Soft Reversible Actuator based on Shape Memory Polymer

Che Tan

Syracuse University

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Abstract

My research employs two shape memory polymer based approaches to develop thermally-triggered soft reversible actuators. Our approaches throughout this thesis aim at developing soft actuators with both simple and complex geometries that have the spatial control over actuation shapes, which makes them desirable for a broad range of applications.

In this thesis, we employed a porous poly (ε-caprolactone) (PCL) shape memory polymer foam infiltrated with PDMS elastomeric matrix to fabricate the actuators. Thermal/mechanical characterizations were used to demonstrate good thermal properties and thermomechanical behavior of materials and composites. Scanning electron microscopy was conducted to illustrate the morphology of the composite actuators and PCL foam. Thermomechanical experiments and self-actuation tests were performed to demonstrate the good reversible actuation of the composite actuators.
Soft Reversible Actuators based on Shape Memory Polymer

By

Che Tan

(Master of Science)

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Chapter 1: Introduction

1.1 Motivation: Soft Reversible Actuator

Soft reversible actuation is an emerging research area that attracts a lot of attention currently. Comparing to the conventional rigid actuators, soft actuators feature inherent compliance, high flexibility, light weight and low production cost which makes them ideal for several applications. Due to the cyclic strain they can provide, soft actuators can be used as substrate for dynamic cell culture\(^4\). Due to their high compliance and flexibility, soft actuators can be used as material for soft robotics\(^{21,23}\). Soft actuators have also attracted a lot of attention in the biomedical device industry, for instance, artificial muscle fabrication\(^1,20\). So far, there are mainly two approaches to develop soft reversible actuators: molecular approach and laminate approach.

1.1.1 Molecular Approach

Several researchers have been developing self-reversible actuator via molecular approach. In this approach, polymer with a broach range of melting temperature is utilized. Zhou et al introduced a strategy for reversible actuation which can be applied to traditional semi-crystalline elastomers. Its shape reversibility is realized by partial melting of crystallites, leaving a latent template behind, that in turn, inverts recovery of the original shape on cooling\(^27\). Behl et al developed a temperature-memory polymer actuator based on a semi-crystalline
polymer network which provides a broad $T_m$ range. Its reversible actuation is achieved by combining a re-shapeable actuation skeleton at an upper $T_m$ range with a temperature-controlled crystallization-induced elongation and melting-induced contraction at a lower $T_m$ range\textsuperscript{2}.

1.1.2 Laminate Approach

Researchers also introduced laminate approach for self-reversible actuators fabrication. Chen and co-workers developed bilayer composite composed of a pre-programed shape memory polyurethane (SMPU) and an un-stretched polyurethane substrate. Reversible bending is achieved through the release of elastic strain of pre-programed SMPU upon heating and the recovery of elastic strain of polyurethane substrate upon cooling\textsuperscript{5}. Westbrook et al developed a reversible shape memory composite where a pre-stretched one way shape memory polymer is embedded in an elastomeric matrix. This composite demonstrates reversible bending actuation upon heating/cooling cycles\textsuperscript{10}. The mechanism of this approach is that the actuator usually has two layers: one rubber biasing layer and one stretched semi-crystalline two-way shape memory polymer layer. Upon heating, the stretched polymer intends to recover to its original shape, thus put the actuator in bending configuration and put stress in rubber layer. Upon cooling, the stored stress in rubber layer will push the actuator to return to its flat configuration. The limitation of this approach is that actuators can only achieve bending actuation.
1.2 Shape Memory Polymer

Shape memory polymers (SMPs) are a class of stimuli-responsive materials that can undergo programmed changes in shape and mechanical properties upon application of an external stimulus such as heat, light, electrical current, magnetic field, pH, or solvent. The most common triggering mechanism for SMPs remains direct heating. A typical one-way shape memory cycle consists of four steps: (1) deforming the SMP at an elevated temperature above its thermal transition temperature; (2) cooling the SMP below its thermal transition temperature while maintaining the deformation to fix the programmed deformation; (3) unloading to observe shape fixing; (4) heating above the thermal transition temperature to trigger recovery. As such, one-way SMPs are capable of undergoing a single programmed shape change between one temporary shape and the programmed shape as shown in Scheme 1. One-way shape memory polymers are mostly wide studied shape memory polymer and are applicable in a broad range of fields. For instance, they can be used as self-healing materials where they demonstrate the crack closure and healing effect. They can also be used for many space applications (e.g. deployable structure for space applications). Medical application is the field where one-way shape memory polymers are most widely used. For instance, several commercialized minimally invasive surgery solutions are based on shape memory polymers (e.g. thrombus removal device). However, one-way shape memory polymers fail to realize reversible actuation, thus, they cannot be used for reversible shape change based applications.
1.2.1 Two Way Shape Memory Polymer

A recent advance in SMP research has led to the development of two-way shape memory polymers, or polymers that can change shape reversibly\textsuperscript{6, 10}. This effect has been most commonly exploited using liquid-crystal elastomers\textsuperscript{3}, which have been developed with fast thermal- and photo-actuation\textsuperscript{11, 25}. Liquid-crystal elastomers have also been reported to exhibit large reversible actuation strains exceeding 300\%\textsuperscript{24}. A cheaper, alternative class of reversible actuators was recently developed, where semi-crystalline SMPs were observed to undergo a phenomenon termed “stretch-induced crystallization”\textsuperscript{6, 10}. Cross-linked SMPs exhibit tensile elongation upon cooling and undergo tensile contraction upon heating in the extent of a constant external stress as shown in Scheme 2. However, for broader applications, it is desirable to achieve the reversible actuation without external stress applied. In order to address the issue, self-reversible actuators have been investigated.

1.3 Scope of Thesis

The aim of this thesis is to employ different approaches based on shape memory polymer to develop thermally-triggered soft reversible actuators. It is important to note that our approaches throughout this thesis were to develop soft actuators with both simple and complex geometries that have the spatial control over actuation shapes, which makes them desirable for a broad range of applications.
1.3.1 Shape Memory Foam-based Reversible Actuator

Firstly, development and characterization of foam-based reversible actuators was studied. In Chapter 2, a foam-based composite approach which combines a shape memory polymer and elastomeric matrix to fabricate a group of foam-based actuators that are capable of achieving both linear and bending actuation upon application of a simple thermal trigger. This approach is demonstrated in a composite system consisting of a porous poly (ε-caprolactone) (PCL) shape memory polymer foam infiltrated with PDMS elastomeric matrix. Self-reversible actuation is achieved through a combination of shape memory recovery of the PCL foam upon heating and stretch-induced crystallization of the PCL foam upon cooling, where the PDMS matrix applies the required internal biasing stress for stretch-induced crystallization. Composite structure, thermal properties, and thermomechanical behavior were evaluated. Scanning electron microscopy was conducted to study the morphology of the SMP foam and reversible actuator. Thermomechanical experiments and self-actuation tests were done to demonstrate reversible actuation of samples upon heating/cooling cycles and to prove that these actuators could achieve the spatial control of desired shapes.

1.3.2 Shape Memory Film-Based Reversible Actuator

In Chapter 3, a film-based bilayer approach was introduced to fabricate soft reversible actuators. PCL film is a two-way shape memory polymeric material that has strain-induced crystallization results in significant elongation upon cooling and subsequent network melting upon heating which results in contraction under a constant external stress. In order to achieve
two-way shape memory effect without the application of an external force. We combined PCL films with elastomeric matrix to prepare the laminate actuator using a bilayer preparation approach. Instead of achieving only bending actuation like other laminated actuators do, the actuators fabricated though our approach can realize complex actuation. We also collaborated with Dr. Qi’s research group in Georgia Tech to develop models that can simulate and predict the reversible actuation of our actuators.

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1.5 Schemes, Figures and Tables

Scheme 1: Schematic of one-way shape memory. a) The SMP is heated above a transition temperature and is deformed upon heating. b) The deformed SMP is “fixed” by cooling below the transition temperature upon an application of external force. c) The permanent shape is recovered by heating the unloaded SMP above its transition temperature.
Scheme 2: Schematic of two way shape memory polymer. a) The SMP is heated above a transition temperature and is deformed upon an application of an external force. b) The SMP is cooled to exhibit tensile elongation via “stretch-induced crystallization” of SMP under an external force. c) The SMP is heated to initiate a tensile contraction in the extent of a constant external stress.
Chapter 2. Shape Memory Foam-based Reversible Actuator

2.1 Synopsis

Shape memory foam is a porous material that can be fabricated via modified porogen-leaching technique. Like other one-way shape memory materials, shape memory foam has the ability to remember the permanent shape after being fixed at a temporary shape. Furthermore, it features the advantages of inherent compliance, high flexibility and light weight. However, its application so far has been limited to one-way shape memory effect based applications, which is not ideal for a broader range of applications (e.g. reversible shape change based application). To address this issue, we introduce a novel approach which combines a porous poly (ε-caprolactone) (PCL) shape memory polymer foam infiltrated with PDMS elastomeric matrix, where PCL foam provides the shape memory recovery behavior and PDMS matrix applies the required internal biasing stress for stretch-induced crystallization. It is found that the reversible actuator fabricated via this approach could achieve good reversible actuation and achieve the spatial control of desired actuation shapes. Also, the actuators demonstrate the high compliance and flexibility as well as functionality.

