Mechanically Active Electrospun Materials

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Abstract

Electrospinning, a technique used to fabricate small diameter polymer fibers, has been employed to develop unique, active materials falling under two categories: (1) shape memory elastomeric composites (SMECs) and (2) water responsive fiber mats. (1) Previous work has characterized in detail the properties and behavior of traditional SMECs with isotropic fibers embedded in an elastomer matrix. The current work has two goals: (i) characterize laminated anisotropic SMECs and (ii) develop a fabrication process that is scalable for commercial SMEC manufacturing. The former ((i)) requires electrospinning aligned polymer fibers. The aligned fibers are similarly embedded in an elastomer matrix and stacked at various fiber orientations. The resulting laminated composite has a unique response to tensile deformation: after stretching and releasing, the composite curls. This curling response was characterized based on fiber orientation. The latter goal ((ii)) required use of a dual-electrospinning process to simultaneously electrospin two polymers. This fabrication approach incorporated only industrially relevant processing techniques, enabling the possibility of commercial application of a shape memory rubber. Furthermore, the approach had the added benefit of increased control over composition and material properties. (2) The strong elongational forces experienced by polymer chains during the electrospinning process induce molecular alignment along the length of electrospun fibers. Such orientation is maintained in the fibers as the polymer vitrifies. Consequently, residual stress is stored in electrospun fiber mats and can be recovered by heating through the polymer’s glass transition temperature. Alternatively, the glass transition temperature can be depressed by introducing a plasticizing agent. Poly(vinyl acetate) (PVAc) is plasticized by water, and its glass transition temperature is lowered below
room temperature. Therefore, the residual stress can be relaxed at room temperature simply by hydrating the PVAc fibers. This work investigated the response of PVAc to the application of water on one surface. More specifically, the folding of films of PVAc fibrous webs in response to water lines drawn locally on the mat surface was quantified and characterized based on fiber mat characteristics.
Mechanically Active Electrospun Materials

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**Scheme 1-2** Electrospinning setup used to electrospin isotropic fibers.

**Scheme 2-1** (a) Electrospinning setup used to electrospin aligned PVAc fibers. The addition of the copper plate creates a more uniform electric field that influences the direction of the jet, promoting fiber alignment. (b) Cross-section of the charged copper plate showing the relative placement of the needle and the plate. The syringe needle is placed through a hole (6 mm diameter) in the plate with approximately 1 cm of the needle extending through the hole. Schematic is not to scale.

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**Scheme 2-3** (a) Diagram showing the effect of stretching a single layer ASMEC. The angles $\theta$ and $\phi$ are indicated and represent the fiber angle and the in-plane rotation angle, respectively. (b) Diagram showing the effect of stretching a bilayer ASMEC. Upon unloading, the fixing mismatch in bilayer ASMECs leads to the curvature phenomenon. There is no mismatch between the layers for $\Delta \theta = 0^\circ$ which leads to a straight sample post stretching. Alternatively, different curvatures are observed for $\Delta \theta \neq 0^\circ$ due to the mismatch between the layers. The curled sample in (b) had $\Delta \theta = 45^\circ$. Upon heating, all samples return to their original shape. Scale bars represent 5 mm.

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**Scheme 3-2** Schematic showing the dual electrospinning setup, which contains two syringes containing different polymer solutions placed on opposing sides of the collector drum. The polymers are simultaneously electrospun, or dual-spun, forming composite mats.

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Table 3-4 Fixing and recovery ratios for the PCL/POSS-TPU and PCL/Pellethane SMECs.

Table 4-1 Summary of the average Young’s modulus values for dry and hydrated PVAc fiber mats with various fiber orientations.

Table A1-1 70-30 PCL1k-POSS TPU synthesis summary.
Chapter 1. Introduction

1.1 Shape Memory Polymers

Shape memory polymers (SMPs) comprise a unique class of polymers that have the ability to fix a temporary shape until they are triggered to return to their original shapes by an external stimulus. The stimulus activating the shape changing mechanism can be heat, solvent, electrical current, light, magnetic fields, or a change in pH. By far, thermally responsive SMPs is the subclass that has been studied the most.

Thermally responsive SMPs are triggered to change shape when heated through a transition temperature. The typical shape memory cycle for a heat-triggered SMP involves five steps: (1) The polymer is heated above a transition temperature, such as its melting temperature ($T_m$) or glass transition temperature ($T_g$); (2) At the elevated temperature, the polymer is deformed to a temporary shape. Often, a polymer strip is stretched to a prescribed strain; (3) With the load maintained, the polymer is cooled below the transition temperature in order to fix the temporary shape; (4) The load is removed, and the free standing polymer maintains the programmed shape; (5) The polymer is heated above the transition temperature and returns to its original form. Scheme 1-1 illustrates the shape memory cycle previously described. A 3D plot of stress, temperature, and strain is often used to display the shape memory capability. An example shape memory curve is provided in Figure 1-1. Labeling in the graph corresponds to the previously described steps in the shape memory cycle.

In a shape memory cycle, there are two important mechanisms involved: shape fixing and shape recovery. The ability to fix a temporary shape depends on the immobility of polymer
chains. In a heat triggered SMP, immobility can arise from chain crystallization or vitrification. Crystallization, or the formation of polymer crystals, occurs only in semi-crystalline polymers, in which enough regularity in chain structure exists to form tightly packed, ordered crystal structures. Crystal formation or dissolution occurs when the polymer is cooled below or heated above its $T_m$, respectively. The polymer crystals act as physical crosslinks that hold the polymer in the temporary shape. Chain vitrification occurs when a polymer is cooled below its $T_g$. Due to thermal contraction, a significant loss in free volume occurs as a polymer cools below $T_g$. The loss in free volume, in conjunction with physical barriers, such as chain entanglements, and the reduced thermal, or kinetic, energy, effectively ‘freezes’ the polymer chains in place. It is noted that while chain movement is restricted below $T_g$, chain rearrangements do proceed. The process by which chain motion occurs below $T_g$ is referred to as physical aging\textsuperscript{18-19} and will not be considered in the scope of this thesis. The fixing ratio, $R_f$, defines the polymers ability to maintain the programmed shape and is calculated using Eq. (1-1),

$$R_f(\%) = \frac{\varepsilon_f - \varepsilon_i}{\varepsilon_d - \varepsilon_i} \times 100$$ \hspace{1cm} (1-1)

where $\varepsilon_f$ is the fixed strain, or the strain after unloading, $\varepsilon_i$ is the initial strain prior to deformation, and $\varepsilon_d$ is the deformed strain, or the strain prior to unloading. An ideal SMP has a $R_f$ of 100 %. The fixing ability is assessed qualitatively by the slope of the stress-temperature-strain graph (Figure 1-1) at step (4). A flat slope during unloading represents good fixing, while a negative slope indicates a decrease in strain, or imperfect shape fixing.

The second mechanism in shape memory, shape recovery, is dependent on crosslinks within the polymer. A SMP can be physically or chemically crosslinked. Physical crosslinks
result from chain entanglements within the polymer, and have been shown to, if the molecular weight of the SMP is relatively high, effectively promote shape recovery.\textsuperscript{20} Physical crosslinks can also be in the form of crystalline regions within the polymer.\textsuperscript{21-22} As with in shape fixing, the bonds formed between chains in the crystals help to maintain the macrostructural shape of the polymer. However, here, the crystalline regions are formed prior to deformation, and thus aid in the recovery of the permanent shape. Similarly, covalent crosslinks promote shape recovery through chemical bonds between chains.\textsuperscript{23-24} Macrostructural deformation of a covalently crosslinked polymer results in deformation of the chemical bonds. When the deformation is fixed in the SMP, the bond angles remain in a non-equilibrium state. When the SMP is then heated above its $T_g$, for example, the chains are no longer vitrified, and the bond angles return to the equilibrium state, promoting bulk shape recovery. Similar to the $R_f$, a recovery ratio, $R_r$, is defined as

$$R_r(\%) = \frac{\varepsilon_f - \varepsilon_r}{\varepsilon_f - \varepsilon_i} \times 100$$

(1-2)

where $\varepsilon_r$ is the strain after recovery. An ideal SMP has 100 % recovery.

Due to their smart, shape-shifting ability, SMPs have been sought for a wide range of applications spanning the medical, space, textile, and structural industries.\textsuperscript{17} Several applications have subsequently been described to highlight the diverse uses for SMPs. SMP stents have been actively studied for medical use due to their ability to simplify the surgical placement procedure.\textsuperscript{25-27} SMP stents can be fixed in a temporary folded, rolled, or elongated shape which reduces the stent diameter, easing the maneuver and placement of the stent at the conduit site. Furthermore, the exact SMP can be selected such that the degradation time
matches the intended usable lifetime of the stent, the modulus more closely matches that of
the surrounding tissue (compared to metallic stent alternatives), and in the case of drug eluting
stents, the SMP can control the rate of drug release. Together, the advantages of SMP stents
increase the functionality of such devices and decrease the complications associated with the
medical procedure. In the textile industry, SMPs have been used to develop sports clothing
with variable permeability. As described by Vili,28 an SMP laminate membrane activates at
elevated temperature to allow breathability and water evaporation. Alternatively, Birjandi
Nejad et al.29 recently reported on a rigid SMP composite system with the ability to “self-heal”
cracks in the material. Upon the application of heat, a propagated crack closed via SM recovery
and then healed, and the mechanical properties proved to match those of the virgin state. The
SMP composite was intended as a coating for building materials to increase the material
lifetime and corrosion resistance.

1.2 Shape Memory Elastomeric Composites

Thermally responsive SMPs are the most commonly studied class of SMPs. The shape
changing mechanism is performed around a transition temperature, often a $T_g$, and relies on
vitrification of the chains upon cooling to fix the temporary shape. Consequently, SMPs in their
fixed state are relatively stiff. A need exists for soft SMPs with mechanical properties that more
closely match those of human tissue.

Composite systems are often utilized when the desired material properties cannot be
met by a single material. The nature of composites gives freedom in design, enabling the
selection of material components with the necessary properties for a given application. The
challenge becomes determining the ideal method of combining and processing the composite in order to extract those properties from the components. As will be discussed in Chapter 3, different processing methods can lead to significant differences in material performance. Further, the properties of composite systems are often quite tunable, as variation in composition alters the degree to which each material contributes to the overall system. In order to achieve a soft SMP, our group has developed a composite system composed of polymer fibers enveloped by an elastomeric matrix. The polymer fibers were prepared via electrospinning.

Electrospinning is the process of applying a voltage to a polymer solution in order to draw micro- to nanoscale fibers. A schematic of an electrospinning setup is shown in Scheme 1-2. A polymer solution is contained within a plastic syringe, and a high voltage power supply charges the syringe needle. Electrostatic repulsion of the charged solution counteracts the surface tension, and a cone of solution forms at the needle tip. At a critical point, when electrostatic repulsion overcomes the surface tension, a jet of solution is ejected from the cone and travels towards the grounded collector drum. As the jet travels through the air, it experiences strong elongational forces that stretch the jet, reducing the diameter. Simultaneously, solvent evaporates from the jet, further reducing the diameter of the jet and increasing the surface charge density. If the surface charge density exceeds a threshold, the jet can split into multiple smaller jets. This process can repeat several times before the fibers are collected. Additionally, due to the relative volatility of the solvents used in the polymer solution and the short path length for mass transfer (due to the small jet diameter), the solvent
Electrospun fiber mats are highly porous, making them ideal for applications including cell culture, wound dressing, and membrane filtration. Our group took advantage of the porosity of electrospun fiber mats to develop a shape memory elastomeric composite (SMEC) system that is soft and rubbery, yet has shape memory capabilities. Infiltration of the porous mat with a crosslinkable elastomer gave the right balance of elastic contraction and shape fixing abilities to maintain low moduli and high elasticity, but also enable SM effects. Such combination of properties lend the SMECs to potential applications in medical devices or as soft actuators.

1.3 Water Responsive Shape Memory Polymers

The use of heat-triggered SMPs for medical applications is limited by the temperature required for activation. While thermally responsive SMPs are ideal for their relatively quick shape changing ability, which is typically within seconds (though it depends on the triggering temperature), most SMPs trigger either at too low or too high of a temperature to be used within the body. Therefore, the SMPs must be chosen or modified to trigger at temperatures typically between 40 and 60 °C. Activation temperatures below the specified range can result in premature activation, i.e. before the SMP reaches its destination in the body, it can be triggered to recover, since body temperature is around 37 °C. The risk of such a scenario causing surgical complications outweighs the benefits provided by using SMPs in the first place. Alternatively, SMPs that trigger above 60 °C, activate at temperatures that can cause damage to
surrounding tissue. As such, alternative methods to trigger shape change have been explored. Namely, water responsive SMPs have received attention for their potential to resolve issues associated with heat triggering in the body.

Water responsive SMPs are triggered to change shape upon hydration due to effects from diffusion of water molecules into the chain structure. In $T_g$-based SMPs, water molecules diffuse into the polymer and disrupt chain packing. Such effect can be observed as swelling of the polymer and is accompanied by a reduction in the $T_g$. Huang et al.$^5$ reported a reduction in $T_g$ of up to 35 °C for a polyurethane based polymer. Furthermore, the $T_g$ showed a dependence on the hydration time which correlated to the water uptake. Similarly, for $T_m$-based SMPs, water absorption can break up crystal structures, causing recovery of deformation programmed into that phase. Jung et al.$^{44}$ and Gu and Mather$^4$ studied PEG-based polyurethane copolymers that responded to hydration. Specifically, the hydrophilic PEG phase absorbed water, resulting in dissolution of the PEG crystals. Jung et al.$^{44}$ reported only partial SM recovery in RT water over a 5 min period. Gu and Mather used a combination of (1) “wet fixing” in which the SMP was programmed in the hydrated state and then fixed by drying and (2) porous fiber mats to improve the recovery and actuation speed upon hydration, respectively. Recovery speeds were minimized to 1.3 s, but the recovery ratios still only reached 83 %. Nevertheless, such effects from water uptake for $T_g$ and $T_m$ based SMPs can be exploited to recover the permanent shape of deformed medical devices once in the body. In the case of $T_g$ based SMPs, as the $T_g$ is depressed below body temperature, the recovery would be stimulated. While in most cases, the water triggered recovery is relatively slow, this result could be utilized to allow surgeons
enough time to place the device before triggering recovery. Additionally, a combination of heat and water triggering could be utilized to reduce the actuation time.

1.4 Scope of Thesis

This thesis details the use of electrospinning to develop stimuli-responsive materials. Each chapter utilizes a modified electrospinning setup to adjust the properties of the fiber mat for the desired application. Chapter 2 (adapted from Robertson et al. *Soft Matter*, 2015 [45]) focuses on the incorporation of aligned electrospun fibers into a soft, elastomeric matrix to develop an anisotropic composite system. Material selection and further processing allow for extreme non-affine shape change after simple room temperature deformation. The goal of Chapter 3 was to develop a scalable fabrication process for shape memory elastomeric composites. This chapter details the use of a dual-electrospinning setup to simply prepare composite fiber mats. The versatility of the approach is explored through variation of composition and material components. In a different realm, Chapter 4 explores a water-responsive fiber mat which shrinks when hydrated. Control of water placement led to the development of water-triggered origami, in which water was used to fold mats into 3-dimensional structures.

Throughout the study, focus will be placed on material processing and characterization. The fundamental properties and response of each system are characterized first in order to explain more complex behaviors later studied. Applications for each system will be explored in more or less detail to provide context for the developed material.
1.5 References


1.6 Schemes, Figures, and Tables

Scheme 1-1 A typical shape memory cycle for a thermally responsive shape memory polymer. The original polymer (a) is heated above its transition temperature (b) and a load is applied to deform the sample (c). With the load maintained, the sample is cooled below the transition temperature (d) to fix the strain and then is unloaded (e). In order to recover the fixed strain, the polymer is heated above its transition temperature (f), and the sample returns to its original form.
Figure 1-1 A typical one-way shape memory plot of stress, temperature, and strain for a heat triggered SMP. Steps in the shape memory cycle correspond to (1) heating, (2) deformation, (3) shape fixing, (4) unloading, and (5) shape recovery. The polymer used to demonstrate the 1WSM plot was an epoxy-based SMP.
Scheme 1-2 Electrospinning setup used to electrospin isotropic fibers.
Chapter 2. Mechanically Programmed Shape Memory Elastomeric Composites

2.1 Synopsis

Soft, anisotropic materials, such as the myocardium in the heart and the extracellular matrix surrounding cells, are commonly found in nature. The anisotropy of such materials leads to specialized responses and is imperative to the material functionality, yet few soft materials have been developed that exhibit similar anisotropy. This chapter focuses on the development of an anisotropic shape memory elastomeric composite (ASMEC) with unique functionality. Aligned polymer fibers embedded in an elastomeric matrix have been shown to exhibit anisotropy in mechanical and shape memory properties. Specifically, the capability of the glassy fibers to reinforce the composite and fix a temporary shape depends on the fiber angle. Thus, tensile mechanical programming of layered ASMECs with various fiber orientations results in the formation of curled geometries due to a mismatch in fixed strain. This response is a breakthrough in the realm of mechanical programming, since non-affine shape change is achieved by simply stretching the layered ASMECs at RT. This chapter will demonstrate that the pitch and curvature of the curled geometries depends on the fiber orientations and the degree of strain programmed into the material. In validation of experimental results, a simple bilayer model was applied and proved to capture the observed phenomena, supporting our conclusions and ensuring attainability of predictable curling geometries.

2.2 Introduction

In the context of SMPs, soft and anisotropic materials can play a vital role in the field of biomaterials. Most fabricated elastomeric materials are isotropic while there is a need for
elastomeric materials that mimic the anisotropic properties observed in nature in materials such as tendons, wood, or bat wings. Further, the extracellular matrix found in the human body is comprised of Type III collagen and elastin small diameter fibers arranged in an anisotropic manner. Another example is myocardium in heart muscle tissue. Researchers have tried to replicate the cardiac anisotropy synthetically. Engelmayr et al. synthesized an anisotropic elastomeric scaffold using poly(glycerol sebacate) and demonstrated the development of cell alignment using this material. Plants are also among the biological systems that demonstrate anisotropy. Passiflora edulis, for example, have long, curly tendrils that form both spirals and helices. Godinho et al. modeled this behavior using synthetic liquid crystalline cellulosic fibers. The curling of such materials with complex geometries can be quantified by measuring the pitch and radius of curvature. Armon et al. used these parameters to describe the geometry of opened Bauhinia variegata seed pods. This type of seed has valves composed of two fibrous layers, with fiber orientations at ±45° with respect to the longitudinal direction of the pod. Opening of the pods is triggered by shrinkage due to changes in humidity. As the valves shrink, curling is observed due to differences in the recovery direction between the two layers. The difference in recovery directions is a result of the anisotropy of the aligned fiber layers. Studying and understanding these anisotropic biological materials helps scientists to fabricate smart biomaterials for biomedical applications. In recent years, anisotropic polymers, anisotropic liquid crystalline elastomers, and anisotropic elastomeric composites with shape memory (SM) properties have been widely studied.

Rodriguez et al. recently introduced an anisotropic elastomeric composite with SM properties. In this approach, the anisotropic SM elastomeric composite (ASMEC) was
constructed through electrospinning aligned fibers of poly(vinyl acetate) (PVAc) and infiltrating Sylgard 184 silicone into the fiber mat. While Sylgard 184 is capable of “memorizing” a permanent shape, it lacks the ability to fix a temporary shape when in the elastomeric state. To enable shape fixing in the elastomer, PVAc fibers were introduced; the PVAc served as the SM fixing polymer and Sylgard 184 served as the soft matrix assisting in SM recovery. This combination allowed for an overall elastomeric behavior of the composite material. The fiber mat was fabricated to have an anisotropic behavior, and its mechanical properties were dependent on the fiber direction. Specifically, the Young’s modulus, which is a measure of a material’s stiffness, depended on the fiber direction. This anisotropy translated to the composite, and it was demonstrated that the ability to fix a temporary shape depended on the PVAc fiber orientation in the ASMEC. When the composite material was stretched in the direction of the polymer fibers, as opposed to the direction perpendicular to the fiber orientation, for example, a higher fixing ratio was attained.

For the present study, a new concept of mechanically programming complex temporary shapes into SMPs is introduced. The process dramatically simplifies the SM cycle and simultaneously introduces a significant technical challenge of accurate shape prescription. The aforementioned study by Rodriguez et al. led to the realization that if two ASMECs are layered with their fiber angles varied, after uni-axially stretching the composite, the shape recovery of the bilayer ASMEC is non-uniform through the thickness. Therefore, the non-uniform shape recovery causes non-affine shape change, and the bilayer composite curls. This transformation from 2D to 3D is remarkable, considering programming requires solely uni-axial tensile deformation without heating; i.e., obviating the time consuming heat/deform/cool sequence of
standard shape memory programming. While similar shape changes have been obtained previously, there are several advantages to the current approach that make it more suitable for a range of applications.\textsuperscript{14-15} For example, Jeong et al. developed a layered composite system that selectively swells in response to solvent polarity.\textsuperscript{14} Through manipulation of the layered geometry, helices were formed upon solvent exposure. Limitations to this approach include the maintenance of the solvent environment and the long time scale required to reverse the shape change. Similarly, Kohlmeyer et al. chemically modified Nafion strips to form helices in response to a change in temperature.\textsuperscript{15} While the thermal environment need not be maintained, significant changes in pH are required to enable and reverse the shape change. Furthermore, the Nafion strip must undergo a typical shape memory cycle prior to chemical modification, making the overall process more labor intensive. This chapter will demonstrate that upon removal of a tensile load, the curvature of a soft, elastic, anisotropic composite with laminae of varying fiber orientations is a consequence of the fixing mismatch resulting from the fiber angle of each layer. Both sample preparation and activation of the shape changing mechanism are simple: room temperature (RT) tensile deformation triggers the formation of helical structures and heating reverses the shape change. The ability to achieve this response at RT makes programming the composite very easy and is one aspect that makes the system so unique. However, the programmed shape lacks an affine relationship with the mechanically deformed shape achieved during loading, which makes it challenging to obtain a prescribed shape. In order to overcome this challenge, a model was applied that predicts the key characteristic of the programmed shape. The curling will be quantified by measurements of curvature and pitch for each bilayer ASMEC, and it will be related to the fiber orientations.
Furthermore, the application of a simple model allows achievement of predictable geometry of curling via mechanical programming of anisotropic composites with different fiber angles.

2.3 Experimental

2.3.1 Materials

Poly(vinyl acetate) (PVAc) (Mw = 260,000 g/mol) was purchased from Scientific Polymer Products, Inc. N,N-Dimethylformamide (anhydrous, 99.8) (DMF) was purchased from Sigma Aldrich. Methanol was purchased and used as received from Fisher Scientific. Poly(dimethylsiloxane) (Sylgard 184) was purchased from Dow Corning and stored in a refrigerator prior to use.

