

**THE EFFECT OF MOISTURE ABSORPTION ON THE PHYSICAL
PROPERTIES OF POLYURETHANE SHAPE MEMORY POLYMER FOAMS**

A Thesis

by

YA-JEN YU

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2011

Major Subject: Biomedical Engineering

**THE EFFECT OF MOISTURE ABSORPTION ON THE PHYSICAL
PROPERTIES OF POLYURETHANE SHAPE MEMORY POLYMER FOAMS**

A Thesis

by

YA-JEN YU

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Approved by:

| | |
|---------------------|------------------------------|
| Chair of Committee, | Duncan J. Maitland |
| Committee Members, | Elizabeth Cosgriff-Hernández |
| | Melissa A. Grunlan |
| Head of Department, | Gerard L. Côté |

May 2011

Major Subject: Biomedical Engineering

ABSTRACT

The Effect of Moisture Absorption on the Physical Properties of Polyurethane Shape
Memory Polymer Foams.

(May 2011)

Ya-Jen Yu, B.S., Feng Chia University; M.S., National Taiwan University

Chair of Advisory Committee: Dr. Duncan J. Maitland

The effect of moisture absorption on the glass transition temperature (T_g) and stress/strain behavior of network polyurethane shape memory polymer (SMP) foams has been investigated. With our ultimate goal of engineering polyurethane SMP foams for use in blood contacting environments, we have investigated the effects of moisture exposure on the physical properties of polyurethane foams. To our best knowledge, this study is the first to investigate the effects of moisture absorption at varying humidity levels (non-immersion and immersion) on the physical properties of polyurethane SMP foams. The SMP foams were exposed to differing humidity levels for varying lengths of time, and they exhibited a maximum water uptake of 8.0% (by mass) after exposure to 100% relative humidity for 96 h. Differential scanning calorimetry results demonstrated that water absorption significantly decreased the T_g of the foam, with a maximum water uptake shifting the T_g from 67 °C to 5 °C. Samples that were immersed in water for 96 h and immediately subjected to tensile testing exhibited 100% increases in failure strains and 500% decreases in failure stresses; however, in all cases of time and humidity

exposure, the plasticization effect was reversible upon placing moisture-saturated samples in 40% humidity environments for 24 h.

ACKNOWLEDGEMENTS

I am extremely grateful to my advisor, Professor Duncan J. Maitland, for his vital encouragement and guidance throughout my graduate studies and research. His patience and enthusiasm in research had motivated me. In addition, he was always accessible and willing to help me with my research.

In addition to my advisor, I would like to thank the rest of my committee members, Professors Elizabeth Cosgriff-Hernández and Melissa A. Grunlan, for their time in reviewing this thesis and for their thoughtful advice and feedback.

I also thank my fellow labmates, Keith Hearon, Jennifer Rodriguez, Brent Volk and Amanda Connor, for my research. They also inspire me in research through our interactions and discussions in the lab.

Last but not the least, my deepest gratitude goes to my fiancée, Chia-Lan Liu, and my family; most especially, my fiancée who spiritually supported me throughout my pursuit of a higher education.

TABLE OF CONTENTS

| | Page |
|--|------|
| ABSTRACT | iii |
| ACKNOWLEDGEMENTS | v |
| TABLE OF CONTENTS | vi |
| LIST OF FIGURES | vii |
| LIST OF TABLES | ix |
| 1. INTRODUCTION | 1 |
| 2. EXPERIMENTAL | 6 |
| 2.1 Polyurethane foam synthesis and sample preparation | 6 |
| 2.2 Characterization | 7 |
| 2.2.1 Moisture uptake | 7 |
| 2.2.2 Glass transition temperature shift | 7 |
| 2.2.3 Infrared band shift | 8 |
| 2.2.4 Stress/strain behavior | 8 |
| 2.2.5 Shape memory effect | 9 |
| 3. RESULTS AND DISCUSSION | 10 |
| 3.1 Moisture uptake | 10 |
| 3.2 Glass transition temperature shift | 12 |
| 3.3 Infrared band shift | 15 |
| 3.4 Stress/strain behavior | 21 |
| 3.5 Shape memory effect | 23 |
| 4. CONCLUSIONS | 25 |
| REFERENCES | 26 |
| VITA | 29 |

LIST OF FIGURES

| | Page | |
|-----------|--|----|
| Figure 1 | Schematic representation of the molecular mechanism of the thermally induced shape-memory effect for (a) a multiblock copolymer with $T_{\text{trans}}=T_m$; (b) a covalently cross-linked polymer with $T_{\text{trans}}=T_m$; (c) a polymer network with $T_{\text{trans}}=T_g$. If the increase in temperature is higher than T_{trans} of the switching segments, these segments are flexible (shown in red) and the polymer can be deformed elastically. The temporary shape is fixed by cooling down below T_{trans} (shown in blue). If the polymer is heated up again, the permanent shape is recovered (The figure is modified from Lendlein A and Kelch S [4] to draw)..... | 2 |
| Figure 2 | The effect of humidity exposure time up moisture absorption, measured by TGA. | 11 |
| Figure 3 | The effect of humidity exposure time on moisture absorption, measured by mass ratio analysis. | 11 |
| Figure 4 | The effect of moisture absorption of T_g | 13 |
| Figure 5 | Change in T_g in a moisture absorption for up to 96 h, placing samples into environment chamber with 40% humidity at 25 °C for 1 day, 2 days, 5days. | 14 |
| Figure 6 | The relationship of T_g versus weight ratio of water. | 14 |
| Figure 7 | FTIR spectra of N-H stretching region of polyurethane foam with differing water uptake levels for up to 96 h. | 17 |
| Figure 8 | FTIR spectra of C=O stretching region of polyurethane foam with differing water uptake levels for up to 96 h. | 18 |
| Figure 9 | Effects of water on the hydrogen bonding in polyurethane polymer (The figure is modified from Yang B et al. [8] to draw). | 18 |
| Figure 10 | FTIR spectra of N-H stretching region of polyurethane foam with differing water uptake levels for up to 96 h, placing samples into environment chamber with 40% humidity at 25 °C for 1 day. | 19 |
| Figure 11 | FTIR spectra of C=O stretching region of polyurethane foam with differing water uptake levels for up to 96 h, placing samples into environment chamber with 40% humidity at 25 °C for 1 day. | 20 |

| | Page |
|--|------|
| Figure 12 Recovery upon heating (Sample with condition of 100% humidity at 25 °C)..... | 23 |
| Figure 13 Recovery upon heating (Sample with condition of 100% humidity at 37 °C)..... | 24 |

LIST OF TABLES

| | Page |
|--|------|
| Table 1 (a) Original N-H stretch, (b) Dry polyurethane SMP foams, (c) Polyurethane SMP foams exposed to moisture. | 19 |
| Table 2 Mechanical property of polyurethane foams with different humidities absorption..... | 22 |

1. INTRODUCTION

Shape memory polymers (SMPs) are smart materials that can store a metastable geometry or geometries and then actuate to a primary geometry after introduction to a stimulus such as heat or moisture. Because of this capability, SMPs have attracted increasing attention from the scientific community and are being proposed for numerous applications in diverse arenas, ranging from the aerospace to biomedical industries [1]. SMP foams are of particular interest because they exhibit large volume expansions upon actuation [2]. Raytheon is currently investigating SMP foams for implementation in aerospace applications, and an SMP foam-based biomedical implant device for treating aneurisms is currently being developed [3]. Neat SMPs and SMP foams can be manufactured to respond to specific stimuli such as heat [4], light [5], electric fields [6], magnetic fields [7], and moisture [8]. Currently, thermo-responsive SMPs have received the most attention for implementation in device-based applications [9].

