistry and Physics*, 214, 1189-1194.
- LENDLEIN, A. 2010. *Shape-memory polymers*, Heidelberg, Dordrecht, London, New York, Springer.
- LENG, J. & DU, R. 2005. A deformation method for shoe last customization. *Computer-Aided Design and Applications*, 2, 11-18.
- LENG, J. & DU, R. 2006. A CAD approach for designing customized shoe last. *Computer-aided Design and Applications*, 3, 377-384.

- LIU, C., QIN, H. & MATHER, P. 2007. Review of progress in shape-memory polymers. *Journal of Materials Chemistry*, 17, 1543-1558.
- LIU, N., HUANG, W., PHEE, S. & TONG, T. 2008. The formation of micro-protrusions atop a thermo-responsive shape memory polymer. *Smart Materials and Structures*, 17, 057001.
- LIU, N. & HUANG, W. M. 2006a. Comments on "Incomplete transformation induced multiple-step transformation in TiNi shape memory alloys" [Scripta Mater 2005;53:335]. *Scripta Materialia*, 55, 493-495.
- LIU, N. & HUANG, W. M. 2006b. DSC study on temperature memory effect of NiTi shape memory alloy. *Transactions of Nonferrous Metals Society of China*, 16, S37-S41.
- LIU, X., CHAKRABORTY, A. & LUO, C. 2010. Fabrication of micropatterns on the sidewalls of a thermal shape memory polystyrene block. *Journal of Micromechanics and Microengineering*, 20, 095025.
- LIU, Y., DU, H., LIU, L. & LENG, J. 2014. Shape memory polymers and their composites in aerospace applications: a review. *Smart Materials and Structures*, 23, 023001.
- LO, M.-J. 2008. Innovative shaped memory insole structure with re-adjustable supporting pads. U.S. Patent No. 7,373,740.
- LUXIMON, A., GOONETILLEKE, R. & TSUI, K. 2003. Foot landmarking for footwear customization. *Ergonomics*, 46, 364-383.
- LUXIMON, A., GOONETILLEKE, R. S. & TSUI, K.-L. 2001. A fit metric for footwear customization. *Proceedings of the 2001 World Congress on Mass Customization and Personalization*.
- LUXIMON, A. & LUXIMON, Y. 2009. Shoe-last design innovation for better shoe fitting. *Computers in Industry*, 60, 621-628.
- MATHER, P. T., LUO, X. & ROUSSEAU, I. A. 2009. Shape memory polymer research. *Annual Review of Materials Research*, 39, 445-471.
- MATSUMURA, K., HYON, S. H., NAKAJIMA, N., PENG, C. & TSUTSUMI, S. 2000. Surface modification of poly (ethylene - co - vinyl alcohol)(EVA). Part I. Introduction of carboxyl groups and immobilization of collagen. *Journal of Biomedical Materials Research*, 50, 512-517.
- MELTON, K. 1990. Ni-Ti based shape memory alloys. *Engineering Aspects of Shape Memory Alloys*, 344, 21-25.
- METCALFE, A., DESFAITS, A. C., SALAZKIN, I., YAHIA, L., SOKOLOWSKI, W. M. & RAYMOND, J. 2003. Cold hibernated elastic memory foams for endovascular interventions. *Biomaterials*, 24, 491-497.
- MILLER, F. A., WIRSCHING, M. T. & HOSICK, F. A. 1975. Size adjustable ski boot. US Patent 3,922,800.
- MIYAZAKI, S., FU, Y. Q. & HUANG, W. M. 2009. *Thin film shape memory alloys: fundamentals and device applications*, Cambridge University Press.

- MONTARNAL, D., CAPELOT, M., TOURNILHAC, F. & LEIBLER, L. 2011. Silica-like malleable materials from permanent organic networks. *Science*, 334, 965-968.
- ÖLANDER, A. 1932. An electrochemical investigation of solid cadmium-gold alloys. *Journal of the American Chemical Society*, 54, 3819-3833.
- OTSUKA, K. & REN, X. 2005. Physical metallurgy of Ti–Ni-based shape memory alloys. *Progress in Materials Science*, 50, 511-678.
- OTSUKA, K. & WAYMAN, C. 1998. Mechanism of shape memory effect and superelasticity. *Shape Memory Materials*, 27-49.
- OTSUKA, K. & WAYMAN, C. M. 1999. *Shape memory materials*, Cambridge university press.
- PEI, Z., YANG, Y., CHEN, Q., WEI, Y. & JI, Y. 2016. Regional shape control of strategically assembled multishape memory vitrimers. *Advanced Materials*, 28, 156-160.
- PELTON, B., SLATER, T. & PELTON, A. Effects of hydrogen in TiNi. Proceedings of the Second International Conference on Shape Memory and Superelastic Technologies, 1997. 395-400.
- PURNAWALI, H., XU, W., ZHAO, Y., DING, Z., WANG, C. C., HUANG, W. M. & FAN, H. 2012. Poly (methyl methacrylate) for active disassembly. *Smart Materials and Structures*, 21, 075006.
- RATNA, D. & KARGER-KOCSIS, J. 2008. Recent advances in shape memory polymers and composites: a review. *Journal of Materials Science*, 43, 254-269.
- REN, X. & OTSUKA, K. 1997. Origin of rubber-like behaviour in metal alloys. *Nature*, 389, 579-582.
- ROUT, N., ZHANG, Y. F., KHANDUAL, A. & LUXIMON, A. 2010. 3D foot scan to custom shoe last. *Special Issue of International Journal of Computer and Communication Technology*, 1, 14-18.
- RUPÉREZ, M. J., MONSERRAT, C., ALEMANY, S., JUAN, M. C. & ALCANÍZ, M. 2010. Contact model, fit process and, foot animation for the virtual simulator of the footwear comfort. *Computer-Aided Design*, 42, 425-431.
- SALLES, A. S. & GYI, D. E. 2013. An evaluation of personalised insoles developed using additive manufacturing. *Journal of Sports Sciences*, 31, 442-450.
- SALVEKAR, A. V., ZHOU, Y., HUANG, W. M., WONG, Y. S., VENKATRAMAN, S. S., SHEN, Z., ZHU, G. & CUI, H. P. 2015. Shape/temperature memory phenomena in un-crosslinked poly-ε-caprolactone (PCL). *European Polymer Journal*, 72, 282-295.
- SAUTER, T., LUTZOW, K., SCHOSSIG, M., KOSMELLA, H., WEIGEL, T., KRATZ, K. & LENDLEIN, A. 2012. Shape-Memory Properties of Polyetherurethane Foams Prepared by Thermally Induced Phase Separation. *Advanced Engineering Materials*, 14, 818-824.
- SHI, Y., YOONESSI, M. & WEISS, R. 2013. High temperature shape memory polymers. *Macromolecules*, 46, 4160-4167.