2.2 Introduction

Shape memory polymers (SMPs) are a class of stimuli-responsive materials that can undergo programmed changes in shape and mechanical properties upon application of an external stimulus. Among all the external stimuli, heat remains the most
common triggering mechanism for SMPs. A typical one-way shape memory material can be fixed at a temporary shape, but recover to its permanent shape upon application of an external stimulus. One-way shape memory materials have varied forms such as electrospun fiber mat, film, and foam. Among them, shape memory polymer foams have attracted a lot of attention, for they feature high porosity, high compliance and high shape change flexibility. Baker et al. developed a highly porous SMP foam which is able to change shape upon body temperature triggering to address the requirement of 3D scaffold for tissue engineering. Torbati et al. introduced a SMP composite foam capable of triple shape memory behavior fabricated via a simple procedure. Maitland et al. developed laser-triggered deployed SMP foam for the treatment of aneurysms.

Though one-way shape memory polymers have a broad range of applications such as self-healing materials, space applications and medical devices, to achieve reversible shape change, an additional programming step is required for these polymers. Recent research in SMP has focus on the development of two-way shape memory polymers, a class of polymers that can change shape reversibly. For instance, semi-crystalline SMPs were observed to undergo a phenomenon termed “stretch-induced crystallization”, where they exhibit tensile elongation upon cooling and undergo tensile contraction upon heating in the extent of a constant external stress. However, an external stress is required in this case to achieve the two-way shape memory effect.
To address this inconvenience, reversible actuators have been developed. So far, the mainly employed two approaches to develop self-reversible actuators are molecular approach and laminate approach. However, several efforts have focused on developing reversible actuators via a composite approach. For instance, ionic polymer-metal composites (IPMC) combine ionic polymer with metal electrode, where the large ionic current give IPMC actuator a powerful actuation when applying a voltage \(^{16,17}\). IPMC actuators feature the advantages of low voltage drive, large bending actuation and softness.

In this chapter, we developed a composite approach of fabricating reversible actuators that is different from those approaches mentioned above. This approach employs a porous poly-(\(\varepsilon\)-caprolactone) (PCL) shape memory polymer foam infiltrated with PDMS elastomeric matrix, where the reversible actuation is achieved through a combination of shape memory recovery of the PCL foam upon heating and stretch-induced crystallization of the PCL foam triggered by internal biasing stress of PDMS matrix upon cooling. In what follows, composite structure, thermal properties, and thermomechanical behavior were evaluated. Scanning electron microscopy was conducted to study the morphology of the composite actuators and PCL foam. Thermomechanical experiments and self-actuation tests were performed to demonstrate the reversible actuation of the composite actuators.
2.3 Experimental

2.3.1 Materials

Poly(ε-caprolactone) diol (Mw=8,000 g/mol) was purchased from Abcr Inc. Benzene anhydrous (99.8%), acryloyl chloride (98%), triethylamine, hexane, tetrathiul, dichloromethane (DCM), 2,2-dimethoxy-2-phenylacetophenone photoinitiator (DMPA), dibutyltin dilaurate and NaCl salt were purchased from Sigma-Aldrich. All chemicals were used as received.

2.3.2 Functionalization of PCL diol (Mw=8,000 g/mol)

Functionalization of PCL diol was carried out by end-capping with acryloyl chloride, as previously reported by Rodriguez et al. Briefly, PCL diol (Mw=8,000 g/mol) was dissolved in benzene anhydrous under nitrogen purge. Trimethylamine and acryloyl chloride were added to the reaction flask at 2.5 times the moles of PCL diol. The reaction was carried out for 3 h, after which time NaCl salt by-product was removed by filtration and the functionalized PCL macromer was precipitated in excess hexanes. The final yield of PCL macromer was 94%.

2.3.3 Modified Porogen Leaching Technique

A modified porogen-leaching technique, similar to the process established by Baker et al. for PCL-co-PEG foam, was employed to make the PCL foam. 6.0 g of salt with 300-500
µm diameter was added to a 30mL glass vial. The glass vial was put in a Styrofoam box (9.25 x 6.25 x 8.25 in) which containing a beaker with 2L water at approximately 40 °C. The Styrofoam box was closed for 24 h, then the glass vial was took out of the box and placed at RT for 1 hour to dry. Following drying, a fused puck of salt remained, to which the polymer solution was added.

2.3.4 Fabrication of PCL Foam

To prepare highly porous PCL foams, we used end-linking of telechelic macromers with thiol-ene chemistry, combined with a modified porogen-leaching process. The fusion of salt particles, prior to PCL crosslinking reaction, was performed to improve pore interconnectivity. The functionalized PCL was dissolved in DCM together with tetrathiol cross-linker and DMPA photo initiator. This mixture was added to the fused salt template at the weight ratio of 1:9 (polymer: salt). Then, UV curing was performed to cross-link the functionalized PCL as shown in Schematic 4. After cross-linking, NaCl salt was extracted in the water, yielding highly porous PCL foams.

2.3.5 Fabrication of PCL-Gelest Composite

2.3.5.1 Linear Actuator

As shown in Scheme 3(A), foams were sliced into rectangular bars with a dimension of 17 mm x 4 mm x 2.5 mm (length x width x thickness). Each bar was uniaxially stretched to
50% strain at 80 °C in an isothermal oven, and then fixed in a 4 °C freezer for 5 min. PDMS matrix was prepared with a composition of base, crosslinker and dibulylin dilaurate at weight ratio of 100:1.8:3. The PDMS matrix was then vacuum infiltrated into the stretched foam bar and cured at 37 °C for 7 d.

2.3.5.2 Bending Actuator

As shown in Scheme 3(B), foams were sliced into rectangular bars and heated to 80 °C for 3 mins. Then, foam bars were stretched and curled around a 4 ml glass vial with a diameter of 15 mm. The curled geometry was fixed by placing the bars in cold water at 10 °C for 2 min. After vacuum drying overnight, the bending-shaped foam was vacuum infiltrated with the PDMS matrix using the same composition described above, and the composite was cured at 37 °C for 7 d.

2.3.5.3 S-shaped Actuator

To demonstrate that the foam-based actuators have the spatial control over the actuation shape. We developed an S-shaped actuator where we programmed the actuator with one end be bent in one direction and the other end be bent in the opposite direction. The foam was sliced into rectangular bars, heated to 80 °C for 3 mins. Then, it was initially fixed in a curled state on one end, in the meanwhile, fixed the other end in the opposite direction by wrapping around a glass vial with a diameter of 27 mm. After vacuum drying overnight, the S-shaped foam was
vacuum infiltrated with the PDMS matrix (composition weight ratio: base: crosslinker: Dibulylin is 100:1.8:3), and cured at 37 °C for 7 d.

2.3.5.4 Clip-shaped Actuator

To demonstrate the functionality of the self-reversible bending actuators, we fabricated a clip-shaped actuator and conducted the demonstration of self-actuation. Two bending actuators were used to fabricate the clip-shaped actuator. They were connected to each other on one end, two sticks were placed beside the connected area of these two bending actuators and tape was used to wrap around the sticks and connected area to stabilize the clip actuator.

2.3.6 Thermal Characterization

To determine the crystallization temperature, melting temperature and percent crystallinity of the PCL foam, differential scanning calorimetry (DSC) was performed. DSC experiments were conducted using a Q200 (TA instrument, inc.). 3-5 mg samples were put in pans and heated from -20°C to 80 °C at rate of 5 °C/min, and then cooled to -20 °C at a rate of 5 °C/min.

2.3.7 Scanning Electron Microscopy

To determine the microscopic architecture of the foam and composite, scanning electron microscopy (SEM) was performed on un-stretched PCL foams, stretched PCL foams
and PCL-PDMS composites. Samples were freeze-fractured and the top and cross-sectional views of each sample were examined.

2.3.8 Dynamic mechanical analysis

Thermomechanical properties of PCL foam, PDMS matrix and PCL-PDMS composite were characterized using a Q800 Dynamic Mechanical Analyzer (DMA) (TA Instrument Inc). Pure PCL foams and PCL-PDMS composites were cut into rectangular-shape bars with dimension of 17 mm x 4 mm x 2.5 mm (length x width x thickness) and PDMS matrix was cut into dogbone-shape before testing with a 6.25 mm gauge length, 1.5 mm gauge width and 1 mm thickness.