Traditional thermo-responsive, two-shape SMPs are heated above a transition temperature, T_{trans} , deformed, and subsequently cooled below T_{trans} to fix a secondary geometry. The secondary geometry is maintained because thermodynamic barriers prevent the polymer chains from relaxing and returning to their original state of higher entropy, which the chains automatically assumed during initial polymerization or processing. T_{trans} can be a glass transition temperature (T_g), a crystalline melt temperature (T_m), or another transition temperature [4]. After heating above T_{trans} , a deformed SMP

This thesis follows the style of *Smart Materials and Structures*.

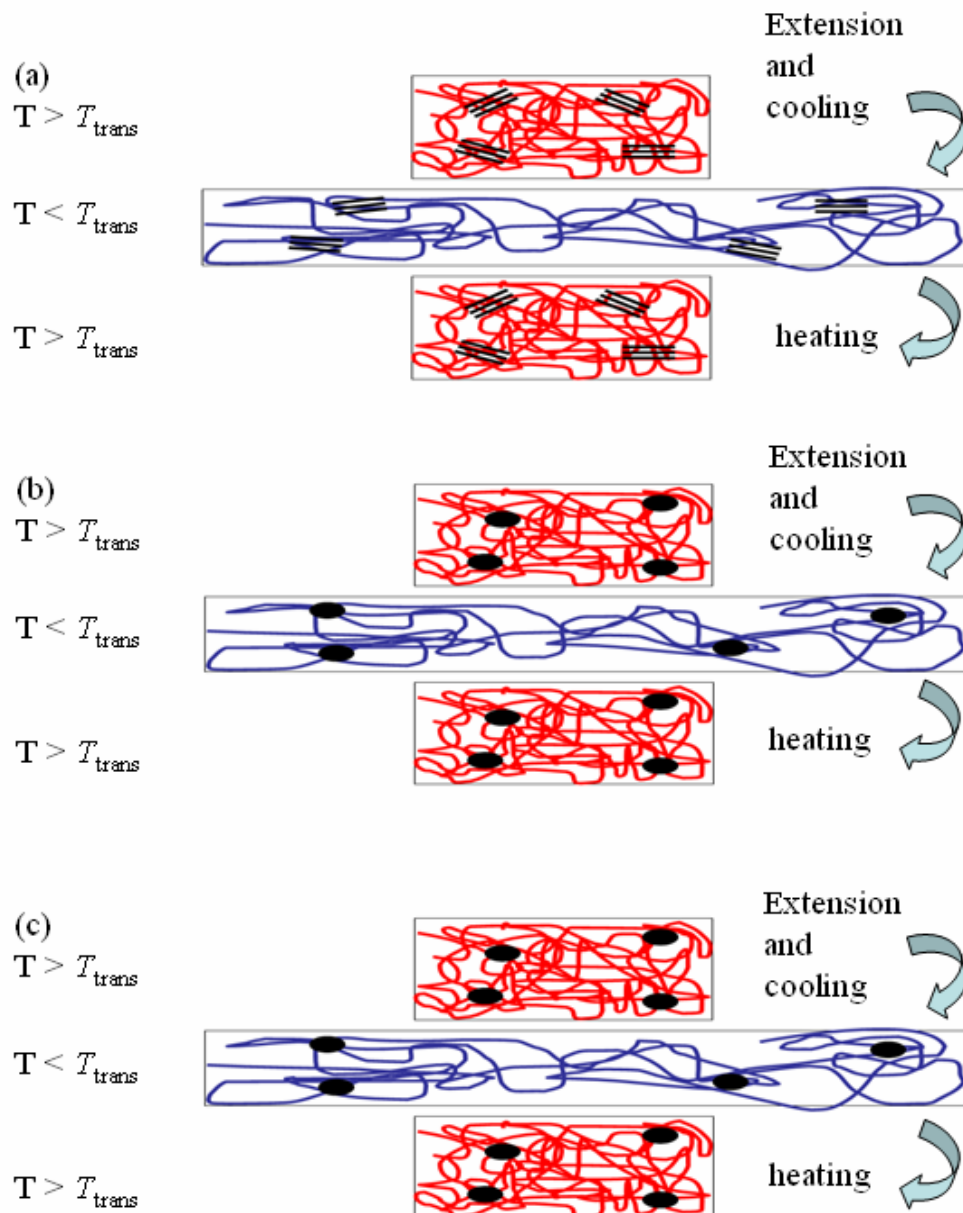


Figure 1 Schematic representation of the molecular mechanism of the thermally induced shape-memory effect for (a) a multiblock copolymer with $T_{\text{trans}} = T_m$; (b) a covalently cross-linked polymer with $T_{\text{trans}} = T_m$; (c) a polymer network with $T_{\text{trans}} = T_g$. If the increase in temperature is higher than T_{trans} of the switching segments, these segments are flexible (shown in red) and the polymer can be deformed elastically. The temporary shape is fixed by cooling down below T_{trans} (shown in blue). If the polymer is heated up again, the permanent shape is recovered [4] (The figure is modified from Lendlein A and Kelch S [4] to draw).

returns to its high-entropy state, which is the original geometry. At the molecular level, netpoints such as covalent crosslinks, crystalline phases, and chain entanglements enhance the SMP systems by keeping polymer chains from sliding past one another while the polymer is heated above T_{trans} in Figure 1 [10].

Previous studies on polyurethane SMPs have focused on synthesis [11-12], structural modeling [13], thermo-mechanical characterization [14], and moisture effects [15]. Yang investigated the effects of moisture absorption on shifting the glass transition temperature to lower values and the corresponding stress-strain behavior of neat polyurethane SMPs. Yang's studies revealed that absorbed water in polyurethanes falls into two categories: bound water and free water. Bound water, which acts as a plasticizer by occupying hydrogen bonding sites between interchain carbamate N-H and C=O groups, significantly lowers T_g and therefore significantly alters stress-strain behavior. Free water, on the other hand, has much less of a plasticizing effect for polyurethanes. In the full FTIR spectrum of polyurethane SMPs, the infrared band of the hydrogen-bonded C=O stretching shifts slightly to a lower frequency after immersion because of firm hydrogen bonding. In contrast, the infrared band of hydrogen-bonded N-H stretching shifts to a higher frequency with the increase in immersion time because of loosely bound water having weaker hydrogen bonding. Xu et al. focused on the moisture effect to decrease the T_g and hardness of attapulgite clay reinforced polyurethane shape memory nanocomposites [16]. With moisture effect on nanocomposites, the results show that heating treatments for nano-powders result in moisture loss. Also, the decrease in the number of surface hydroxyl groups generates a crystallized and bundled structure. The decrease in the

moisture content of SMPs reinforced with attapulgite clay is improved by increasing the interfacial bonding between polymer and filler.