- SOKOLOWSKI, W., METCALFE, A., HAYASHI, S., YAHIA, L. H. & RAYMOND, J. 2007. Medical applications of shape memory polymers. *Biomedical Materials*, 2, S23.
- SUN, L. & HUANG, W. 2010a. Thermo/moisture responsive shape-memory polymer for possible surgery/operation inside living cells in future. *Materials & Design*, 31, 2684-2689.
- SUN, L., HUANG, W., WANG, T., CHEN, H., RENATA, C., HE, L., LV, P. & WANG, C. 2017. An overview of elastic polymeric shape memory materials for comfort fitting. *Materials & Design*, 136, 238-248.
- SUN, L. & HUANG, W. M. 2010b. Mechanisms of the multi-shape memory effect and temperature memory effect in shape memory polymers. *Soft Matter*, 6, 4403-4406.
- SUN, L., HUANG, W. M. & CHEAH, J. Y. 2010. The temperature memory effect and the influence of thermo-mechanical cycling in shape memory alloys. *Smart Materials and Structures*, 19, 055005.
- SUN, L., HUANG, W. M., DING, Z., ZHAO, Y., WANG, C. C., PURNAWALI, H. & TANG, C. 2012. Stimulus-responsive shape memory materials: a review. *Materials & Design*, 33, 577-640.
- SUN, L., HUANG, W. M., LU, H., LIM, K. J., ZHOU, Y., WANG, T. X. & GAO, X. Y. 2014a. Heating - Responsive Shape - Memory Effect in Thermoplastic Polyurethanes with Low Melt - Flow Index. *Macromolecular Chemistry and Physics*, 215, 2430-2436.
- SUN, L., HUANG, W. M., LU, H. B., WANG, C. C. & ZHANG, J. L. 2014b. Shape memory technology for active assembly/ disassembly: fundamentals, techniques and example applications. *Assembly Automation*, 34, 78-93.
- SUN, L., WANG, T. X., LEOW, W. C., HUANG, W. M., CUI, H. & GAO, X. Y. 2016. Temperature memory effect in differential scanning calorimeter test in thermoplastic polyurethane. *Journal of Polymer Research*, 23, 63.
- TADAKI, T. 1998. Cu-based shape memory alloys. *Shape memory materials*, 97-116.
- TEY, S. J., HUANG, W. M. & SOKOLOWSKI, W. M. 2001. Influence of long-term storage in cold hibernation on strain recovery and recovery stress of polyurethane shape memory polymer foam. *Smart Materials & Structures*, 10, 321-325.
- TOBUSHI, H., MATSUI, R., HAYASHI, S. & SHIMADA, D. 2004. The influence of shape-holding conditions on shape recovery of polyurethane-shape memory polymer foams. *Smart Materials & Structures*, 13, 881-887.
- TOENSMEIER, P. A. 2005. Shape memory polymers reshape product design. *Plastics Engineering*, 61, 10-11.
- WANG, C., HUANG, W., DING, Z., ZHAO, Y., PURNAWALI, H., ZHENG, L., FAN, H. & HE, C. 2012a. Rubber-like shape memory polymeric materials with repeatable thermal-assisted healing function. *Smart Materials and Structures*, 21, 115010.

- WANG, C. C., DING, Z., PURNAWALI, H., HUANG, W. M., FAN, H. & SUN, L. 2012b. Repeated instant self-healing shape memory composites. *Journal of Materials Engineering and Performance*, 21, 2663-2669.
- WANG, C. C., HUANG, W. M., DING, Z., ZHAO, Y. & PURNAWALI, H. 2012c. Cooling-/water-responsive shape memory hybrids. *Composites Science and Technology*, 72, 1178-1182.
- WANG, J., ZHANG, H., LU, G. & LIU, Z. 2011a. Rapid parametric design methods for shoe-last customization. *The International Journal of Advanced Manufacturing Technology*, 54, 173-186.
- WANG, T., HUANG, W., AW, J., HE, L. & VETTORELLO, M. 2016a. Comfort Fitting Using Shape Memory Polymeric Foam. *Journal of Testing and Evaluation*, 45, 1201-1212.
- WANG, T. X., HUANG, W. M., CHEN, H., XIAO, R., LU, H. B. & KANG, S. F. 2016b. Temperature Memory Effect and Its Stability Revealed via Differential Scanning Calorimetry in Ethylene-Vinyl Acetate Within Glass Transition Range. *Journal of Polymer Science Part B: Polymer Physics*, 54, 1731-1737.
- WANG, T. X., RENATA, C., CHEN, H. M. & HUANG, W. M. 2017. Elastic Shape Memory Hybrids Programmable at Around Body-Temperature for Comfort Fitting. *Polymers*, 9, 674.
- WANG, W., WANG, W., CHEN, X., JING, X. & SU, Z. 2009. Hydrogen bonding and crystallization in biodegradable multiblock poly (ester urethane) copolymer. *Journal of Polymer Science Part B: Polymer Physics*, 47, 685-695.
- WANG, X., ZHAO, J., CHEN, M., MA, L., ZHAO, X., DANG, Z.-M. & WANG, Z. 2013. Improved self-healing of polyethylene/carbon black nanocomposites by their shape memory effect. *The Journal of Physical Chemistry B*, 117, 1467-1474.
- WANG, Z., HANSEN, C., GE, Q., MARUF, S. H., AHN, D. U., QI, H. J. & DING, Y. 2011b. Programmable, Pattern - Memorizing Polymer Surface. *Advanced Materials*, 23, 3669-3673.
- WEERASINGHE, T. W. & GOONETILLEKE, R. S. 2011. Getting to the bottom of footwear customization. *Journal of Systems Science and Systems Engineering*, 20, 310-322.
- WEISS, R., IZZO, E. & MANDELBAUM, S. 2008. New design of shape memory polymers: mixtures of an elastomeric ionomer and low molar mass fatty acids and their salts. *Macromolecules*, 41, 2978-2980.
- WISCHKE, C. & LENDLEIN, A. 2010. Shape-memory polymers as drug carriers—a multifunctional system. *Pharmaceutical Research*, 27, 527-529.
- WONG, A. S., LI, Y. & ZHANG, X. 2004. Influence of fabric mechanical property on clothing dynamic pressure distribution and pressure comfort on tight-fit sportswear. *Sen'i Gakkaishi*, 60, 293-299.
- WU, X., HUANG, W. & TAN, H. 2013. Characterization of shape recovery via creeping and shape memory effect in ether-vinyl acetate copolymer (EVA). *Journal of Polymer Research*, 20, 150.