2.3.8.1 One-way shape memory test

To determine the shape fixing and shape recovery of the PCL foam, PCL-PDMS composite and PDMS matrix, one-way shape memory characterization was performed. Samples were heated to 80 °C at 3 °C/min and held isothermally for 2 min. Then uniaxially stretched to 20 % strain and cooled to -20 °C at 3 °C/min isothermal for 2 min to fix the temporary shape. Sample fixing was determined by unloading and shape recovery was determined by heating the sample back to 80 °C. This was repeated for 3 cycles.
2.3.8.2 Two-way shape memory test

To determine the two-way shape memory behavior of PCL foam, PCL-PDMS composites and PDMS matrix, two-way shape memory tests were performed. Samples were uniaxially stretched to 30%. The stress applied to deform the samples to 30% strain was maintained and samples were cooled to -20 °C and held isothermally for 3 min. Then, samples were heated again to 80 °C and then cooled to -20 °C to observe reversible actuation.

2.3.8.3 Self-actuation test

Self-actuation tests were performed on samples to determine whether they have reversible actuation upon heating and cooling cycles. No external stress was applied on the sample. Samples were heated from room temperature to 80 °C at 3 °C/min and then cooled to -20 °C at 3°C/min. Samples were subjected to 3 heating/cooling cycles.

2.3.9 Self-actuation demonstration

To further determine the reversible actuation of PCL-PDMS composites, we conducted self-actuation tests in hot/cold water. Hot water (70 °C) and cold water (10 °C) were prepared before testing. Completely cured PCL-PDMS composites were prepared for testing.

2.3.9.1 Bending Actuator

The actuator was put in the hot water to study its recovery upon heating and reverse
motion upon cooling. Photos and video were taken to record the self-reversible actuation procedure. Curvature of the actuators was measured at different time points (e.g. before heating, after heating, after cooling) during the tests. Circles are drawn to fit the bending configuration of actuators as shown in Scheme 3, radius of the cycle is measured based on a scale ruler. Curvature of each actuator is calculated via 1/ Radius of the circle. Also, the open/close gap of actuators at different time points during tests were measured as shown in Scheme 4.

2.4 Results and Discussion

2.4.1 Thermal Characterization

DSC experiments were conducted to study the thermal properties of the composites (both stretched and un-stretched composites), pure PCL foam and pure PDMS matrix. 1st cooling and 2nd heating thermal traces are shown in Figure 1. Heating and cooling rates were 10 °C/min for all samples. From the results, we notice that for PCL foam and PCL-PDMS composites, during the heating process, there are two melting points. But for PDMS matrix, there is only one melting point (Tm of PDMS is -4.05 °C). For PCL foam, the main Tm is around 45.3 °C. For PCL-PDMS composites, Tm is around 44.9 °C (for un-stretched composite) and 45 °C (for stretched composite). During the cooling process, the Tc for PCL foam is around 21.6 °C, and Tc for un-stretched composite and stretched composite is around 20.8 °C and 20.6 °C, respectively. The thermal properties are summarized in Table 1. The results show that after the foams were infiltrated with PDMS, Tm and Tc remain almost the same. We also calculated the crystallinity percentage of the foam, which is about 30%. PCL weight-% were also calculated, assuming 30% PCL foam crystallinity%, yielding 21% for un-stretched composite
and 43% for stretched composite. The difference of PCL wt % between un-stretched and stretched composite reveals that by stretching the foam, the pore space decreases, allowing us to infiltrate less PDMS matrix. Consequently, the PCL wt % increases. PCL wt % is important for us to optimize the actuation for the composite.

2.4.2 Morphology

Figures 2 and 3 shows the SEM micrograph of each sample from both top-view and cross-section view. Before stretching, the foam has open and interconnected pores, which allow us to infiltrate it with PDMS matrix. After stretching the foam, we noticed that although the pore space of the foam decreased, it still has open and interconnected pores. For the composite sample, from the top-view micrograph, we noticed that all the pores on the surface were filled up with PDMS. By looking at the cross-section micrograph of composite, we noticed the middle of the sample is also filled up with PDMS. Thus, we can conclude that the infiltration of PDMS into PCL foam is complete.

2.4.3 Dynamic Mechanical Analysis

2.4.3.1 One-way shape memory test

To understand the fixing and recovery behavior of PCL foam, PDMS matrix, and composite (un-stretched), one way shape memory DMA tests were performed. Result for pure PCL foam is shown in Figure 4(a), good fixing behavior and good recovery behavior were
observed. Figure 4(b) shows the result for PDMS matrix, which indicates there is no fixing and recovery behavior for PDMS matrix only. Figure 4(c) also shows the result for un-stretched composites, good fixing and recovery behavior are also observed, but not perfect.

2.4.3.2 Two-way shape memory test

To study the two-way shape memory behavior of samples, two way shape memory tests were conducted. From the Figure 4(a), we had noticed that there is strain-induced crystallization during cooling process for both PCL foam and un-stretched composite. This behavior indicated that these materials should possess two way shape memory effects. Therefore, two way shape memory DMA tests were conducted to study the two way shape memory behavior of these materials. Figure 5(a), (c) show typical two way shape memory traces for PCL foam and un-stretched composite respectively, which indicate these two have two way shape memory behavior. Figure 5(b) shows PDMS matrix itself has no two way shape memory behavior.

2.4.3.3 Self-actuation Test

Results for self-actuation tests are shown in Figure 6 and 7. Figure 6 are the test results for un-stretched foam, stretched foam and PDMS matrix. These results show that there is only thermal expansion and cooling shrinkage for these samples, no self-actuation exists. Figure 6 shows the test result for stretched composite, we noticed there is an initial contraction upon heating because of the stretched shape memory foam followed by a quick thermal expansion.
Then, there is cooling-induced elongation and heating induced shrinkage, which indicate this composite have self-reversible actuation of 5% strain.

2.4.4 Demonstration of self-actuation

2.4.4.1 Bending Actuator

Self-reversible actuation of a bending actuator was demonstrated in hot/cold water. The result is shown in Figure 8 and Supplemental Video 1. When heating in 70 °C hot water, we noticed the actuator gradually changed toward the flat configuration. And then, after putting the actuator in 15 °C cold water, it returned back to bending configuration. The result remains the same for multiple cycles.

2.4.4.2 S-shaped Actuator

Self-actuation of the S-shaped actuator was demonstrated in hot (70°C)/cold (15°C) water as shown in Supplemental Video 2. When immersed in hot water, the actuator gradually change shape toward flat configuration; when immersed in cold water, the actuator returned to the S configuration. The result remains the same for multiple cycles.

2.4.4.3 Clip-shaped Actuator

Self-actuation of clip-shaped actuator was demonstrated in hot (70°C)/cold (15°C) water, two metal rings were placed on the bottom of cold water. As shown in Supplemental
Video 3, when put the actuator in hot water, the “clip” was open up, when put in cold water, the “clip” gradually closed while pick up a ring in water. Then, after we put it back into the hot water, the “clip” opened again and dropped off the ring in the hot water. The result remains the same for multiple cycles.

2.5 Conclusions

In the study, we prepared self-biasing reversible actuator using a foam-based composite approach. PCL foam provides the strain-induced crystallization while PDMS matrix provides the self-biasing force. Using this approach, we’ve been able to achieve both linear and bending actuation. Thermal properties, morphology, mechanical properties of PCL foam, PDMS matrix and PCL-PDMS composite were characterized. The traditional linear reversible actuation and bending reversible actuation of PCL-PDMS actuators are presented in this work. In addition, actuators with more complex geometries, including clip-shape and claw-shape, were prepared to demonstrate special control of desired shapes. Ease of fabrication, good mechanical properties and good self-reversible actuation were observed to prove geometrically complex actuation events. Further study is required to improve the actuation strain and to develop actuators with more complex geometry.

Our foam based approach is crucial among other approaches for fabricating reversible actuators. Comparing to current approaches of fabricating self-reversible actuator (e.g. laminate approach and liquid crystalline approach), laminate approach can only achieve bending actuator and liquid crystalline approach can only achieve linear actuator. However,
our approach can achieve both linear and bending actuators instead of being restricted to only one configuration. Moreover, by arranging bending actuators in certain ways, we already achieved functional actuators like the clip-shaped one. In the future, we are going to try more complex configurations. These current achievements make our approach different than others, showing great potential of foam-based actuator to realize flexible special-controlled actuator. Moreover, the fabrication process is easy and the cost is low.

Soft actuation is an emerging research area that attracts a lot of attention now. Comparing to the conventional rigid actuators, soft actuators have new feature of softness, light and high flexibility, which has a wide range application in field of robotics and automation. In this work, we developed a kind of soft actuator which demonstrates good actuation during temperature change. Besides, our bending actuators can be configured to fabricate functional soft actuators (e.g. clip shaped actuator). The good actuation and spatial control of our soft actuators make them ideal for a great deal of applications.