The above discussion indicates that hydrogen bonding has a significant influence on the T_g and mechanical properties of PU SMPs before and after water absorption. Hydrogen bonding has effects on polar groups, such as those contained in dry nylon 6,6. Dry nylon 6,6 ($T_g = 50\text{ }^\circ\text{C}$) has a higher glass transition than dry polycaprolactone ($T_g = -60\text{ }^\circ\text{C}$) because of its ability to form hydrogen bonds between the carbonyl oxygen and the amide hydrogen atoms within the polymer chain. These hydrogen bonding forces can decrease the chain mobility to result in a higher transition point. Also, in nylon 6,6, the planar amide (-CO-NH-) groups are very polar, so nylon forms multiple hydrogen bonds among adjacent strands to have higher crystallinity.

Although Yang's studies and those of others have effectively characterized the effects of moisture absorption on the thermal and thermo-mechanical properties of urethane SMPs [16-17], these studies have been limited to neat polyurethane SMPs. Research related to the effect of moisture exposure on polyurethane foams has examined moisture diffusion rate and mechanical property changes [18-19]; however, the effect of moisture uptake on the shape memory behavior of polyurethane foams has yet to be evaluated.

In this study, we evaluated the effect of moisture absorption on the T_g and stress/strain behavior of polyurethane SMP foams made from a urethane SMP composition described in Wilson 2007 [4]. The composition of SMP foams was synthesized by hexamethylene diisocyanate (HDI), N,N,N',N'-tetrakis(2-hydroxypropyl) ethylenediamine (HPED), and triethanolamine (TEA). Moisture uptake at different temperatures and humidity levels were measured using thermogravimetric analysis (TGA) and mass ratio analysis. Fourier

transform infrared (FTIR) was used to analyze the interactions of the absorbed water with the N-H groups and C=O groups of the urethane foams. Some water molecules absorbed in the polyurethane SMP foams bridge the gaps between the hydrogen bonded N-H and C=O groups to cause the IR absorbance shift. Moisture-induced T_g effects were measured using differential scanning calorimetry (DSC). T_g shift effects decide whether the polymer can maintain the deformed shape in the “package” and “in vivo” conditions or not. The effect of water uptake on the stress/strain and shape memory behavior of the foams was evaluated by strain to failure and free strain recovery experiments.

2. EXPERIMENTAL

2.1 Polyurethane foam synthesis and sample preparation

Polyurethane SMP foams were prepared based on a technique developed by Dr. Thomas S. Wilson at Lawrence Livermore National Laboratory. Prepolymers were made from hexamethylene diisocyanate (HDI, 98%, TCI America), N,N,N',N'-tetrakis(2-hydroxypropyl) ethylenediamine (HPED, 98%, TCI America), and triethanolamine (TEA, 99%, Sigma-Aldrich). Foams were formulated from the prepolymers by adding the following surfactants, catalysts, and blowing agents in a Flackteck 150 DAC speed mixer for 15 s at 3400 rpm: DC-5179 (Air Products), DC-I990 (Air Products), T131 (Air Products), BL-22 (Air Products), DI water and Enovate (Honeywell Corp.) For foaming, an overall NCO/OH ratio of 1.05 was used.

After sample preparation, the polyurethane foams were dried at 90 °C for 12 h at 1 torr to remove residual moisture. The samples were then placed in a CSZ MCBH-1.2-.33-.33-H/AC environmental chamber at a controlled temperature of 25 °C, with controlled humidities of 40 %, 60 %, and 80% (simulating the general environment condition for “package”) for time periods of 0.5 h, 1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 12 h, 24 h, 48h, and 96 h. For sample preparation at 100% humidity, the samples were immersed into a water bath at control temperatures of 25 °C or 37 °C (simulating the “in vivo” condition) for time periods of 12 h, 24 h, 48 h, and 96 h.

2.2 Characterization

2.2.1 Moisture uptake

TGA analysis was used to measure the water uptake of samples exposed to various humidities for time periods of 12 h, 24 h, 48 h, and 96 h. TGA was run on 10-15 mg samples in a TA Instruments Q80 thermogravimetric analyzer. TGA samples, tested in triplicate, were heated from 30 °C to 400 °C at 10 °C/min. In order to accurately evaluate the time it took the foams to reach moisture saturation at each humidity level, a second set of foam samples was subjected to mass ratio analysis. Five specimens of each sample were massed, exposed to the different humidity levels for 0.5 h, 1 h, 2 h, 3 h, 4 h, 5 h, and 6 h, and re-massed immediately after removal from the environmental chamber.

2.2.2 Glass transition temperature shift

DSC experiments were run using a TA Instruments Q200 differential scanning calorimeter from -40 °C to 80 °C at 10 °C/min on 5-10 mg samples to evaluate the effect of moisture absorption on T_g . To determine whether the T_g shift was reversible, samples that had been exposed to various humidity levels for 96 h were put back in the environmental chamber at 40% humidity for 1 day, 2 days, and 5 days, after which DSC experiments were run with the same experimental procedures described above.

2.2.3 Infrared band shift

The interactions between absorbed water molecules and hydrogen-bonded N-H and C=O groups were analyzed using a Bruker Tensor 27 FTIR spectrometer. A control foam sample that had not been exposed to moisture was run in addition to the humidified samples. FTIR spectra were collected by averaging 150 scans with a resolution of 4 cm^{-1} and a wavenumber range of 600 cm^{-1} to 4000 cm^{-1} . To determine whether the shifts in the IR spectra were reversible, samples that had been exposed to various humidity levels for 96 h were put back in the environmental chamber at 40% humidity for 1 day, 2 days, and 5 days, after which FTIR experiments were run with the same experimental procedures described above.

2.2.4 Stress/strain behavior

Strain to failure experiments were carried out on $60 \times 15 \times 6$ mm polyurethane foam samples using an MTS Insight 30 Universal Tensile Tester. In accordance with ASTM D638 Standard Test Method for the Tensile Properties of Plastics, samples were mounted in epoxy blocks and exposed to different humidity levels for 96 h. These samples were then immediately subjected to strain to failure experiments at a constant strain rate of 50 mm/min at $25\text{ }^{\circ}\text{C}$. To determine whether the moisture-induced changes in stress-strain behavior were reversible, samples that had been exposed to various humidity levels for 96 h were put back in the environmental chamber at 40% humidity for 1 day, after which

strain to failure experiments were run with the same experimental procedures described above.