2.3.2 Electrospinning Method

For sample preparation, 2 g of PVAc were dissolved in 10 mL of a 7:3 volume ratio methanol:DMF mixture to achieve a 20 wt% PVAc solution. The solution was electrospun using the modified electrospinning setup shown in Scheme 2-1. By introducing a charged copper plate with the plate face perpendicular to the syringe needle, the direction of the jet can be influenced. The metal plate creates a more uniform electric field, and when used in conjunction with a high drum rotation speed, fiber mats with aligned fibers are spun.

In order to electrospin the aligned fibers, the PVAc solution was pumped at 0.5 mL h⁻¹. A voltage of +14 kV was applied to the syringe needle, and a voltage of +12 kV was applied to the copper plate. The grounded metal collector drum (-0.5 kV) rotated at 3000 rpm, and the distance between the needle tip and the collector drum was 8 cm. Electrospinning was run for
8-10 h. After removal, the fiber mat was dried in a vacuum oven at room temperature (RT) for 24 h.

2.3.3 Anisotropic Single Layer Composite Fabrication

An elastomeric composite was prepared by applying a 10:1 mass ratio base:curing agent of a two-part Sylgard 184 (hereafter “Sylgard”) mixture to the porous fiber mat. The Sylgard was applied to one side of the fiber mat with a spatula, and a heavy roller was used to remove excess and evenly distribute the mixture. The fiber mat was turned over, and the process was repeated. The infiltrated fiber mat was put into a vacuum oven (ca. 760 mm Hg) at RT for 1 h to assist the fiber infiltration and to remove air bubbles from the Sylgard. After removal from the vacuum oven, the composite material was cured at 30 °C for 48 h.

2.3.4 Anisotropic Bilayer Composite Fabrication

Squares (30 mm in length) were cut from the anisotropic single layer composite at various fiber angles (θ = 0°, 22.5°, 45°, 67.5°, and 90°). The reported angles are indicative of the angle between the direction of the fibers and the cutting direction in the PVAc fiber mats. Two plies were stacked and adhered with Sylgard, and the excess Sylgard was removed by running a heavy roller over the top layer. The prepared bilayers had layers with fiber angles of 0°/0°, 0°/22.5°, 0°/45°, 0°/67.5°, and 0°/90° (top fiber orientation/bottom fiber orientation). Since each prepared bilayer had one layer with 0° orientation, hereafter the term “Δθ” which refers to the difference in fiber angle between the two layers (Δθ = 0°, 22.5°, 45°, 67.5°, and 90°) will be used. A schematic of this layering process is shown in Scheme 2-2. The bilayers were put in a vacuum oven (ca. 760 mm Hg) for 1 h to remove air bubbles from the Sylgard layer in between
the two plies. After removing, the bilayers were cured at 30 °C for 48 h and then post cured at 60 °C for 16 h to ensure that the Sylgard crosslinking was complete.

2.3.5 Scanning Electron Microscopy

A JEOL JSM-5600 Scanning Electron Microscope (SEM) was used to examine the microstructural morphology and topography of the anisotropic composites. SEM was performed on the PVAc fiber mats, single layer ASMECs, and bilayer ASMECs. All samples were sputter coated with gold for 45 s prior to the SEM analysis. SEM micrographs of the surface of the electrospun aligned PVAc fiber mats were taken in order to verify fiber alignment. The surface and the transverse and longitudinal cross-sections of the infiltrated fiber mat and the bilayer composite were also visualized. SEM micrographs of the bilayer cross-sections were used to measure the thickness of the Sylgard layer that was used to adhere the two plies. ImageJ software (Version 1.46) was used for PVAc fiber diameter and Sylgard thickness measurements.

2.3.6 Thermal Analysis

Thermal properties of samples were characterized using Differential Scanning Calorimetry (DSC); (Q200 TA Instrument). Samples were heated from -60 °C to 160 °C to remove the thermal history, cooled to -60 °C, and finally heated to 160 °C at the rate of 10 °C min⁻¹ to determine the Tgs. The second cooling and heating were studied and reported. DSC was performed on PVAc fiber mats, neat Sylgard, and the bilayer ASMECs in order to measure the transition temperatures.
2.3.7 Mechanical Testing

To calculate the Young’s modulus of the PVAc fiber mats and the single and bilayer ASMECs, dog bones (ASTM D638 Type IV, scaled down by a factor of 4), with a gauge length of 6.25 mm and width of 1.5 mm, were cut from the samples. The dog bones from the PVAc fiber mats and single layer ASMECs were cut with $\theta = 0^\circ$, $22.5^\circ$, $45^\circ$, $67.5^\circ$, and $90^\circ$; and the dog bones were cut from the bilayer ASMECs with $\Delta \theta = 0^\circ$, $22.5^\circ$, $45^\circ$, $67.5^\circ$, and $90^\circ$. These angles correspond to the angle between the direction parallel to the fibers and the loading direction. The samples were stretched at 25 $^\circ$C using a Linkam TST350 tensile stress testing system at 33 $\mu$m s$^{-1}$ until failure. The Linkam system measures the force required to stretch the sample and the distance the sample has been stretched. From this data, stress-strain curves were generated. The stress was calculated using Eq. (2-1):

$$\sigma (\text{MPa}) = \frac{F}{A}$$

where $\sigma$ is the engineering stress, $F$ is the force (N), and $A$ is the cross sectional area of the sample prior to stretching (mm$^2$). The strain was calculated using Eq. (2-2):

$$\varepsilon (%) = \frac{\Delta L}{L} \times 100$$

where $\varepsilon$ is the engineering strain, $\Delta L$ is the distance the sample has been stretched (mm), and $L$ is the initial length of the sample prior to stretching (mm). The Young’s modulus was measured as the slope of the stress-strain curve in the linear, elastic region.

2.3.8 Reversible Plasticity Shape Memory (RPSM)

Reversible plasticity shape memory (RPSM) of single layer ASMECs were quantified using a Q800 TA Dynamic Mechanical Analyzer (DMA). A RPSM method was developed to describe
the reversal of elastic and plastic deformation upon a thermal stimulus. This method helps to understand and compare the fixing and recovery ratios of each single layer ASMEC with different θ relative to the direction of stretching at RT. Prior to testing, thermal histories of the samples were removed by heating to 60 °C for 20 min, followed by cooling to RT for 5 min. Dog bone specimens were cut at different θ using a dog bone die. For this experiment, the DMA was set to controlled force mode in a tensile configuration. A preload force of 0.001 N was used, and the sample was first equilibrated at 25 °C. After being held isothermal for 3 min, the sample was set to be stretched to 75 % strain by ramping the force at 0.02 N min⁻¹ (Step 1). In the stretched state, the sample was held isothermal for 1 min and then the force was ramped to 0.001 N at a rate of 0.05 N min⁻¹ for unloading (Step 2). The sample was again held isothermal for 1 min, after which the temperature was ramped at 2 °C min⁻¹ to 60 °C for shape recovery (Step 3). At 60 °C, the sample was held isothermal for 3 min to allow time for shape recovery. The temperature was then ramped at 2 °C min⁻¹ to 25 °C to complete the first SM cycle (Step 4). All steps were repeated two more times for a total of 3 RPSM cycles, and a minimum of 3 samples with each fiber orientation were tested. The degree of fixing (Rᶠ) and degree of shape recovery (Rʳ) were calculated for each cycle based on Eq. (1-1) and Eq. (1-2), respectively.

2.3.9 Curvature and Pitch Analysis of Mechanically Activated Shape Change

In order to determine the relationship between fiber orientation and the curling phenomenon, 30 (l) x 2.5 (w) mm rectangular strips were cut from the bilayer ASMECs. Typical sample thicknesses were between 0.6 and 0.7 mm. Using the Linkam system, the rectangular strips were stretched at a rate of 33 μm s⁻¹ at RT to strains of either 40, 50, 75, or 100 %. These
strains were chosen to study the breadth of curvature achieved under varying conditions. After reaching the desired strain, each specimen was unclamped, and the curling was observed. Images of the curled specimens were taken for further analysis.

In order to quantify the curling of the bilayers, pitch and radius of curvature were measured. Image J (Version 1.46), was used to obtain quantitative measurements for the pitch and radius of curvature. The pitch was obtained by measuring the distance between consecutive peaks or troughs of the curled sample, and the radius of curvature was obtained by measuring the diameter of the sample in its curled state and dividing by 2. The radius of curvature was converted to a normalized curvature for better comparison between samples, as will be discussed later. The normalized experimental curvature, $\kappa_{\text{exp}}$, was calculated as

$$\kappa_{\text{exp}} = \frac{t_1 + t_2}{R}$$  \hspace{1cm} (2-3)

where $t_1$ and $t_2$ (mm) are the thicknesses each ASMEC layer in the bilayer and $R$ (mm) is the measured radius of curvature.

2.3.10 Modeling of Curvature

From the extensive research that has been done on curling of bimetallic strips, it is known that the curvature of bilayers undergoing a mismatch strain is highly dependent on the thickness of each layer.\textsuperscript{16} For bimetallic strips, the following equation has been developed, relating the radius of curvature, $R$, to the flexural rigidity, $EI$, and the bending moment, $M$.

$$R(\text{mm}) = \frac{EI}{M} = \frac{E_1^2 t_1^4 + E_2^2 t_2^4 + 4E_1E_2t_1^3t_2 + 4E_1E_2t_1t_2^3 + 6E_1E_2t_1^2t_2^2}{6E_1E_2t_1t_2(t_1 + t_2)(\varepsilon_{T_1} - \varepsilon_{T_2})}$$  \hspace{1cm} (2-4)

with $E_x$, $t_x$, and $\varepsilon_{T_x}$ indicating the Young’s Modulus, the thickness, and the thermal strain of layer $x$, respectively. In our study, a mismatch in strain between the two layers arises from a
difference in the fixed strain after unloading the bilayer system rather than a difference in thermal strain. Therefore, Eq. (2-4) is modified to relate the radius of curvature to the fixed strain mismatch in the bilayer system, $\varepsilon_{fx}$, to obtain Eq. (2-5).

$$R(\text{mm}) = \frac{E_1^2 t_1^4 + E_2^2 t_2^4 + 4E_1 E_2 t_1^2 t_2 + 4E_1 E_2 t_1 t_2^3 + 6E_1 E_2 t_1^2 t_2^2}{6E_1 E_2 t_1 t_2 (t_1 + t_2)(\varepsilon_{f_1} - \varepsilon_{f_2})} \quad (2-5)$$

The fixed strain after stretching, $\varepsilon_{fl}$, for layer $i$ is given by

$$\varepsilon_{fl}(1) = \frac{R_{fi} \varepsilon}{100^2} \quad (2-6)$$

where $R_{fi}$ (%) and $\varepsilon$ (%) are the fixing ratio of layer $i$ and the strain to which the sample is stretched, respectively. In examining Eq. (2-5), it is clear that the radius of curvature has a complex dependence on the sample thickness. For the experiments conducted in this study, the thickness of each layer ($t_1, t_2$) was matched to be equal, $t_1=t_2=t$, and therefore Eq. (2-5) can be reduced to Eq. (2-7).

$$R(\text{mm}) = \frac{E_1^2 t + E_2^2 t + 14E_1 E_2 t}{12E_1 E_2 (\varepsilon_{f_1} - \varepsilon_{f_2})} \quad (2-7)$$

For comparison to the $\kappa_{\text{exp}}$, $R$ was converted to the normalized theoretical curvature, $\kappa_{\text{the}}$, using Eq. (2-8).

$$\kappa_{\text{the}}(1) = \frac{t_1 + t_2}{R} = \frac{2t}{R} = \frac{24E_1 E_2 (\varepsilon_{f_1} - \varepsilon_{f_2})}{E_1^2 + E_2^2 + 14E_1 E_2} \quad (2-8)$$

2.4 Results

Anisotropic PVAc fiber mats, single layer ASMECs, and bilayer ASMECs at different fiber angles were fabricated using the methods prescribed in the experimental section (Section 2.3) and shown in Scheme 2-1 and Scheme 2-2. Fiber mat and single layer ASMECs were tested at
various fiber orientations ($\theta = 0^\circ, 22.5^\circ, 45^\circ, 67.5^\circ, \text{ and } 90^\circ$). Similarly, the prepared bilayer ASMECs contained layers with fiber angles of $0^\circ/0^\circ$, $0^\circ/22.5^\circ$, $0^\circ/45^\circ$, $0^\circ/67.5^\circ$, and $0^\circ/90^\circ$ (top fiber orientation/bottom fiber orientation). Since each prepared bilayer had one layer with $0^\circ$ orientation, we will hereafter use the term “$\Delta \theta$” which refers to the difference in fiber angle between the two layers ($\Delta \theta = 0^\circ, 22.5^\circ, 45^\circ, 67.5^\circ, \text{ and } 90^\circ$).

Figure 2-1 shows representative SEM micrographs of an aligned PVAc fiber mat, single layer ASMEC, and bilayer ASMEC. SEM images of PVAc fiber mats were used to demonstrate the fiber alignment and to measure the average fiber diameters. In general, the fibers were all oriented in the same direction, with minimal outliers (Figure 2-1a). It is noted that the SEM image of the aligned fibers was taken at an angle, and therefore, the fibers appear to be oriented at a $45^\circ$ angle. The average PVAc fiber diameter was $0.81 \pm 0.21 \mu m$. A total of 150 measurements from two samples were used to calculate the average fiber diameter. SEM images of the single layer ASMEC showed a smooth layer of Sylgard on the surface (Figure 2-1b) and complete infiltration of Sylgard throughout the thickness of the fiber mat (Figure 2-1b and d). SEM images of the bilayer ASMEC cross sections showed a thin layer of Sylgard used for laminating the two layers (Figure 2-1e and f). Further, the cross sectional images showed that Sylgard provided good lamination, which is evident at the Sylgard-composite interface. It was necessary to measure the thin layer within the bilayer system to demonstrate its minimal effect on the curling phenomenon, as this will be discussed later. Based on measurements from 5 samples, the Sylgard thickness adhering the two lamina was calculated to be less than 16 % of the overall thicknesses of the bilayer ASMECs.
2.4.1 Thermal Analysis

The DSC first cooling and second heating traces for the PVAc fiber mat, neat Sylgard, and the bilayer composite can be seen in Figure 2-2. The measured glass transition temperatures (T_g) are 42 °C and 46 °C for the PVAc fiber mat and the bilayer composite, respectively. The T_g of Sylgard cannot be determined from the DSC results, but it is known to be -114 °C from prior studies.17 These results support the previous study from our group that showed the inclusion of a PVAc fiber mat within a Sylgard matrix raises the T_g.3

2.4.2 Mechanical Analysis

The Young’s moduli of the fiber mats and the single layer and bilayer ASMECs were measured using the Linkam TST 350 tensile stress testing system. Representative stress-strain curves for the aligned fibers and the single and bilayer composites for each fiber angle are shown in Figure 2-3. Figure 2-3a shows that a higher yield stress was attained for the fiber mats with fibers oriented at θ = 0°. In general, the yield stress decreased as the fiber orientation increased (from θ = 0° to θ = 90°) as a result of the reduced capacity of the fibers to bear the load when θ ≠ 0°. A similar trend was observed in the single layer ASMECs (Figure 2-3b). Notably, the maximum stress that was achieved for the single layer ASMEC was lower when compared to its fiber mat state. It is postulated that this decrease is due to the decrease in fiber volume fraction when Sylgard was infiltrated due to the increase in spacing between the anisotropic fibers. Figure 2-3c shows representative stress-strain curves for the bilayer ASMEC system and reveals that the yield stress did not show a clear dependence of fiber orientation. However, the bilayer ASMECs with Δθ = 0° and 22.5° exhibited the highest yield
stresses, suggesting, again, that higher stresses are achieved when fibers are oriented in, or close to, the direction of loading. More studies need to be conducted to study the mechanical nature of the bilayer system when uni-axially loaded.

In studying the initial slopes of the stress-strain curves, it is evident that the Young’s moduli of the PVAc fiber mats and single layer ASMECs decreased as \( \theta \) increased (Table 2-1). For \( \theta = 0^\circ \), the fibers are aligned in the direction of loading and bear the entire load, increasing the stiffness of the fiber mat. However, for \( \theta = 90^\circ \), the fibers are perpendicular to the loading direction and are being pulled apart from each other. Therefore, the fibers bear little load, decreasing the stiffness of the overall material. These two phenomena were also studied and observed by Rodriguez et al.\(^3\) The introduction of the elastomeric Sylgard, with an average Young’s modulus of 0.7 MPa, greatly altered the mechanical properties of the electrospun PVAc fiber mats, reducing the Young’s modulus by an order of magnitude. The fiber mats had Young’s moduli in the range of 20 - 200 MPa, and the single layer ASMEC had Young’s moduli in the range of 3 - 30 MPa. As stated prior, this decrease in mechanical properties is postulated to be due to the decrease in fiber volume fraction in the material because of significant dilation from the Sylgard intake into the fiber mat. The Young’s moduli for the bilayer system did not have a clear dependence on \( \Delta \theta \), and a narrow range of moduli was observed. The bilayer ASMECs with \( \Delta \theta = 0^\circ \) and 22.5° had the highest moduli at 17 MPa and the bilayer ASMEC with \( \Delta \theta = 45^\circ \) had the lowest modulus at 11 MPa. The lack of dependence on \( \Delta \theta \) may be explained by the complexity of the bilayer system, which will not be explored in the scope of the present study. In comparing the two composite systems, it was found that the single and bilayer ASMECs have Young’s moduli of the same magnitude; the single and bilayer ASMECs have
similar stress-strain behaviors during loading, but more investigation needs to be conducted to fully understand the tensile behavior of the bilayer system.

2.4.3 Reversible Plasticity of Single Layer Composites

A reversible plasticity shape memory (RPSM) method was used to characterize the shape memory properties of the single layer ASMECs as a function of $\theta$ relative to the direction of uni-axial stretching. Representative stress-temperature-strain 3D plots are shown in Figure 2-4. Upon uni-axially stretching at RT, which is below the $T_g$ of the PVAc fibers but above the $T_g$ of the Sylgard, each specimen was deformed both elastically and plastically. This deformation assists in further orienting the anisotropic fibers and drives the chain conformation to a lower entropy state. Upon unloading, the temporarily fixed deformation was measured and each specimen was heated to 60 °C to observe the shape recovery and then cooled to RT to complete the RPSM cycle.

The fixing ratio ($R_f$) was affected by plastic deformation of PVAc fibers below their $T_g$ and also depended on the angle, $\theta$, relative to the direction of uni-axial stretching. As $\theta$ increased from 0° to 90°, $R_f$ decreased from 85 % to 50 % under the effect of elastic contractile force of the Sylgard matrix that became dominant over the orientated fibers’ plastic deformation. Sylgard is an elastomeric rubber, as opposed to PVAc fibers that are glassy (amorphous) polymer fibers. Below the PVAc’s $T_g$, the fibers are able to prevent the elastomer matrix from contracting and returning to its high entropy state by reinforcing the composite. However, the ability to reinforce the composite diminishes when the fibers are oriented perpendicular, as opposed to parallel, to the loading direction. The recovery ratio ($R_r$) for all single layer ASMECs tested were found to be higher than 96 % for cycles two and three but as
low as 78 to 88 % for cycle one. Sylgard was tested as a control, and its fixing ratio was close to 0 % due to its elastic nature. Therefore, the recovery ration, as conventionally defined, could not be calculated. The \( R_f \) and \( R_r \) values are tabulated for each fiber orientation in Table 2-2.

2.4.4 Mechanically Programmed Shape Change of Bilayer ASMECs

Curvature in bilayer systems arises when a mismatch of strain between the two layers exists. For example, in substrate/coating systems a strain mismatch often arises when subjected to a temperature change due to differences in the thermal expansion coefficients of the substrate and coating,\(^{16}\) resulting in bending of the bilayer system. In the ASMEC bilayer systems reported herein, a mismatch in strain arises from the difference in the elastic recovery of each layer, resulting in bending of the bilayer. Scheme 2-3 demonstrates the effect of fiber orientation on the behavior of the single and bilayer ASMECs subjected to tensile deformation. In-plane rotation of the bilayers with different fiber orientations leads to helix formation.

The following characterization aims to relate the curvature and pitch to the fiber orientation of bilayer ASMECs. Each sample was first stretched uni-axially at RT to the desired strain using the Linkam tensile stage. The tensile load was varied to determine the level to which curvature and pitch depend on strain. Therefore, samples were stretched to either 40, 50, 75, or 100% strain. Remarkably, upon unclamping, a non-affine shape change occurred, as the samples changed from flat strips to helices. Attaining a similar shape change in typical SMPs requires both thermal control and manual manipulation of the SMP into the curled form. Thus, tensile mechanical programming at RT drastically simplifies the programming process. A representative set of images of curled bilayer ASMECs stretched to 40, 50, 75, and 100 % strain are shown in Figure 2-5. Inspection of these results quickly indicates mechanical (not thermo-
mechanical) programming of complex, 3D shapes, offering dramatic acceleration of shape forming processes from initially flat films. For $\Delta \theta = 0^\circ$, where the relative angle between the fibers and the stretching direction was 0° for both layers, the fixing ratios were the same. Therefore, there was no mismatch between the layers, and the sample remained straight post-stretching. On the other hand, for $\Delta \theta \neq 0^\circ$, the fixing ratio of each layer was different since there was a mismatch between the fixed lengths that led to a curled state. In studying the images in Figure 2-5, it can be seen qualitatively that the pitch and radius of curvature tend to decrease with increasing $\Delta \theta$.

After deforming four different samples to 40, 50, 75, and 100% strain, the curling was quantified by measuring the radius of curvature and pitch. The circles and lines drawn in Figure 2-6a demonstrate how the measurements of radius of curvature and pitch were obtained using ImageJ software. Analysis of the images revealed that the curvature was highly dependent on sample thickness, and therefore, the values were normalized (Eq. (2-3)) for comparison purpose to better observe the relationship between fiber orientation and curvature.

Figure 2-6b and c show the results for the pitch and normalized curvature as a function of fiber orientation. It is observed that the pitch decreases with increasing $\Delta \theta$ while the normalized curvature increases with increasing $\Delta \theta$. Therefore, a tighter curl was achieved when the difference in fiber orientation between the layers was maximized. The dependence on fiber orientation can also be explained in our RPSM observation discussed earlier. Note that no curvature measurements were reported for $\Delta \theta = 0^\circ$ since the samples remained in a flat state. Also the quantitative pitch analysis for the $\Delta \theta = 22.5^\circ$ at 40% strain was not reported because at lower strain the specimens made less than one complete curl. Therefore, the distance between
consecutive peaks or troughs could not be measured. In addition to the dependence on $\Delta \theta$, the pitch and normalized radius showed a dependence on strain; the normalized curvature increased and the pitch decreased with increasing strain. It is noted that, for all cases, the curled bilayers activated by strain at RT are recoverable to their equilibrium, flat state by heating above PVAc’s $T_g$ (Scheme 2-3b).