2.6 References

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22. Tao Xie, and Ingrid A Rousseau, 'Facile Tailoring of Thermal Transition Temperatures of Epoxy Shape Memory Polymers', *Polymer*, 50 (2009), 1852-56.
2.8 Schemes, Figures and Tables

**Scheme 1.** Concept and brief fabrication process of a) linear b) bending composite actuators.
Scheme 2. Schematic for crosslinking of semi-crystalline PCL with shape memory capability via thiol-ene chemistry.
Scheme 3. Curvature measurement of actuator during actuation test

Curvature = 1/ Radius
Scheme 4. Gap measurement of actuators during actuation test
Figure 1. DSC thermograms (1st cooling and 2nd heating) of (a) PDMS matrix (1.9 wt% crosslinker), (b) PCL foam, (c) un-stretched PCL/PDMS composite, and (d) PCL/PDMS composite stretched 30%. Incorporation of PDMS does not affect the Tm or Tc of the PCL. Heating rates are 10 °C/min for heating and cooling.
### Table 1. Summary of the thermal properties determined by DSC experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{m,1}(^oC)$</th>
<th>$T_{m,2}(^oC)$</th>
<th>$\Delta H_m$(J/g)</th>
<th>$T_{c,1}(^oC)$</th>
<th>$T_{c,2}$ ($^oC$)</th>
<th>$\Delta H_c$(J/g)</th>
<th>Crystallinity (%)</th>
<th>PCL wt-%$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL Foam</td>
<td>45.3</td>
<td>50.5</td>
<td>41.6</td>
<td>21.6</td>
<td>21.6</td>
<td>42.0</td>
<td>30%</td>
<td>100</td>
</tr>
<tr>
<td>PDMS (1.9 wt% crosslinker)</td>
<td>-4.05</td>
<td>-</td>
<td>1.13</td>
<td>-23.0</td>
<td>-</td>
<td>1.34</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Unstretched PCL-PDMS Composite</td>
<td>44.9</td>
<td>50.7</td>
<td>8.76</td>
<td>20.8</td>
<td>20.8</td>
<td>10.3</td>
<td>21.0</td>
<td></td>
</tr>
<tr>
<td>30% stretched PCL-PDMS Composite</td>
<td>45.0</td>
<td>50.9</td>
<td>17.9</td>
<td>20.6</td>
<td>20.6</td>
<td>16.0</td>
<td>43.0</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Calculated assuming 30% PCL crystallinity $\Rightarrow$ PCL wt-% = $100*(\Delta H_m/41.6)$
Figure 2. SEM micrographs of (left) un-stretched PCL foam, (middle) PCL foam stretched 30%, and (right) PCL/PDMS composite stretched 30% reveal that for both the (top row) top surface and (bottom row) cross-section PDMS completely fills the open, interconnected pores of the PCL foam. Pore size decreases upon stretching the PCL foam but remains open enough to enable infiltration of the PDMS matrix. Double-headed arrow indicates the direction of PCL stretching for the top surface; for the bottom surface the stretch direction is into the page. Scale bar is 200 μm.
Figure 3. Zoomed in SEM micrographs of (left) unstretched PCL foam, (middle) PCL foam stretched 30%, and (right) PCL/PDMS composite stretched 30% reveal that for both the (top row) top surface and (bottom row) cross-section PDMS completely fills the open, interconnected pores of the PCL foam. Pore size decreases upon stretching the PCL foam but remains open enough to enable infiltration of the PDMS matrix. For the bottom surface the stretch direction is into the page. Scale bar is 500 μm.
Figure 4. One-way shape memory characterization of (A) PCL Foam, (B) PDMS matrix (1.9 wt% crosslinker), (C) Un-stretched PCL-PDMS (1.9 wt% crosslinker) composite. The beginning of the cycles are marked by the asterisk (*) symbol. Samples were deformed at 80 °C (deformation), cooled to -20 °C and unloaded (fixing), followed by continuous heating to 80 °C (recovery). The arrows denote the various stages, specifically (1) deformation, (2) fixing, (3) unloading, and (4) recovery.
Figure 5. Two-way shape memory characterization of (A) PCL foam, (B) PDMS matrix (1.9 wt% crosslinker), and (C) un-stretched PCL/PDMS composite reveal that the PCL foam and un-stretched PCL/PDMS composite have two-way shape memory, as indicated from the elongation upon cooling, while the PDMS matrix alone does not. The beginning of the cycles are marked by the asterisk (*) symbol. Samples were heated from room temperature to 80 °C at 3 °C/min and cooled to -20 °C at 3 °C/min for 3 cycles.
Figure 6. Self-actuation characterization (heating/cooling cycles) of (A) un-stretched PCL foam, (B) 20% stretched PCL foam, (C) PDMS matrix (with 1.9 wt% crosslinker) reveals that show neither the PCL foam alone or PDMS matrix exhibits reversible actuation. The stretched foam initially recovers the 20% strain, but does not reversibly actuate. The beginning of the experiment is marked by the asterisk (*) symbol. Sample was heated from room temperature to 80 °C at 3 °C/min and cooled to -20 °C at 3 °C/min for 3 cycles.
Figure 7. Self-actuation characterization (heating/cooling cycles, no stress is applied on the sample) of PCL/PDMS composite stretched 20% reveals that reversible actuation of 5% strain was achieved between cooling and heating cycles. The composite recovers the 20% strain upon first heat and subsequently reversibly actuates when heating to 80 °C and cooling to −20 °C at a rate of 3 °C/min. The beginning of the experiment is marked by the asterisk (*) symbol. Sample was heated and cooled for 3 cycles.
Figure 8. Bending actuation of a PCL/PDMS composite initially curled shows that upon heating the composite uncurls, and upon subsequent cooling the composite reversibly curls. The PCL foam was initially fixed in a curled state by wrapping around a glass vial with a diameter of 27 mm. The composite was heated in 70 °C water and cooled in 15 °C water for 10 min.
<table>
<thead>
<tr>
<th>Cycle</th>
<th>Before 1&lt;sup&gt;st&lt;/sup&gt; Heating</th>
<th>After 1&lt;sup&gt;st&lt;/sup&gt; Heating</th>
<th>After 1&lt;sup&gt;st&lt;/sup&gt; Cooling</th>
<th>After 2&lt;sup&gt;nd&lt;/sup&gt; Heating</th>
<th>After 2&lt;sup&gt;nd&lt;/sup&gt; Cooling</th>
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<tbody>
<tr>
<td>Radius (mm)</td>
<td>10.3</td>
<td>11.2</td>
<td>10.5</td>
<td>11.4</td>
<td>10.6</td>
</tr>
<tr>
<td>Curvature</td>
<td>0.0971</td>
<td>0.0893</td>
<td>0.0952</td>
<td>0.0877</td>
<td>0.0943</td>
</tr>
</tbody>
</table>
**Table 3** Summary of length of the bending actuator during test in Figure 7

<table>
<thead>
<tr>
<th>Results</th>
<th>Before 1&lt;sup&gt;st&lt;/sup&gt; heating</th>
<th>After 1&lt;sup&gt;st&lt;/sup&gt; heating</th>
<th>After 1&lt;sup&gt;st&lt;/sup&gt; cooling</th>
<th>After 2&lt;sup&gt;nd&lt;/sup&gt; heating</th>
<th>After 2&lt;sup&gt;nd&lt;/sup&gt; cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gap length (mm)</td>
<td>2.16</td>
<td>7.28</td>
<td>3.51</td>
<td>7.31</td>
<td>3.49</td>
</tr>
</tbody>
</table>
Chapter 3. Shape Memory Film-based Reversible Actuator

3.1 Synopsis

Shape memory polymers are a class of well-studied materials which have a broad range applications as well as simple fabrication process\textsuperscript{9, 10, 16}. SMPs in film form have been used as materials for laminate structure actuators. The laminated actuators can achieve reversible actuation without application of an external stress\textsuperscript{4}, which allows reversible actuation based applications (e.g. actuators, artificial muscles). However, they are restricted to bending actuation only. To address this issue, we introduce a novel approach which combines the poly(\(\varepsilon\)-caprolactone) (PCL) shape memory polymer films with an elastomeric matrix in a variety of complex configurations. It is found that the laminated reversible actuators fabricated via this approach could achieve good reversible actuation and realize complex actuation.

3.2 Introduction

Two way shape memory polymers are a class of smart materials that has attracted a lot of attention within the past decade\textsuperscript{11}. They can realize reversible actuation under an application of an external force, which does not require an additional programming step as one-way shape memory polymers do. For instance, Chung et al developed a novel semicrystalline poly(cyclooctene) (PCO) based two-way shape memory polymer which undergoes a phenomenon termed “stretch-induced crystallization”, where the polymer exhibits elongation upon cooling and contraction upon heating under the condition of a constant external stress\textsuperscript{5}. 
However, there is a demand for applications based on reversible actuation without use of external stress (e.g. actuators, artificial muscles). Therefore, a lot of novel materials have been developed to address this demand. So far, there are two main approaches: molecular approach\textsuperscript{2-17} and laminate approach.