2.2.5 Shape memory effect

Free strain recovery experiments were carried out on 60 x 15 x 6 mm polyurethane foam samples in an MTS Insight 30 Universal Tensile Tester with a thermal chamber. In accordance with ASTM D3574-08 Standard Test Method for Polyurethane Foams, samples were mounted on epoxy blocks and exposed to 100% humidity for 96 h (one sample at 25 °C, and another at 37 °C). The samples were then gripped in the tensile tester, heated to 80 °C at 1 °C/min, and strained to 15%, 25%, and 35%. The strained samples were then cooled to 25 °C at 1 °C/min to fix the respective strains. Then, for free strain recovery, the bottoms of the samples were unclamped inside the thermal chamber, and the samples were heated to 80 °C at 1 °C/min to determine recoverable strain, which was measured by a laser extensometer. Percent recoverable strain, or recovery ratio, is calculated according to Equation (1),

$$\text{Recovery Ratio} = \text{Recovered length} / \text{Initial length} * 100 \quad (1)$$

3. RESULTS AND DISCUSSION

3.1 Moisture uptake

Results for percent moisture uptake as measured by TGA and mass ratio analysis are provided in Figures 2 and 3, respectively. For 40%, 60%, and 80% relative humidities, moisture absorption increased with humidity exposure time until 6 h, after which it generally remained constant. For the samples exposed to 100% humidity (i.e., immersion in water), reaching maximum water uptake took longer. As Figure 2 demonstrates, the maximum water uptake after 96 h at 25 °C in the 100% relative humidity environment was 8%, and this value did not change significantly when the temperature in the environmental chamber was increased to 37 °C. However, increased temperature did increase the moisture absorption rate [20]. The 37 °C sample reached maximum water uptake at 20 h, while the 25 °C sample did not reach maximum water uptake until 96 h. As expected, moisture absorption and moisture saturation levels were dependent on moisture exposure time, humidity level, and temperature. Our results prove that moisture saturation is dependent on the ambient humidity level that at higher humidity levels, more water uptake is possible [21].

Figures 2 and 3 show the moisture absorption with water immersion is different from non-immersion water absorption. Even though the environmental chamber provides 100% humidity, the 100% humidity absorption is not equivalent to water immersion. Our finding agrees with Loos et al., who showed that different environmental exposure affects the water absorption behavior [22].

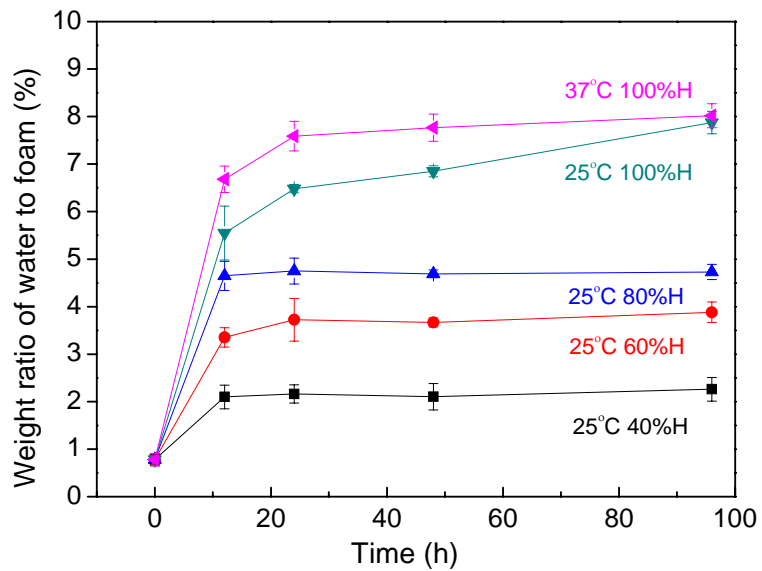


Figure 2 The effect of humidity exposure time up moisture absorption, measured by TGA.

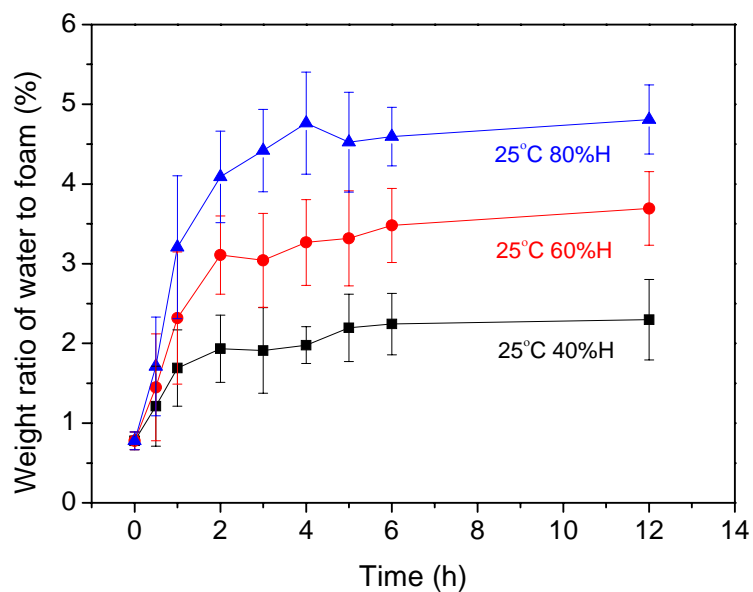


Figure 3 The effect of humidity exposure time on moisture absorption, measured by mass ratio analysis.

3.2. Glass transition temperature shift

The glass transition temperatures of all samples decreased upon moisture absorption, as shown in Figure 4. After 12 h, the T_g 's of the foams generally reached a plateau. A maximum shift in T_g occurred for the 100% humidity foams (both 25 °C and 37 °C), where the T_g dropped from 67 °C to 5 °C after 96 h. The moisture effects on T_g were reversible, as shown in Figure 5. Samples that were exposed to humidity for 96 h and then placed in the environmental chamber at 40% humidity exhibited significant moisture loss after 1 day. The absorbed moisture for all samples was approximately the same after one day (2.2%). This value of 2.2% corresponds to the initial absorbed moisture value for the foam exposed to 40% relative humidity that is plotted in Figure 2. This moisture loss was accompanied by an increase in T_g : after being placed in the environmental chamber at 40% humidity for one day, the T_g 's of all samples increased to roughly the same value: 42 °C, the T_g value for the initial foam exposed to 40% humidity that is plotted in Figure 5.

The PU foams characterized in this work are homogeneous, amorphous foams that exhibit a single T_g , 67 °C, which decreases as water is absorbed by the foam. The Gordon-Taylor equation predicts the effect of absorbed water on the glass transition temperature of polymers,

$$T_g = \frac{W_1 T_{g1} + k(1 - W_1) T_{g2}}{W_1 + k(1 - W_1)} \quad (2)$$

where W_1 is the weight fraction of water, T_{g1} is the T_g of water, and T_{g2} is T_g of the polymer. The constant k is equal to $\Delta C_{p2} / \Delta C_{p1}$, which are the respective heat capacities for the materials in the equation with T_{g1} and T_{g2} . Equation 2 predicts that absorbed

moisture, W_1 , will lower T_g . The increase in W_1 value accompanies an increase in k . Lim 1999 reported the equation describing the law of regular solution in the binary system and may not be appropriate for specific interaction between the polymers and water. However it is still widely accepted to describe the absorbed water dropped the T_g largely [23]. In the Figure 6, our system indicates that T_g decreases with the increase of the weight of water to foams but not in a linear manner. Also, we fit the experimental data to find the function between T_g and weight ratio of water to foam to express the following equation:

$$T_g = 86.112 * \exp(-(\text{weight ratio of water to foam})/5.868) - 17.529 \quad (3)$$