- WUTTIG, M., LI, J. & CRACIUNESCU, C. 2001. A new ferromagnetic shape memory alloy system. *Scripta Materialia*, 44, 2393-2397.
- XIAO, R. 2016. Modeling solvent-activated shape-memory behaviors based on an analogy between solvent and temperature. *RSC Advances*, 6, 6378-6383.
- XIAO, R., GUO, J., SAFRANSKI, D. L. & NGUYEN, T. D. 2015a. Solvent-driven temperature memory and multiple shape memory effects. *Soft Matter*, 11, 3977-3985.
- XIAO, R., YAKACKI, C. M., GUO, J., FRICK, C. P. & NGUYEN, T. D. 2015b. A predictive parameter for the shape memory behavior of thermoplastic polymers. *Journal of Polymer Science Part B: Polymer Physics*, 54, 1405-1414.
- XIE, T. & ROUSSEAU, I. A. 2009. Facile tailoring of thermal transition temperatures of epoxy shape memory polymers. *Polymer*, 50, 1852-1856.
- XIONG, S., GOONETILLEKE, R. S., ZHAO, J., LI, W. & WITANA, C. P. 2009. Foot deformations under different load-bearing conditions and their relationships to stature and body weight. *Anthropological Science*, 117, 77-88.
- XIONG, S., ZHAO, J., JIANG, Z. & DONG, M. 2010. A computer-aided design system for foot-feature-based shoe last customization. *The International Journal of Advanced Manufacturing Technology*, 46, 11-19.
- XUE, L., DAI, S. & LI, Z. 2010. Biodegradable shape-memory block co-polymers for fast self-expandable stents. *Biomaterials*, 31, 8132-8140.
- YAKACKI, C. M., SHANDAS, R., SAFRANSKI, D., ORTEGA, A. M., SASSAMAN, K. & GALL, K. 2008. Strong, Tailored, Biocompatible Shape - Memory Polymer Networks. *Advanced Functional Materials*, 18, 2428-2435.
- YAMAUCHI, K., OHKATA, I., TSUCHIYA, K. & MIYAZAKI, S. 2011. *Shape memory and superelastic alloys: Applications and technologies*, Elsevier.
- YANG, B., HUANG, W., LI, C. & LI, L. 2006. Effects of moisture on the thermomechanical properties of a polyurethane shape memory polymer. *Polymer*, 47, 1348-1356.
- YANG, F., ZHANG, S. & LI, J. C. 1997. Impression recovery of amorphous polymers. *Journal of Electronic Materials*, 26, 859.
- ZHANG, D., PETERSEN, K. M. & GRUNLAN, M. A. 2012a. Inorganic-organic shape memory polymer (SMP) foams with highly tunable properties. *ACS Applied Materials & Interfaces*, 5, 186-191.
- ZHANG, Y., LUXIMON, A., PATTANAYAK, A. K. & ZHANG, M. 2012b. Shoe-last design exploration and customization. *Journal of the Textile Institute*, 103, 541-548.
- ZHAO, Q., ZOU, W., LUO, Y. & XIE, T. 2016. Shape memory polymer network with thermally distinct elasticity and plasticity. *Science Advances*, 2, e1501297.
- ZHAO, Y., HUANG, W. & FU, Y. 2011. Formation of micro/nano-scale wrinkling patterns atop shape memory polymers. *Journal of Micromechanics and Microengineering*, 21, 067007.
- ZOTZMANN, J., BEHL, M., HOFMANN, D. & LENDLEIN, A. 2010. Reversible Triple - Shape Effect of Polymer Networks Containing

Polypentadecalactone - and Poly (ϵ - caprolactone) - Segments. *Advanced Materials*, 22, 3424-3429.

Appendix A

Differential scanning calorimeter (DSC) result of a typical elastic 3D printing filament bought from Esun Industrial Co., Ltd, (Shenzhen, China) is presented in Figure A.1. The diameter of this filament is 1.75 mm. A TA Q200 DSC machine from TA Instrument (New Castle, DE, USA) was used to conduct the test from -80°C to 220°C at a heating/cooling rate of 10°C/min. As revealed, two glass transitions occur at around -45°C and 80°C, respectively. Trough and peak at around 170°C upon heating and 90°C upon cooling represent melting and crystallization, respectively. Thus, the second T_g at around 80°C can be utilized to trigger the shape memory effect for this filament.

Figure A.1 DSC result of the elastic 3D printing filament at heating/cooling rate of 10°C/min.

A Shimadzu (Tokyo, Japan) AG-10NX to 10kNXplus tensile tester with a 1 KN load cell was used to conduct the uni-axial cyclic tensile tests at room temperature (about 23°C) for this elastic 3D printing filament. Five cycles with a maximum strain of 20%,

40%, 60%, 80% and 100% in each cycle were carried out. Strain rate of $10^{-2}/s$ was used during the whole test. The result is plotted in Figure A.2.

Figure A.2 Typical stress vs. strain relationships under uni-axial cyclic tension at room temperature for the elastic 3D printing filament from Esun Industrial Co., Ltd.

As we can see, small residual strain after unloading is found in each cycle. As observed, sample recovered back its original length right after being taken out from the clamps. Thus, we may conclude the 3D printing filament has good elasticity at room temperature.

The shape memory performance of the same elastic 3D printing filament is reported in Figure A.3. A TA Q800 dynamic mechanical analysis (DMA) machine from TA Instrument (New Castle, DE, USA) was used to carry out the test in film tension mode. A sample of 3D printing filament was firstly heated to around 90°C (above the second

glass transition) and then gradually stretched to approximately 30% strain. Cooling and then unloading were applied subsequently to fix the temporary shape. To trigger the shape recovery, sample was reheated to around 95°C. With a maximum strain of 30% after loading, around 24% and 11% residual strain are found after unloading and reheating, respectively, which indicates a shape fixity ratio of approximately 80% and shape recovery ratio of 54.2%.

Figure A.3 Shape memory cycle for an elastic 3D printing filament from Esun Industrial Co., Ltd.

Figure A.4 shows a piece of 3D printed shoe using this 3D printing filament. Figure A.4(a) is the overall view of the shoe. Cavities are designed on the shoe to intentionally increase the capability of elastic deformation of the shoe. Figure A.4(b) is the shoe on feet and Figure A.4(c) demonstrates the shoe can be easily bent. As the transition temperature of this elastic filament is far above human body temperature, thus it is not applicable for direct contact with human body. According to the wearer, although the

shoe is highly elastic, it is still too hard for human foot as uncomfortable feeling emerges after long time wearing.

(a)

(b)

(c)

Figure A.4 3D printed shoe using the same printing filament as that in Figure A.1 and Figure A.2. (a) Overall view of the shoe; (b) shoe on feet; (c) elastic bending of the shoe on feet.

Appendix B

B.1 Introduction

A recent study of a thermoplastic polyurethane (TPU) around its melting temperature range via differential scanning calorimetry (DSC), in which the required sample size is very small (about 10s mg level), reveals the temperature memory effect (TME) as that observed in shape memory alloys (SMAs) (Huang et al., 2012). Similar to that reported in (Bothe et al., 2013), the melting/crystalline transition is attributed to the polyester segment in this TPU.

Since the melting transition is essentially similar to that of the reverse martensitic transition (from martensite to austenite upon heating), in which latent heat is involved, it is not a big surprise to see similar TME in a thermoplastic polymer within its melting transition temperature range. However, it is unclear whether the glass transition, which is the common feature of most polymers, could be utilized to achieve the same memory effect.