The laminate approach is an approach that combines pre-stretched SMP layer with an elastomeric matrix layer to form the bi-layered structure\textsuperscript{7,15}. The mechanism of this approach is that laminated actuator usually has two layers: one rubber biasing layer and one stretched semi-crystalline two-way shape memory polymer layer. Upon heating, the stretched polymer intends to recover to its original shape, this puts the actuator in a bending configuration with stress applied to the rubber layer. Then upon cooling, the stored stress in rubber layer drives the actuator return to flat configuration accommodated by elongation of the SMP during crystallization. Westbrook et al developed a reversible shape memory composite where a pre-stretched one way shape memory polymer is embedded in an elastomeric matrix. This composite exhibited a reversible bending actuation upon heating/cooling cycles\textsuperscript{7}. Chen and co-workers developed bilayer composite composed of a pre-programed shape memory polyurethane (SMPU) and an un-stretched polyurethane substrate. Reversible bending was achieved through the release of elastic strain of pre-programed SMPU upon heating and the recovery of elastic strain of polyurethane substrate upon cooling\textsuperscript{4}. However, the laminate approach can only be able to fabricate the bending actuator, which limits the applications of this approach.
Poly (ε-caprolactone) (PCL) is a widely studied polymeric material\textsuperscript{1–3}. It is a biodegradable polyester material and can be degraded in physiological condition (e.g. human body condition), thus, it attracts a great deal of attention for its use of biocompatible material\textsuperscript{6}. For instance, PCL is FDA-approved for biomedical applications, such as drug delivery vehicle\textsuperscript{12}, suture\textsuperscript{14} and tissue engineering scaffold\textsuperscript{8}. It also well-used for shape memory materials. For instance, Rodriguez et al developed a shape memory associated self-healing consisting of cross-linked PCL network with linear PCL network\textsuperscript{13}. Zhu et al introduced a class of poly(ε-caprolactone) (PCL) with different molecular weight crosslinked by γ-radiation. The polymers they developed exhibit a typical one-way shape memory effect with good fixing rate and recovery rate\textsuperscript{18}.

In this chapter, we developed a novel laminate approach capable of fabricating bilayer-based actuators with both simple bending geometry and more complex geometries. This approach employs poly (ε-caprolactone) (PCL) shape memory polymer films embedded within elastomeric matrix, where the reversible actuation is achieved through a combination of shape memory recovery of the PCL film upon heating and stretch-induced crystallization of the PCL film triggered by internal biasing stress of elastomeric matrix upon cooling. Actuators with complex geometries were fabricated by arranging the stretched PCL film in different ways during the mold assembly process. In what follows, thermal properties and thermomechanical behavior were evaluated. Self-actuation demonstrations were performed to demonstrate the reversible actuation of these novel laminated actuators.
3.3 Experimental

3.3.1 Materials

Poly(ε-caprolactone) diol (Mw=8,000 g/mol) was purchased from Abcr Inc. Benzene anhydrous (99.8%), acryloyl chloride (98%), triethylamine, hexane, tetrathiol, dichloromethane (DCM), 2,2-dimethoxy-2-phenylacetophenone photoinitiator (DMPA), tert-butyl acrylate (tBA) and poly(ethylene glycol) dimethacrylate (PEGDMA) were purchased from Sigma-Aldrich. All chemicals were used as received.

3.3.2 Functionalization of PCL diol (Mw=8,000 g/mol)

Functionalization of PCL diol was carried out by end-capping with acryloyl chloride, as previously reported by Rodriguez et al\textsuperscript{13}. Briefly, PCL diol (Mw=8,000 g/mol) was dissolved in benzene anhydrous under nitrogen purge. Trimethylamine and acryloyl chloride were added to the reaction flask at 2.5 times the moles of PCL diol. The reaction was carried out for 3 h, after which time HCL salt by-product was removed by filtration and the functionalized PCL macromer was precipitated in excess hexanes. The final yield of PCL macromer was 94%.

3.3.3 Film Fabrication Mold

A film fabrication mold was developed to enable quick and convenient film fabrication. As shown in Figure 1, two glass slides, an aluminum spacer and several clamps were utilized to assemble this mold. This mold was designed to crosslink the polymer via UV curing. By
simply varying the dimension of the aluminum spacer and glass slides, we are able to fabricate film with different sizes.

3.3.4 Fabrication of PCL Film

To prepare PCL films, we used end-linking of telechelic macromers with thiol-ene chemistry as shown in Scheme 1, combined with a film fabrication process as shown in Figure 2. Films were fabricated within a glass mold described above via UV crosslinking. The functionalized PCL was dissolved in DCM mixed with tetrathiol cross-linker and DMPA photo initiator at the molar ratio of 2:1 (PCL: tetrathiol) and 1 weight-% DMPA. This mixture was then injected into the glass mold and UV curing was performed to cross-link functionalized PCL. After cross-linking, the PCL films were taken out of mold and dried in vacuum oven over night.

3.3.5 Fabrication of PCL-tBA/PEGDMA Bilayer Actuators

3.3.5.1 Bending Actuator

Films were cut into rectangular strip with dimension of 25 mm x 5 mm x 0.65 mm (length x width x thickness). Each strip was uniaxially stretched to 100% strain at 80 °C in an isothermal oven, and then fixed in a 4 °C freezer for 5 min to achieve a temporary shape. Those stretched film strips were then fixed on the inner surface of glass slides using double-sided tape in varying pattern before the assembling process of the mold as shown in Scheme 2.
Elastomeric matrix tBA/PEGDMA was prepared with a composition of tBA, PEGDMA and DMPA at weight ratio of 45: 55: 0.2. The mixed tBA/PEGDMA matrix was then injected into the assembled mold bearing the PCL film. Then, a UV curing process was performed following the protocol of turning on UV light for 1 min and turning off UV light for 1 min, and repeated this curing cycle for 20 times. In this manner, the temperature remained below the melting point of PCL, thereby preventing premature recovery of the films.

3.3.5.2 Saddle-shaped Actuator

As shown in Scheme 3, films were cut into rectangular strip with dimension of 10 mm x 5 mm x 0.65 mm (length x width x thickness). Each strip was uniaxially stretched to a certain strain at 80 °C in an isothermal oven, and then fixed in a 4 °C freezer for 5 min to achieve a temporary shape. One stretched film strip was fixed on the bottom surface of the mold while another stretched film was fixed under the top surface of the mold in the perpendicular position of the bottom film. Right after the assembling process of the mold, matrix tBA/PEGDMA was prepared with a composition of tBA, PEGDMA and DMPA at weight ratio of 45: 55: 0.2. The mixed tBA/PEGDMA matrix solution was then injected into the assembled mold. After that, UV curing process was performed following the protocol of turning on UV light for 1 min and turning off UV light for 1 min, and repeated this curing cycle for 20 times.
3.3.5.3 S-shaped Actuator

As shown in Scheme 4, films were cut into rectangular strip with dimension of 10 mm x 5 mm x 0.65 mm (length x width x thickness). Each strip was uniaxially stretched to 100% strain at 80 °C in an isothermal oven, and then fixed in a 4 °C freezer for 5 min to achieve a temporary shape. One stretch film strip was fixed on the bottom surface of the mold while another stretched film was fixed under the top surface of the mold. These two strips were aligned but not overlapped each other. Right after the assembling process of the mold, matrix tBA/PEGDMA was prepared with a composition of tBA, PEGDMA and DMPA at weight ratio of 45: 55: 0.2. The mixed tBA/PEGDMA matrix solution was then injected into the assembled mold. After that, UV curing process was performed following the protocol of turning on UV light for 1 min and turning off UV light for 1 min, and repeated this curing cycle for 20 times.

3.3.5.4 Curl-shaped Actuator

As shown in Scheme 5, a film was cut into rectangular strip with dimension of 30 mm x 5 mm x 0.65 mm (length x width x thickness). It was uniaxially stretched to 100% strain at 80 °C in an isothermal oven, and then fixed in a 4 °C freezer to achieve for 5 min a temporary shape. After stretching, the film strip was fixed on the bottom surface in diagonal direction cross the aluminum spacer. Right after the assembling process of the mold, matrix tBA/PEGDMA was prepared with a composition of tBA, PEGDMA and DMPA at weight ratio of 45: 55: 0.2. The mixed tBA/PEGDMA matrix solution was then injected into the assembled
mold. After that, UV curing process was performed following the protocol of turning on UV light for 1 min and turning off UV light for 1 min, and repeated this curing cycle for 20 times.

3.3.5.5 Actuators with more complex geometries

To demonstrate that our film-based bilayer approach can achieve actuators for more complex actuation, we developed actuators with more complex geometries including triangle-shaped, W-shaped and X-shaped actuators. Matrix composition, stretched strain of film and UV curing speed were changed to prevent the cracking of matrix and pulling out of films during curing process and self-actuation tests.