### 2.4.5 Comparing Theoretical Predictions of Curvature to Experimental Results

The observation of non-affine shape programming is very different from those demonstrated in most SMPs to date where a programmed shape shows affinity to the applied mechanical deformation. For example, an applied stretching deformation programs the SMP into a stretched shape. The non-affine shape change opens a new design space for a wide range of potential applications, but at the same time imposes challenges on how to achieve desired shape change. Eq. (2-8) was used to predict the normalized curvature of the bilayer ASMECs, and the calculated values were compared to our experimental data (Figure 2-7). For both the experimentally measured and theoretically calculated normalized curvature, a trend of increasing curvature with increasing $\Delta \theta$ is observed. Furthermore, the curvature increases with increasing strain programmed into the bilayer. While the experimentally measured values agree well with the predicted values from the model, some inaccuracies may arise from the assumptions made in applying the model. As mentioned previously, and as seen from Eq. (2-8), the radius of curvature is highly sensitive to the thicknesses of each laminae. Therefore, even slight differences in the thickness of each layer, which were disregarded when making the assumption that each layer was equal to half of the total thickness of the bilayer sample, could contribute to the discrepancy between the theoretical and experimental results. Due to the
Poisson effect, these thickness values also change based on the strain induced into the bilayer system, which is not accounted for in the model. Additionally, the Sylgard layer that adheres the two layers together may add to the complexity of the composite, causing it to behave as a tri-layer system. Further studies are required to test this hypothesis. Nevertheless, the model was able to predict the trend in curvature that was seen in the bilayer ASMEC system. A more complex model, designed specifically for this system, has been developed by collaborators at Georgia Tech. Since the model accounts for the mechanical nature of the ASMEC system, it more accurately predicted the curvature and has the added ability to predict the pitch.

2.4.6 Bilayer ASMEC Shapes

Given the observed dependence of curling on the fiber orientation, we realized a potential for the construction of interesting 3D structures simply by cutting shapes out of a bilayer ASMEC sheet using lines selected strategically relative to the anisotropy directions. Using a sheet with $\Delta \theta = 90^\circ$, a 3-pronged “propeller”, a triangle, and a circle were cut from the mat. The orientation of cutting for each shape is shown in Figure 2-8a. Each prong of the propeller and each side of the triangle was stretched individually. The circle was stretched in small segments, working around the shape. The arrows in Figure 2-8a indicate stretching for each shape. Photographs of the shapes prior to deformation and of the 3D structures obtained after the mechanically programmed shape change are shown in Figure 2-8b and c, respectively. For the propeller, the prong with fiber orientations of $0^\circ/90^\circ$ (with respect to the stretching direction), curled after deformation with no pitch. This is consistent with the results reported previously. The two prongs cut diagonally across the mat have fiber orientations of $+60^\circ/-30^\circ$ and $-60^\circ/+30^\circ$ relative to the axes of the prongs. Here, a sign convention was adopted since
one layer is no longer in the 0° direction. After deformation, these two prongs curled and formed helicoids due to the difference in recovery between the two layers. Furthermore, each helicoid is roughly a mirror image of the other due to the opposite signs in the fiber orientations. For the triangle, one side had fiber orientations of 0°/90°. Since an equilateral triangle was cut, the other two sides, again, had fiber orientations of +60°/-30° and -60°/+30°. After deformation, all sides curled, but were constrained at the ends due to the connection to the other sides of the triangle. The 0°/90° side formed an arch shape, and the +60°/-30° and -60°/+30°, which would have formed helicoids if unconstrained, curled back towards the third side. Finally, a circle was cut from the bilayer ASMEC with $\Delta \theta = 90°$. After deformation, the circle formed a saddle-like structure, with arches forming through the segments where the tangent to the circle is parallel to one of the fiber orientations (and perpendicular to the other). The concavity of the arch depended on the position of the layer with a relative fiber orientation of 90°. As explained previously, due to the lower fixing of a 90° layer compared to a 0° layer, the bilayer curls towards the 90° ply. All 3D shapes recovered to their flat forms upon heating above the $T_g$ of PVAc. It is clear that more interesting 3D structures can be obtained by adjusting the initial cut shape and varying the fiber orientations of the layers.

2.5 Conclusions

A unique anisotropic SM composites that can be mechanically programmed from 2D films to 3D complex shapes at RT was introduced. Achieving the non-affine shape change with a simple tensile programming step is atypical for SMPs, which normally require significant manipulation and thermal control to achieve such a drastic shape change. This unique characteristic can be used for fabrication of composites with predictable SM behavior that
target specific biomedical and aerospace applications. Furthermore, the programmed 3D shape can be triggered to return to its equilibrium, flat shape by heating through the T_g of PVAc, adding the advantages of reversibility and repetitive programming. Results showed dependence of Young’s modulus on fiber orientation for anisotropic PVAc fibers and for single and bilayer ASMEC systems. RPSM was used to quantify the dependence of fixing and recovery on the fiber angle for single layer composites. Due to the dependence of fixing on the fiber orientation, mechanically programmed bilayer ASMECs curled, and the pitch and radius curvature were analyzed qualitatively and quantitatively for all fiber orientations deformed to various strains. The radius of curvature and pitch decreased in response to a mismatch in strain caused by an increase in Δθ. A simple theoretical model was developed to predict the observed dependence of shape fixity, curvature, and pitch on the fiber orientation and applied strains and showed good agreement with experimental data. These mechanically programmed shape memory elastomeric composites are a class of smart, soft materials that can be used in aerospace, active cell culture,19 stent, and catheter20 applications.

2.6 References


Scheme 2-1 (a) Electrospinning setup used to electrospin aligned PVAc fibers. The addition of the copper plate creates a more uniform electric field that influences the direction of the jet, promoting fiber alignment. (b) Cross-section of the charged copper plate showing the relative placement of the needle and the plate. The syringe needle is placed through a hole (6 mm diameter) in the plate with approximately 1 cm of the needle extending through the hole. Schematic is not to scale.
Scheme 2-2 Fabrication of single layer and bilayer anisotropic shape memory elastomeric composites (ASMECs). Aligned PVAc fibers were electrospun and subsequently infiltrated with Sylgard to form the single layer ASMECs. Square sections with various fiber orientations ($\theta$) were adhered with a layer of Sylgard between them to form the bilayer ASMECs.
Figure 2-1 SEM micrographs of (a) aligned PVAc fiber mat, (b) single layer ASMEC surface, (c) single layer ASMEC perpendicular cross-section, (d) single layer ASMEC parallel cross-section, (e) bilayer ASMEC perpendicular cross-section, and (f) bilayer ASMEC parallel cross-section. It is noted that the SEM image of the aligned fibers was taken at an angle.
Figure 2-2 DSC first cooling and second heating curves for (a) a PVAc fiber mat, (b) neat Sylgard, and (c) an ASMEC bilayer composite. The measured glass transition temperatures ($T_g$) are 42°C and 46°C for the PVAc fiber mat and the bilayer composite, respectively. The $T_g$ of Sylgard cannot be determined from the DSC results, but it is known to be -115°C from prior studies.
Figure 2-3 Representative stress-strain curves (first column) and magnified views of the elastic deformation (second column) for (a) anisotropic PVAc fiber mats (b) single layer composites, and (c) bilayer composites with fiber orientations ($\theta$ or $\Delta \theta$) of 0° (black), 22.5° (red), 45° (green), 67.5° (blue), and 90° (pink). Noise in the magnified views of (a) and (b) is due to the small thicknesses of the fiber mats and single layer ASMECs and the limited resolution of the Linkam system. The vertical dotted lines in (c) indicate strains to which the bilayer composites were stretched for mechanically activated shape change.
Table 2-1 Average Young’s modulus values for PVAc fiber mats, single layer ASMECs, and bilayer ASMECs.

<table>
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<tr>
<th>$\theta/\Delta\theta$ (°)</th>
<th>E (MPa), Fiber Mat</th>
<th>STDEV</th>
<th>E (MPa), Single Layer A-SMEC</th>
<th>STDEV</th>
<th>E (MPa), Bilayer A-SMEC</th>
<th>STDEV</th>
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<td>17.4</td>
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<td>1.3</td>
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</tr>
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<td>5.5</td>
<td>1.1</td>
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<td>3.9</td>
<td>0.6</td>
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**Figure 2-4** Reversible plasticity shape-memory (RPSM) 3D plots of single layer ASMECs with fiber orientation angles of: (a) 0°, (b) 22.5°, (c) 45°, (d) 67.5°, (e) 90°, and (f) neat Sylgard. Each plot shows three cycles. Projection of cycles onto strain vs. stress and strain vs. temperature planes are shown. Samples were loaded at RT (1), unloaded at RT for fixing (ii), heated to 60 °C for recovery (iii), and cooled to RT (iv).
Table 2-2 Average fixing ($R_f$) and recovery ($R_r$) ratio measurements from the three cycles of the reversible plasticity shape-memory (RPSM) analysis of single layer ASMECs with different fiber angles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cycle</th>
<th>$R_f$ (%)</th>
<th>STDEV</th>
<th>$R_r$ (%)</th>
<th>STDEV</th>
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<td>4</td>
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Scheme 2-3 (a) Diagram showing the effect of stretching a single layer ASMEC. The angles $\theta$ and $\varphi$ are indicated and represent the fiber angle and the in-plane rotation angle, respectively. (b) Diagram showing the effect of stretching a bilayer ASMEC. Upon unloading, the fixing mismatch in bilayer ASMECs leads to the curvature phenomenon. There is no mismatch between the layers for $\Delta \theta = 0^\circ$ which leads to a straight sample post stretching. Alternatively, different curvatures are observed for $\Delta \theta \neq 0^\circ$ due to the mismatch between the layers. The curled sample in (b) had $\Delta \theta = 45^\circ$. Upon heating, all samples return to their original shape. Scale bars represent 5 mm.
Figure 2-5 Representative images of curled bilayer ASMECs stretched to a) 40, b) 50, c) 75, and d) 100 % strain indicating the pitch in the corresponding top row and the radius of curvature in the bottom row. Δθ is indicated in the top left corner of each image. Scale bars represent 4 mm.
Figure 2-6 (a) Representation of the method used to experimentally measure the curvature and pitch. (b) Average experimental measurements for normalized curvature as a function of $\Delta \theta$. (c) Average experimental measurements for the pitch as a function of $\Delta \theta$. The bilayer ASMECs were stretched to 40 (red), 50 (green), 75 (blue) and 100 (pink) % strain.
Figure 2-7 Comparison of the experimental (----●--) and theoretical (--■--) results for normalized curvature as a function of $\Delta \theta$ for bilayer ASMECs stretched to 40 (red), 50 (green), 75 (blue) and 100 (pink) % strain.
Figure 2-8 3D structures obtained from cutting shapes out of a bilayer ASMEC sheet with $\Delta \theta = 90^\circ$. Images show (a) a schematic of the cutting (solid lines) and stretching (arrows) orientations, (b) the shapes prior to deformation, and (c) the 3D structures obtained after mechanically programmed shape change for (i) the propeller, (ii) triangle, and (iii) circle.
Chapter 3. Dual-Spun Thermoplastic Shape Memory Elastomeric Composites

3.1 Synopsis

This chapter aims to develop a scalable method to fabricate shape memory elastomeric composites (SMECs). Previously developed SMEC fabrication methods utilize processing techniques that impose limitations on the SMEC’s production at a larger scale. The multi-step method involves labor-intensive processing steps and requires up to several days for complete fabrication. The current work presents a simple strategy to prepare SMECs more efficiently and with more control over the composition, thus allowing for adjustment of material properties to meet requirements for a variety of applications. The dual-electrospinning approach provides further versatility in that it can be applied to fabricate composites consisting of any combination of electrospinnable polymers. In this chapter, the feasibility of fabricating SMECs via dual-electrospinning is investigated, and control of the thermal, mechanical, and shape memory properties through composition is demonstrated. Two SMEC systems are compared, in part, to exemplify the versatility of the approach. In other words, components can be chosen for specific properties which lead to unique functionality of the composite. In this case, poly(ε-caprolactone) was chosen for its reversible adhesive properties.

3.2 Introduction

Soft SMPs lend themselves to a broad range of applications. Most commonly, soft SMPs are sought for biomedical applications, in which they are used in devices such as stents,\textsuperscript{1-3} vascular grafts, and surgical sutures.\textsuperscript{4} In such instances, SM is exploited to reduce the invasiveness of the medical procedure necessary to place the device. The SMP device can be
rolled, folded, or compressed to reduce its size, easing the maneuvering and placement process. Further, for soft SMPs, a low modulus is advantageous, as it more closely matches the mechanical properties of native tissue in the body. Beyond medical applications, soft SMPs have also found applications in actuators, textiles, and self-healing materials.

The need for a switching mechanism, which is used to lock in the temporary shape and later allow recovery of the permanent shape, imposes limitations in material properties of SMPs. Commonly utilized \( T_g \)-based SMPs rely on chain vitrification to fix the temporary shape, and chain entanglements (in sufficiently high molecular weight polymers) serve as physical crosslinks, enabling shape recovery upon heating. However, vitrification and shape fixing are accompanied by a 1-2 order of magnitude increase in modulus. Consequently, the modulus of such an SMP in the fixed state is around 1-10 GPa, or about 2-5 orders of magnitude higher than the modulus of soft tissue. In many cases, the modulus of an implanted medical device needs to closely match the mechanical properties of the surrounding tissue so as to impose minimal damage and to allow healing.

Recently, researchers have sought to develop soft, elastic systems with shape memory capabilities. Significant efforts have been made in the fields of liquid crystalline elastomers, shape memory hydrogels, block copolymers, and polymer composites. Luo et al. developed a composite system in which a silicone elastomer was used to imbibe a web of polymer fibers. Specifically, the polymer system (the precursor to the system used in Chapter 2) was composed of polydimethylsiloxane (PDMS; Sylgard 184) and poly(e-caprolactone) (PCL), a semi-crystalline polymer with a \( T_g \) below RT. The crosslinked PDMS formed a matrix around electrospun PCL fibers, and the SM was performed around PCL’s \( T_m \). Encasement of the PCL in
the PDMS allowed the composite to maintain its form when heated above PCL’s $T_m$. Moreover, recrystallization of the PCL after deformation counteracted the elastic contraction of the PDMS matrix, allowing the composite to fix a temporary shape. To trigger recovery of the composite, the PCL was remelted, allowing contraction of the elastic matrix.

While the soft and elastic PDMS/PCL system introduced by Luo et al.\textsuperscript{18} exhibited excellent mechanical and SM properties, the crosslinked PDMS restricts its widespread use. Firstly, crosslinked polymers by nature, are thermosets, or polymers whose shapes, once set, cannot be redefined (Note: Here, “shape” is referring to the permanent form of the polymer, not a temporary shape held in a SM cycle.). Such a property imposes manufacturing limitations, as thermosets cannot be processed via extrusion or injection or compression molding, for example. While the PDMS was applied in its liquid precursor state, once the components are mixed, the crosslinking process begins. Therefore, there is a usable lifetime, or “pot life”, in which the viscosity of the mixture is low enough for processing. Heat can accelerate curing, further limiting the available processing methods. Moreover, the process used to apply the PDMS is relatively labor intensive and time consuming, making it non-ideal for commercial manufacturing; a spatula was used to spread and remove excess PDMS, requiring careful attention not to damage the fiber mat. Further, the curing process used to crosslink the PDMS required more than 48 h, which is, again, non-ideal for commercial manufacturing. Ultimately, the PDMS is not a biodegradable polymer, and in many instances, both biocompatibility and biodegradation are required to eliminate the need for a secondary device-removal surgery.
Here, we aim to develop a composite system with similar material properties (low
modulus, high extensibility, and shape memory capabilities) that is fabricated using easily
scalable methods for commercial manufacturing. We turn to dual-electrospinning and hot
compaction to prepare the shape memory elastomeric composites (SMECs). The dual-
electrospinning process,\textsuperscript{21-22} which simultaneously electrospins two polymers, one aiding in
fixing and the other providing the “memory”, is advantageous in that not only is it industrially
relevant, but it also allows for tuning of the relative composition of the two polymers.
Furthermore, it can easily be applied to fabricate composites using any two electrospinnable
polymers, therefore broadening the range of achievable properties.\textsuperscript{23} For the current work,
two systems have been studied, one composed of PCL and a synthesized thermoplastic
polyurethane elastomer (TPU), and the other composed of PCL and Pellethane® 5863-80A, a
commercially available TPU. The thermal, mechanical, and shape memory properties of the
two SMEC systems are compared in the subsequent sections. Furthermore, the reversible
adhesive performance, a unique property of some PCL-containing systems, has been studied for
the SMEC prepared with the synthesized TPU.

Reversible adhesives are materials that can be used to adhere two surfaces and later be
triggered to release, or debond.\textsuperscript{24-26} PCL has been shown to exhibit excellent adhesive
properties when crystallized on the surface of the material to which it is meant to be
adhered.\textsuperscript{25, 27} However, PCL itself, is not a good reversible adhesive, because when it is
remelted, though it will allow easy debonding between two surfaces, the liquid PCL remains on
the surface of the contacting materials. By incorporating the PCL into a composite, liquid PCL
can more easily be lifted from the surface, though remaining residue is probable. Luo et al.
developed a rigid reversible adhesive composed of epoxy and PCL. A highly interconnected 2-phase system was achieved through polymerization induced phase separation. When heated through PCL’s T_m, due to greater thermal expansion by PCL than by the epoxy, the PCL “bled” from the composite and enriched the surface. Upon recrystallization, the composite displayed excellent bonding ability, with bond strengths reaching 600 N cm^{-2}. Alternatively, Xie and Xiao utilized a composite system with shape memory capabilities to assist in delaminating the adhesive from the contacting surface. The rigid adhesive, with a permanently curved shape, was fixed into a temporary flat shape. After adhering to a surface, recovery of the permanent shape assisted in peeling the adhesive from the surface. However, the attained bond strengths were significantly lower than the system developed by Luo et al. and plateaued at around 60 N cm^{-2}. Here, we introduce a soft reversible adhesive with similar capabilities, but with the added benefit of being able to conform to the shape of the adhering surface due to its flexible nature. Furthermore, the shape memory properties were exploited to assist in delamination of the reversible adhesive.

3.3 Experimental

3.3.1 Materials

Poly(ε-caprolactone) (M_n = 70 – 90 kg mol^{-1}), hexamethylene diisocyanate (HDI), dimethylformamide (DMF), and deuterated chloroform (chloroform-D) were purchased from Sigma Aldrich. Toluene, n-hexanes, chloroform, tetrahydrofuran (THF), and acetone were purchased from Fisher. Isobutyl tin POMS® and 1,2-propane diol isobutyl polyhedral oligomeric silsesquioxane (POSS) were purchased from Hybrid Plastics. Poly(ε-caprolactone) diol (PCL1k,
MW = 1.25 kg mol⁻¹) was purchased from Polysciences, Inc., and Pellethane® 5863-80A was kindly supplied by Lubrizol Corp. PCL1k, POSS, and isobutyl tin POMS were dried in a RT vacuum oven (ca. 760 mm Hg) for 24 h and toluene was distilled prior to use. All other materials were used as received.

3.3.2 Thermoplastic Polyurethane Elastomer Synthesis

A 70:30 mass ratio PCL1k-POSS multiblock polyurethane (hereafter, “POSS-TPU”) was synthesized in a simple one pot reaction. Within a dried Schlenk flask and under a N₂ purge, the PCL1k and POSS were dissolved in toluene to obtain a 10 % (w/v) solution. After heating to 50 °C, HDI was added to obtain a 0.95:1 molar ratio HDI:monomer. Additionally, 0.1 wt% (relative to the mass of monomer) isobutyl tin POMS (catalyst) was added, and the solution was heated to 100 °C. HDI was subsequently added in 12 µL increments over a period of 3 days to reach a final molar ratio of HDI:monomer of 1.05:1. Incremental addition of HDI was used to maximize the molecular weight of the synthesized polymer. The toluene solution containing the polymer was cooled to room temperature and then precipitated in n-hexanes (1:4 volume ratio toluene:n-hexanes) over a bath of cold acetone and dry ice. Excess toluene and n-hexanes was poured off, and the precipitated POSS-TPU was washed with DI water to remove any water soluble contaminants. The POSS-TPU was then dried at 40 °C for 2 days and further dried in a RT vacuum oven (ca. 760 mm Hg) for 24 h to remove any excess solvent. The reaction scheme is provided in Scheme 3-1.
3.3.3 Synthesis Characterization

The molecular weight of the synthesized POSS-TPU was determined using gel permeation chromatography (GPC). The GPC setup was equipped with a Waters 2414 refractive index detector and a Wyatt miniDAWN TREOS light scattering detector. A dilute solution of the POSS-TPU was prepared by dissolving 2-4 mg POSS-TPU in 1 mL THF, and a 30 µL injection of the filtered (0.2 µm PTFE filter) solution was run through the polystyrene separating column (ResiPore©) for 30 min. Peaks in light scattering and refractive index were analyzed using Astra 5.3.4 software to determine the average molecular weight of the synthesized POSS-TPU.

Proton nuclear magnetic resonance spectroscopy (1H NMR, Bruker Avance III HD 400 MHz spectrometer equipped with a 5 mm outer diameter Prodigy probe) was used to determine the relative incorporation of PCL1k and POSS in the synthesized POSS-TPU. Approximately 10 mg POSS-TPU were dissolved in 1 mL chloroform-D, and the solution was exposed to a standard 1D pulse sequence with a 30° pulse and a relaxation delay time of 1 s. The 1H NMR chamber temperature was 25 °C.

3.3.4 Dual-Electrospinning Method

A dual-electrospinning setup (Scheme 3-2) was used to simultaneously electrospin two polymers for SMEC fabrication. Here, both polymers were electrospun and collected on the same mandrel to obtain a well-dispersed composite fiber mat. The two syringes containing the polymer solutions were placed on opposite sides of the mandrel in order to minimize effects from interaction of the electric fields. The tip-of-the-needle-to-mandrel distances were kept
constant at approximately 6 cm for all fiber mats. The flow rates of the syringes were controlled by separate pumps, and thus could be set independently, allowing for control over the relative weight fraction of each polymer in the composite fiber mat.