The purpose of this appendix is to investigate the TME via DSC in a commercial thermoplastic EVA, at around its glass transition temperature range. In addition, due to the strong influence of the micro-Brownian motion in polymers within the glass transition temperature range, we also study the effects of heating holding time on the resulted TME.

The TME investigated via DSC, in which there is no macroscopic shape switching involved, may be considered as the first step toward revealing the possibility of applying EVA in the field of comfort fitting.

B.2 Material and experimental

Figure B.1 presents the typical DSC result of a TPU studied in (Sun et al., 2016), in which there are two thermal cycles. The first one is from 0°C (point A) to 46°C (point B) and then back to 0°C, and the subsequent cycle is from 0°C to 70°C and then back to 0°C. The heating stop temperature (T_s , which is 46°C in this particular case) in the first cycle is actually within the melting temperature range of this polymer. However, when compared with the grey dotted line, which is the result of a full thermal cycle without any previous heating stop within the melting range, the melting start temperature in the second thermal cycle is apparently increased to a higher temperature level, which may be denoted by the turning point (T_t) as marked in Figure B.1. It is found that the difference between T_t and T_s (ΔT) is about a constant if the heating/cooling rate is fixed, so that the TME via DSC, which has been only observed in SMAs in the past, is proved to be applicable to the melting transition range of a polymer.

Figure B.1 Typical DSC result of thermoplastic polyurethane with one heating stop at 46°C. Black dashed line: thermal cycle from 0°C (A) to 45°C (B) to 0°C (A); black line: subsequent thermal cycle from 0°C (A) to 70°C to 0°C (A). (Reproduced from (Sun et al., 2016))

The EVA (Cosmothene, H2181, as-received in pellet form) used in this study was bought from Polyolefin PTE Ltd., Singapore. According to the data provided by the company, its weight percent of vinyl acetate is 18%, and the Vicat Softening Point is 63°C. Its excellent thermo-responsive SME has been reported in (Wu et al., 2013).

A DSC Q200 (TA Instruments) was used for all DSC tests conducted in this study. Unless otherwise stated, the applied ramping rate was a constant of 5°C/min to get rid of the influence of heating/cooling rate, which is a common phenomenon in DSC test. The starting temperature of all tests was always 0°C. Around 6 mg of pellets was used in each test. All samples were pre-heated to 120°C to eliminate the influence of the previous thermo-mechanical history.

Figure B.2 presents the typical result of a full thermal cycle between 0°C and 120°C. As we can see, the melting transition of this EVA is at around 85°C upon heating, while crystallization occurs at around 70°C upon cooling. A close-look of the DSC curve in the inset of Figure B.2 reveals that there is a straight line segment upon heating from 45°C to 70°C, which is seemingly the glass transition. However, there might be some overlapping of glass transition and melting. According to the systematical investigation on the SME of this EVA upon uni-axial stretching to up to 100% at 35, 55 and 75°C, respectively, reported in (Wu et al., 2013), this EVA, which is thermo-elastic, is able to fully recover from 20% pre-stretching at 55°C after heating to 55°C. Even after 100% pre-stretching at 75°C, the recovery is still over 80% upon heating to 75°C. Hence, even there is any melting at 75°C, it should not be significant. In addition, the Vicat softening point of this EVA is 63°C. Thus, herein, we may define 45°C to 70°C as the glass transition range of this EVA. From comfort fitting point of view and to be more cautious, the highest heating stop temperature applied in the course of this study was 60°C.

Figure B.2 DSC result of a full thermal cycle. Inset: zoom-in view of the glass transition range upon heating. (Reproduced from (Wang et al., 2016b))

Two types of TME tests were carried out. In the first type, there was only one stop temperature (single-stop test); and in the second type, there were three stop temperatures (triple-stop test), i.e., there were three thermal cycles (all started from 0°C and finished at 0°C) before final heating (also started at 0°C). In both types of tests, 50°C, 55°C and 60°C, which are all within the glass transition temperature range, were selected as the heating stop temperatures in thermal cycling.

In the cases of triple-stop test, three stop temperatures (50°C, 55°C and 60°C) might follow a descend order (i.e., 60°C in the first thermal cycle, 55°C in the second cycle and then 50°C in the final cycle), an ascend order (i.e., 50°C, 55°C and then 60°C), or in a “random” order of 50°C, 60°C and then 55°C.

In the tests to investigate the influence of heating holding at a prescribed heating stop temperature, heating was stopped at the prescribed temperature and then this temperature was maintained for one hour or three hours before cooling.

B.3 Results analysis and discussion

B.3.1 Single-stop test

The results of the final heating process of all single-stop tests are plotted in Figure B.3. For comparison, the result of the experiment without heating stop is also included. Note that hereinafter, solid grey line always refers to the result without heating stop (taken from Figure B.2).

Figure B.3 DSC results in the final heating process of single-stop tests. (Reproduced from (Wang et al., 2016b))

As compared with the curve without heating stop (solid grey line), the results of the single-stop tests are all featured by an apparent new segment, which deviates from the solid grey line. The deviation appears to occur only within a certain temperature range. The apparent turning points of deviation are estimated and indicated by arrows in Figure B.3. It can be seen that the exact location of the turning point depends on the previous heating stop temperature (T_s), and is seemingly always a couple of degrees higher than the previous heating stop temperature, which reveals the typical feature of the TME. Upon further heating, the DSC curve returns back to the “normal” track as that without heating stop.

Figure B.4 plots the experimental results of single-stop tests with a holding time of one hour or three hours, together with the results without holding (taken from Figure B.2)

for comparison. The apparent turning points are also marked by arrows. It can be concluded that with heating holding, the turning point shifts to a higher temperature, in particular at higher T_S . Furthermore, with a longer heating holding period, the deviation becomes more significant, i.e., the deviation segment shifts to a higher temperature region and it covers a wider temperature range as well.

Figure B.4 DSC results of single-stop tests with heating holding time of one or three hours. (a) $T_S = 50^\circ\text{C}$; (b) $T_S = 55^\circ\text{C}$; and (c) $T_S = 60^\circ\text{C}$. The experimental results of without holding are taken from Figure B.2 for comparison. (Reproduced from (Wang et al., 2016b))

In order to confirm above observed TME happens at lower heating/cooling speed as well, two more tests were carried out at 3°C/min and 1°C/min, respectively, with T_s at 55°C. The results of the final heating process are plotted in Figure B.5, together with that at 5°C/min for comparison. It is clear that when the heating/cooling speed is reduced, the TME persists, but the magnitude is reduced.