3.3.5.6 W-shaped Actuator

As shown in Scheme 6, films were cut into rectangular strips with dimension of 10 mm x 5 mm x 0.65 mm (length x width x thickness). It was uniaxially stretched to 40% strain at 80 °C in an isothermal oven, and then fixed in a 4 °C freezer for 5 min to achieve a temporary shape. After stretching, two film strips were aligned on the bottom surface with a space between them. One film strip was fixed under the top surface of the mold covering the space between those bottom films. Right after the assembling process of the mold, matrix tBA/PEGDMA was prepared with a composition of tBA, PEGDMA and DMPA at weight ratio of 55: 45: 0.08. The mixed tBA/PEGDMA matrix solution was then injected into the assembled mold. After that, UV curing process was performed following the protocol of turning on UV light for 40 s and turning off UV light for 1 min, and repeated this curing cycle for 30 times.
3.3.5.7 Triangle-shaped Actuator

Films were cut into rectangular strips with dimension of 30 mm x 5 mm x 0.65 mm (length x width x thickness). It was uniaxially stretched to 40% strain at 80 °C in an isothermal oven, and then fixed in a 4 °C freezer for 5 min to achieve a temporary shape. After stretching, three film strips were fixed on the bottom surface aligned in triangle arrangement. Right after the assembling process of the mold, matrix tBA/PEGDMA was prepared with a composition of tBA, PEGDMA and DMPA at weight ratio of 55: 45: 0.08. The mixed tBA/PEGDMA matrix solution was then injected into the assembled mold. After that, UV curing process was performed following the protocol of turning on UV light for 40 s and turning off UV light for 1 min, and repeated this curing cycle for 30 times.

3.3.5.8 X-shaped Actuator

Films were cut into rectangular strips with dimension of 35 mm x 5 mm x 0.65 mm (length x width x thickness). It was uniaxially stretched to 40% strain at 80 °C in an isothermal oven, and then fixed in a 4 °C freezer for 5 min to achieve a temporary shape. After stretching, four films were fixed on the bottom of actuator arranged in X shape. Right after the assembling process of the mold, matrix tBA/PEGDMA was prepared with a composition of tBA, PEGDMA and DMPA at weight ratio of 55: 45: 0.08. The mixed tBA/PEGDMA matrix solution was then injected into the assembled mold. After that, UV curing process was
performed following the protocol of turning on UV light for 40 s and turning off UV light for 1 min, and repeated this curing cycle for 30 times.

### 3.3.6 Thermal Characterization

To determine the crystallization temperature, melting temperature of the PCL film and glass temperature of tBA/PEGDMA matrix, differential scanning calorimetry (DSC) was performed. DSC experiments were conducted using a Q200 (TA instrument, Inc.). 3-5 mg samples were put in pans and heated from -10 °C to 80 °C at rate of 5 °C/min and then cooled to -10 °C at a rate of 5 °C/min for PCL films. Matrix samples were heated from -60 °C to 80 °C at rate of 5 °C/min and then cooled to -60 °C at a rate of 5 °C/min.

### 3.3.7 Dynamic mechanical analysis

Thermomechanical properties of PCL film and tBA/PEGDMA matrix were characterized using a Q800 Dynamic Mechanical Analyzer (DMA) (TA Instrument Inc). Both PCL films and tBA/PEGDMA matrix were cut into dogbone-shape before testing with a 6.25 mm gauge length, 1.5 mm gauge width and 1 mm thickness.

#### 3.3.7.1 One-way shape memory test

To determine the shape fixing and shape recovery behavior of PCL film and tBA/PEGDMA matrix, one-way shape memory characterization was performed. Samples were
heated to 80 °C at 3 °C/min and held isothermally for 2 min. Then uniaxially stretched to 30 % strain and cooled to -20 °C at 3 °C/min isothermal for 2 min to fix the temporary shape. Sample fixing was determined by unloading and shape recovery was determined by heating the sample back to 80 °C. This was repeated for 3 cycles.

3.3.7.2 Two-way shape memory test

To determine the two-way shape memory behavior of PCL film and tBA/PEGDMA matrix, two-way shape memory tests were performed. Samples were uniaxially stretched to 30%. The stress applied to deform the samples to 30% strain was maintained and samples were cooled to -20 °C and held isothermally for 3 min. Then, samples were heated again to 80 °C and then cooled to -20 °C to observe reversible actuation.

3.3.7.3 Self-actuation test

Self-actuation tests were performed on samples to determine whether PCL films and tBA/PEGDMA matrix have reversible actuation upon heating and cooling cycles. No external stress was applied on the sample during the tests. Samples were heated from room temperature to 80 °C at a rate of 3 °C/min and then cooled to -20 °C at a rate of 3 °C/min. Samples were subjected to 3 heating/cooling cycles.
3.3.8 Self-actuation demonstration

To determine the reversible actuation of PCL-tBA/PEGDMA bilayer actuators, we conducted the self-actuation tests in hot/cold water. Hot water (70 °C) and cold water (10 °C) were prepared before testing. Because the crystallization temperature of PCL film is above RT, the bilayer actuators are expected to actuate at RT. So, we also conducted the self-actuation test in hot water/RT. Completely cured actuators were prepared for testing.

3.3.8.1 Bending Actuator

For hot/cold water test, the actuators were placed in the hot water for 30 s for recovery of the stretched PCL film and then placed in cold water for 1 min for crystallization-induced actuation. For hot water/RT test, the actuators were placed in the hot water for 30 s for recovery of the stretched PCL film and then placed in cold water for 3 min for crystallization-induced actuation. Photos and videos were taken to document the self-reversible actuation process of the bending actuators. We measured the curvature of sample at varying time points to quantify the reversible actuation.

3.3.8.2 Actuators with complex geometries

For hot/cold water test, the actuators were placed in the hot water for 30 s for recovery of the stretched PCL film and then placed in cold water for 1 min for crystallization-induced actuation. For hot water/RT test, the actuators were placed in the hot water for 30 s for recovery of the stretched PCL film and then placed in cold water for 3 min for crystallization-induced actuation.
actuation. Photos and videos were taken to document the self-reversible actuation process of the bending actuators. We measured the curvature of sample at different film area at varying time point to quantify the reversible actuation.

3.4 Results and Discussion

3.4.1 Thermal Characterization

DSC experiments were conducted to study the thermal properties of the PCL film and tBA/PEGDMA matrix. 1st cooling and 2nd heating thermal traces are shown in Figure 3. Heating and cooling rate are 10 °C/min for all samples. From the results, we notice that during the heating process, for regular PCL film, the T<sub>m</sub> is 43.7 °C. For PCL film after a hot/cold water cycle, the T<sub>m</sub> decreased to 27.7 °C. For PCL film after a hot water/RT cycle, the T<sub>m</sub> is 28.1 °C. For tBA/PEGDMA matrix, the T<sub>g</sub> is -12 °C. The T<sub>m</sub> of PCL film slightly changed after hot/cold water or hot water/RT process, which indicates the process does not affect the T<sub>m</sub> of PCL film. During the cooling process, the T<sub>c</sub> for regular PCL film is 43.7 °C, the T<sub>c</sub> for PCL film that was processed through a hot/cold water cycle is 46.9 °C, the T<sub>c</sub> for PCL film that was processed through a hot water/RT cycle is 47.2 °C. The T<sub>c</sub> of PCL film only slightly changed after hot/cold water or hot water/RT process, which indicates the process does not affect the T<sub>c</sub> of PCL film.
3.4.2 Dynamic Mechanical Analysis

3.4.2.1 One-way shape memory test

To understand the fixing and recovery behavior of PCL film and tBA/PEGDMA matrix, one way shape memory DMA tests were performed. Results for PCL film is shown in Figure 4(A), good fixing behavior and good recovery behavior were observed. However, for tBA/PEGDMA matrix as shown in Figure 4(B) and (C), we noticed that matrix in Figure 4(B) has good fixing and matrix in Figure 4(c) has poor fixing. Both of them have good recovery behavior. However, the matrix in actuator is not used for its shape memory response.

3.4.2.2 Two-way shape memory test

From the Figure 4(A), we also noticed that there is strain-induced crystallization during cooling process for PCL film, which indicates this material may possess two way shape memory effects. Therefore, two way shape memory DMA tests were conducted to study the two way shape memory behavior of these materials. Figure 5(A) shows typical two way shape memory track under a constant stress of 0.1 MPa for PCL film which indicate it has two way shape memory behavior. Figure 5(B) and (C) show tBA/PEGDMA matrix have cooling shrinkage and heating expansion under an external stress of 0.25 MPa, which indicates no two way shape memory behavior for both matrix.
3.4.2.3 Self-actuation Test

Results for self-actuation tests are shown in Figure 6. Figure 6 (a) is the test results for un-stretched PCL film and Figure 6 (b) and (c) are for tBA/PEGDMA matrix. These results showed that there was only thermal expansion and cooling shrinkage, no self-actuation was observed for these samples. We also observed an interesting behavior of PCL film as shown in Figure 6(a): during the first heating cycle, the strain of PCL film increased rapidly comparing to the 2nd and 3rd cycle. The reason for this is unknown.

3.4.3 Demonstration of self-actuation

3.4.3.1 Bending Actuator

Self-reversible actuation of a bending actuator was demonstrated via hot/cold water test. The results are shown in Figure 7 and Supplemental Video 4. For hot/cold water test, we noticed the actuator gradually changed toward bending configuration. When placed the actuator in 15 °C cold water, it returned back to flat configuration. This result remains the same for multiple cycles. As shown in Table 1, we quantified the actuation by measuring the curvature of the actuator at different times during heating/cooling.