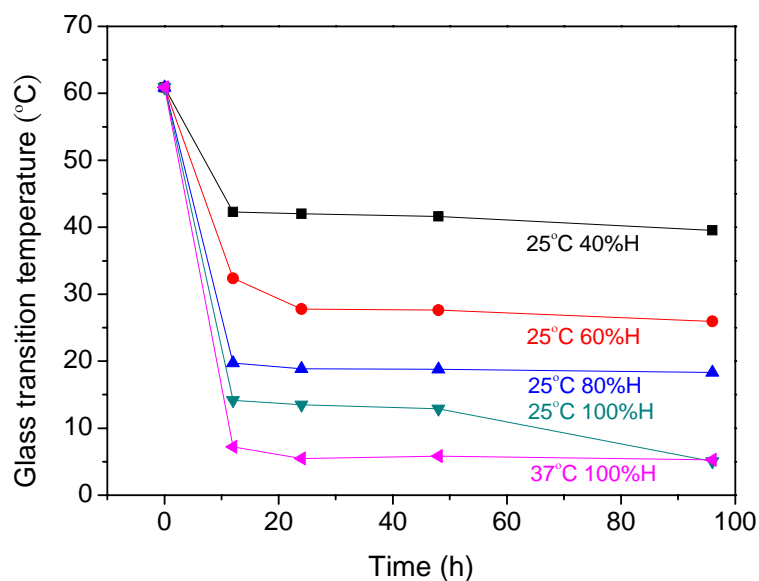


Figure 4 The effect of moisture absorption of T_g .

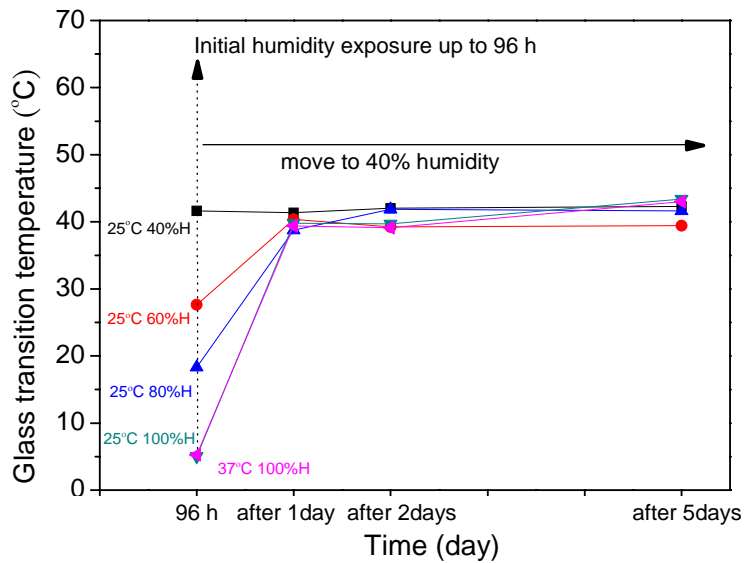


Figure 5 Change in T_g in a moisture absorption for up to 96 h, placing samples into environment chamber with 40% humidity at 25 °C for 1 day, 2 days, 5 days.

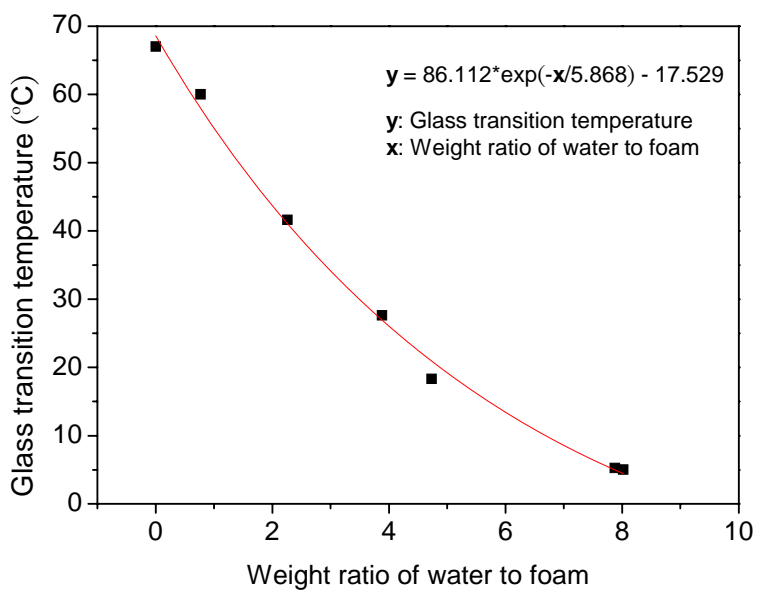


Figure 6 The relationship of T_g versus weight ratio of water.

3.3. Infrared band shift

The control foam sample that was not exposed to humidity exhibited a bond N-H stretch intensity peak at 3307 cm^{-1} . As Figure 7 indicates, the bond N-H stretch intensity peaks were shifted both to higher wavenumbers and higher intensities with increasing moisture absorption, with the 100% humidity samples exhibiting N-H stretch intensity peaks at approximately 3332 cm^{-1} . Figure 8 shows the effect of absorbed moisture on the carbamate and urea C=O stretch intensity peaks, occurring at 1687 cm^{-1} and 1647 cm^{-1} , respectively. Although increased water content resulted in increased intensities for the respective C=O peaks, observable shifts in wavenumber did not occur.

In a moisture-free polyurethane foam, hydrogen bonding occurs between carbamate N-H and C=O groups. After moisture absorption, the hydrogens in water molecules can either form hydrogen bonding bridges between two carbamate C=O groups or occupy the hydrogen bonding sites at carbamate N-H groups that can be explained by the schematic model in Figure 9 [23]. Hydrogen bonds formed with the N-H groups cause the N-H infrared bands to increase in intensity and shift to higher wavenumbers because loosely bound water weakens the hydrogen bonding (shown in Table 1). Such behavior is apparent in the IR spectra in Figure 7 for our polyurethane SMP foams. In contrast, the hydrogen bonds formed with the C=O groups cause the C=O infrared bands to increase in intensity and shift to lower wavenumbers [24]. Although our foams exhibited increased carbamate C=O peak intensities with increasing moisture absorption, no discernable shift in wavenumber was apparent.

One possible explanation for this behavior is that the chemical structure of the polyurethane foams characterized in this work is significantly different from that of other

urethanes: there are no traditional hard and soft segments. Also, our foaming process includes the addition of water, which results in an increased urea content and even more hydrogen bonding interactions. The foams are entirely comprised of 6-carbon-long diisocyanates and low-molecular weight tri-and-tetrafunctional alcohols, so the ratio of carbamate and urea linkages to the total number of molecules in the polymer is much higher than that of an SMP with an oligomeric soft segment. Since each carbamate linkage has two hydrogen bonding sites (C=O and N-H; three in the case of urea linkages), our foams have significantly more hydrogen bonding sites than a polyurethane with, for example, a polyethylene oxide or polybutadiene soft segment. The urethane and urea in this study could have so great a number of bound carbonyls before moisture absorption that, even after maximum moisture absorption, there could still be no discernable shift in wavenumber. This theory could also explain why there are no apparent free carbonyl peaks in our IR spectrum. Since bound carbonyl peaks are significantly broader than free carbonyl peaks, it is possible that the broadness and intensity of the bound carbonyl peaks makes it impossible to observe the free carbonyl peaks [25-26].