Figure B.5 Comparison of the DSC curves in the final heating process at three different heating/cooling speeds. (Reproduced from (Wang et al., 2016b))

B.3.2 Triple-stop test

Figure B.6 reveals the results of two particular triple-stop tests. In one test, the three heating stop temperatures followed a descend order, i.e., 60°C in the first thermal cycle, 55°C in the second cycle and 50°C in the third cycle; while in the other test, the three stop temperatures followed an ascend order, i.e., 50°C in the first cycle, 55°C in the second cycle and 60°C in the third cycle.

Figure B.6 DSC results of triple-stop tests in descend and ascend orders. (Reproduced from (Wang et al., 2016b))

It is observed that if the heating stop temperatures follow an ascend order, the influence of the previous two heating stop temperatures in the final heating process is almost fully removed, and only the effect of the last heating stop temperature, which is also the highest among the three heating stop temperatures, can be observed. On the other hand, if the heating stop temperatures follow a descend order, the influence of all three heating stop temperatures is noticeable, while the last heating stop temperature, which is also the highest heating stop temperature, is far more significant than the other two. The apparent turning points corresponding to the heating stop temperature of 60°C in both tests are slightly different.

In addition to above two tests, in which the heating stop temperatures following a either descend or ascend order, three more triple-stop tests were carried out in which the

heating stop temperatures were in a kind of random manner, i.e., 50°C in the first cycle, 60°C in the second cycle and 55°C in the third cycle. Among them, in two tests, there was a heating holding period of one hour at 50°C or 55°C. All results in the final heating process are plotted in Figure B.7.

Figure B.7 DSC results of triple-stop tests with heating holding time indicated in the legend. (Reproduced from (Wang et al., 2016b))

As we can see, in all three tests it is difficult to spot the influence of the heating stop temperature of 50°C even with a heating holding time of one hour at this temperature. On the other hand, although a heating stop temperature of 55°C was applied in the last cycle, which was after a heating stop temperature of 60°C was applied in the previous (second) cycle, both heating stop temperatures of 55°C and 60°C always induce remarkable deviation so that their influence can be easily identified in the final heating process. Heating holding at either 55°C or 50°C causes apparent distortion in the

resulted DSC curves, and thus, both turning points corresponding to heating stop temperatures of 55°C and 60°C may shift to a higher temperature range.

B.3.3 Analysis and further discussion

A summary of the relationship between T_s and ΔT of all tests in this study is presented in Figure B.8. The influence of single heating stop and heating holding is schematically illustrated in Figure B.9.

Figure B.8 Relationship between ΔT and T_s of all tests. (Reproduced from (Wang et al., 2016b))

Figure B.9 Illustration of the influence of T_s and heating holding in the DSC curve of the final heating process. (Reproduced from (Wang et al., 2016b))

Based on the results in Figure B.8 and illustration in Figure B.9, the following general trends can be concluded.

— ***Without heating holding***

- a. In a single-stop test, ΔT is roughly a constant and seemingly decreases only slightly with the increase of T_s .
- b. A higher heating stop temperature is able to eliminate the influence of the previous lower heating stop temperature(s).
- c. A lower heating stop temperature results in an additional deviation in the DSC result of the final heating process.

Consequently, in the case of the triple-stop test in which T_s s follow a descend order, we can identify three ΔT s, and they share the same general trend as that of single-stop test.

The TME via DSC in this polymer (based on the glass transition) only induces a kind of deviation when compared with the curve of non-heating stop. This pattern is different from what reported in (Sun et al., 2016), in which the transition is melting and the polymer is a thermoplastic polyurethane with low melt flow index (Sun et al., 2014a). Note that the observed pattern associated with the TME in (Sun et al., 2016) is similar to that in most SMAs under the reverse martensitic transformation (Liu and Huang, 2006b, Sun et al., 2010).

In comparison with the TME (via DSC test) in SMA (Liu and Huang, 2006a, Liu and Huang, 2006b, Sun et al., 2010) and in the polymer based on melting transition (Sun et al., 2016), it can be concluded that a)-c) are common features shared by all of them.

— ***With heating holding***

- i. Holding at a particular heating stop temperature for a period of time is able to enhance the influence of this heating stop temperature and in the meantime, increase the corresponding ΔT in the final heating process (refer to Figure B.8).
- ii. However, even with heating holding, if the heating stop temperature in the following thermal cycle is higher, the influence of heating holding at this temperature can be fully eliminated.

- iii. With heating holding, a lower heating stop temperature in the following thermal cycle can enhance the corresponding deviation in the final DSC curve, while the influence of other heating stop temperature(s), if applicable, becomes less significant.

Note that due to the nature of micro-Brownian motion, polymers in glass transition are featured by a kind of temperature-time equivalent relationship, i.e., the influence of a lower heating temperature of a longer period of heating time is equivalent to that of a higher heating temperature of a shorter period of heating time.

B.4 Conclusion remarks

The TME via DSC test is revealed in a commercial thermoplastic EVA around its T_g in both single-stop and triple-stop tests. It is found that in the case of single-stop test, a higher T_s , which is within the glass transition range, may reduce ΔT slightly. In the case of triple-stop test, same as that in SMAs and the reported polymer within its melting temperature range, a higher heating stop temperature is able to eliminate the influence of the previous heating stop at lower temperature(s), while a lower heating stop temperature in the following cycle is able to produce an additional deviation in the DSC result of the final heating process.

Thus, together with what previously reported in (Sun et al., 2016), the TME via DSC test without involving any macroscopic shape change could be a general feature of polymers, which is applicable in both the melting transition and the glass transition.

On the other hand, due to the nature of micro-Brownian motion in polymers in the glass transition, which is different from the reversible martensitic transformation in SMAs, heating holding at a prescribe temperature can not only effectively enhance the influence of this heating stop temperature, but also increase the corresponding ΔT .

Appendix C

C.1 Introduction

Normally, the permanent shape of thermoset materials is not able to be reshaped once synthesized or cross-linked, while oppositely, reshaping of the permanent shape can be easily achieved in thermoplastics. The term of vitrimer was first introduced by Leibler and his colleagues (Montarnal et al., 2011) to described a group of polymers, which are between thermoset and thermoplastic (Jurowska and Jurowski, 2015). So far, the shape memory effect (SME) in both thermoset and thermoplastic polymers have been reported in the literature and plenty of engineering polymers have been verified to intrinsically have superior shape memory performance (Hussein and Harrison, 2008, Huang et al., 2012, Purnawali et al., 2012, Yang et al., 1997, Wang et al., 2017, Wu et al., 2013, Sun et al., 2014a, Wang et al., 2016a). However, the SME in vitrimers or vitrimer-like polymers have yet been well explored (Pei et al., 2016, Zhao et al., 2016).

In this appendix, a systematic characterization of heating-responsive shape memory behavior in a vitrimer-like polyurethane (PU) is conducted and the underlying working mechanism is investigated.

C.2 Material, sample preparation and experimental

The polyurethane used in the course of study is TPU 262A bought in pellet form originally from Taiwan PU Corporation, Taiwan. The pellets were firstly heated to

130°C, which is well above the melting point of this TPU and then hot-pressed into a flat piece around 1 mm thick. Subsequently, strips with 20 mm length and 5 mm width were cut from it for a series of dynamic mechanical analysis (DMA) tests.