3.4.3.2 S-shaped Actuator

Self-actuation of S-shaped actuator was demonstrated via hot/cold water test and hot water/RT test. The results are shown in Figure 8, Figure 9 and Supplemental Video 5 and 6.
For hot/cold water test, when placed the actuator in hot water, we noticed that it gradually changed toward S configuration. When placed the actuator in 15 °C cold water, it returned back to flat configuration. For hot water/RT test, the action process is similar, but it also took longer for actuator to return to flat configuration at RT than in cold water. These results remain the same for multiple cycles. As shown in Table 2, we also quantified the actuation by measuring the curvature of the actuator at different time during heating/cooling cycle.

### 3.4.3.3 Saddle-shaped Actuator

Self-actuation of Saddle-shaped actuator was also demonstrated via hot/cold water test and hot water/RT test. The results are shown in Figure 10, Figure 11 and Supplemental Video 7-10. For the hot/cold water test, when placed the actuator in hot water, we noticed that it gradually changed toward saddle configuration. When placed the actuator in 15 °C cold water, it returned back to flat configuration. For hot water/RT test, the action process is similar, but it also took longer for actuator to return to flat configuration at RT than in cold water. These results remain the same for multiple cycles. As shown in Table 3, we also quantified the actuation by measuring the curvature of the actuator at different time during heating/cooling cycle. Since before heating and after cooling the actuator was in almost flat configuration, radius and curvature was not measured here.
3.4.3.4 W-shaped Actuator

Self-actuation of W-shaped actuator was also demonstrated via hot/cold water test and hot water/RT test. The result is shown in Figure 12, Figure 13 and Supplemental Video 11 and 12. For hot/cold water test, when placed the actuator in hot water, we noticed that it gradually changed toward W-shaped configuration. When placed the actuator in 15 °C cold water, it returned back to flat configuration. For hot water/RT test, the action process is similar, but it also took longer for actuator to return to flat configuration at RT than in cold water. These results remains the same for multiple cycles. As shown in Table 4, we also quantified the actuation by measuring the curvature of the actuator at different time during heating/cooling cycle.

3.4.3.5 Other Actuators

Furthermore, actuators with Curl-shaped, Triangle-shaped and X-shaped geometries were also developed to demonstrate the spatial control over actuation shapes of this novel laminate approach. Reversible actuation tests were performed to qualitatively study the actuation behavior of these actuators. As shown in Figure 14, 15 and 16 and Supplemental Video 13-19, these complex shaped actuators did have reversible actuation during heating/cooling tests.

3.5 Conclusions

A film-matrix based laminate approach is applied to fabricate self-reversible actuators using PCL film as semi-crystallized cross-linked polymer network and tBA/PEGDMA as
elastomeric matrix. Thermal properties, mechanical properties of PCL film, tBA/PEGDMA matrix were characterized. The simple bending actuator as well as actuators with complex geometries are presented in this work. Ease of fabrication, good mechanical properties and good self-reversible actuation were observed to prove geometrically complex actuation events. Further study is required to improve the actuation strain and to develop actuators with more complex geometry.

Our novel film-based laminate approach is significant among other approaches for fabricating reversible actuators. So far, most laminate approaches are limited to bending actuators, however, our approach can realize both bending actuation and complex actuation. This spatial control of actuation shape is achieved by simply changing the geometries of actuators during mold assembling process. So far, we have developed several complex actuators based on this approach to show the great potential of them to realize flexible special-controlled actuators. Besides, we have cooperated with another group to develop several mathematic models to simulate and predict the actuation of our actuators. In addition to the mentioned advantages, our approach also shows easy and quick fabrication process while maintaining a low fabrication cost.
3.6 References


Figure 1. Film fabrication mold: (a) shows the elements for assembling the mold, (b) the top view of the mold after assembling, (c) shows the side view of the mold.
Scheme 1. Schematic for crosslinking of semi-crystalline PCL with shape memory capability via thiol-ene chemistry.
Figure 2. Fabrication process of PCL film.

Inject PCL, tetrathiol, DMPA mixture into mold

UV

(c)
**Scheme 2.** Geometry of bending actuator.

Note: Films are in purple
Matrix is in grey

Note: Films are in purple
Matrix is in grey

Note: Films are in purple
Matrix is in grey
Scheme 5. Geometry of Curl-shaped actuator.

Side View
Note: Films are in purple
Matrix is in grey

Top View

Note: Films are in purple
Matrix is in grey
Figure 3. DSC thermograms (1st cooling and 2nd heating) of Tm of (a) PCL film, (b) PCL film after hot/cold water test, (c) PCL film after hot water/RT test, and (d) Tg of tBA/PEGDMA matrix. Hot/cold water test or Hot water/RT test does not affect the Tm or Tc of the PCL. Heating rates are 10 °C/min for heating and cooling.
Figure 4. One-way shape memory characterization of (A) PCL Film, (B) 0.08% tBA/PEGDMA matrix, (C) 0.2% tBA/PEGDMA matrix. The beginning of the cycles are marked by the asterisk (*) symbol. Samples were deformed at 80 °C (deformation), cooled to -20 °C and unloaded (fixing), followed by continuous heating to 80 °C (recovery). The arrows denote the various stages, specifically (1) deformation, (2) fixing, (3) unloading, and (4) recovery.
Figure 5. Two-way shape memory characterization of (A) PCL film, (B) 0.2% tBA/PEGDMA Matrix (C) 0.08% tBA/PEGDMA matrix reveal that the PCL film has two-way shape memory, as indicated from the elongation upon cooling, while the matrix alone do not. The beginning of the cycles are marked by the asterisk (*) symbol. Samples were heated from room temperature to 80 °C at 3 °C/min and cooled to -20 °C at 3 °C/min for 3 cycles.
Figure 6. Self-actuation characterization (heating/cooling cycles) of (A) PCL film, (B) 0.2% tBA/PEGDMA Matrix , (C) 0.08% tBA/PEGDMA matrix show neither the film alone or the matrix exhibits reversible actuation. The beginning of the cycles are marked by the asterisk (*) symbol. Samples were heated from room temperature to 80 °C at 3 °C/min and cooled to -20 °C at 3 °C/min for 3 cycles.
Figure 7. Bending actuation of a PCL-tBA/PEGDMA bilayer actuator initially curled shows that upon heating the actuator curls, and upon subsequent cooling the composite reversibly uncurls. The actuator was heated in 70 °C water and cooled at RT for 10 min.
Table 1 Summary of radius and curvature for bending actuator in Figure 7 during Hot water/RT Test

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Before heating</th>
<th>After heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius (mm)</td>
<td>95.1</td>
<td>36.2</td>
</tr>
<tr>
<td>Curvature (mm^{-1})</td>
<td>0.0011</td>
<td>0.0276</td>
</tr>
</tbody>
</table>
Figure 8. Actuation of a PCL-tBA/PEGDMA S-shaped actuator shows that upon heating the actuator turns into S shape, and upon subsequent cooling the composite reversibly flattens. The actuator was heated in 70 °C water and cooled in 15 °C water for 5 min.
Figure 9. Actuation of a PCL-tBA/PEGDMA S-shaped actuator shows that upon heating the actuator turns into S shape, and upon subsequent cooling the composite reversibly flattens. The actuator was heated in 70 °C water and cooled at RT for 10 min.
**Table 2** Summary of radius and curvature for S-shaped Actuator in Figure 7 during Hot water/RT Test

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Before heating</th>
<th>After heating</th>
<th>After cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius (mm)</td>
<td>22.9</td>
<td>13.9</td>
<td>22.8</td>
</tr>
<tr>
<td>Curvature (mm⁻¹)</td>
<td>0.0437</td>
<td>0.0719</td>
<td>0.0439</td>
</tr>
</tbody>
</table>
Figure 10. Actuation of a PCL-tBA/PEGDMA Saddle-shaped actuator shows that upon heating the actuator turns into Saddle shape, and upon subsequent cooling the composite reversibly flattens. The actuator was heated in 70 °C water and cooled in 15 °C water for 5 min.
Figure 11. Actuation of a PCL-tBA/PEGDMA Saddle-shaped actuator shows that upon heating the actuator turns into Saddle shape, and upon subsequent cooling the composite reversibly flattens. The actuator was heated in 70 °C water and cooled at RT for 10 min.
Table 3 Summary of radius and curvature for Saddle-shaped Actuator in Figure 7 during Hot water/RT Test