Two types of SMECs were fabricated for this study: one composed of PCL and the synthesized POSS-TPU and the other composed of PCL and Pellethane® 5863-80A (hereafter, “Pellethane”). Additionally, for each type, the weight percentage of PCL in the SMEC was varied from 0 to 40 wt% in order to examine the effect of composition on the thermal, mechanical, and shape memory properties of the SMECs. To obtain the desired weight fraction of PCL in the SMEC, the electrospinning parameters were adjusted accordingly. Table 3-1 lists the compositions of the electrospinning solutions and the voltages and flow rates used to dual-spin the SMECs.

3.3.5 Film Formation

A Carver 3851-0 hot press was used to compression mold the SMEC films from the dual-spun fiber mats. The fibers were first folded over on themselves several times to achieve a thicker stack of fibers (~1 mm thickness). The stack was loaded in the press at room temperature and then heated to 80 °C to melt the PCL. A 1 metric ton force was applied after this heating to compress the film and ensure complete infiltration of the PCL in the elastomeric fibers. After 15 min, the pressure was released to minimize compression of the elastomer fibers, and the film was slowly cooled to RT.
3.3.6 Preparation of Blended SMECs

Blended SMECs were prepared via solvent casting and compression molding for comparison to the dual-spun SMECs. PCL and Pellethane polymer pellets (used as received) were dissolved in a 60:40 THF:DMF volume ratio solution to obtain a 10 % (w/v) solution. The relative weight fractions of PCL and Pellethane were varied to match those of the dual-spun SMECs and to study the range of attainable properties. To ensure complete dissolution and mixing of both polymers, the solution was stirred overnight at RT. Once completely mixed, the solution was poured into a Teflon® dish, and the solvent was allowed to evaporate for 2 days. The dish containing the polymer solution was heated to 40 °C to accelerate solvent evaporation. The blended polymer film was dried in a RT vacuum oven (ca. 760 mm Hg) overnight to remove any residual solvent. For better comparison to the dual-spun SMECs and to improve the uniformity of the films, the solvent cast PCL/Pellethane films were subsequently compression molded at 160 °C for 15 min under 1 metric ton applied load. The films were slowly cooled to RT.

3.3.7 Thermal Analysis

A TA Instruments Q500 Thermogravimetric Analyzer (TGA) was used to observe changes in the degradation profiles of the SMECs with increasing PCL content and to estimate the PCL weight percentages. A high resolution program was used to better distinguish degradation events. The heating rate is variable and depends on the instantaneous weight loss rate. If the sample weight is stable, the heating rate is high, with a maximum at the set value. As the rate of weight loss increases, the heating rate is decreased. Maximum heating rate of 20 °C min\(^{-1}\)
and 50 °C min⁻¹ were used to for the PCL/POSS-TPU and PCL/Pellethane SMECs, respectively, and a resolution number of 4 and a sensitivity value of 1 were used for both systems.

High resolution TGA was used to estimate the weight fraction of PCL in the composites since it separates degradation events. In this work, the end of a degradation event has been defined as the point where the heating rate reaches a peak, i.e. since the rate of weight loss is at a minimum, the heating rate reaches a maximum. At a given point, a comparison of the remaining weight fraction of a SMEC to those of the neat components, gives the percentage of PCL in the composite. More specifically, Eq. (3-1) was used to estimate the composition of the SMECs:

$$w_{SMEC} = x \cdot w_{PCL} + (1 - x)w_{elastomer}$$  \hspace{1cm} (3-1)

where $w$ is the remaining weight fraction of the specified component and $x$ is the PCL weight fraction.

A TA Instruments Q200 Differential Scanning Calorimeter (DSC) was used to determine the transition temperatures of the SMECs and to again estimate the weight percentage of PCL in the SMECs. DSC cycles were run from -80 °C to 150 °C for the PCL/POSS-TPU SMECs and from -80 to 200 °C for the PCL/Pellethane SMECs. All heating and cooling rates were 10 °C min⁻¹. The second heating cycles were analyzed so that all samples had similar thermal histories. The weight percentage of PCL in the SMEC was estimated by comparing the heat of melting, $\Delta H_m$, of the neat PCL with the heat of melting of the PCL in the SMEC:

$$\text{wt}\% \text{ PCL} = \frac{\Delta H_{m,SMEC}}{\Delta H_{m,PCL}} \cdot 100$$  \hspace{1cm} (3-2)
3.3.8 Scanning Electron Microscopy

Scanning electron microscopy (SEM; JEOL JSM-5600) was used to study the morphology of the fibers and SMECs. SEM analysis was performed on the as-spun composite fibers, the dual-spun SMEC surfaces, the dual-spun SMEC cross-sections, and the blended SMEC surfaces. Surfaces were gold sputtered for 45 s prior to visualization to enhance image quality. Typically, an accelerating voltage of 8 kV and a working distance of 20 mm were used for imaging.

3.3.9 Wide Angle X-ray Scattering

To study the nanostructure of the SMECs, wide angle X-ray scattering was employed. A Rigaku generator (MicroMax-002+) was used with an accelerating voltage of 45 kV and a current of 0.88 mA to produce X-rays with a wavelength of 1.5405 Å. Under vacuum, samples were exposed to radiation for 1 h. The sample-to-detector distance was fixed at 122.7, resulting in scatter angles in the range of $5^\circ < 2\theta < 40^\circ$. A FujiFilm FLA7000 reader was used to collect the scattered X-ray diffraction patterns, and SAXSgui software (version 2.03.04) was used for analysis.

3.3.10 Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) was performed on the SMECs and their components using a TA Instruments Q800 dynamic mechanical analyzer. Dog bone (ASTM D638, 1/4-scale) samples were cut from the films with a custom made punch (Test Resources, Inc.). Each sample was quenched to -70 °C, held isothermally for 10 min, and then heated at 3 °C min$^{-1}$ to 160 °C. An oscillatory stress was applied with a frequency of 1 Hz and a displacement amplitude of 15 µm.
3.3.11 Tensile Testing

A Test Resources Model 100P Universal Testing Machine was used to measure the Young’s moduli of the SMECs and their components at room temperature. Dog bone (ASTM D638, ¼-scale) samples were stretched at 33 µm s⁻¹ to failure. Stress-strain curves were generated, and the Young’s modulus was calculated from the stress and strain data in the linear region of the curve using Eq. (3-3):

$$E(\text{MPa}) = \frac{d\sigma}{d\varepsilon}$$ (3-3)

where $E$ is the Young’s modulus, $\sigma$ is the engineering stress, and $\varepsilon$ is the engineering strain.

3.3.12 Shape Memory Testing

The shape memory properties of the SMECs were investigated using the DMA in controlled force mode. Dog bone (ASTM D638, ¼-scale) shaped samples were stretched at 60 °C to 20 % strain by ramping the force at 0.02 N min⁻¹. The temperature was then ramped at 3 °C min⁻¹ to 20 °C and held isothermal for 10 min, fixing the sample more or less. The sample was then returned to the unconstrained state by ramping the force at 0.05 N min⁻¹ to 0.001 N (preload force). To recover the permanent shapes, the samples were heated at 3 °C min⁻¹ to 80 °C. This cycle was repeated two times to yield a three-cycle shape memory program. The fixing and recovery ratios for each cycle were calculated using Eqs. (1-1) and (1-2).

3.3.13 Reversible Adhesive Testing

The adhesive properties of the PCL/POSS-TPU SMECs were characterized using the compression DMA in controlled force mode. Disc shaped samples (4.76 mm diameter) were
placed between polished (600 grit) steel compression clamps. At 20 °C, the force was ramped at 0.5 N min\(^{-1}\) to 1 N. The temperature was then ramped at 5 °C min\(^{-1}\) to 70 °C to melt the PCL. After a 10 min isothermal hold, the temperature was cooled back to 20 °C at 3 °C min\(^{-1}\). The temperature was held at 20 °C for 10 min to allow time for the PCL to crystallize, adhering the SMEC to the clamps. The apparent pull-off strength was measured by unloading the sample at 0.5 N min\(^{-1}\). After reaching an equilibrium point (0 N force), the force ramping continued, putting the sample into tension. At the point that the force applied by the clamps overcame the adhesive strength, the SMEC delaminated from the clamp. The sample thickness and force were recorded throughout the experiment, and at the point of delamination, an apparent and dramatic increase in thickness was observed, as the clamps were suddenly separated. The measured force at that point was divided by the initial cross-sectional area (0.18 cm\(^2\)), to calculate the apparent pull-off strength. The SMECs with varying PCL content were tested to reveal the effect of composition on the adhesive strength. Furthermore, for the SMEC containing 12 wt% PCL, the effect of the applied load was studied. In this case, the initial force was varied between 0.1 (preload force) and 3 N. The steel clamps were cleaned between each run with acetone and a Kimwipe® to remove any residual PCL on the surface.

The SMECs’ adhesion, which relies on PCL crystallization, can be reversed by melting the PCL. Therefore, the *reversible* adhesive properties were studied by altering the method previously described. After crystallizing the PCL, the temperature was again ramped at 5 °C min\(^{-1}\) to 70 °C, remelting the PCL. To ensure the PCL was fully melted, the sample was held at 70 °C for 10 min before the force was unloaded to measure the apparent pull-off strength at the elevated temperature.
The SM properties of the SMECs were exploited to further enhance the reversibility of the SMECs’ adhesion. A rectangular strip (18 (l) x 4.5 (w) x 1 mm (t)) of the SMEC containing 12 wt% PCL was first fixed into a temporary elongated shape. The SM method used was similar to that detailed in Section 3.3.12, except 50% strain was programmed and the sample was removed in the fixed state, i.e. it was not heated to 80 °C after programming. Squares (4 mm (l)) were cut from the strained rectangle and the reversible adhesive test described previously was used to measure the pull-off strength of the SMECs.

3.4 Results

3.4.1 Synthesis Characterization

A PCL1k-POSS TPU was synthesized for dual-electrospinning SMECs. The POSS-TPU, which precipitated in long, stringy sections, was analyzed with GPC and $^1$H NMR after drying to determine the molecular weight and relative incorporation of the constituents. A high molecular weight was necessary in order for the POSS-TPU to provide sufficient elasticity for shape recovery and to allow for high elongation. The influence of molecular weight on elasticity and strain-to-failure is studied in more detail in Appendix 1. Mechanical Properties of PCL1k and POSS-Based Thermoplastic Polyurethane Elastomers. From GPC analysis, a high molecular weight was confirmed. The $M_w$ was 300 kg mol$^{-1}$ with a relatively low polydispersity index of 1.67.

$^1$H NMR was used to compare the relative incorporation of the PCL1k and POSS to the intended composition (70:30 PCL1k:POSS mass ratio). The obtained spectrum is provided in Figure 3-1. Figure 3-1 also includes the chemical structure of the POSS-TPU and indicates the
protons and corresponding peaks used in analysis. Namely, the ratio of the normalized signals at 2.3 and 0.6 ppm gave the molar ratio PCL1k to POSS which was then converted to a mass ratio. Comparison indicated a slightly higher incorporation of PCL1k than POSS, with a calculated mass ratio of 77:23.

3.4.2 Thermal Analysis

High resolution TGA was used to compare the thermal stabilities of the SMECs and to estimate the weight percentage of PCL in the SMECs. The high resolution TGA profiles are provided in Figure 3-2. All SMECs were stable high temperatures and did not experience mass loss until above 250 °C. For estimation of the composition, the degradation events of the SMEC components would ideally occur at different temperatures, with one component degrading completely prior to the degradation of the other component. However, in the case of the PCL/POSS-TPU and PCL/Pellethane SMECs, the degradation profiles are more complex. The neat POSS-TPU degraded almost completely at around 280 °C, and the neat PCL degraded almost completely at around 350 °C. While it was expected that two degradation events would occur for the PCL/POSS-TPU SMECs (one at 280 °C and the other at 350 °C), only one degradation step was observed at around 290 °C. This result is hypothesized to be a kinetic effect. Since the heating rate slowed as the POSS-TPU began degrading, the SMECs remained at ~290 °C for the duration of the POSS-TPU degradation. This increased time at the elevated temperature (compared to the neat PCL which maintained at faster heating rate until around 350 °C) was sufficient for PCL degradation to also begin. For this reason, a slower maximum heating rate was chosen (20 °C min⁻¹ compared to 50 °C min⁻¹ for the PCL/Pellethane SMECs) with the intent being to lower the POSS-TPU degradation temperature and separate the PCL
and POSS-TPU degradation events. However, as previously described, the SMECs exhibited only one mass loss event, and all SMECs lost about 80% of their initial masses at around 290 °C. The remaining mass gradually burned off during heating to 600 °C. Further studies are necessary to determine if further lowering the heating rate allows for separation of PCL and POSS-TPU degradation.

While the degradation profiles for the PCL/Pellethane SMECs were similarly complicated, the PCL content was able to be estimated for this system. In studying the degradation profile for neat Pellethane (Figure 3-2b and c, (i)), there were two major degradation events, one at 300 °C and the other at 370 °C, which are indicated by the drops in the remaining weight percentage. Additionally, there was a minor event which resulted in a small drop in weight percentage (15%) and occurred at an intermediate temperature (355 °C). It was expected that the PCL degradation would occur separately since neat PCL was observed to degrade at 380 °C using the same high resolution TGA method (Note: This temperature is higher than the temperature reported previously for PCL degradation (350 °C). The increase in degradation temperature is due to the faster heating rate used with the PCL/Pellethane system.). However, PCL degradation in the SMECs occurred simultaneously with the first major Pellethane degradation event. This conclusion was drawn based on the decreasing weight percentage of the SMECs in the 320 - 370 °C temperature range (after the first mass loss event) with increasing PCL content. Further, while 4 degradation events were expected had all events occurred separately, with the exception of the SMEC with 2 wt% PCL, only 2 events were observed. Therefore, events combined to form one event with a larger drop in weight percentage, and the minor Pellethane degradation event was no longer distinguishable, i.e.
there was no slowing of the heating rate, and rather, the mass loss occurred gradually during heating. The 2 wt% PCL SMEC had 3 degradation events, as the minor Pellethane degradation event was separate from the first event (PCL and Pellethane). Due to the low PCL content, this SMEC exhibited a thermal response closer to that of neat Pellethane.

As noted previously, the end of a degradation event was designated as the temperature at which a local maximum in heating rate was achieved. Figure 3-3 shows remaining weight percentage and heating rate as functions of temperature plotted on the same graph for the PCL/Pellethane SMEC with 26 wt% PCL. The remaining weight percentage after the first mass loss event (combined PCL and Pellethane degradation) was compared to the remaining weight percentage of Pellethane after its first major and degradation event (77.7 %) and to that of PCL after its degradation event (1.5 %). Inserting those values into Eq. (3-2), gives the estimated weight fraction of PCL. Estimated PCL content based on high resolution TGA content is tabulated in Table 3-2. The values are relatively close to those obtained through DSC analysis (as will subsequently be discussed) and to the nominal values. Disagreement between the estimated and nominal values for the dual-spun SMECs can be partially accounted for by errors in electrospinning. At times, needles clogged, lowering the effective mass flow rate of that component, and also, due to the high voltages and whipping forces experienced by the polymer jets, not all fibers were collected on the drum. A fraction of the fibers deposited on the surrounding walls and surfaces, again altering the relative mass ratio. Such issues can be at least partially alleviated by further optimizing the electrospinning conditions and by increasing the size of the collector drum (to increase the fraction of fibers collected).
DSC second heating curves (Figure 3-4) were studied to measure the transition temperatures of the SMECs and the neat components and to estimate the weight percentage of PCL contained in the SMECs. For both systems, the SMECs exhibited the neat components’ transitions at unchanged temperatures. This indicated that the two components remained in discrete phases after processing. PCL/POSS-TPU SMECs exhibited transitions at -54, 20, 56, and 116°C, corresponding to PCL1k’s $T_g$, PCL1k’s $T_m$ (in the POSS-TPU), PCL’s $T_m$, and POSS’s $T_m$, and the PCL/Pellethane SMECs exhibited transitions at -30, 56, and 157 °C, corresponding to Pellethane’s $T_g$, PCL’s $T_m$, and Pellethane’s $T_m$. It is noted that the blended PCL/Pellethane SMECs also exhibited unchanged transition temperatures. While the blended SMECs were theoretically mixed at the molecular level when dissolved in solvent, phase separation occurred during solvent casting and compression molding, enabling separation of the transition temperatures. Since it was ultimately concluded (based on consistent transition temperatures and WAXS analysis detailed in Section 3.3.9) that the PCL crystalline domains were unaltered by the presence of the elastomers, the PCL content was estimated by dividing the enthalpy of melting of the PCL in the SMEC to that of neat PCL (Eq. (3-2)). As expected, the enthalpy of melting of the PCL phase increased with increasing PCL content. Since with more PCL there are more PCL crystals, more energy is required to transition the PCL into a melt. Thus, the ratio of enthalpies (Eq. (3-2)) gives an estimate of PCL content, assuming equivalent crystallinity degree. The calculated values (Table 3-2) were relatively close to the nominal values and the values calculated from high resolution TGA.
3.4.3 Scanning Electron Microscopy

SEM was used to study the morphology of the dual-spun fibers and the SMEC films. The composite fibers for both the PCL/POSS-TPU and PCL/Pellethane SMECs had highly uniform fibers (Figure 3-5a and Figure 3-6a, respectively). The elastomer and PCL fibers were indistinguishable, but previous studies have shown that the fibers of each polymer are well dispersed and intertwined. Dual-electrospinning allows for the preparation of homogeneous composites, with the two polymers in discrete phases but mixed at small length scales (on the order of 1 µm). SEM images of the hot compacted SMEC films (Figure 3-5b and c and Figure 3-6b and c) revealed that the Pellethane and POSS-TPU remained in the fiber phase after processing, while PCL became the matrix surrounding the fibers. The composite fibers were compacted at 80 °C, which is above the Tm of PCL, but below the Tm of Pellethane and the POSS-TPU. Therefore, the PCL melted, infiltrating the elastomer fibers and forming a dense film. Fewer fibers were apparent for the PCL/POSS-TPU SMECs, which is hypothesized to be due to partial melting of the fibers. Since the synthesized POSS-TPU is composed of PCL1k and POSS and it exhibits a Tm at 20 °C, hot compaction at 80 °C ensured complete melting of the PCL1k phase. Therefore, the fiber morphology was affected, but some fibers were apparent in SEM images and the mechanical stability observed in DMA provided evidence that the fiber/matrix morphology remained. Cross-sectional SEM images (Figure 3-5c and Figure 3-6c) showed that the void space between electrospun fibers was filled with PCL. This fiber/matrix morphology is advantageous for shape memory performance, as will be discussed in Section 3.4.7. The blended PCL/Pellethane SMECs had smooth surfaces with minimal texture and defects (Figure 3-7).
3.4.4 Wide Angle X-ray Scattering

Blending of polymers at small length scales can disrupt molecular arrangement of the polymer chains.\textsuperscript{32-34} Such disruption can result in altered transition temperatures or hindered crystal formation. As was shown in Section 3.4.2, the PCL and elastomer transition temperatures were all observed in the SMECs, and the respective temperatures were unaltered. To further verify that the crystal structures of the polymers in the SMECs were unaffected by the processing methods, WAXS was utilized. The WAXS patterns and corresponding diffractograms for the PCL/POSS-TPU and PCL/Pellethane SMECs can be seen in Figure 3-8 and Figure 3-9. The neat POSS-TPU shows a sharp inner ring, corresponding to diffraction at POSS crystal planes. While the PCL1k also crystallized (as evidenced by the presence of a DSC melting peak), no sharp crystalline ring was observed due to the low crystallinity of the PCL1k phase. The neat PCL film had 2 characteristic crystalline rings corresponding to the (110) and (200) crystalline planes of the PCL unit cell.\textsuperscript{35} For the PCL/POSS-TPU SMECs, the intensities of the PCL rings and POSS ring increased and decreased, respectively, with increasing PCL content. In comparing the normalized intensity diffractograms for the SMECs, the relative heights of the characteristic PCL peaks increased accordingly. Furthermore, the crystalline \textit{d}-spacings (for both PCL and POSS) were consistent between the SMECs and the neat components. Therefore, the crystal structure appeared unaltered by processing, and it was assumed that the relative crystallinity of the PCL phase was consistent among samples, thus justifying the gravimetric DSC analysis of PCL content. Similar results were obtained for both the dual-spun and blended PCL/Pellethane SMECs, except no crystalline ring was evident for the Pellethane. Therefore, the PCL rings became more distinct and the
Pellethane amorphous halo faded as the SMECs increased in PCL content. For both the dual-spun and blended PCL/Pellethane SMECs, the PCL diffraction angles (2θ) were unaffected by the incorporation of Pellethane, again suggesting that the PCL and Pellethane microdomains were discrete and there was no interference with crystallization.

3.4.5 Dynamic Mechanical Analysis

Understanding the temperature dependence of modulus is essential in assessing a material for a given application. DMA was used to relate the storage modulus to temperature and to reveal the effect of composition on the thermomechanical behavior of the SMECs. Figure 3-10 shows storage modulus as a function of temperature for the PCL/POSS-TPU and PCL/Pellethane SMECs and the neat components. The PCL, which is above its T_g at RT (25 °C), had a RT storage modulus of 150 MPa. After going through its melting transition, the storage modulus dropped drastically (below the sensitivity of the DMA), as the PCL flowed as a liquid. The lack of a rubbery plateau indicated that neat PCL would not exhibit SM properties, thus necessitating incorporation of an elastomer. Both the POSS-TPU and Pellethane had low moduli at RT (15 and 8.3 MPa, respectively), and exhibited storage modulus drops corresponding to the transition temperatures determined by DSC. Importantly, at temperatures well above PCL’s T_m, the elastomers maintained a rubbery plateau. Such mechanical stability is necessary for SM performance.