Additionally, some TPU 262A pellets were fully dissolved in acetone (99% purity) at a concentration of 20 grams/100 mL after stirring for 24 hours. Thereafter, the solution was carefully poured on a Petri dish in air at around 22°C for 24 hours to ensure complete evaporation of acetone. Subsequently, a flat piece of TPU 262A was obtained and samples of the same size (20 mm long and 5 mm wide) were cut from it for DMA tests.

Figure C.1(a) is the differential scanning calorimetry (DSC) result of TPU 262A upon thermal cycling between -50°C and 200°C at a temperature ramping rate of 10°C/min using a Q200 DSC machine from TA Instrument (New Castle, DE, USA). Two cycles are included here as it is a must to primarily eliminate the thermal history in the material, and only the second cycle (red line) is useful for analysis. A trough and a peak are observed representing melting upon heating and crystallization upon cooling, respectively. Therefore, the melting of TPU 262A may be determined to end at around 60°C. Although crystallization temperature of this material is below room temperature (22°C) according to Figure C.1(a), as we have observed, given enough time, it crystallizes at room temperature, which is similar to the polycaprolactone (PCL) reported in (Salvekar et al., 2015).

Figure C.1 (a) DSC result of TPU 262A at heating/cooling rate of 10°C/min and (b) DMA result of TPU 262A at heating rate of 1°C/min.

A Q800 DMA machine also from TA Instruments (New Castle, DE, USA) was used to determine the storage modulus and tangent delta of TPU 262A. The scanning temperature range was from room temperature to 115°C at a ramping rate of 1°C/min and a frequency of 1 Hz in film tension mode. The result is shown in Figure C.1(b). Similar to that of the DSC result, the melting ends at around 60°C as the storage modulus drops to almost 0 MPa at this point. In the course of this study, we focus on melting as transition for triggering the SME in this material. The programming was carried out at above 60°C.

The demonstration of the SME is shown in Figure C.2. The original strip of about 45 mm long and 2 mm thick (Figure C.2a) was firstly heated to about 65°C in an oven and then stretched to approximately 95 mm. The strip became transparent, but was still in solid state at 65°C, as shown in Figure C.2(b). The manually stretched sample kept the deformed shape after cooling for hardening. Upon heating to 65°C again, according to

Figure C.2(c), the sample became transparent again and shortened back to around 45 mm. It turned to opaque appearance after gradual crystallization at room temperature (Figure C.2d). Upon reheating to 110°C, which is well above its melting range, the sample became slightly flowable and thus was not able to maintain the shape as observed in Figure C.2(e).

Figure C.2 Demonstration of the SME in TPU 262A. (a) Original TPU strip; (b) after stretching at 65°C and then cooling for hardening; (c) upon reheating to 65°C; (d) after crystallization; and (e) upon further reheating to 110°C and then cooling for crystallization.

The same DMA machine was used for investigation of the strips of 20 mm long and 5 mm thick. Firstly, the clamped sample was heated to a prescribed temperature (65°C,

80°C, 90°C, 100°C, 105°C, 108°C or 110°C) inside the furnace of the DMA machine. A tensile force was then gradually increased until the strain reached around 25% ($\pm 10\%$). The door of the furnace was subsequently opened to allow air-cooling to maintain the deformed shape. Until the sample was fully crystallized (opaque), furnace was closed and then the tensile force was released. The next step was to reheat to the previous programming temperature for shape recovery.

C.3 Experimental results and analysis

Figure C.3 presents the results of one shape memory cycle obtained from DMA tests at different programming temperatures (T_d) for comparison. Apparently, the temporary shapes of all samples are well maintained after programming. The results of one shape memory cycle of the samples previously dissolved in acetone are shown in Figure C.4.

Although shape fixity ratio can directly obtained from Figure C.3 and Figure C.4, in terms of shape recovery ratio, it was noticed that sample tended to be pulled out of clamps, which resulted in strain that is not recoverable upon heating. Thus, the gauge length of all samples reported in Figure C.3 was also manually measured by a Vernier caliper before and after testing. Shape recovery ratio and shape fixity ratio as a function of programming temperature of all tests is plotted in Figure C.5.

Figure C.3 Results of one shape memory cycle programmed at 65°C (a), 80°C (b), 90°C (c), 100°C (d), and 105°C (e).

Figure C.4 Results of one shape memory cycle programmed at 65°C (a), 80°C (b), 90°C (c), 100°C (d), 105°C (e), 108°C (f), and 110°C (g) of samples after being dissolved in acetone.

Shape fixity ratios are 100% for all the samples with and without acetone treatment. The overall trends for shape recovery ratio are similar for both types of samples with and without acetone treatment (dissolving in acetone). Via manual measurement, better shape recovery in samples programmed below 80°C is observed. Dramatic decrease in shape recovery ratios in samples programmed at 80°C and above. Although the results of samples with acetone treatment are slightly different from those without acetone treatment, lower shape recovery ratio is always found at higher programming temperature and all samples are only able to recover very little at high programming temperature. As such, we may conclude that this material is vitrimer.

Figure C.5 The relationship between shape recovery/fixity ratio and programming temperature (T_d) in samples with and without dissolving in acetone.

C.4 Further investigation

To further investigate the SME in TPU 262A, the original TPU 262A samples were firstly heated to 120°C and then cooled to prescribed temperatures (T_d), namely 90°C, 75°C and 50°C for stretching by hands to 100% strain. After cooling back to room temperature, the restrained samples were released. The shape recovery was subsequently triggered by reheating gradually to pre-determined temperatures, while the residual strain was recorded in each step. The reheating temperature is termed as T_r . Two more tests with the same preheating (T_p) and programming temperature (90°C and 75°C) was also conducted. The results are summarized in Figure C.6 in terms of shape recovery ratio against reheating temperature.

Figure C.6 The relationship between shape recovery ratio and reheating temperature (T_r) for preheated and then deformed TPU 262A samples. Legend is in $T_p:T_d$ format, where T_p and T_d indicate the preheating and programming temperatures, respectively.

As we can see, the 75:75 sample shows almost 100% shape recovery ratio and it is slightly lower for 90:90. Such a result is consistent with the conclusion obtained from Figure C.5, in which the shape recovery performance starts to downgrade when the programming is conducted at over 80°C. Notice that the shape recovery ratios for 75:75 and 90:90 sample exceed 100% upon reheating to over 110°C, which is due to the self-flowing of the material at such high temperatures. On the other hand, the 120:90 sample has the lowest shape recovery ratio and 120:75 sample performs slightly better, while remarkable increase in the shape recovery ratio is found in the 120:50 sample. It reveals the regaining of the SME in TPU 262A as its shape recovery performance is gradually meliorating with the decreasing of the programming temperature. However, comparing with the results in Figure C.5, in which the shape recovery ratio is over 70% upon directly heating to 90°C and then programming, it is much lower (less than 10%) for the sample pre-heated to 120°C and then cooled down to 90°C (refer to 120:90 sample) for programming. Moreover, it shows only slightly higher in shape recovery ratio for the 120:75 sample and remarkable increase is found only if further cooling down to 50°C for programming (refer to the 120:50 sample).