We found the moisture-induced shifts of the N-H peaks in the IR spectra peak to be reversible. Yang, et al. demonstrated such reversibility by driving off absorbed moisture by heating polyurethane samples [8]. We demonstrated a similar effect by placing moisture-saturated samples in a lower humidity environment (40% humidity). The N-H peaks shift back to 3307 cm^{-1} in the Figure 10, and the C=O peaks shift back to lower intensities after exposure to 40% humidity at $25\text{ }^{\circ}\text{C}$ in the Figure 11. Although moisture appears to evaporate from our foams with relative ease (Yang, et al. heated neat

polyurethane at different temperatures to drive off moisture), this observation does not necessarily indicate that there are weaker hydrogen bonding interactions in our urethane than in other urethanes. Urethane foams have significantly more surface area than neat urethane films, so the significant moisture evaporation from the foams could simply be a result of increased surface area.

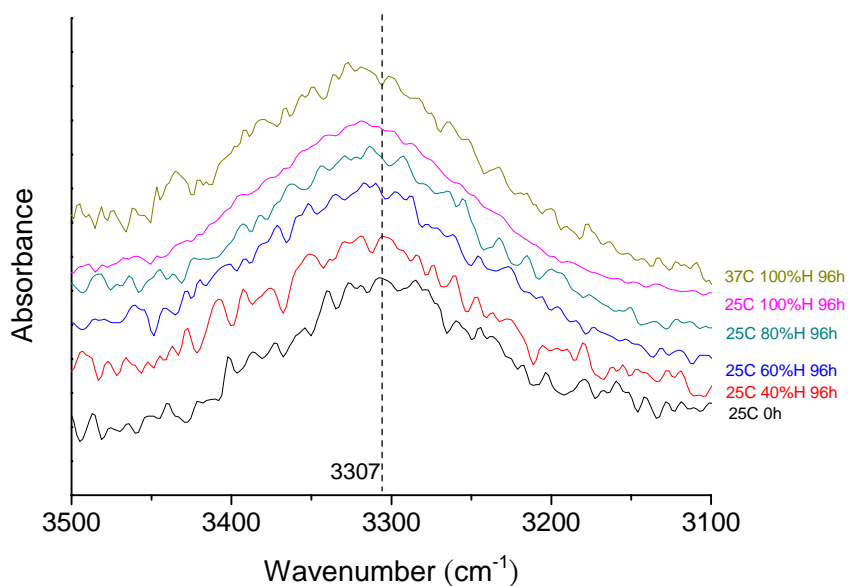
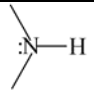
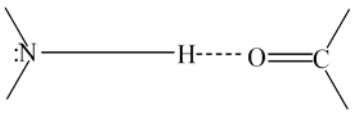
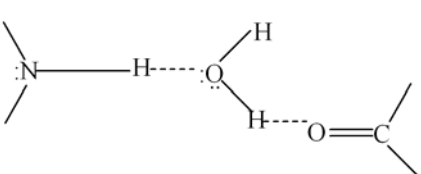


Figure 7 FTIR spectra of N-H stretching region of polyurethane foam with differing water uptake levels for up to 96 h.

Table 1 (a) Original N-H stretch, (b) Dry polyurethane SMP foams, (c) Polyurethane SMP foams exposed to moisture.

| | |
|---|---|
| (a)  | N-H stretch has strong bond |
| (b)  | Hydrogen bonding weakens N-H stretch, lowers its force constant, the bond N-H stretch intensity peaks shift to lower frequency |
| (c)  | Loosely bound water molecule weakens hydrogen bond, it results in the bond N-H stretch intensity peaks shift back to higher frequency |

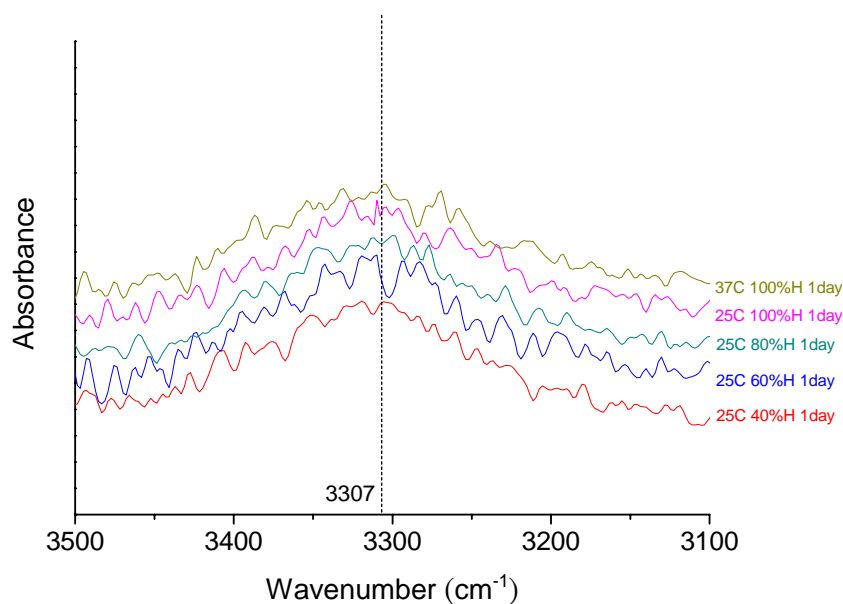


Figure 10 FTIR spectra of N-H stretching region of polyurethane foam with differing water uptake levels for up to 96 h, placing samples into environment chamber with 40% humidity at 25 °C for 1 day.

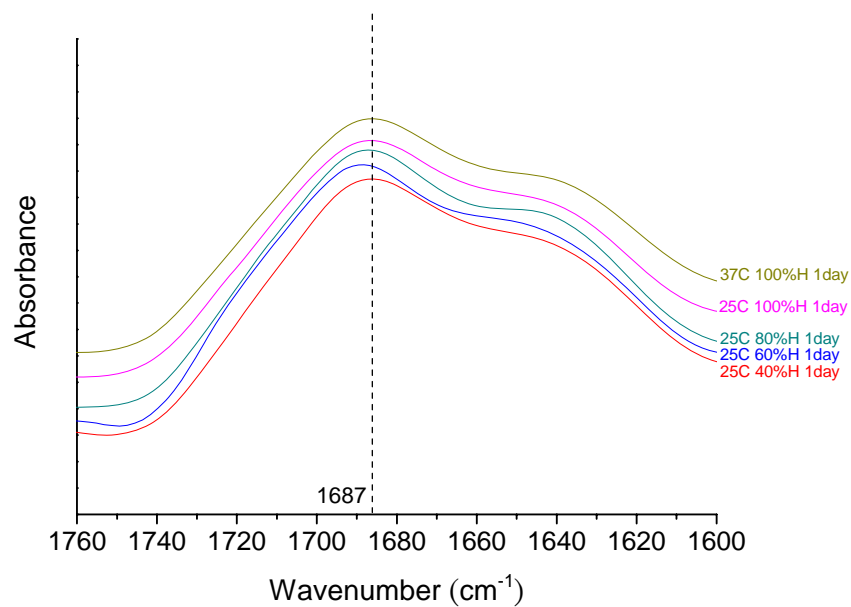


Figure 11 FTIR spectra of C=O stretching region of polyurethane foam with differing water uptake levels for up to 96 h, placing samples into environment chamber with 40% humidity at 25 °C for 1 day.