DMA of the SMECs highlighted an important advantage of the dual-electrospinning SMEC approach: the ability to tune mechanical properties through control of the relative composition. For all of the SMEC systems studied, the RT storage modulus tended to increase
with increasing PCL content. Values for RT storage modulus are tabulated for the different SMEC compositions in **Table 3-3**. The increase in modulus followed directly from the increased volume fraction of the higher modulus component, PCL. The PCL/POSS-TPU composites exhibited intermediate moduli in the -40 – 50 °C range; the exception being that the moduli of the 3 SMECs with the lowest PCL content dropped below the modulus of the neat POSS-TPU in the 10 – 50 °C range. Since the PCL content in these samples accounts for only a small percentage of the material (12 % or less by DSC), it is expected that complete infiltration of the POSS-TPU fibers was not obtained, i.e. there was not enough PCL present to fill all void spaces between the POSS-TPU fibers. Therefore, voids in the materials reduced the effective moduli of the SMECs. However, this hypothesis was not confirmed via SEM. More importantly, while the SMECs dropped in storage moduli at PCL’s T_m, rubbery plateaus were achieved for all compositions; the elastomer fibers provided the mechanical support necessary to prevent the SMECs from deforming and flowing once the PCL melted. This result was exploited for SM. Similar results were obtained for the PCL/Pellethane SMECs, but the temperature range for intermediate moduli was narrowed to -10 to 50 °C due to the higher T_g of the Pellethane compared to the POSS-TPU. Furthermore, the dual-spun and blended systems had similar DMA profiles, and the moduli values were comparable. The solvent cast PCL/Pellethane SMEC with the highest PCL content, however, had a slightly lower modulus above PCL’s T_m, and the modulus dropped below the sensitivity of the instrument at around 80 °C. This result is hypothesized to be an effect of the phase separation of the PCL and Pellethane. As discussed in **Section 2.4.1**, phase separation occurred during solvent casting and compression molding. The size of the separated domains was not studied, but it is expected that with more PCL, the PCL
domains became larger. Therefore, above PCL’s $T_m$, larger regions of the SMEC were melted, providing no mechanical support to the system. Such effect has consequences on SM performance, as will be discussed in Section 3.4.7.

3.4.6 Tensile Testing

The tensile response of the SMECs (Figure 3-11) stretched at a constant rate was studied using a Test Resources mechanical tester. After stretching the samples to failure, the Young’s moduli and strain-to-failures were studied to gain a better understanding of the tensile behavior of the SMECs with varying PCL content. The characteristic stress-strain curve for neat PCL was observed, with a relatively high initial slope (120 MPa) followed by a yield point at which necking occurred. Subsequently, the gauge length region of the dog bone was elongated until the sample failed. The strain-to-failure for PCL was relatively high at over 2500 % strain. The synthesized POSS-TPU had a much lower Young’s modulus around 6.3 MPa, and the strain-to-failure was around 2200 % strain. Similarly, Pellethane had a Young’s modulus around 6.7 MPa, and its strain to failure was even lower at about 1500 % strain. In general, the SMECs had Young’s moduli between those of the neat components, as was also observed in DMA. The exceptions were again, the PCL/POSS-TPU SMECs with the lowest PCL content. The presence of voids in the films, which was discussed in Section 3.4.5, could explain the lower Young’s moduli. In studying the strain-to-failures of the SMECs, no clear dependence on PCL content was observed. However, in general, the SMECs failed at strains lower than the neat elastomers. The premature failure is likely due to effects from voids and interfacial boundaries between PCL and the elastomer. Any nonuniformity in the material leads to stress concentration, which is responsible for early failure. Nevertheless, the SMECs had relatively high strain-to-failures,
typically above 1000 % strain. Such high elongation and low moduli justify classification of the SMECs as “elastomeric”. It is also noted that no significant differences in tensile behavior between the dual-spun and blended PCL/Pellethane SMECs were observed.

3.4.7 Shape Memory Testing

Due to the presence of rubbery plateaus above the melting point of PCL in the SMECs, shape memory capabilities were expected. Since the shape fixing is performed around PCL’s T_m, the elastomer must hold the composite together, and prevent it from flowing as a liquid, during deformation. The rubbery plateaus indicated that the elastomer provided enough support to the system to give it mechanical integrity when the PCL was melted. In the shape memory cycle, PCL crystallization assisted in fixing a temporary shape, counteracting the elastic contraction of the POSS-TPU or Pellethane. Remelting the PCL allowed recovery of the permanent shape as the elastomer fibers contracted within the liquid PCL matrix.

The tensile SM properties of the SMECs were analyzed using the DMA in controlled force mode. 3D stress-temperature-strain plots are provided in Figure 3-12, Figure 3-13, and Figure 3-14 for the PCL/POSS-TPU, PCL/Pellethane, and blended PCL/Pellethane SMECs, respectively. All samples were stretched and fixed at 20 % strain. However, upon unloading, the ability of the PCL crystallites to prevent the elastic contraction of the elastomer fibers showed a strong dependence on the relative composition of the SMEC. Specifically, the fixing ability increased with increasing PCL content. Such a result was expected since with increasing PCL content, a smaller volume fraction of the material (fewer elastomer fibers) tries to contract and a larger fraction crystallizes, preventing recovery. The fixing ratios ranged between 20 and
100 % for all SMEC types studied. In general, for comparable PCL content, the PCL/POSS-TPU SMECs had higher fixing ratios than the PCL/Pellethane SMECs. It is hypothesized that the POSS-TPU also aided in shape fixing, as the PCL1k T_m was around 20 °C. Any partial crystallization of the PCL1k would assist in shape fixing. Pellethane’s T_g and T_m were well below and above the temperature range spanned in the SM cycle, so Pellethane vitrification or crystallization were not expected to aid in shape fixing. Comparing the dual-spun and blended PCL/Pellethane SMEC systems, the dual-spun SMECs averaged about 10 % higher fixing ratios. Furthermore, the SM properties of the blended SMEC with 31 wt% PCL were not reported here because inconsistencies were observed in SM performance. Three samples of the 31 wt% PCL SMEC (blended) were tested for SM properties. Of the 3, 2 samples yielded during the first deformation step. As the PCL was melted, the samples were so soft that even the small forces that were applied stretched the samples to strains beyond the limit of the instrument. The third sample tested showed great SM properties with excellent fixing and recovery. However, due to the inconsistent performance, the values were not reported. Such inconsistency is likely caused by an inhomogeneous morphology. As was discussed previously, the PCL and Pellethane phase separated during processing, and it is expected that the separation led to PCL rich and Pellethane rich sections of the SMEC film. In studying the recovery of the SMECs, it was calculated that the dual-spun SMECs (both the PCL/POSS-TPU and PCL/Pellethane systems) had average recovery ratios above 97 %. The blended PCL/Pellethane SMECs, however, had recovery ratios ranging between 89 and 96 %. In addition to the recovery ratios being lower than the dual-spun SMECs, the standard deviations were also larger in magnitude. This variability in performance can again be explained by inhomogeneity in film morphology. A
A summary of the fixing and recovery ratios for the different SMEC compositions is provided in Figure 3-15 and Table 3-4.

3.4.8 Reversible Adhesive Testing

Due to the incorporation of PCL into the SMECs, reversible adhesive properties were expected for the SMECs. When PCL crystallizes in contact with a material such as steel, it adheres to the surface. The adhesive properties of the PCL/POSS-TPU SMEC system (the PCL/Pellethane SMECs were not included in this testing) were quantified using a compression clamp in the DMA. As described in Section 3.3.13, the disc shaped samples were first compressed to a prescribed force. Subsequently, the sample was heated to melt the PCL and then cooled to crystallize the PCL and form the adhesive bond. After allowing time for crystallization, the force was ramped back to 0 N and into negative values, thus placing the sample in tension until delamination from the plate surface. Figure 3-16 shows an example of the raw data obtained during an adhesive test for the PCL/POSS-TPU SMEC containing 12 wt% PCL. During the initial loading step, the SMEC was placed into compression, and a corresponding decrease in strain was observed. As the sample was heated through the PCL melting point, the magnitude of the strain increased further, since the sample was softened and more easily compressed. Cooling the sample (to crystallize the PCL) was accompanied by thermal contraction, and the sample thickness decreased even further. As the compressive force was decreased and the sample is placed into tension, a portion of the strain was recovered. The tensile force ramp continued, but the sample thickness plateaued until a sudden and dramatic increase in strain (tensile) was observed due to delamination of the clamp from the sample. The force at this point was normalized by the initial sample area (Note: Any
changes in sample area associated with compression of the sample were not taken into account when calculating the surface area in contact with the steel clamps.) to obtain the apparent pull-off strength.

The apparent pull-off strength was measured for the various PCL/POSS-TPU SMEC compositions to determine the effect of PCL content on adhesive performance (Figure 3-17a). The neat POSS-TPU was also tested as a control and to establish a baseline for adhesive strength. The SMEC with only 2 wt% PCL and the neat POSS-TPU performed similarly, with apparent pull-off strengths of about 5 N cm\(^2\). Adhesion of the neat POSS-TPU to the clamp is expected to be due to partial crystallization of the PCL1k. The minimal increase in adhesive strength for the 2 wt% PCL SMEC can be explained by incomplete surface coverage of PCL. Since the PCL accounted for such a small percentage of the material, it is likely that the contacting surface of the SMEC (to the clamp) was predominately the POSS-TPU. The SMECs with higher PCL content (>12 wt%) adhered more securely to the steel clamps. The pull-off strengths for the higher PCL content SMECs were all around 24 N cm\(^2\). The lack of dependence on PCL content at these compositions suggests that the surfaces were equally saturated with PCL.

The effect of the applied force on the adhesive strength of the PCL/POSS-TPU SMECs was studied by varying the load applied during the bonding step between 0.1 and 3 N. For the 12 wt% PCL SMEC, the bond strength was observed to increase as the applied load was increased (Figure 3-17b), suggesting that the SMEC system functions as a pressure sensitive adhesive. This result is hypothesized to be due to effects from squeezing the samples to higher degrees. At low forces, the clamp only lightly touched the sample surface. Therefore, the
sample diameter was essentially unchanged. Furthermore, only the PCL initially on the surface of the sample contacted the clamp during the adhesive test. When higher forces were used, however, the sample was compressed to higher strains. Such deformation is expected to be accompanied by an increase in diameter, which increases the surface area in contact with the clamp. Additionally, if there were regions of the sample surface that were lacking PCL, the high forces assisted in spreading the PCL along the surface. This, again, increased the effective surface area assisting in adhesion (since the POSS-TPU was shown to only minimally adhere to the steel clamp). Increasing the force from 0.1 to 3 N increased the apparent pull-off strength 9-fold.

Compared to the adhesive system developed by Luo et al., the POSS-TPU/SMEC system exhibited much lower adhesive strengths. With that said, Luo et al. indicated a strong dependence of adhesive strength on crystallization time. In the SMEC systems, a 10 min isothermal hold was utilized, but Luo et al. varied the crystallization time from 20 to 40 min. Therefore, it is expected that the adhering strength for the SMEC system would similarly increase with crystallization time and the values would more closely match those obtained by Luo et al. On the other hand, the maximum bond strength achieved (45 N cm\(^{-2}\)) more closely matched the strengths achieved by Xie and Xiao (60 N cm\(^{-2}\)). The major advantage of the SMEC adhesive system over the rigid adhesives studied by Luo et al. and Xie and Xiao is the ability of the SMEC to conform to textured or oddly shaped surfaces. For example, the SMEC could be curled around a spherical shape to increase the contact area compared that obtainable from a straight, rigid adhesive applied to a curved surface.
The reversibility of the SMEC adhesives was demonstrated by delaminating the SMECs at elevated temperature. In this case, the PCL crystals which had adhered to the clamp surface were remelted to allow easier delamination. The apparent pull-off strengths for the various SMEC compositions were compared to those measured for the crystallized state. While the apparent pull-off strengths at elevated temperature were all less than half of their respective strength in the crystallized state, the strengths were unsatisfactorily high. The liquid PCL caused the surface of the SMECs to be sticky, thus still promoting adhesion. Hence, the SM properties of the SMECs were exploited to reduce the contacting surface area at the point of delamination. Pre-fixed samples from the 12 wt% PCL SMEC were tested using the same reversible adhesive testing method. During the first heating ramp to melt the PCL, shape recovery was prevented, as the sample was constrained by the applied compressive load. Subsequently, the sample was cooled and heated again and then unloaded. During unloading, as the force applied to the sample decreased to around 0 N, the sample was able to recover the fixed strain. Internal movement of the sample surface in a direction normal to the tensile (delamination) direction, combined with the reduced contacting surface area, aided in delaminating the sample from the clamp surface. The apparent pull-off strength was reduced to less than 1 N cm\(^{-2}\). Furthermore, the ability to manipulate (bend, twist, etc.) the SMEC while in the fixed elongated shape is beneficial for adhesion to odd shapes, and was not possible with the previously studied, rigid shape memory adhesive system.\(^{31}\) Such shape memory assisted delamination has high potential in practical applications.
3.5 Conclusions

Dual-electrospinning was used to simultaneously electrospin two polymers which separately aided in shape fixing and shape memory. The resulting composite fibers were processed simply by compression molding to form dense SMEC films. Demonstrated control over the relative composition of the SMECs translated to control over the thermal, mechanical, SM, and adhesive properties. This new approach to fabricate SMECs drastically simplifies the fabrication process, enabling large-scale manufacturing of SM rubbers. We envision such materials will find broad application in the biomedical field, with the SMECs used in bulk or as coatings for vascular grafts, stents, or catheters. Furthermore, the reversible adhesive SMECs could be useful in manufacturing packaging, repair, and home improvement applications. For example, in packaging of microwavable foods, the SMEC films could be used to self-delaminate during warming, thus eliminating the need to pre-cut the packaging and preventing bursting of the container if consumers forget that preparation step. While SMECs developed here already show promising versatility, the highlight of the dual-electrospinning approach is the ability to individually select components for specific properties necessary for a given application.

3.6 References


23. Birjandi Nejad, H.; Robertson, J. M.; Mather, P. T., Interwoven polymer composites via dual-electrospinning with shape memory and self-healing properties. *MRS Communications 2015, 5 (02), 211-221*


3.7 Schemes, Figures, and Tables

**Scheme 3-1** Multiblock PCL1k-POSS polyurethane synthesis mechanism.

1,2 Propane diol Isobutyl POSS + 1k PCL diol

Hexamethylene Diisocyanate

Isobutyl tin POMS in Toluene, 100 °C → Precipitate in Hexane → Wash in DI water → Multiblock PCL1k-POSS Polyurethane
Scheme 3-2 Schematic showing the dual electrospinning setup, which contains two syringes containing different polymer solutions placed on opposing sides of the collector drum. The polymers are simultaneously electrospun, or dual-spun, forming composite mats.
Table 3-1 Electrospinning solution compositions and electrospinning parameters used to dual-spin SMECs

<table>
<thead>
<tr>
<th>Electrospinning solution</th>
<th>Electrospinning Conditions</th>
<th>Electrospinning parameters</th>
<th>PCL/POSS-TPU SMECs</th>
<th>PCL/Pellethane SMECs</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL solution</td>
<td>20 % (w/v), 80:20 (volume) chloroform:DMF</td>
<td>2 wt% PCL</td>
<td>PCL – 0.1 mL h⁻¹, 10 kV</td>
<td>PCL – 0.2 mL h⁻¹, 15 kV</td>
</tr>
<tr>
<td></td>
<td></td>
<td>POSS-TPU solution</td>
<td>POSS-TPU – 6.0 mL h⁻¹, 14.5 kV</td>
<td>Pellethane – 7.6 mL h⁻¹, 16 kV</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 wt% PCL</td>
<td>PCL – 0.2 mL h⁻¹, 10 kV</td>
<td>PCL – 0.3 mL h⁻¹, 12 kV</td>
</tr>
<tr>
<td></td>
<td></td>
<td>POSS-TPU solution</td>
<td>POSS-TPU – 5.0 mL h⁻¹, 14.5 kV</td>
<td>Pellethane – 5.4 mL h⁻¹, 15 kV</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 wt% PCL</td>
<td>PCL – 0.8 mL h⁻¹, 11 kV</td>
<td>PCL – 0.4 mL h⁻¹, 12 kV</td>
</tr>
<tr>
<td></td>
<td></td>
<td>POSS-TPU solution</td>
<td>POSS-TPU – 5.0 mL h⁻¹, 14.5 kV</td>
<td>Pellethane – 4.0 mL h⁻¹, 14 kV</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15 wt% PCL</td>
<td>PCL – 0.4 mL h⁻¹, 10 kV</td>
<td>PCL – 0.4 mL h⁻¹, 12 kV</td>
</tr>
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<td></td>
<td></td>
<td>POSS-TPU solution</td>
<td>POSS-TPU – 1.5 mL h⁻¹, 14 kV</td>
<td>Pellethane – 3.6 mL h⁻¹, 14 kV</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20 wt% PCL</td>
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<td>PCL – 0.6 mL h⁻¹, 12 kV</td>
</tr>
<tr>
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<td></td>
<td>POSS-TPU solution</td>
<td>POSS-TPU – 3 mL h⁻¹, 12 kV</td>
<td>Pellethane – 3.6 mL h⁻¹, 14 kV</td>
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<td>25 wt% PCL</td>
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<td></td>
<td></td>
<td>Pellethane solution</td>
<td>Pellethane – 3.6 mL h⁻¹, 14 kV</td>
<td>Pellethane – 3.6 mL h⁻¹, 14 kV</td>
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</table>
Figure 3-1 $^1$H NMR spectrum for the synthesized PCL1k-POSS TPU. The ratio of peak integrals for peaks (a) and (b) were compared to determine the relative incorporation of PCL1k and POSS. The protons associated with the labeled peaks are indicated above the spectrum on the POSS-TPU structure.
Figure 3-2 High resolution TGA profiles for (a) the PCL/POSS-TPU SMECs, (b) the PCL/Pellethane SMECs, and (c) the blended PCL/Pellethane SMECs. In (a), (i) is the neat POSS-TPU, and in (b) and (c), (i) is neat Pellethane. In (a), (b), and (c), (vii) is neat PCL. (i) through (vi) correspond to SMECs with increasing PCL content as detailed in Table 3-2.
Figure 3-3 High resolution TGA mass loss and heating rate curves as a function of temperature for the PCL/Pellethane SMEC with 26 wt% PCL (by DSC analysis). Indicated in the graph are the 2 mass loss events, (i) and (ii). Event (i) combines PCL and Pellethane degradation, and event (ii) is associated with Pellethane. The end of each event was chosen as the peak in heating rate.
Table 3-2 Estimated PCL content in the SMECs based on high resolution TGA and DSC analyses.

<table>
<thead>
<tr>
<th>Nominal PCL Wt%</th>
<th>PCL Wt% (TGA)</th>
<th>PCL Wt% (DSC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL/POSS TPU</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>0.2</td>
</tr>
<tr>
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<td>26</td>
<td>-</td>
<td>17</td>
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<tr>
<td>31</td>
<td>-</td>
<td>38</td>
</tr>
<tr>
<td>PCL/Pellethane (Dual-Spun)</td>
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<td></td>
</tr>
<tr>
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<td>PCL/Pellethane (Blended)</td>
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<tr>
<td>31</td>
<td>33</td>
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</tbody>
</table>
(a) Heat Flow (W/g) (Exo Up)

Temperature (°C)

(b) Heat Flow (W/g) (Exo Up)

Temperature (°C)
Figure 3-4 DSC second heating curves for (a) the PCL/POSS-TPU SMECs, (b) the PCL/Pellethane SMECs, and (c) the blended PCL/Pellethane SMECs. In (a), (i) is the neat POSS-TPU, and in (b) and (c), (i) is neat Pellethane. In (a), (b), and (c), (vii) is neat PCL. (i) through (vi) correspond to SMECs with increasing PCL content as detailed in Table 3-2. Samples with increasing PCL content exhibit PCL melting peaks of greater magnitude, i.e. a higher enthalpy of melting. All heating and cooling rates were 10 °C min⁻¹.
Figure 3-5 Scanning electron microscopy images of the (a) fibers, (b) film surface, and (c) film cross-section of the PCL/POSS-TPU SMECs with (i) 0.2, (ii) 2, (iii) 12, (iv) 17, and (v) 38 wt% PCL.
Figure 3-6 Scanning electron microscopy images of the (a) fibers, (b) film surface, and (c) film cross-section of the PCL/Pellethane SMECs with (i) 2, (ii) 5, (iii) 16, (iv) 26, and (v) 31 wt% PCL.
Figure 3-7 Scanning electron microscopy images of the surfaces of the blended PCL/Pellethane SMEC films with (i) 2, (ii) 5, (iii) 16, (iv) 26, and (v) 31 wt% PCL.
Figure 3-8 WAXS patterns for (a) the PCL/POSS-TPU SMECs, (b) the PCL/Pellethane SMECs, and (c) the blended PCL/Pellethane SMECs. In (a), (i) is the neat POSS-TPU, and in (b) and (c), (i) is neat Pellethane. In (a), (b), and (c), (vii) is neat PCL. (i) through (vi) correspond to SMECs with increasing PCL content as detailed in Table 3-2.
Figure 3-9 WAXS diffractograms showing crystallinity peaks for (a) the PCL/POSS-TPU SMECs, (b) the PCL/Pellethane SMECs, and (c) the blended PCL/Pellethane SMECs. In (a), (i) is the neat POSS-TPU, and in (b) and (c), (i) is neat Pellethane. In (a), (b), and (c), (vii) is neat PCL. (i) through (vi) correspond to SMECs with increasing PCL content as detailed in Table 3-2.
Figure 3-10 Dynamic mechanical analysis of (a) the PCL/POSS-TPU SMECs and (b) the PCL/Pellethane SMECs. In (a), (i) is the neat POSS-TPU, and in (b) and (c), (i) is neat Pellethane. In (a), (b), and (c), (vii) is neat PCL. (i) through (vi) correspond to SMECs with increasing PCL content as detailed in Table 3-2. Storage modulus as a function of temperature is plotted for each composition studied. The relative drop in storage modulus at PCL’s melting point is observed to increase in magnitude with increasing PCL content.
**Table 3-3** Summary of room temperature mechanical properties of the SMECs with varying composition.