It appears that the SME in this material depends heavily on the thermal history during programming. To understand the underlying mechanism of such a thermal history dependent phenomenon, further experiments were conducted.

The micro-structure of TPU 262A was detected by ^1H Nuclear Magnetic Resonance (NMR) (Bruker Unity-400) as shown in Figure C.7. Tetramethylsilane (TMS) was used

as the internal standard and acetone- d_6 was used as solvent. It appears that TPU 262A is composed by poly (1,4-butylene adipate glycol) (PBA), diphenyl-methane-diisocyanate (MDI), and 1,4-butylene glycol (BDO). PBA segments form the soft domain and MDI and BDO segments serve as the hard segments. The ratio of soft segments to hard segments is obtained as about 28/3.

Figure C.7 ^1H NMR spectrum in acetone- d_6 .

X-ray Diffractometry (XRD) results of samples upon heating to different temperatures were obtained and then analyzed by Rigaku Smartlab. The applied scanning range was 10° to 40° . The spectra were collected upon heating TPU 262A from 25°C to 110°C .

As shown in Figure C.8, at room temperature (around 23°C), TPU 262A exhibits obvious diffraction at 2θ values of 21.76° , 22.42° , and 24.02° , which attribute to the crystalline segments of PBA in soft domain. Upon heating to 80°C , the diffraction of crystal disappears and only the amorphous diffraction is observed, corresponding to the

completed melting of TPU 262A, which agrees with the DSC result. Moreover, the intensity of amorphous diffraction decreases with the increase of temperature to 110°C upon heating. It indicates the decrease in the aggregation interaction in the hard segments from temperature of 80 to 110°C. According to Figure C.7, the hard segments are formed by MDI and BOD, thus, we may conclude that the hydrogen bonding formed by N-H and C=O in urethane affects the aggregation interaction in the hard domain. These hydrogen bonding interactions is further investigated by Fourier Transform Infrared Spectroscopy (FTIR).

Figure C.8 XRD spectra of TPU 262A recorded at 25°C, 80°C and, 110°C upon heating.

FTIR spectra were recorded with a Bruker Vertex 70 spectrometer at some pre-determined temperatures controlled by a Harrick ATC-02402 temperature controller. Dried particles of TPU 262A was dissolved in acetone at a concentration of 2%(w/v), and then a thin film was prepared by casting the solution on a KBr plate at 60°C. This

film was held between two KBr plates in a heating cell and then heated from 30°C to 180°C. After reaching each desired temperature and isothermy for one minute, the sample was scanned sixty times at a resolution of 4 cm^{-1} .

Figure C.9 reveals the FTIR spectrum of TPU 262A recorded at room temperature. This spectrum is mainly featured by the N-H stretching vibrations at 3500-3200 cm^{-1} , the C-H stretching vibrations at 3100-2800 cm^{-1} , the C=O stretching at 1820-1640 cm^{-1} , the N-H in-plane bending at 1540 cm^{-1} , and the skeletal vibrations at 1450-1000 cm^{-1} , and 970-870 cm^{-1} .

Figure C.9 FTIR spectrum of TPU 262A recorded at room temperature. Insets show the N-H stretching (3500-3200 cm^{-1}) and the C=O stretching (1860-1620 cm^{-1}) regions.

As the focus of this study is on the hydrogen bonding interactions in the hard domain, two spectral regions are more of our interest: the N-H stretching vibrations at 3500-3200 cm^{-1} , and the C=O stretching vibrations at 1860-1620 cm^{-1} .

The N-H Stretching Region

The N-H stretching region of the FTIR spectra displayed on a transmittance scale and recorded upon heating is shown in Figure C.10. The infrared bands at 3446 and 3340 are assigned to the stretching modes of the “free” and hydrogen bonded N-H groups, respectively. The frequencies of these two bands are remarkably similar to those observed in polyurethanes with polyester as the soft segments. Dramatic change in band area as temperature increases is obvious. Over the temperature range from 30°C to 120°C, the peak position of the “free” N-H stretching band is almost constant at 3446 cm^{-1} , while the area of the “free” band gradually decreases as the temperature increases to above 80°C, while it is almost constant from 30°C to 60°C. This is similar to that reported for polyurethanes (Wang et al., 2009).

The peak position and area of the hydrogen bonded N-H stretching as temperature increases shares the same trend. The peak position remains as a constant upon heating from 30°C to 60°C, and then shifts from 3340 to 3362 cm^{-1} upon further heating from 80°C to 120°C, which indicates a decrease in the strength of the hydrogen bonds above 80°C. The area of hydrogen bonded N-H stretching stays high, and keeps almost

constant at below 60°C, while a steep decrease takes place upon heating to over 80°C, which indicates the hard domains gradually turn to amorphous.

Figure C.10 FTIR spectra of TPU 262A in the N-H stretching region recorded upon heating from 30°C to 120°C.

The C=O stretching Region

According to the structure analysis, the C=O stretching bands include two components, the ester C=O and the urethane C=O stretching. The latter is further composed of three sub-components corresponding to the “free”, disordered hydrogen bonded, and ordered hydrogen bonded C=O stretching, respectively. The “free” C=O groups are not bonded by hydrogen bonds, whereas the disordered and ordered hydrogen bonded ones are the hydrogen bonded groups associated with amorphous phase and crystalline phase, respectively.

Figure C.11 reveals the FTIR spectrum in the C=O stretching region of TPU 262A on a transmittance scale as temperature increases. Only a wide band is observed within 1820-1640 cm^{-1} , which may attribute to the overlap of the ester C=O stretching in the range of 1780-1740 cm^{-1} and the urethane C=O stretching from 1740-1660 cm^{-1} . However, the shift of the peak position and the change of peak shape are apparent. The band at 1720 cm^{-1} is caused by the “free” C=O groups, while the disordered hydrogen bonded C=O and the ordered hydrogen bonded C=O attribute to the bands at 1700 cm^{-1} and 1685 cm^{-1} , respectively. In Figure C.11, the bands at 1700 cm^{-1} and 1685 cm^{-1} can be clearly observed upon heating from 30°C to 60°C. These two bands gradually vanish upon further heating from 80°C to 120°C, which implies the degradation in the intensity of hydrogen bonded C=O.

Figure C.11 FTIR spectra of TPU 262A in the C=O stretching region recorded as a function of temperature upon heating from 30°C to 120°C.