3.4. Stress/strain behavior

Tensile testing data for all samples is provided in Table 2. Strain to failure results demonstrated that absorbed moisture significantly plasticized the urethane foams [27], although this plasticization effect proved to be reversible. Upon exposing the foam to humidity, the water molecules can act as a plasticizer that not only decreases the T_g , but also increase the breaking strain. The increase in water content corresponding with the decrease in stress and the increase in strain may result from the hydrogen bonding between polymer chains. As previous mentioned the water molecules can separate into two parts: one is free water that can freely transfer from holes to polymer chains, and the other one is bound water that can interact with functional groups of material. Extensive moisture absorption leads to the increase in bound water to interact with functional groups of PU foams. Water molecules, penetrating the inner structure of PU foams, act as a plasticizer to generate hydrogen bonding between N-H and C=O groups to permit polymer chains of molecules to move freely. In our research, the samples that were exposed to various humidities and then placed in the room temperature for 1 day exhibited failure strains on the order of 20% and failure stresses on the order of 50 kPa. The samples were exposed to 100% humidity, and then immediately tested within 1 h exhibited failure strains on the order of 30-40% and failure stresses on the order of 15 kPa. Similar trends occurred for Young's modulus values. The observed plasticization effect was in accordance with the results of Yang's studies on the effects of moisture on the stress/strain behavior of neat polyurethanes.

Table 2 Mechanical property of polyurethane foams with different humidities absorption.

| | Breaking strain (%) | Breaking tensile strength (kPa) | Young modulus (kPa) |
|---------------------------|---------------------|---------------------------------|---------------------|
| 25C-40%H-96h-after 1 day | 21 ± 7 | 52 ± 11 | 281 ± 117 |
| 25C-60%H-96h-after 1 day | 18 ± 5 | 50 ± 12 | 282 ± 56 |
| 25C-80%H-96h-after 1 day | 18 ± 6 | 43 ± 13 | 275 ± 143 |
| 25C-100%H-96h-after 1 day | 23 ± 5 | 55 ± 13 | 247 ± 77 |
| 37C-100%H-96h-after 1 day | 21 ± 6 | 43 ± 11 | 226 ± 108 |
| 25C-100%H-96h-immediately | 31 ± 1 | 17 ± 1 | 52 ± 2 |
| 37C-100%H-96h-immediately | 41 ± 12 | 14 ± 5 | 35 ± 13 |

(Average ± Standard deviation; n=10)

3.5 Shape memory effect

Free strain recovery results for samples exposed to 100% humidity at 25 °C and 37 °C for 96 h are provided in Figures 12 and 13. For 15% and 25% strains, the observed recovery ratio was approximately 95%. For 35% strains, the recovery ratio decreased to 87%. Since the polyurethane foams characterized in this work were highly crosslinked, even strains as low as 35% could result in localized permanent deformations and destruction of foam cells [28].

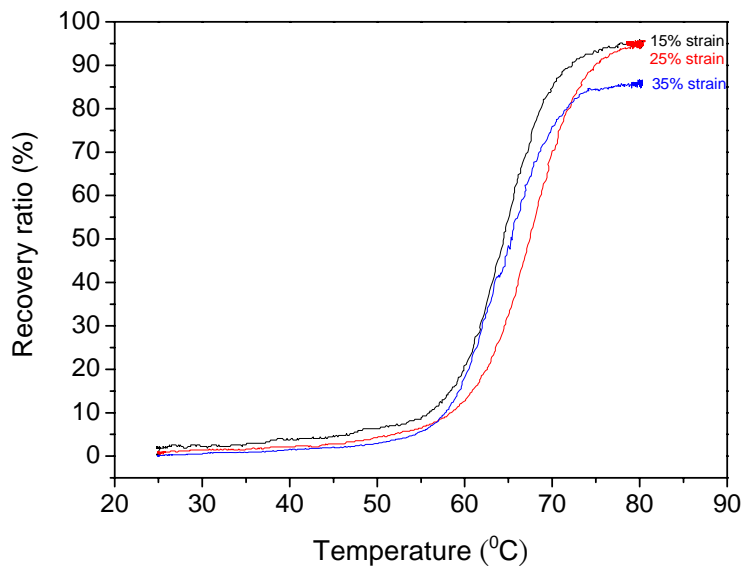


Figure 12 Recovery upon heating (Sample with condition of 100% humidity at 25 °C).

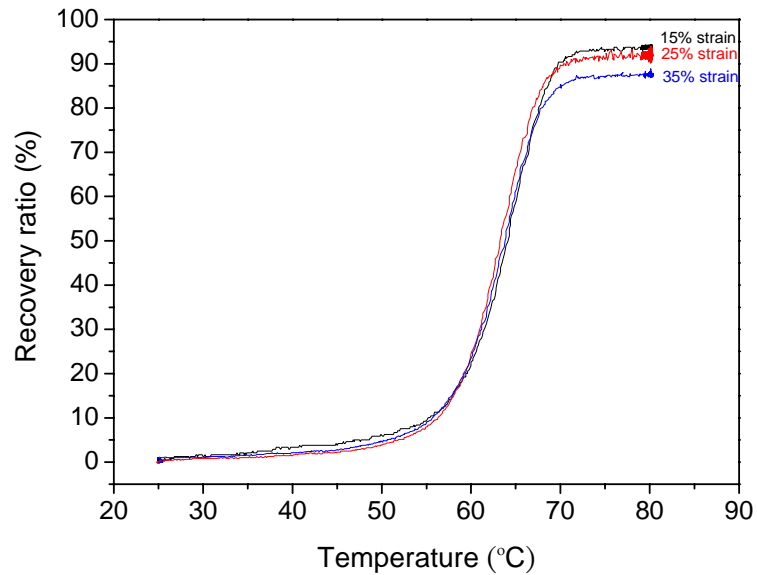


Figure 13 Recovery upon heating (Sample with condition of 100% humidity at 37 °C).

4. CONCLUSIONS

The water uptake of the polyurethane SMP foams characterized in this work increased with increased humidity exposure time, increased humidity, and increased temperature. The maximum water uptake was 8%, which occurred after exposure to 100% humidity for 96 h at room temperature and for 20 h at 37 °C. At humidities less than or equal to 80%, moisture saturation occurred after 6 h.

The T_g of the polyurethane foams decreased upon moisture absorption, and a maximum shift from 67 °C to 5 °C occurred after 8% water uptake. This T_g shift affected a transformation from glassy to viscoelastic behavior when the SMP foams were subjected to tensile testing at 25 °C. Both the T_g shifts and the resulting mechanical behavior transformations were reversible upon placing the foams in a 40% humidity environment for 24 h.

Recovery ratios approaching 100% for samples strained to 25% or less demonstrate that the SMP foams characterized in this work are potentially useful for applications where complete tensile strain recovery is necessary.