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Before heating</th>
<th>After heating</th>
<th>After cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius (mm) (Front View)</td>
<td>-</td>
<td>19.5</td>
<td>-</td>
</tr>
<tr>
<td>Curvature (Front View)</td>
<td>-</td>
<td>0.0513</td>
<td>-</td>
</tr>
<tr>
<td>Radius (mm) (Side View)</td>
<td>-</td>
<td>39.9</td>
<td>-</td>
</tr>
<tr>
<td>Curvature (Side View)</td>
<td>-</td>
<td>0.0251</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: Since before heating and after cooling the actuator was in almost flat configuration, radius and curvature was not measured here.
**Figure 12.** Actuation of a PCL-tBA/PEGDMA W-shaped actuator shows that upon heating the actuator turns into W shape, and upon subsequent cooling the composite reversibly flattens. The actuator was heated in 70 °C water and cooled in 15 °C water for 5 min.
Figure 13. Actuation of a PCL-tBA/PEGDMA W-shaped actuator shows that upon heating the actuator turns into W shape, and upon subsequent cooling the composite reversibly flattens. The actuator was heated in 70 °C water and cooled at RT for 10 min.
Table 4. Summary of radius and curvature for W-shaped Actuator in Figure 7 during Hot water/RT Test

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Before heating</th>
<th>After heating</th>
<th>After cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius(mm)</td>
<td>42.8</td>
<td>39.0</td>
<td>42.2</td>
</tr>
<tr>
<td>Curvature</td>
<td>0.0234</td>
<td>0.0256</td>
<td>0.0237</td>
</tr>
</tbody>
</table>
Figure 14. Actuation of a PCL-tBA/PEGDMA Curl-shaped actuator shows that upon heating the actuator turns into Curl shape, and upon subsequent cooling the composite reversibly flattens. The actuator was heated in 70 °C water and cooled at RT for 10 min.
Figure 15. Actuation of a PCL-tBA/PEGDMA Triangle-shaped actuator shows that upon heating the actuator turns into triangle shape, and upon subsequent cooling the composite reversibly flattens. The actuator was heated in 70 °C water and cooled at RT for 10 min.
Figure 16. Actuation of a PCL-tBA/PEGDMA X-shaped actuator shows that upon heating the actuator turns into x shape, and upon subsequent cooling the composite reversibly flattens. The actuator was heated in 70 °C water and cooled at RT for 10 min.
Chapter 4. Conclusions and Future Directions

4.1 Overall Conclusions

The work contained in this thesis has introduced two novel approaches of fabricating soft reversible actuators based on two-way shape memory polymers. The first approach is a foam-based composite approach that combines a shape memory polymer and elastomeric PDMS matrix to fabricate a group of foam-based actuators that are capable of achieving both linear and bending actuation upon application of a simple thermal trigger. The second approach is a film-based bilayer approach which combines the poly(ε-caprolactone) (PCL) shape memory polymer films with elastomeric matrix. The laminate reversible actuators fabricated via this approach could achieve good reversible actuation and realize complex actuation.

4.2 Shape Memory Foam-based Reversible Actuator

4.2.1 Summary and Conclusions

In Chapter 2, a group of foam-based actuators consisting of a porous poly(ε-caprolactone) (PCL) shape memory polymer foam infiltrated with PDMS elastomeric matrix are reported. These actuators are capable of achieving both linear and bending actuation upon application of a simple thermal trigger. Composite structure, thermal properties and thermomechanical behavior were evaluated. Scanning electron microscopy revealed complete infiltration of the PDMS matrix into the porous voids within the foam. Thermomechanical experiments and self-actuation tests revealed that the actuators have good reversible actuation
upon heating/cooling cycles. Results also demonstrated that the degree of actuation dependent on the programming conditions of the PCL foam. Furthermore, these actuators could achieve the spatial control of desired shape changes. These foam-based actuators are expected to enable new application in biomedical research including dynamic cell culture, artificial muscle and biomedical soft devices, as well as robotics.

4.2.2 Future Work

Despite the observation that our foam-based actuators can realize both linear and bending actuation comparing to other reversible actuators, there is still a limitation to this foam-based approach. The reversible strain can only reach to about 5% for linear actuator and the observed actuation for bending actuator was also not apparent neither. In other words, the actuator cannot actuate to its temporary shape perfectly. The reason for the low actuation might be that the recovery of the foam does not exert enough compressive stress on the matrix when heating; therefore, the stored stress cannot elongate the composite sufficiently when cooling. Another reason might be that the porosity of the foam is small so that the matrix is not sufficiently stiff to elongate the composite during cooling process. Our future work will aim at improving the actuation strain of this foam-based actuator. We can optimize the ratio of semi-crystalline polymer to matrix, or, we can improve crystallinity of the polymer, which will improve the strain-induced crystallization. For example, instead of PCL, we can use other polymer that has more crystallinity and can achieve more strain-induced crystallization to improve actuation strain. Besides, we can adjust the modulus of the foam to optimize the
actuation. Finally, we can adjust the stretched strain to maximize the actuation, for stretched strain does affect the PDMS matrix amount we infiltrate into the foam.

4.3 Shape Memory Film-based Reversible Actuator

4.3.1 Summary and Conclusions

In Chapter 3, a novel laminate approach employs a poly (ε-caprolactone) (PCL) shape memory polymer film embedded within elastomeric matrix, where the reversible actuation is achieved through a combination of shape memory recovery of the PCL film upon heating and stretch-induced crystallization of the PCL film triggered by internal biasing stress of elastomeric matrix upon cooling. This novel laminate approach is capable of fabricating bilayer-based actuators with both simple bending geometry and more complex geometries via arranging the stretched PCL film in different ways during the mold assemble process. Thermal properties and thermomechanical behavior were evaluated. Self-actuation demonstration revealed that the actuators have good reversible actuation upon heating/cooling cycles and upon heating/RT cycles. Results also demonstrated that degree of actuation is dependent on the programming strain of the PCL film, the amount of matrix and the dimension of the actuator. Furthermore, these actuators could achieve the spatial control of desired shapes by simply varying the geometries of actuators.
4.3.2 Future Work

Although we can achieve both bending actuation and complex actuation via our film-based approach, limitations remain. The actuations of these actuators were not large in amplitude. Moreover, as the geometry of the actuator becomes more complex, the high actuation becomes harder to achieve. The reason for this issue might be that when the geometry of the actuator will affect its reversible actuation. In our experiments, we adjusted the stretched strain of film, the amount of matrix, matrix composition to optimize the actuation. However, if the geometry of the actuator is very complex, additional parameters should be considered. To solve this problem, our future work will focus on optimizing the actuation using mathematical modeling. We plan to co-work with Dr. H, Qi’s group in Georgia Tech to develop the models that simulate the actuation of our actuators, then investigate different parameters in the model (e.g. stretched strain of film, dimensions of film and matrix, actuator configuration) to find out the optimized combination of parameters that gives the most predicted actuation. After that, we will make the corresponding actuators and compare the experimental to the theoretical model we developed. We also plan to explore some application of these bilayer actuators. For instance, we can purchase internal heaters (e.g. Kapton™ heaters from Minco/Omega) and integrate them into the bilayer system. After incorporation of heaters, we can then design a “hand” where each finger is an actuator (e.g. combines 5 simple bending actuators in a hand design). Thus, upon heating the fingers will “bend”, upon cooling the fingers will extend based on the reversible actuation behavior.
Vita

Che Tan

121 Lafayette Rd, apt 518, Syracuse, NY 13205

(315)560-6983 ctan03@syr.edu

EDUCATION

M.S. in Biomedical Engineering (January 2013 to Present)
L.C. Smith College of Engineering and Computer Science, Syracuse University, NY

Bachelor in Pharmacy (September 2008 to July 2012)
School of Pharmacy, Chongqing Medical University, Chongqing, China

SKILLS

Lab Techniques: Polymer Chemistry, Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA)

Computer Application: Microsoft Office, SigmaPlot, EndNote, Adobe Photoshop & illustrator

Communicative Skill / Interpersonal Skills / Teamwork Spirit

INDUSTRY EXPERIENCE

Research Intern, Chongqing Huanrui Biotechnology Co., Ltd, Chongqing, China (June 2010 to September 2010)
- Participated in the material base research of the goat horn extractive
- Detected pyroglutamic acid in goat horn extractive
- Developed a method for determining the content of pyroglutamic acid

ACADEMIC PROJECTS

Graduate Researcher, Syracuse University, Syracuse, U.S.A (June 2013 to Present)
- Soft reversible actuators based on shape memory polymer

Research Assistant, State Biopharmaceutical Research Center, Chongqing, China (January 2011 to September 2011)
- Selected the units of effective & protective antigen glucosyltransferases of Streptococcus Mutans
- Took two important genes to construct fusion gene and expressed the corresponding recombinant protein

Research Assistant, School of Pharmacy, Chongqing Medical University, Chongqing, China (November 2011 to June 2012)
- Prepared Vinorelbine liposome
- Combined Vinorelbine liposome with Methylene Blue to overcome tumor drug resistance of Nasopharyngeal Carcinoma

Research Assistant, Bioengineering Department, Chongqing University, Chongqing, China (June 2012 to August 2012)
- Monitored release behavior of two different chemotherapeutic drugs from Chitosan nanoparticles