From the variation of N-H stretching and urethane C=O stretching upon heating, it can be concluded that the hydrogen bonding interactions in the hard domain remain constant at below 60°C, and then gradually decrease as the temperature increases to over 80°C. In such a way, the hard domain is able to help the recovery of the permanent shape, if programming is carried out at below 60°C, while it gradually loses its function when the programming temperature is increased from 80°C to 120°C, which essentially contributes to such a vitrimer-like phenomenon in this shape memory material.

A schematic illustration of the phase transition process of TPU 262A during heating is proposed in Figure C.12. As it shows, the soft and hard segment are initially in crystalline and glassy states, respectively. Upon heating to 60°C, the soft segment melts to help to fix the temporary shape during programming, while the hard segment remains glassy to store the elastic energy for shape recovery. However, upon heating to between 80°C and 110°C, the hard segment is in the transition process from elastic to viscous. Under such a situation, the hard segment starts to lose its elasticity and thus degradation in shape recovery performance occurs. If the temperature rises to even higher (e.g. 120°C), the hard segment is dominated by viscosity, which results in almost complete vanishing of the SME.

Figure C.12 Schematic illustration of the phase transition process in TPU 262A upon heating.

Similar to temperature increase, acetone can also affect the hydrogen bonding interactions. The interactions between acetone molecules and TPU destroy the hydrogen bonding between C=O in urethane and N-H groups, resulting in the incapability of aggregation of hard segments, thus dissolving takes place. Once acetone is evaporated, the C=O in urethane and N-H reconnect to restore hydrogen bonding, which is able to aggregate the hard segments together again to enable the shape memory function.

The DMA result shown in Figure C.1(b) is replotted in Figure C.13 to reveal the strain vs. temperature relationship. Four insets are included as the zoom-in views of temperature ranges from 44°C to 46°C, from 89°C to 91°C, from 99°C to 101°C, and from 107°C to 109°C, respectively.

Figure C.13 The relationship between strain and temperature according to the DMA tests shown in Figure C.1(b).

Clearly, the material is nearly elastic within 44°C to 46°C with the strain ranging from 7.054% to 7.064% upon cyclic stretching. Although its elasticity is well maintained after melting, the range of strain variation gradually increases upon heating to higher temperatures due to the softening of material as the insets between 89°C to 91°C and 99°C to 101°C reveal. At last, the material loses its elasticity as it shows almost no elastic recovery upon cyclic loading and thus, the strain keeps increasing to about 150% as the inset from 107°C to 109°C shows.

C.5 Conclusion remarks

In this appendix, a vitrimer-like TPU is investigated for its SME. Dynamic mechanical analysis is utilized to carry out most of the experiments on the samples with and without

acetone treatment. It can be concluded that the SME of this TPU starts to degrade when the temperature is over around 80°C. Any deformation at around 105°C results in almost 100% permanent plastic deformation. Additionally, the pre-heated samples start to regain the SME upon cooling to lower temperatures. The micro-structure of this TPU is identified as PBA segments form the soft domain, while MDI and BDO segments are the hard segments.

List of publications

1. Wang, T. X., Renata, C., Chen, H. M., & Huang, W. M. (2017). *Elastic Shape Memory Hybrids Programmable at Around Body-Temperature for Comfort Fitting*. *Polymers*, 9(12), 674.
2. Wang, T. X., Huang, W. M., Zhao, Y., Ding, Z., & Li, Y. (2017). *Shape Memory Phenomenon In Metallic Materials*. *International Journal of Recent Development in Civil & Environmental Engineering*, 3(2), 28-32.
3. Wang, T. X., & Huang, W. M. (2017). *Shape Memory Alloys for Monitoring Minor Over-Heating/Cooling Based on the Temperature Memory Effect via Differential Scanning Calorimetry: A Review of Recent Progress*. *Shape Memory and Superelasticity*, 3(4), 414-421.
4. Wang, T. X., Huang, W. M., Aw, J. E., He, L. W., & Vettorello, M. (2016). *Comfort fitting using shape memory polymeric foam*. *Journal of Testing and Evaluation*, 45(4), 1201-1212.
5. Wang, T. X., Huang, W. M., Chen, H. M., Xiao, R., Lu, H. B., & Kang, S. F. (2016). *Temperature Memory Effect and Its Stability Revealed via Differential Scanning Calorimetry in Ethylene-Vinyl Acetate Within Glass Transition Range*. *Journal of Polymer Science Part B: Polymer Physics*, 54(17), 1731-1737.
6. Wu, X. L., Wang, T. X., Huang, W. M., & Zhao, Y. (2017). *Thermo-Responsive Shape-Memory Effect and Surface Features in Polycarbonate (PC)*. *Applied Sciences*, 7(8), 848.
7. Sun, L., Huang, W. M., Wang, T. X., Chen, H. M., Renata, C., He, L. W., & Wang, C. C. (2017). *An overview of elastic polymeric shape memory materials for comfort fitting*. *Materials & Design*, 136, 238-248.
8. Sun, L., Wang, T. X., Leow, W. C., Huang, W. M., Cui, H., & Gao, X. Y. (2016). *Temperature memory effect in differential scanning calorimeter test in thermoplastic polyurethane*. *Journal of Polymer Research* 23(3): 1-8.
9. Tang, C., Wang, T. X., Huang, W. M., Sun, L., & Gao, X. Y. (2016). *Temperature sensors based on the temperature memory effect in shape memory alloys to check minor over-heating*. *Sensors and Actuators A: Physical* 238(2), 337-343.
10. Sun, L., Wang, T. X., Leow, W. C., Huang, W. M., Cui, H., & Gao, X. Y. (2016). *Temperature memory effect in differential scanning calorimeter test in thermoplastic polyurethane*. *Journal of Polymer Research*, 23(3), 63.
11. Sun, L., Huang, W. M., Lu, H., Lim, K. J., Zhou, Y., Wang, T. X., & Gao, X. Y. (2014). *Heating - Responsive Shape - Memory Effect in Thermoplastic Polyurethanes with Low Melt - Flow Index*. *Macromolecular Chemistry and Physics* 215.24 (2014): 2430-2436.
12. Wang, T. X., Aw J. E., Weng, Y. W., & Huang, W. M. (2016). *Advanced Shape Memory Technology for Product Design, Manufacturing and Recycling*. *Materials China*, 2016, 35(8): 613-621.

13. Sun, L., Wang, T. X., Huang, W. M., *Monitoring minor over-heating/cooling temperature based on the temperature memory effect in shape memory materials via differential scanning calorimetry: A brief review of the recent progress*, Journal of Thermal Analysis and Calorimetry, 133, 2018, 1649-1661.
14. Sun, L., Wang, T. X., Zakee, Mhibm., Rosli, Msb., Yun, X. L., Huang, W. M., *Self-surface wrinkling atop acrylonitrile butadiene styrene (ABS) via heating-responsive shape memory effect*, Surface Review and Letters, Accepted.
15. Huang, W. M., Wang, T. X. (2016) *Personalised footwear and the manufacture thereof*. PCT No.: SG 10201502071W.