<table>
<thead>
<tr>
<th></th>
<th>Wt% PCL&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Storage Modulus at RT (MPa)</th>
<th>Young's Modulus at RT (MPa)</th>
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<tbody>
<tr>
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<td>15</td>
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<tr>
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</tr>
<tr>
<td>(ii)</td>
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<td>11</td>
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<tr>
<td>(iii)</td>
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<td>16</td>
<td>8.2</td>
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<td>(iv)</td>
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<td>(v)</td>
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</tr>
<tr>
<td>(vi)</td>
<td>38</td>
<td></td>
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</tr>
<tr>
<td>PCL/POSS-TPU</td>
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<td>8.3</td>
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</tr>
<tr>
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<td>10</td>
<td>7.5</td>
</tr>
<tr>
<td>(ii)</td>
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<td>12</td>
<td>8.3</td>
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<td>(vi)</td>
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<td></td>
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<tr>
<td>PCL/Pellethane (Dual-Spun)</td>
<td>100</td>
<td>8.3</td>
<td>6.7</td>
</tr>
<tr>
<td>(i)</td>
<td>0</td>
<td>13</td>
<td>7.1</td>
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<tr>
<td>(ii)</td>
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<td>14</td>
<td>11</td>
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<td>(iii)</td>
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<td>(iv)</td>
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<td>(v)</td>
<td>26</td>
<td>39</td>
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</tr>
<tr>
<td>(vi)</td>
<td>31</td>
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<sup>a</sup>As determined by DSC for the PCL/TPU and dual-spun PCL/Pellethane SMECs. Nominal values are reported for the blended SMECs.
Figure 3-11 Stress-strain curves for (a) the PCL/POSS-TPU SMECs, (b) the PCL/Pellethane SMECs, and (c) the blended PCL/Pellethane SMECs. In (a), (b), and (c), (vii) is neat PCL, and (i) through (vi) correspond to SMECs with increasing PCL content as detailed in Table 3-2. The left column shows the strain-to-failure and the right column magnifies the region of elastic deformation in the SMECs, highlighting that the Young’s modulus increases with increasing PCL content.
Figure 3-12 Shape memory stress-temperature-strain plots of the PCL/POSS-TPU SMECs with (a) 0.2 wt% PCL, (b) 2 wt% PCL, (c) 12 wt% PCL, (d) 17 wt% PCL, and (e) 38 wt% PCL. The steps in the SM cycle are depicted in (a): (i) deformation, (ii) cooling, (iii) unloading, and (iv) shape recovery.
Figure 3.13 Shape memory stress-temperature-strain plots of the PCL/Pellethane SMECs with (a) 2 wt% PCL, (b) 5 wt% PCL, (c) 16 wt% PCL, (d) 26 wt% PCL, and (e) 31 wt% PCL. The steps in the SM cycle are depicted in (a): (i) deformation, (ii) cooling, (iii) unloading, and (iv) shape recovery.
Figure 3-14 Shape memory stress-temperature-strain plots of the blended PCL/Pellethane SMECs with (a) 2 wt% PCL, (b) 5 wt% PCL, (c) 16 wt% PCL, and (d) 26 wt% PCL. The steps in the SM cycle are depicted in (a): (i) deformation, (ii) cooling, (iii) unloading, and (iv) shape recovery.
Figure 3-15 (a) Fixing and (b) recovery ratios as functions of PCL content for (i) PCL/POSS-TPU, (ii) dual-spun PCL/Pellethane, and (iii) blended PCL/Pellethane SMECs.
Table 3-4 Fixing and recovery ratios for the PCL/POSS-TPU and PCL/Pellethane SMECs.

<table>
<thead>
<tr>
<th></th>
<th>Wt% PCL(^a)</th>
<th>(R_f(%))</th>
<th>(R_s(%))</th>
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<tr>
<td><strong>PCL/TPU</strong></td>
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<td>(ii)</td>
<td>0.2</td>
<td>11.9 ± 3.8</td>
<td>103.5 ± 2.6</td>
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<td>(iii)</td>
<td>2</td>
<td>61.8 ± 1.0</td>
<td>101.4 ± 0.3</td>
</tr>
<tr>
<td>(iv)</td>
<td>12</td>
<td>84.0 ± 1.0</td>
<td>104.9 ± 2.8</td>
</tr>
<tr>
<td>(v)</td>
<td>17</td>
<td>93.4 ± 0.3</td>
<td>99.8 ± 1.5</td>
</tr>
<tr>
<td>(vi)</td>
<td>38</td>
<td>97.4 ± 0.0</td>
<td>97.7 ± 2.4</td>
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<td><strong>PCL/Pellethane (Dual-Spun)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ii)</td>
<td>2</td>
<td>36.0 ± 0.6</td>
<td>104.0 ± 1.1</td>
</tr>
<tr>
<td>(iii)</td>
<td>5</td>
<td>46.8 ± 0.3</td>
<td>106.6 ± 3.0</td>
</tr>
<tr>
<td>(iv)</td>
<td>16</td>
<td>75.1 ± 0.4</td>
<td>99.9 ± 0.7</td>
</tr>
<tr>
<td>(v)</td>
<td>26</td>
<td>89.9 ± 0.2</td>
<td>99.8 ± 0.3</td>
</tr>
<tr>
<td>(vi)</td>
<td>31</td>
<td>94.8 ± 0.2</td>
<td>97.7 ± 4.2</td>
</tr>
<tr>
<td><strong>PCL/Pellethane (Blended)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ii)</td>
<td>2</td>
<td>24.0 ± 1.8</td>
<td>95.4 ± 4.8</td>
</tr>
<tr>
<td>(iii)</td>
<td>5</td>
<td>34.0 ± 2.8</td>
<td>90.5 ± 9.0</td>
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<tr>
<td>(iv)</td>
<td>16</td>
<td>66.3 ± 3.7</td>
<td>89.5 ± 10.0</td>
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<tr>
<td>(v)</td>
<td>26</td>
<td>71.8 ± 1.3</td>
<td>95.9 ± 2.6</td>
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<tr>
<td>(vi)</td>
<td>31</td>
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\(^a\)As determined by DSC for the PCL/TPU and dual-spun PCL/Pellethane SMECs. Nominal values are reported for the blended SMECs.
Figure 3-16 Temperature (a), strain (b), and force (c) data acquired during an adhesive test measuring the apparent pull-off strength of the PCL/POSS-TPU SMEC with 12 wt% PCL. (i) The sample is loaded to 1.0 N, (ii) the sample is heated to 70 °C, (iii) the temperature is ramped to 20 °C, and (iv) the force is ramped, putting the sample into tension and eventually delaminating the sample from the clamp.
(a) wt% PCL vs. Apparent Pull-Off Strength

(b) Applied Load (N) vs. Apparent Pull-Off Strength
Figure 3-17 Apparent pull-off strengths for the PCL/POSS-TPU SMECs under various conditions. (a) Comparison of adhesive strength at 20 (gray) and 70 (blue) °C for the SMECs with various PCL content. (b) Effect of applied load on the adhesive strength of the 12 wt% PCL SMEC. (c) Apparent pull-off strength for the 12 wt% PCL SMEC bonded at 1 N at 20 °C (gray), 70 °C (blue), and at 70 °C with SM assisted delamination (red).
Chapter 4. Water-Triggered Origami with a Polymeric Web

4.1 Synopsis

Electrospinning is a versatile technique used to produce small-scale fibers from polymer solutions or melts. Chapter 2 and Chapter 3 detailed the use of electrospinning in the fabrication of shape memory elastomeric composites. This chapter focuses on the effects of electrospinning on molecular orientation. More specifically, the elongational forces experienced during electrospinning impart stresses in the polymer fibers. Such stress can be stored in the fibers upon vitrification and later recovered by heating the fibers above their glass transition temperature. Recovery of the stored stress in electrospun poly(vinyl acetate) (PVAc) fibers results in a significant size reduction of the fiber mat. Alternatively, PVAc fiber mats can be hydrated to similarly recover the stress. Such response to water has been exploited here to develop water-triggered origami, in which PVAc fiber mats are folded by drawing stripes of water along the mat. Strategic placement of the water lines allows for the self-assembly of 3-dimensional structures that mimic paper based origami forms. Electrospun PVAc’s response to hydration has been studied in detail and characterized for both isotropic and anisotropic PVAc fibers.

4.2 Introduction

Technology aims to reduce the degree of manual labor in construction and use. Devices that self-assemble are of particular interest for various applications. As an example, the aerospace field requires effective deployment of self-assembled space structures.\textsuperscript{1-3} Satellites sent into space need to be compact prior to reaching their destination. However, once in
space, sections of the satellite, such as an antenna, can expand in order to increase surface area. Block et al. developed a self-deploying helical antenna that is compact during launch. Once in space, the antenna is released, and it expands to the coiled form in a spring-like fashion. The self-deployment of the antenna allows for a large disproportionality between the antenna and satellite size that would otherwise prevent launching. Another example of using self-folding structures is in the field of drug delivery for delivering therapeutic drugs to targeted areas. Often, self-folding is used to encapsulate or release the drug, but He et al. used a pH responsive polymeric device to increase localization of drug delivery. Swelling in a relatively high pH environment, such as at the intestine wall, caused portions of the device to swell, leading to folding of the edges of the device. The initially flat delivery system gripped onto the intestine wall, increasing the number of attached devices and ensuring localized drug delivery. Here, the self-actuation deployed in response to environmental conditions.

One focus of current research is the development of programmable self-assembling structures. For this technology, computer programming is often required, and program signals are sent into the material, detailing the steps of construction. An advantage of this approach is that after construction, additional programs can be sent to the structure, allowing it to reassemble into another shape. Another approach to self-assembling structures utilizes 4-dimensional (4D) printing, where the fourth dimension is time. In this case, the printed material, or one of the printed materials, responds to an environmental stimulus applied after printing, resulting in a conformational change of the printed object. Drawbacks to this approach include the current size and material limitations of 3D printing and the need for a preconceived ending state; the final shape of the object must be determined prior to printing,
and the shape changing mechanism must be planned to determine the geometry of the printed object.

Origami is among the usable techniques to fabricate self-folding or self-assembling three-dimensional (3D) structures for applications in the aerospace and biomedical fields. Using the origami water-bomb base folding pattern as inspiration, Onal et al. developed a crawling worm robot whose motion is controlled by electrical currents. Fabricated from an initially flat polymer sheet, the robot was constructed by folding the sheet into a cylinder using origami techniques. The addition of shape memory alloy coils, which connected sections of the cylinder, provided the mobility mechanism for the robot. Current through the coils caused heating, which in turn, caused contraction of the robot as it self-folded along the water-bomb base fold pattern. Turning the current off allowed for relaxation of the coils. Successive on-off currents led to the peristaltic crawling motion of the robot. On the other hand, conventional origami techniques can be used with untraditional materials in a way that more closely mimics paper origami. Ryu et al. used light to activate stress relaxation in a pre-strained, photo-responsive material. The application of light led to the formation of free radicals in the photoinitiator within the material, which then reacted with the polymer, causing bonds to dissociate. Since the polymer was previously strained, bond reformation relieved the stress in the system, and the polymer shrunk. The intensity of the light controlled the degree to which the dissociation took place, and thus controlled the shrinkage of the polymer. Since the intensity decreased through the thickness of the sample, a shrinkage gradient formed when light was shined on the surface, leading to bending or folding. Control over the areas exposed
to light allowed Ryu et al. to define the bending locations and mimic paper-based origami in a process termed “photo-origami”.

Here, we use water to trigger localized shrinkage in electrospun poly(vinyl acetate) (PVAc) fiber mats. An advantage of our approach over the light-induced shrinkage method is that the fiber mat does not need to be pre-conditioned. Instead, the processing method, itself, programs stress in the material. The water-triggered shrinkage relies only on the molecular alignment induced by the electrospinning process and on the plasticization effect of water in PVAc.

4.3 Experimental

4.3.1 Materials

Poly(vinyl acetate) (PVAc) (Mw = 260,000 g mol\(^{-1}\)) was purchased from Scientific Polymer Products, Inc, N,N-dimethylformamide (anhydrous, 99.8) (DMF) was purchased from Sigma Aldrich, and methanol was purchased from Fisher Scientific. All materials were used as received.

4.3.2 Electrospinning Method

PVAc fiber mats were prepared via electrospinning. A 20 % (w/v) PVAc solution was used and prepared by dissolving 2 g of PVAc in 10 mL of a 7:3 volume ratio methanol:dimethylformamide mixture. The solution was electrospun using the setups described in Scheme 1-2 and Scheme 2-1 to obtain isotropic and anisotropic fibers, respectively. For all isotropic fiber mats, the negatively biased metal collector drum (-0.5 kV) rotated at 400 rpm, and the distance between the needle tip and collector drum was 8 cm. The
voltage applied to the syringe needle was varied between +6 and +14 kV in order to obtain mats with different fiber diameters, with smaller fiber diameters obtained at higher voltages. The solution flow rate was adjusted between 1.0 and 1.5 mL h\(^{-1}\) in order to balance the flow rate associated with the needle voltage. After removing, the fiber mats were dried in a vacuum oven (ca. 760 mm Hg) at room temperature (RT) for 12 h to remove any residual solvent. In order to produce aligned fibers by electrospinning, the PVAc solution was pumped at 0.5 mL h\(^{-1}\) and a voltage of +14 kV was applied to the syringe needle. Further, a voltage of +12 kV was applied to an intermediate copper plate incorporated to diminish field line divergence. The collector drum rotated at 3000 rpm. Electrospinning was run for varying lengths of time in order to vary the thickness of the resulting fiber mat. All other parameters were kept constant. Again, the fibrous webs were dried in a vacuum oven (ca. 760 mm Hg) at RT for 12 h.

Portions of the fiber mats (isotropic and anisotropic) were hydrated to compare the thermal and mechanical properties of PVAc in the dry and hydrated states. Samples hereafter referred to as “hydrated” were submerged in RT deionized (DI) water for at least 24 h prior to testing to allow sufficient time for water uptake. All dry fiber mats were tested within 24 h to minimize effects from humidity and physical aging.

4.3.3 Differential Scanning Calorimetry

A TA Instruments Q200 differential scanning calorimeter (DSC) was used to measure the glass transition temperature (T\(_g\)) of PVAc fiber mats in the dry (as-spun), hydrated, and post-hydrated (hydrated then dried) states. All samples were equilibrated at -60, then heated to 80
°C to remove the thermal history, and then cooled back to -60 °C. The second heat was run from -60 to 80 °C and was used to measure the glass transition temperatures of each sample.

All heating and cooling rates were 10 °C min⁻¹.

4.3.4 Fiber Mat Shrinkage

Electrospun PVAc fiber mats shrink when hydrated, as stresses stored in the fibers during electrospinning are relaxed. The degree of shrinkage upon hydration was measured by submerging 25.4 mm square sections of the mats in RT DI water. After 24 h of hydration, the new dimensions were measured, and the percent shrinkage, s, was calculated using the following equation:

\[ s(\%) = \frac{L_0 - L}{L_0} \times 100 \]  
\[ (4-1) \]

where \( L_0 \) is the original length (25.4 mm) and \( L \) is the length after shrinkage. Three samples were taken from each tested mat, and from each sample, the percent shrinkage was calculated along each of the 4 edges. The shrinkage values for all four sides were averaged for the isotropic fiber mats, and the shrinkage values for opposing (parallel) sides were averaged for the anisotropic fiber mats. Therefore, 2 average shrinkage values were obtained for the anisotropic PVAc fiber mats, representing the change in length parallel and perpendicular to the fibers.

As a control, a 25.4 mm square PVAc fiber mat was hydrated in cold water for comparison to the samples hydrated at RT. The sample was placed in DI water in the refrigerator for 24 h and subsequently imaged and measured on a chilled metal plate.
4.3.5 Scanning Electron Microscopy

Scanning electron microscopy (SEM) (JEOL JSM-5600) was used to visualize the surface of electrospun fiber mats. SEM micrographs of fiber mats before and after hydration were obtained. Hydrated samples were subsequently dried for 24 h in a vacuum oven prior to visualization. All fiber mats were visualized before hydration in order to measure the average fiber diameter of each mat. Image J software (Version 1.46) was used to measure the fiber diameters. At least 100 measurements were taken from each mat and averaged. Select mats were visualized after hydration to determine the effect of water on the fiber mat morphology. Average fiber diameters for fiber mats post-hydration were obtained using similar methods. All samples were sputter coated with gold for 45 s prior to the SEM analysis. Typical accelerating voltages and working distances were 8 kV and 20 mm, respectively.

4.3.6 Mechanical Testing

The apparent Young’s moduli of dry and hydrated PVAc fiber mats were measured using a Test Resources Model 100P Universal Testing Machine equipped with a 5.6 lbf (25 N) load cell. Dog bone (ASTM D63 Type IV, scaled down by a factor of 4) shaped samples were cut from dry and hydrated fiber mats and stretched at 33 μm s⁻¹ (~32 % min⁻¹) at RT until failure. To maintain hydration, the hydrated samples were submerged in a RT saline (0.9 % (w/v) NaCl) water bath during stretching. Anisotropic fiber mats were tested with the fibers aligned both parallel and perpendicular to the loading direction. The force and displacement were recorded simultaneously and used to generate stress-strain curves. Young’s modulus was determined from the slope of the stress-strain curve in the initial linear, elastic region. Two fiber mats with
various thicknesses and fiber diameters were tested for each state, and 3 samples from each fiber mat were used to gain confidence in the accuracy of the results.

4.3.7 X-ray Diffraction Analysis

A Rigaku SMAX 3000 X-Ray diffraction apparatus was used to identify molecular alignment in the PVAc before and after hydration. A collimated beam of X-rays (\( \lambda = 1.5405 \text{ Å} \)) was generated using an accelerating voltage of 45 kV and a current of 0.88 mA. Under vacuum, samples were exposed to the X-ray beam for 1 h. Small angle X-ray scattering (SAXS) patterns were obtained using a detector distance of 1550 mm. X-ray analysis was performed on isotropic and anisotropic PVAc fibers and PVAc films before and after hydration. Hydrated samples were subsequently dried for 1 day prior to testing. Since anisotropy due to molecular alignment was being probed, azimuthal plots of relative intensity versus azimuthal angle were prepared using SAXSgui software (version 2.03.04).

4.3.8 Fully Constrained Stress

A custom built device (Figure 4-1) was used to measure the fully constrained stress (FCS) generated due to the fiber mat shrinkage in water.\(^{12}\) Rectangular strips, 5 mm in width, were clamped into the device, with the distance between clamps being 21.5 mm. As shown in Figure 4-1, one clamp was fixed vertically, while the other clamp was free to rotate to accommodate the sample length. However, a force sensor was placed against this clamp pole to prevent rotation and sample shrinkage. If the sample tried to shrink, the rotating pole hit the force sensor, applying an equivalent force, but not moving in position. Thus, when the sample was hydrated and tried to shrink, the generated forces were measured. The FCS device was also
equipped with a sensor, which indicated the point at which water contacted the sample, and a funnel for easy filling of the tank with 25 °C water. Isotropic and anisotropic PVAc fiber mats were tested to compare the forces generated. For the anisotropic fiber mats, samples were tested with fibers oriented parallel and perpendicular to direction of force measurement. Experiments were run for 35 min.

The data collected from the force sensor was given in terms of voltage, and thus had to be converted to force measurements. The sensor was calibrated by applying known forces to the sensor. Namely, a string was connected between the two clamps, and a known mass was hung from the string. Various masses were tested, and the voltages were related to the weight of the sample. The calibration curve is provided in Figure 4-2.

From the generated force versus time data, the onset of force generation and the maximum achieved stress were measured and compared for the different fiber orientations. The onset of force generation was obtained by finding the intersection of lines fitted to the data prior to force generation and during the linear increase in force. For the isotropic fiber mats, the values were related to the average fiber diameters of the mats.

4.3.9 Folding Kinetics Testing

The unique shrinking behavior of electrospun PVAc in response to contact with water enables water-triggered folding through selective water placement. The dependence of folding rate on fiber diameter and mat thickness were studied. Rectangles, 30 × 18 mm (l × w) in dimension, were cut from the electrospun fiber mats and measured for thickness using calipers. The cut mat was placed on a Pelletier plate, set to 25 °C, and connected to a TA Instruments AR-G2 rheometer. Using a thin paintbrush, a line of water was drawn down the length of the
mat as indicated in **Scheme 4-1**. Subsequently, 0.05 mL of water was added to the drawn line via syringe and spread evenly with the paintbrush. First drawing the water line with a paintbrush was necessary to wet the surface of the fibers. Without this step, the water from the syringe remained in droplets on the surface of the mat. Videos of the mats folding were taken to later analyze for the folding kinetics. A video tracking software, Tracker (version 4.87), was used to trace the folding over time and obtain folding angle versus time data. The folding angle was subsequently fitted to the following exponential model:

\[
\theta(\degree) = 180 \times [1 - \exp(k \times (t - t_0))] 
\]

(4-2)

where \( \theta \) is the fold angle, \( k \) is a rate parameter, \( t \) is the time, and \( t_0 \) is a time parameter that captures the delay before folding begins. Here, an angle of 0\(^{\circ}\) indicates a flat mat prior to folding, and an angle of 180\(^{\circ}\) indicates a completely folded mat. Additionally, time 0 was designated as the time that the wet paint brush first contacted the fiber mat. Microsoft Excel’s “solver” was used to minimize the sum of the squares of the differences (SSDs) between the model prediction and the measured data through simultaneous adjustment of \( k \) and \( t_0 \).

The effect of the width of the drawn water line was also studied to further examine electrospun PVAc’s response to water contact. Again, using 30 (l) by 18 (w) mm fiber mat rectangles, water lines ranging from 1 to 5 mm in width were drawn using a thin paintbrush. To control the width of the water line, a mask was placed over the fiber mat, only exposing the desired hydration area. After wetting the area with the paintbrush, the mask was removed, and additional water was added using a syringe. The ratio of line width to added water volume was held constant at 1 mm:0.02 mL. Videos of the folding were recorded and later tracked and analyzed to relate the line width to the folding rate.
4.3.10 3-Dimensional Geometries

Traditional paper origami is typically used to build 3D forms. To demonstrate the efficacy of using electrospun PVAc and water in a similar fashion, 3D geometries were assembled. The fiber mats were first cut into a predetermined shapes to allow assembly of the desired structure. Water lines were drawn using the methods described in Section 4.3.9 to form folds in the mats. Strategic water placement and timing were required for self-assembly of the 3D geometries.

4.4 Results

4.4.1 Differential Scanning Calorimetry

DSC was employed to study the effect of water uptake on PVAc’s glass transition. Thermal heating and cooling scans for dry and hydrated PVAc fiber mats can be seen in Figure 4-3. The second heating results indicate T_g's of 44 and 17 °C for dry and hydrated PVAc, respectively. Further, the hydrated PVAc heating and cooling scans showed endothermic and exothermic peaks, respectively, that correspond to the melting and crystallization of water in the sample. The T_g of the hydrated sample was significantly lower than that of the dry sample due to the plasticization effect of water in PVAc. The relatively small water molecules diffuse into the PVAc fibers, disrupting the polymer chain entanglements and increasing space between molecules. The increased free volume in the polymer allows for more mobility of the chains and effectively reduces the glass transition temperature. In this case, the T_g is depressed below RT, a result utilized for water-triggered origami. Further, the T_g depression is reversible, as the polymer can be dried, eliminating the water molecules disrupting the chain structure. As
the water evaporates and the free volume decreases to match that of the pre-hydrated state, the \( T_g \) reverts to its original value. **Figure 4-3c** shows the DSC heating and cooling scans for PVAc fiber mats subjected to 24 h hydration followed by 48 h of drying in a RT vacuum. The PVAc \( T_g \) (44 °C) is comparable to the \( T_g \) of the as-spun PVAc.