REFERENCES

- [1]Behl M and Lendlein A 2007 Shape-memory polymers *Mater. Today* **10** 20-28.
- [2]Huang W M, Lee C W and Teo H P 2006 Thermomechanical behavior of a polyurethane shape memory polymer foam *J. Intell. Mater. Syst. Struct.* **17** 753-60.
- [3]Maitland D J, Small W, Ortega J M, Buckley P R, Rodriguez J, Hartman J and Wilson T S 2007 Prototype laser-activated shape memory polymer foam device for embolic treatment of aneurysms *J. Biomed. Opt.* **12** 030504.
- [4]Lendlein A and Kelch S 2002 Shape-memory polymers *Angew. Chem. Int. Ed.* **41** 2034-57.
- [5]Lendlein A, Jiang H, Junger O and Langer R 2005 Light-induced shape-memory polymers *Nature* **434** 879-82.
- [6]Sahoo N G, Jung Y C, Goo N S and Cho J W 2005 Conducting shape memory polyurethane-polypyrrole composites for an electroactive actuator *Macromol. Mater. Eng.* **290** 1049-55.
- [7]Buckley P R, Mckinley G H, Wilson T S, Small W, Benett W J, Bearinger J P, Mcelfresh M W and Maitland D J 2006 Inductively heated shape memory polymer for the magnetic actuation of medical devices *IEEE Trans. Biomed. Eng.* **53** 2075-83.
- [8]Yang B, Huang W M, Li C and Li L 2006 Effects of moisture on the thermomechanical properties of a polyurethane shape memory polymer *Polymer* **47** 1348-56.
- [9]Small W, Singhal P, Wilson T S and Maitland D J 2010 Biomedical applications of thermally activated shape memory polymers *J. Mater. Chem.* **20** 3356-66.

- [10]Behl M, Razzaq M Y and Lendlein A 2010 Multifunctional shape-memory polymers *Adv. Mater.* **22** 3388-410.
- [11]Wilson T S, Bearinger J P, Herberg J L, Marion J E, Wright W J, Evans C L and Maitland D J 2007 Shape memory polymers based on uniform aliphatic urethane networks *J. Appl. Polym. Sci.* **106** 540-51.
- [12]Hearon K, Gall K, Ware T, Maitland D J, Bearinger J P and Wilson T S 2010 Post-polymerization crosslinked polyurethane shape-memory polymers *J. App. Poly. Sci.* **in press**.
- [13]Volk B L, Lagoudas D C and Chen Y-C 2010 Analysis of the finite deformation response of shape memory polymers: II. 1D calibration and numerical implementation of a finite deformation, thermoelastic model *Smart Mater. Struct.* **19** 075006.
- [14]Tobushi H, Hara H, Yamada E and Hayashi S 1996 Thermomechanical properties in a thin film of shape memory polymer of polyurethane series *Smart Mater. Struct.* **5** 483-91.
- [15]Yang B, Huang W M, Li C, Lee C M and Li L 2004 On the effects of moisture in a polyurethane shape memory polymer *Smart Mater. Struct.* **13** 191-5.
- [16]Xu B, Huang W M, Pei Y T, Chen Z G, Kraft A, Reuben R, De Hosson J T M and Fu Y Q 2009 Mechanical properties of attapulgite clay reinforced polyurethane shape-memory nanocomposites *Eur. Polym. J.* **45** 1904-11.
- [17]Pretsch T, Jakob I and Müller W 2009 Hydrolytic degradation and functional stability of a segmented shape memory poly(ester urethane) *Polym. Degrad. Stab.* **94** 61-73.
- [18]Oertel G 1985 *Polyurethane Handbook* (New York: Hanser).
- [19]Zhao D, Little J C and Cox S S 2004 Characterizing polyurethane foam as a sink for or Source of volatile organic compounds in indoor air *J. Environ. Eng.* **130** 983-89.

- [20] Bassirirad H, Radin J W and Matsuda K 1991 Temperature-dependent water and ion transport properties of barley and sorghum roots : I. relationship to leaf growth plant *Physiol.* **97** 426-32.
- [21] Avilés F and Aguilar-Montero M 2010 Moisture absorption in foam-cored composite sandwich structures *Polym. Compos.* **31** 714-22.
- [22] Alfred C. Loos, George S. Springer, Barbara A. Sanders and Tung R W 1980 Moisture absorption of polyester-E glass composites *J. Compos. Mater.* **14** 142-54.
- [23] Lim L T, Britt I J and Tung M A 1999 Sorption and transport of water vapor in nylon 6,6 film *J. Appl. Polym. Sci.* **71** 197-206.
- [24] Yen F-S, Lin L-L and Hong J-L 1999 Hydrogen-bond interactions between urethane–urethane and urethane–ester linkages in a liquid crystalline poly(ester–urethane) *Macromolecules* **32** 3068-79.
- [25] Mattia J and Painter P 2007 A Comparison of hydrogen bonding and order in a polyurethane and poly(urethane–urea) and their blends with poly(ethylene glycol) *Macromolecules* **40** 1546-54.
- [26] Yilgör E, Burgaz E, Yurtsever E and Yilgör I 2000 Comparison of hydrogen bonding in polydimethylsiloxane and polyether based urethane and urea copolymers *Polymer* **41** 849-57.
- [27] Dhakal H N, Zhang Z Y and Richardson M O W 2007 Effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester composites *Compos. Sci. Technol.* **67** 1674-83.
- [28] Volk B L, Lagoudas D C, Chen Y-C and Whitley K S 2010 Analysis of the finite deformation response of shape memory polymers: I. Thermomechanical characterization *Smart Mater. Struct.* **19** 075005.

VITA

Name: Ya-Jen Yu

Address: Biomedical Engineering
c/o Dr. Duncan J Maitland
Texas A&M University, College Station, TX 77843-3120

Email: yu1122@gmail.com

Education: M.S., Biomedical Engineering, Texas A&M University, USA, 2011

M.S., Material Science and Engineering, National Taiwan University,
Taiwan, 2003 - Process of biomimetic ceramic (Hydroxyapatite)

B.S., Material Science and Engineering, Feng Chia University, Taiwan,
2001- The corrosion behavior of Fe-based shape memory alloy

Working Experience:

Industrial Technology of Research Institute (ITRI) Associate Researcher

Mar. 2007-Mar. 2008 *Medical Electronics and Device Technology Center, ITRI
Oct. 2003-Mar. 2007 *Biomedical Engineering Research Laboratories, ITRI

Achievements:

July 2007-Mar. 2008 *Biogluce for bone tissue repair **Project leader**
(Cooperate with Chang Gung Memorial Hospital)

Jan. 2007-Mar. 2008 *Spinal non-fusion stabilization system **Sub-project leader**
(Cooperate with Chang Gung Memorial Hospital)

Oct. 2005-Oct. 2006 *Marketing analysis and patent portfolio of bone products-
annular repair, nucleus replacement, spine non fusion
stabilization system, lumbar cage, tissue anchor

July 2005-Dec. 2006 *Novel spinal cage development
(Cooperate with Taipei City Hospital)

July 2005-Dec. 2006 *Development of novel shoulder anchor
(Cooperate with National Taiwan University Hospital)

June 2005-Dec.2005 *Biphasic osteochondral repair for articular cartilage regeneration
(Cooperate with National Taiwan University Hospital)

June 2005-July 2005 *Tissue pulverizer

July 2004-Feb. 2005 *The development of the stealthy nano-micelle technology

Oct. 2003-Jun. 2004 *Ion-exchange polymer-metal composite