### 4.4.2 Fiber Mat Shrinkage

During the electrospinning process, the high elongational forces experienced by the polymer jet when ejected from the charged needle induce molecular alignment along the length of the spun fibers. Because of the high degree of order of the extended and oriented chains, the polymer fibers are in a high energy state. This energy, or residual stress, is stored in the polymer as the fibers are vitrified. By heating above \( T_g \), the chains have enough mobility to reconfigure and conform to a lower energy, more random state. As the molecules reconfigure, the fibers shrink in length, causing the bulk mat to shrink. This effect has been reported in the past for PVAc and other electrospun polymers.\(^{13-16}\) In this case, however, heat was not used to cause the shrinkage. Instead, as water was absorbed into the fibers, the \( T_g \) was progressively lowered due to plasticization effects. As the \( T_g \) was depressed below room temperature, the molecular mobility increased to allow chain reconfiguration, and shrinkage occurred.

The degree of shrinkage of electrospun PVAc fiber mats was determined by measuring the length of PVAc squares before and after hydrating. **Figure 4-4** shows images of sections of a mat pre- and post-shrinkage. The PVAc fiber mats were found to shrink to less than half of their original length. Using **Eq. (4-1)**, the shrinkage was calculated to be 64 ± 4 % for the isotropic fibers. The shrinkage was found to be independent of mat characteristics (thickness, fiber diameter), and shrinkage values ranged from 60 to 68 % for all mats. Notably, the size
reduction was highly dependent on the fiber orientation. For the aligned fibers, the fiber mats shrunk more in the direction parallel to the fibers than in the direction perpendicular to the fibers. The respective shrinkage values were $70 \pm 2$ and $50 \pm 4\%$. Since the molecular orientation was along the fiber length, it was expected that the observed anisotropy would occur.

Since the $T_g$ of hydrated PVAc is depressed to around 17 °C, it was expected that hydrating PVAc fibers in refrigerated water would prevent shrinkage. After 24 h of hydration, the fiber mat was observed to maintain its shape (Figure 4-5). More specifically, the shrinkage was calculated to be only $6 \pm 1\%$. Such shrinkage is expected to be due to swelling effects from water absorption. Once the hydrated fiber mat was brought to RT, shrinkage comparable to previously reported results was observed.

4.4.3 Scanning Electron Microscopy

SEM images were obtained for fiber mats before and after hydration (Figure 4-4). Before hydration, the fibers were relatively straight and uniform. After hydration, and shrinkage, the fibers curled and twisted and the average fiber diameter increased. The increase in fiber diameter is explained by constant volume. Since the fibers shrink in length when hydrated, the diameter must increase in order to compensate. It is noted that any swelling due to water uptake should be reversed since the fibers were dried prior to visualization via SEM. The increase in average fiber diameter was calculated as $61 \pm 7\%$. It is also noted at this time that the shrinkage resulted in an increase in fiber density. Such increase is observed in SEM as a reduction in the size of the voids between fibers. The densification of the mat was also observed as a change in brittleness. Before hydration, the fiber mat could be easily folded or
bent without breaking. After hydration, the dried mat became more brittle, and bending the mat typically resulted in cracking or fracture. Since in both cases, the fibers were below their $T_g$, the brittle response was expected. It is hypothesized that the low volume fraction of the fibers in the pre-hydrated state gave the mat compliance. However, since the fiber mat densified after hydration, the mat responded more similarly to a brittle PVAc film.

4.4.4 Mechanical Testing

Engineering stress-strain curves were generated from force and displacement measurements obtained from the Test Resources mechanical tester, which was used to stretch dry and hydrated PVAc fiber mats. Representative curves for each fiber orientation and hydration state can be seen in Figure 4-6. It is noted that only the apparent stress has been reported since the porosities of the mats were not taken into account when calculating the cross-sectional areas. Furthermore, the dependence of mechanical properties on the fiber diameter was not a focus of this research. While no significant differences in tensile behavior were observed for the fiber mats with different average fiber diameters, more research would be needed to confirm if such a dependence does exist. For the current study, the calculated Young’s moduli and the observed elongations at break were averaged across all tested fiber mats (with varying fiber diameters) for a given fiber orientation. The relatively small standard deviations in the average values indicates that this approach is reasonable for the range of fiber diameters tested.

In the dry state, the stress-strain profiles significantly depended on the fiber orientation. As was observed in previous studies,17-18 a significantly higher stress was achieved when the fibers were oriented parallel to the stretching direction as opposed to perpendicular. Further,
the randomly oriented fibers required an intermediate stress for comparable elongations. The
difference in achieved stress is due to the load bearing capacity of the fibers. When the fibers
are oriented in the stretching direction, they are capable of bearing the load, and elongation of
the fibers requires a higher force. Conversely, when the fibers are oriented perpendicular to
the stretching direction, the applied force is used to separate the entangled fibers. Due to the
imperfect alignment of electrospun fibers, out of place fibers (i.e. fibers crossing the alignment
direction) are capable of bearing a load, and they contribute to the achieved stress. For the
isotropic case, since the fibers were oriented in all directions, there was an intermediate load
bearing capacity, and the stress achieved was between that of the fibers oriented parallel and
perpendicular to the stretching direction. The average Young’s moduli for the parallel,

isotropic, and perpendicular fibers in the dry state are tabulated in Table 4-1.

After the fiber mats were shrunk by hydrating for 24 h, dog bone samples were
stretched in a saline water bath to maintain hydration. Because the fibers in the hydrated state
were above their T₆s, the mechanical responses were drastically different from those observed
in the dry state. Namely, much smaller forces were required for deformation and the samples
reached much higher deformations before breaking. The low apparent moduli of the hydrated
fibers are hypothesized to be effects of (1) the physical state of the fibers and (2) the fiber
morphology. The hydrated fibers were stretched in the rubbery state since their T₆ was
reduced below RT due to plasticization from the water molecules. Therefore, the polymer
fibers were softened and required less force to deform. Furthermore, after hydration, the
fibers were raveled, twisted, and curled. Therefore, the initial force required to deform the
fiber mats was likely used to unravel and straighten the fibers. This hypothesis is supported by
the increase in slope observed between 150 and 200 % strain. The change in slope corresponds, we postulate, to the point at which the tensile deformation changed from straightening the fibers to stretching the fibers. Furthermore, the elongation at break was significantly increased for the hydrated samples. The hydrated PVAc typically reached about 1000 % strain or more before failure, while the dry PVAc typically fractured within a few hundred percent strain. Since the hydrated fibers were above their \( T_g \) during testing, the polymer chains could more easily rearrange to accommodate the strain. Polymer chains in the dry fibers, however, had restricted motion due to low free volume below \( T_g \). Thus, the glassy fibers had a brittle response and broke at low strains. Overall, hydrating the fiber mats reduced the strength of the material but increased the overall durability.

4.4.5 X-ray Diffraction Analysis

SAXS analysis was performed in order to verify molecular alignment in electrospun webs. Diffraction patterns for isotropic and anisotropic fibers and a PVAc film were obtained before and after hydration. Hydrated samples were subsequently dried prior to performing the X-ray analysis. The SAXS patterns can be seen in Figure 4-7. The as-spun anisotropic fibers showed indication of order in the SAXS pattern. The central pattern was elongated vertically, which was consistent with the horizontal orientation of the fibers during testing. For the isotropic fibers, the SAXS pattern was more uniform along the azimuth, since the randomly oriented fibers mask the molecular orientation. A slight elongation in the pattern was observed, which is likely due to a small degree of fiber orientation resulting from the rotation of the collector drum. The amorphous nature of the PVAc film resulted in a SAXS pattern with no notable features. After hydrating, the SAXS pattern for the anisotropic fibers became more
uniform along the azimuth, though slight elongation indicated that some molecular orientation remained. The pattern for the isotropic fibers became completely uniform, and the pattern for the PVAc film was unchanged. Azimuthal plots of intensity as a function of angle can be seen in Figure 4-8. The peaks in intensity at around 90° and 270° for the as-spun anisotropic fibers are indicative of the orientation. The peaks decrease significantly in intensity after hydration, which is consistent with the features observed in the SAXS patterns. It is hypothesized that nanovoids within the fiber mats may give rise to the SAXS scattering, but further analysis is necessary in order to reveal and confirm the internal structure responsible for the observed patterns.

4.4.6 Fully Constrained Stress Measurement

Using the custom designed device described in Section 4.3.8, the FCS generated during shrinkage was measured for mats hydrated in 25 °C water. Example plots of the FCS as a function of time are shown in Figure 4-9 for isotropic and anisotropic fibers. In all cases, there was a short time delay before force generation occurred. During this time delay, water diffused into and plasticized the fibers. Once the $T_g$ was depressed below the water temperature, the shrinkage occurred. The force generated during contraction depended significantly on the fiber orientation. When the fibers were aligned parallel to the direction of force measurement, the FCS was about 10 times as high as when the fibers were oriented perpendicular to the measurement direction. Specifically, the average FCS for the parallel and perpendicular fibers were $0.45 \pm 0.10$ and $0.04 \pm 0.01$ MPa, respectively. Since shrinkage occurs along the length of the fibers, this result was expected. The isotropic fibers exhibited an intermediate stress, with an average of $0.07 \pm 0.02$ MPa. It is noted that the measured stress is the apparent engineering
stress, since the fiber volume fraction was not considered and the force was normalized by the initial cross-sectional area. After the initial force generation, the stress was observed to gradually relax over the 30 min testing period. Such relaxation is a result of molecular rearrangement and chain slippage which reduce the contractile force of the fibers.

For the isotropic fiber mats, the contractile response was studied in more detail in order to relate the maximum FCS and the time delay before force generation to the average fiber diameter of the mats. It was expected that fiber mats with smaller fiber diameters would generate higher apparent stresses due to the presumably higher fiber volume fractions (since smaller fibers can pack more tightly). However, no clear dependence was observed (Figure 4-10a). This is likely due to the wide range of fiber diameters found within each fiber mat. Furthermore, a relatively small range of fiber diameters were tested, with all average fiber diameters between 0.4 and 1.0 µm. The time delay before the onset of force generation showed a slight dependence on the average fiber diameter, with longer delays observed for larger fiber diameters (Figure 4-10b). Such dependence can be explained by the diffusion path of water. For larger fiber diameters, the water must diffuse along a longer path (fiber radius) to hydrate the entire fiber. Furthermore, since PVAc is hydrophobic, the diffusion process is relatively slow, and thus an increase in the diffusion path length results in delayed hydration (plasticization) and shrinkage.

4.4.7 Folding Kinetics Testing

Understanding that PVAc fiber mats shrink upon hydration, we realized that if a line of water is drawn on one side of a spun mat, the mat will fold. To our advantage, PVAc is hydrophobic, so permeation of water through the mat is slow. Thus, when water contacts only
one surface, that surface begins to shrink before the water permeates through the mat, and a
gradient of shrinkage forms through the thickness. If a line water is drawn on the surface,
localized shrinkage is obtained, and the mat folds. **Scheme 4-2** illustrates this concept. Using
the method described earlier, isotropic PVAc fiber mats with various characteristics were folded
using water. Time step images of the amazing folding response can be seen in **Figure 4-11**.
Data relating the folding angle to time was obtained using the Tracker software. An example
plot of fold angle over time is provided in **Figure 4-12**. In general, the fiber mats folded
completely within 30 to 600 s, with the time being dependent on the mat characteristics, which
will subsequently be discussed. A delay before folding begins was observed and is
hypothesized to be a combined result of (1) the hydrophobicity of PVAc and (2) the necessity to
plasticize a fraction of the fibers through the thickness in order to trigger folding. PVAc is a
hydrophobic polymer, and thus water uptake is slow compared to hydrophilic polymers.
Furthermore, a fraction of the fibers must be hydrated and in the process of shrinking before
the fiber mat folds. If only the fibers on the very top of the mat shrink, a large enough force is
not generated to overcome the stiffness of the fibers and fold the mat. Thus, folding is also
delayed by water permeation through the fiber mat.

Folding data for all tested fiber mats was fitted to the model given in Eq. (4-2). **Figure
4-12** compares the model fit to the data captured from a folding fiber mat. Good agreement
between the model and experimental data is observed except for at the end of folding, where
the model underpredicts the fold angle. This flaw in the model was consistently observed
across the tested samples. While the exponential model was sufficient in capturing the major
characteristics of the folding, it is noted that in some instances, the folding rate was more
complex than what was captured by the exponential equation. For example, some fiber mats started folding slowly, then folded more rapidly, and finally slowed as the folding neared completion. In such instances, the fold angle versus time trace had a more sigmoidal shape which was not captured by the model. The model only predicts a delay before folding begins followed by an exponential rise. An example of such data can be seen in Figure 4-13 along with the model fit. A more complex model that considers the material properties of PVAc, water diffusion kinetics, and the plasticization effect is being developed, but for the current work, the simple model was used to characterize the folding.

The rate of folding and the time delay before folding began were found to be highly dependent on certain characteristics of the mat. The parameters, k and t₀, which capture the rate and time delay, respectively, are plotted as functions of mat thickness and fiber diameter in Figure 4-14. Increasing the mat thickness led to slower folding rates and longer time delays before folding began. Since the fold angle depends on the fraction of the mat that is shrunk, increasing the mat thickness requires water to permeate and diffuse into a thicker section of fibers in order for the same angle to be obtained. Therefore, more time was necessary for folding, and the rates obtained were lower. Due to the significant drop in folding rate with increasing thickness, it was hypothesized that water permeation through the mat, as opposed to water diffusion into the fibers, was the rate limiting step. Therefore, it was expected that the folding rate would increase with increasing fiber diameter, since the fiber mats are presumably more porous (porosity was not measured, but was expected to be lower for fiber mats with smaller fiber diameters since the fibers can pack more tightly). However, no significant dependence of k or t₀ on fiber diameter was observed. The lack of relation may be
explained by the relatively wide range of fiber diameters (as is evident by a large standard deviation in average fiber diameter) present in each fiber mat.

For the isotropic fiber mats, the effect of water line width on the folding kinetics was also investigated. 1 to 5 mm wide water lines were drawn on fiber mats with varying thicknesses. The rate of folding was observed to increase with increasing width, which we attribute to a larger section of fibers being hydrated and shrinking. Therefore, with a smaller fraction of the fibers shrunk through the thickness of the mat, the gradient and generated force was larger and able to overcome the stiffness of the mat and fold it. Furthermore, the water line width had a more drastic impact on thinner mats, as is indicated by the larger slope in Figure 4-15a. When the 1 mm water lines were drawn on the thicker fiber mats, there were instances in which the mat did not fold to completion. Such a small amount of water was added to the surface of the mat that it did not permeate far enough into the thickness to result in complete folding. Also, the folding rate was so slow, that it is suspected that a portion of the water evaporated over time. In such cases, the mat remained in the partially folded state. The width of the water line also impacted the sharpness of the fold angle. Wider lines resulted in more curling of the fiber mat around the hydration area since a larger area of the mat was involved. The thinner water lines allowed for sharper folding, as the width of the gradient section was much smaller. Images depicting the change in sharpness are provided in Figure 4-15b-d. No significant dependence of the time delay before folding, $t_0$, on water line width was observed.

Anisotropic fiber mats were also tested to observe the response to water application relative to the fiber direction. When the line was drawn perpendicular to the fiber alignment
direction, the fiber mat folded similarly to the isotropic fiber mats. Folding was expected for this case since the fibers shrunk in the folding direction. When the water line was drawn parallel to the fibers, however, a different response was observed. In most instances, in the location of the water, the fiber mat shrunk parallel to the drawn line, which was expected. This resulted in wrinkling of the fiber mat (Figure 4-16a), since the non-wetted portions of the mat did not shrink, and thus were pulled by the center line. In other instances, the fiber mat curled towards the line (Figure 4-16b). Again, since the fibers shrunk in the direction of the line, and since there was a gradient of shrinkage through the thickness, this response was expected. The unexpected case was that in which the fiber mat folded partially, and then one side of the fold curled towards the water (in a similar fashion to case b), causing the other side to curl away from it (Figure 4-16b). It is suspected that the response is due to the imperfect alignment of the fibers. Such anisotropy in behavior could be useful in controlling the response of the fibers in practical applications.

4.4.8 3-Dimensional Geometries

PVAc fiber mats cut into preconceived shapes were used to assemble 3D geometries. A triangle, pyramid, accordion, and water-bomb base were constructed via the application of water to the surface of the fiber mats. A triangle (Figure 4-17a) was constructed from a rectangular piece of the fiber mat. Two evenly spaced parallel lines were drawn on the mat, and the second line was drawn immediately after the first to minimize time between the start of shrinkage. Along each fold, the end of the rectangle folded upward, and the two ends met at the top, forming a triangle. The pyramid (Figure 4-17b) was constructed in a similar fashion, but the initial starting shape was a four-pronged star. An accordion (Figure 4-17c) was formed
from a rectangular piece of fiber mat. As with the triangle, two evenly spaced parallel lines were drawn on the mat, but the second line was drawn on the opposite side of the mat. After drawing the first line, the mat was flipped over, and the second line was drawn. In order to prevent capillary action from causing the water to spread along the underneath of the fiber mat after flipping, the mat was kept lifted from the surface of the Pelletier plate. Interestingly, the fiber mat did not appear to fold along the water line facing the ground. This indicates that gravity assists in the permeation of the water through the mat. Since PVAc is hydrophobic, water is not readily absorbed, and the gravitational force is needed to promote water permeation. Thus, the fiber mat was flipped a second time to allow the second fold to develop. The water-bomb base, a commonly used paper origami preform, was constructed in a similar fashion, but with four lines drawn on each side (Figure 4-17d). The lines alternated sides of the PVAc in a radial pattern centered on the square sheet. The resulting zig-dag plane did not fold as tightly as the typical paper based water-bomb base. This is likely due to constraint imposed by the center of the structure. The eight separate folds met at the center of the square, thus pulling it in different directions. Tension at that point restricted the folding of the structure. Such tension could be alleviated by cutting a small hole from the square. Nevertheless, the water-bomb base and other 3D structures was achieved via water-triggered origami.

4.5 Conclusions

Residual stresses stored in PVAc from the electrospinning process can be relaxed by heating the PVAc through its $T_g$. In this chapter, an alternative method of stress recovery was studied. Namely, hydrating PVAc fibers was shown to plasticize the PVAc, reducing the $T_g$ below RT. As the $T_g$ transitioned below RT, a significant increase in free volume and kinetic
energy allowed molecular rearrangement of the PVAc. Thus, the stress from electrospinning was relaxed, and the fiber mats shrunk to less than half of their original lengths. Such stress relaxation was shown via SAXS to result in a loss of molecular alignment along the fiber direction. This response to water was exploited to develop a water-triggered folding system. Application of water on one surface of the PVAc resulted in the formation of a shrinkage gradient through the thickness of the fiber mat, which led to folding. Fitting folding data to a simple exponential model captured the key aspects of the folding response and revealed that the folding rate was highly dependent on the mat thickness and the width of the drawn water line. Furthermore, fiber orientation dictated the response of the mat, i.e. when water lines were drawn perpendicular to the fiber direction or on isotropic fiber mats, the folding was observed, but when water was drawn along the fiber direction, a variety of responses were achieved. To show the efficacy of water-triggered folding for the construction of 3D structures, patterns of water were applied to cut sheets of PVAc fibers. Through careful water placement and timing, 3D structures were self-assembled in a process we have termed, “water-triggered origami.” We envision that this phenomenon can be used in its current state for a craft alternative to paper origami. Furthermore, the unique shrinkage response could be exploited in development of a humidity sensor. In this case, the PVAc fibers could be triggered to shrink if the humidity gets above a certain level. Further development of this phenomenon could lead to more complex applications. For example, using dual-electrospinning to combine PVAc with a non-water responsive polymer could allow for better control of the final fold angle of the mat after hydration. In this case, a gradient in composition through the thickness could be used to
define the final achieved fold angle, which could be useful for more robust assembly of 3D structures.

4.6 References


12. Yang, P. New Surface and Bulk Shape Memory Effects in Polymers for Biomedical Applications. Syracuse University, 2014.


4.7 Schemes, Figures, and Tables

Scheme 4-1 Water-triggered folding technique, showing (a) a cut isotropic fiber mat, (b) the application of a small amount of water with a paint brush to wet the mat surface, (c) the application of 0.05 mL water with a syringe, and (d) water-triggered folding.
Figure 4-1 Custom built device used to measure the fully constrained stress generated during shrinkage of the PVAc fiber mats. Significant components of the device are labeled on the figure.
Figure 4-2 Calibration curve used to convert the voltage signal from the force sensor to the force generated by fiber mat shrinkage.
Figure 4-3 DSC heating and cooling curves for (a) as-spun PVAc fibers, (b) hydrated PVAc fibers, and (c) PVAc fibers that were hydrated and subsequently dried. The glass transition temperatures of each state are indicated by the vertical dotted lines at 17 °C ((b)) and 44 °C ((a) and (b)). All heating and cooling rates were 10 °C min⁻¹.
Figure 4-4 Photographs and SEM images of isotropic (top row) and anisotropic (bottom row) PVAc fiber mats (a) before and (b) after 24 h hydration. Hydration was accompanied by a drastic reduction in size of the fiber mat and an increase in average fiber diameter. The fiber orientation is indicated by arrows for the anisotropic fiber mats. Scale bar represents 5 mm for all photographs.
**Figure 4-5** Photograph comparing a PVAc fiber mat before (left) and after (right) hydration in refrigerated DI water. Minimal shrinkage was observed compared to PVAc fibers hydrated in RT DI water. Scale bar represents 5 mm.
Figure 4-6 Tensile engineering stress-strain curves for (a) dry and (b) hydrated PVAc fiber mats with parallel (i), isotropic (ii), and perpendicular (iii) fibers. The top row shows the strain-to-failure of the fiber mats, and the bottom row provides a magnified view of the initial region of deformation from which the Young’s modulus was calculated.
Table 4-1 Summary of the average Young’s modulus values for dry and hydrated PVAc fiber mats with various fiber orientations.

<table>
<thead>
<tr>
<th>Hydration State</th>
<th>Fiber Orientation</th>
<th>Young’s Modulus (MPa)</th>
<th>STDEV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Parallel</td>
<td></td>
<td>185</td>
<td>38</td>
</tr>
<tr>
<td>Dry Isotropic</td>
<td></td>
<td>78.0</td>
<td>5.8</td>
</tr>
<tr>
<td>Dry Perpendicular</td>
<td></td>
<td>24.4</td>
<td>8.0</td>
</tr>
<tr>
<td>Hydrated Parallel</td>
<td></td>
<td>0.09</td>
<td>0.02</td>
</tr>
<tr>
<td>Hydrated Isotropic</td>
<td></td>
<td>0.13</td>
<td>0.03</td>
</tr>
<tr>
<td>Hydrated Perpendicular</td>
<td></td>
<td>0.08</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Figure 4-7 SAXS patterns for (a) anisotropic PVAc fibers, (b) isotropic PVAc fibers, and (c) a PVAc film before (left column) and after (right column) hydration. The fiber orientation direction is indicated by arrows for the anisotropic fibers.
Figure 4-8 Azimuthal plots of intensity as a function of angle prepared from the SAXS data of (a) anisotropic fibers (b) isotropic fibers, and (c) a PVAc film before (solid, top) and after (dashed, bottom) hydration.
Figure 4-9 Representative plots of the fully constrained stress generated by water-induced shrinkage of PVAc fibers oriented (i) parallel, (ii) randomly (isotropic), and (iii) perpendicular relative to the stress measurement direction. Plot (a) captures the full 30 min test time and shows the relaxation of the stress over time, and (b) expands the initial 150 s to expose the delay before stress generation.
Figure 4-10 Average (a) fully constrained stress (maximum) and (b) onset time for force generation as functions of the average fiber diameter for isotropic PVAc fiber mats.
Scheme 4-2 Schematic showing the mechanism by which water-triggered origami is achieved. Due to localized hydration and slow water permeation, a gradient of shrinkage forms through the thickness of the fiber mat, causing folding.
Figure 4-11 Time-step images of an isotropic PVAc fiber mat folding after application of water along the length of the mat. Scale bar represents 5 mm for all photographs.
Figure 4-12 Fold angle as a function of time for water triggered folding of a PVAc fiber mat. Experimental data (circle scatter plot) is compared to the fitted exponential model (line plot) used to characterize the folding.
Figure 4-13 Example folding data for a fiber mat that exhibited variable folding rates. The model (line plot) is not able to capture the sigmoidal shape of the experimental data (scatter plot).
Figure 4-14 Time delay ($t_0$, filled) and folding rate ($k$, open) as functions of (a) mat thickness and (b) average fiber diameter for isotropic PVAc fiber mats. The folding characteristics showed a stronger dependence on the thickness of the fiber mat.
Figure 4-15 Effect of water line width on (a) the folding rate and (b)-(d) the sharpness of the fold. In (a), fiber mats with average thicknesses of (i) 0.10, (ii) 0.13, and (iii) 0.19 mm were tested. The pictures show folded fiber mats (0.13 mm average thickness) after (b) 1 mm, (c) 3 mm, and (d) 5 mm wide water lines were drawn on the mats.
Figure 4-16 Aligned PVAc fiber mats after water lines were drawn parallel to the fiber direction. The fiber mats responded by either (a) wrinkling, (b) curling, or (c) partially folding then curling. Top and bottom rows show different perspectives of the same fiber mat.
Figure 4-17 3D geometries constructed using water-triggered origami. Assembled structures include (a) a triangle, (b) a pyramid, (c) an accordion, and (d) a water-bomb base. The top row shows schematics of the cut PVAc fiber mats and indicates the placement of water lines. Black dotted lines indicate water drawn on top of the mat and gray dotted lines indicate water lines drawn on the reverse side. The middle row shows images of the mats during the assembly process, and the bottom row shows the final folded structures. For (c) and (d), between the middle and bottom rows, the fiber mats were flipped to the opposite side.
Chapter 5. Summary

5.1 Conclusions

The work detailed in this thesis utilized electrospun fibers in the development of dynamic and active materials. The polymers from which the fibers were spun were chosen for their specific thermal and mechanical properties to enable the sought after functionality. Chapters 2 and 3 exploited the porous nature of electrospun materials in the development of soft shape memory composite systems, while Chapter 4 utilized the residual stress inherently stored in electrospun fibers to develop a unique water responsive system. This work shows the versatility in electrospinning and only touches upon the broad range of applications for which electrospinning can be used.

5.1.1 Mechanically Activated Shape Memory Elastomeric Composites

Chapter 2 detailed the use of aligned poly(vinyl acetate) (PVAc) fibers in the fabrication of laminated shape memory elastomeric composites (SMECs). The aligned fibers were infiltrated with a crosslinkable elastomer which promoted shape recovery, while the PVAc fiber phase aided in shape fixing. Due to the anisotropy of the PVAc fibers, the single layer SMECs exhibited directionally dependent properties. Most importantly, the Young’s modulus and the reversible plasticity shape fixing ability significantly varied with fiber orientation. A higher modulus was measured with the fibers oriented in the loading direction as opposed to when the fibers were oriented perpendicular to the fiber direction. Such result is due to the load bearing capacity of the fibers. Similarly, the ability of the fibers to counteract the contraction of the elastomer matrix after room temperature (RT) deformation was directionally dependent.
With the fibers oriented parallel to the tensile direction, the plastic deformation of the PVAc resisted elastic contraction and fixed 85 % of the deformed strain. On the other hand, when the fibers were oriented perpendicular to the tensile direction, only 50 % of the deformed strain was fixed. Intermediate fiber orientations corresponded to intermediate fixing ratios.

Anisotropy in the fixing ability of the SMECs resulted in unique shape change for the laminated SMECs. Specifically, laminating the anisotropic SMECs (ASMECs) at varying fiber orientations led to the formation of curled geometries after simple tensile deformation. Due to the directional dependence of the fixing ratio, layers of the laminated ASMECs with different fiber orientations had different fixed lengths after stretching. Therefore, to accommodate the difference in length, the laminated ASMEC curled towards the ply with the lower fixing ratio. The curling attributes, namely the curvature and pitch of the helical structures, were related to the difference in fiber orientation. As the difference in fiber angle of the two layers increased, the curvature increased and the pitch decreased, i.e. the curling was tighter. This result follows directly from the greater difference in fixed lengths between the two ASMEC layers. Furthermore, all structures were recoverable to their initial flat form by heating above PVAc’s $T_g$.

Adaptation of the model developed for the curling of bimetallic strips showed that prediction of the curvature based on the fiber orientation and thickness of each layer was possible. Such result could be applied to design 3D structures with predictable form. Although the model was not used to predict structure in this study, some of the attainable 3D shapes were formed from initially flat laminated ASMECs in the form of a propeller, a triangle, and a
circle. Interesting geometries were attained due to the fiber orientations involved and the constraint imposed from the continuous forms.

5.1.2 Dual-Spun Thermoplastic Shape Memory Elastomeric Composites

Chapter 3 innovated the SMEC fabrication process, utilizing only industrially relevant processing techniques so as to enable large scale production of shape memory rubbers. A dual-electrospinning setup was developed to simultaneously electrospin the two polymers which separately promoted shape fixing and shape recovery. In doing so, the crosslinkable elastomer traditionally used in SMEC fabrication was replaced with a thermoplastic polyurethane elastomer. The advantages of changing to dual-electrospinning and thermoplastic elastomers include (1) elimination of the fiber infiltration step in which the polymer fibers were imbibed with the elastomer precursor, (2) elimination of the crosslinking process which required several days for complete curing, and (3) control over the relative composition of the shape fixing and shape recovery polymers. It was demonstrated that by altering the flow rates of the two polymers during dual-electrospinning, the composition could be controlled. As such, the mechanical properties could be tuned to meet those of a specific application. However, it was shown that there is a trade-off between modulus and shape memory performance. If a lower modulus is sought, more of the elastomer should be incorporated into the composite (as opposed to the higher modulus shape fixing polymer), but the ability of the composite to withstand elastic contraction and fix a temporary shape diminishes with decreasing content of the shape fixing polymer. Furthermore, the dual-electrospinning process was compared to a blend approach in which the two polymers were initially mixed at the molecular level. Due to phase separation, the blended polymers showed variable performance, indicating
inhomogeneity within the film. Therefore, the dual-electrospinning process was preferred for fabrication of a homogeneous composite.

Potentially the most advantageous attribute of the dual-electrospinning process is its versatility. Dual-electrospinning can be applied to any two electrospinnable polymers to achieve well-dispersed, intertwined composites. As such, the two polymers can be chosen to meet the needs of specific applications, and dual-electrospinning is not limited to SMEC fabrication. This concept was touched upon by comparing the properties of two SMEC systems. Furthermore, one system was chosen for its unique ability to function as a reversible adhesive. The control over composition was again used to tune the adhesive performance, though a threshold in performance was reached at an intermediate composition.

5.1.3 Water-Triggered Origami with a Polymeric Web

Chapter 4 detailed the use of a water responsive electrospun fiber mat to mimic paper-based origami. Due to the strong elongational forces experienced during electrospinning, residual stress can be stored in electrospun fibers. Upon heating, that stress is recovered, and the fiber mat shrinks. For the PVAc system studied, water plasticization depresses the $T_g$ below RT, thus enabling water-triggered shrinkage at RT. The properties of the fiber mats in the wet and dry states were compared, and specifically, the Young’s modulus was observed to decrease by 3-4 orders of magnitude upon hydration. The shrinkage effect was exploited to develop a water-triggered origami system in which the PVAc fiber mats folded in response to drawn lines of water on the mat surface. As the water permeated through the mat and diffused into the fibers, a gradient of shrinkage formed, causing folding. The mat thickness was determined to
be the characteristic of the mat that predominantly controlled the rate of folding. Further, the folding rate could be adjusted by varying the width of the drawn water line. Wider lines resulted in faster folding, as they caused a larger area to shrink, thus magnifying the shrinkage gradient. Applying this concept to strategically cut sheets of PVAc fiber mats, multiple water lines were drawn to assemble 3D geometries that mimicked paper-based origami.

5.2 Future Work

5.2.1 Mechanically Activated Shape Memory Elastomeric Composites

Chirality is a commonly observed phenomenon in nature that exists at both the microscale and macroscale. For example, molecular structures can be chiral, with the different orientations referred to as enantiomers. Therapeutic drugs with different chiralities have been shown to have profoundly different effects in the body.\(^1\) For example, one chirality may be therapeutic while the other is toxic. Furthermore, DNA is a chiral macromolecule with defined handedness. On a larger length scale, shells and plant vines show chirality with preferred orientations.\(^2\) As science often draws inspiration from nature, the development of chiral materials for various applications is of interest.

The bilayer laminated ASMECs developed in Chapter 2 exhibited chirality, as the helical structures had handedness defined by the relative orientation of the ASMEC layers. As the next steps in material development, it would be interesting to study the response of a multilayer (>2) laminated ASMEC. After tensile deformation, such a material would be expected to exhibit an even more complex response involving both twisting and curling. The twisting would result from in plane rotation of the composites after tensile deformation, and the curling would likely
be defined by the top and bottom layers of the laminated stack. As an alternative to the stacking approach, the electrospinning setup could be modified in order to electrospin a fiber mat with varying fiber angles through the thickness of the mat. For example, the collector drum, in addition to rotating in the direction of fiber collection, could rotate normal to the collection direction. Such rotation would occur over the course of electrospinning, i.e. in order to get a 90° variation in preferred fiber orientations, the drum would rotate 90° over the 8-12 h collection period. The gradient in fiber orientation through the thickness would be continuous, and its properties would be interesting to compare to the multilayer laminated composites suggested previously.

5.2.2 Dual-Spun Thermoplastic Shape Memory Elastomeric Composites

As discussed in Chapter 2, anisotropy in material properties is often desirable, as directionally dependent materials are commonly found in nature. Aligned fibers can be electrospun (Scheme 2-1) by increasing the rotation speed of the collector drum and by adding a charged copper plate that creates a more uniform electric field, thus influencing the direction of the charged polymer jet. By modifying the current dual-electrospinning setup, i.e. by increasing the drum rotation and adding charged copper plates around the needles, dual-spun \emph{aligned} fibers can be attained, thus enabling dual-spun anisotropic SMECs (ASMECs). Due to the reversed morphology (in the original ASMEC, the shape fixing polymer was contained in an elastomeric matrix, and in the dual-spun ASMEC, the elastomer would serve as the fiber phase within a matrix of the shape fixing polymer), it would be interesting to compare the properties of the dual-spun ASMEC to those of the ASMEC developed in Chapter 2.
The dual-electrospinning approach to SMEC fabrication resulted in switching of the fiber and matrix phases. The dual-spun SMECs had the shape fixing polymer as the matrix, which was exploited for the reversible adhesive application. However, in some cases, having the shape fixing polymer as the matrix may be non-ideal. For the PCL based system, this can be understood, as adherence of the SMEC to the contacting surface upon crystallization could be undesirable. One approach that could be used to resolve such an issue is coaxial electrospinning. The needle used in coaxial electrospinning has an inside core and an outside sheath, allowing for the electrospinning of composite fibers. In the case of the SMECs, the shape fixing polymer could be contained within an elastomer sheath. Such morphology would contain the shape fixing polymer when melted or softened and would prevent contact between the core and surrounding surfaces. Furthermore, the fiber structure in a core-sheath SMEC would be maintained. In contrast, the previously studied SMECs were dense films in usable form. The fibrous SMEC would be interesting to study as its apparent modulus would presumably be even lower than the current SMECs due to the reduced volume fraction. Additionally, the porous fiber morphology could lend the SMECs to a new range of applications including cell culture and wound dressing.

As discussed previously, one of the main advantages of dual-electrospinning is its versatility. Dual-electrospinning can be used to prepare homogenous composites of any two electrospinnable polymers. However, this concept is not limited to only two electrospinning jets. A third electrospinning jet could be added to prepare composites of 3 polymers. Such a tri-electrospinning setup could be used to electrospin quadruple SM composites, or composites capable of having three temporary shapes and one permanent shape. For example, a

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poly(methyl methacrylate) (PMMA), PCL, PVAc composite could be electrospun together. Such a composite should, with the optimal relative composition, be able to fix temporary shapes due to PMMA vitrification, PCL crystallization, and PVAc vitrification. By heating above PMMA’s $T_g$, then deforming and cooling, temporary shape 1 could be fixed. Deforming again at a temperature above PCL’s $T_m$ but below PMMA’s $T_g$ and then cooling should fix a second temporary shape. And finally, deforming above PVAc’s $T_g$ but below PCL’s $T_m$, and then cooling, a third temporary shape should be fixed. Upon heating, consecutive recovery of the fixed shapes and the permanent shape could be observed. Quadruple SMP composites could find new applications requiring complex shape change due to the increased functionality.

5.2.3 Water-Triggered Origami with a Polymeric Web

A potential drawback to the current water-triggered origami approach is the sensitivity of the entire fiber mat to water. If the entire mat is submerged in water, the isotropic fiber mat shrinks equally in length along all sides. Due to the homogenous shrinkage, folding does not occur. Furthermore, if excess water is used to fold the fiber mat, as the water spreads throughout the mat and is absorbed by the fibers, the entire mat shrinks. In such instances, folding may occur first, but then the folded structure is observed to shrink in size over time. To better control the response of the fiber mat, and to maintain the overall size of the mat, a composite fiber mat could be electrospun. Utilizing the dual-electrospinning setup, PVAc could be simultaneously electrospun with a water insensitive or a water swellable polymer. In either case, a gradient fiber mat could be electrospun with the additional polymer concentrated on the bottom of the mat and PVAc concentrated on the top. When water is applied on the surface of such a mat, the PVAc should shrink, while the fibers composed of the other polymer...
should maintain their shape. Thus, the overall size of the mat should be maintained due to constraint imposed by the presence of the additional polymer. Furthermore, if a water swellable polymer is incorporated into the web, the folding rate may be increased, as both sides of the mat would be contributing to folding, with the bottom swelling and the top (PVAc) shrinking.

An alternative route to explore with water-triggered origami is reversible folding. Fully constrained stress measurement revealed that the stress generated during hydration induced shrinkage relaxes with time. If a biasing layer were added to the PVAc, stress relaxation should allow unfolding. For example, if a bilayer composite were prepared with an elastomer bottom layer and a fibrous PVAc top layer, upon application of water to the top surface, the composite could fold (or curl) in response to PVAc shrinkage. Folding would stretch the bottom elastomer layer, putting it into a state of tension. If the thickness and modulus of the elastomer were balanced with the contractile stress generated during shrinkage, upon relaxation of that stress, the elastomer could trigger unfolding. Such reversibility could be useful in certain applications.

5.3 References


Appendix 1. Mechanical Properties of PCL and POSS-Based Thermoplastic Polyurethane Elastomers

A1.1 Mechanical Testing

Multiple syntheses of multiblock poly(ε-caprolactone)-polyhedral oligomeric silsesquioxane polyurethanes (POSS-TPUs) were performed following similar procedures as those outlined in Section 3.3.2 (see comments in Table A1-1 for exact reaction conditions). The resulting products had a range of molecular weights, as is summarized in Table A1-1.

The dependence of the Young’s modulus and strain to failure on the molecular weight of the POSS-TPUs was tested using the Linkam TST350 tensile stage. Dog bone (ASTM D638, ¼-scale) shaped samples were stretched at 33 µm s⁻¹ to failure or to the limits of the instrument. The Young’s modulus was calculated using Eq. (3-3) from the stress and strain data in the elastic region. The strain to failure was taken as the strain at which the stress returned to 0 N for samples that failed during testing. At least three samples were tested for each synthesis (molecular weight).

The stress-strain curves of syntheses 6 and 11 (Mₙ = 18.3 and 62.8, respectively) are presented in Figure A1-1. The higher molecular weight POSS-TPU shows a slightly higher Young’s modulus, as seen by the steeper increase in stress at low strains. This higher modulus can be explained by increased entanglements between polymer chains. At low molecular weights, the chains are able to slip past each other, providing less resistance to deformation. For similar reasons, the strain-to-failure of the low molecular weight samples is observed to be at significantly lower strains. However, it is noted that the majority of tested POSS-TPUs
reached the limits of the Linkam without failing. The Young’s modulus and strain to failure of the POSS-TPUs are plotted as functions of molecular weight in Figure A1-2.

A1.2 Elasticity Testing

The dependence of the elasticity of the POSS-TPUs on molecular weight was also investigated. Ideally, elastomers return to their original lengths immediately after stretching and releasing. However, due to chain slippage and plastic deformation of the crystalline regions, incomplete recovery is observed for the POSS-TPUs after stretching. To determine the impact of molecular weight on the elasticity of the POSS-TPUs, a TA Instruments AR-G2 rheometer was used in a tensile mode. Custom made clamps were used to stretch dog bone samples. The samples were first stretched to 100 % strain at 33 µm s⁻¹. Immediately after reaching 100 % strain, the clamp direction was reversed, and the sample was brought back to 0 % strain at a 33 µm s⁻¹. After a 10 min hold, the sample was stretched again to 50 % strain, and then unloaded back to 0 % strain. Two more cycles were repeated at 50 % strain to complete the program. Two types of measurements were made from the stress and strain data: elasticity ratios and recovery ratios. Here, we define the elasticity ratio, $R_e$, as follows:

$$R_e(\%) = \frac{\varepsilon_m - \varepsilon_e}{\varepsilon_m - \varepsilon_i} \times 100$$  \hspace{1cm} (A1-1)

where $\varepsilon_m$, $\varepsilon_e$, and $\varepsilon_i$ are the maximum strain reached during the cycle, the strain at 0 N force (after unloading), and the initial strain at the beginning of the cycle, respectively. The recovery ratio, similar to the shape memory recovery ratio, $R_R$, was calculated using Eq. (A1-2):

$$R_R(\%) = \frac{\varepsilon_m - \varepsilon_R}{\varepsilon_m - \varepsilon_i} \times 100$$  \hspace{1cm} (A1-2)
where $\varepsilon_R$ is the strain at which the stress increases in the next cycle. $R_e$ measures the immediate recovery of the POSS-TPU, while $R_R$ captures the time-dependent recovery. $R_R$ is necessary due to the viscoelastic nature of polymers. Upon unloading to 0 stress, the POSS-TPUs do not recover completely, but during the isothermal hold, recovery continues.

**Figure A1-3** shows the generated stress-strain curves for syntheses 6 and 11 ($M_n = 18.3$ and 62.8 kg mol$^{-1}$, respectively). The lower elasticity of the lower molecular weight POSS-TPU is observed by the slightly steeper decrease in stress upon unloading in the first stretching cycle. The more rapid decrease in stress indicates more chain slippage and thus, less elastic recovery. However, it is noted that the improved elasticity with the higher molecular weight POSS-TPU is only slight. After the stretch to 100 % strain, the lower molecular weight sample remained deformed to about 43 % strain, while the higher molecular weight sample recovered to about 37 % strain. It is hypothesized that the range of molecular weights tested was too narrow to observe a significant increase in elasticity. If a significantly higher molecular weight POSS-TPU, such as one with a $M_n$ of 200 kg mol$^{-1}$ or higher, were tested, it is expected that the elasticity would show significant improvement. Ideally, the loading and unloading traces would overlap completely, indicating 100 % elasticity. The elasticity and recovery ratios are plotted as functions of molecular weight in **Figure A1-4**. As the molecular weight increases, the ratios for the first cycle increase slightly, though all values are between 50 and 70 % ($R_e$) and 60 and 80 % ($R_R$). After the first cycle at high deformation, the subsequent stretches to 50 % strain showed improved elasticity and recovery. Both ratios were observed to be independent of molecular weight. The elasticity ratio averaged around 85 %, and the recovery ratio averaged around 100 % for stretching cycles 2-4. The improved elasticity and recovery after the initial deformation in
likely a result of (1) the smaller deformation and (2) the initial prestretch. In cycles 2-4, the samples were stretched to 50 % strain, while in cycle 1, they were stretched to 100 % strain. Due to the smaller deformation, less chain slippage is induced, therefore resulting in improved elasticity. Furthermore, the prestretch to 100 % strain plastically deformed the samples, and partial recovery was promoted by chain entanglements. Subsequent stretches to strains less than 100 % did not further plastically deform the samples, and thus, 100 % recovery was expected (and observed on average).
### A1.3 Schemes, Figures, and Tables

**Table A1-1** 70-30 PCL1k-POSS TPU synthesis summary.

<table>
<thead>
<tr>
<th>Mass Ratio (NMR)</th>
<th>M_n (kg mol(^{-1}))</th>
<th>M_w (kg mol(^{-1}))</th>
<th>T_g,PCL (°C)</th>
<th>T_m,PCL (°C)</th>
<th>ΔH_m,PCL (J g(^{-1}))</th>
<th>T_m,POSS (°C)</th>
<th>ΔH_m,POSS (J g(^{-1}))</th>
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Figure A1-1 Stress-strain curves showing (a) the attainable strains and (b) the initial slope (Young’s modulus) for (i) a relatively low molecular weight POSS-TPU (synthesis 6) and (ii) a relatively high molecular weight POSS-TPU (synthesis 11). The low molecular weight film broke around 100 % strain, while the higher molecular weight film stretched to the limits of the instrument.
Figure A1-2 (a) Young’s modulus and (b) strain-to-failure as functions of number average molecular weight ($M_n$, left column) and weight average molecular weight ($M_w$, right column). Increasing molecular weight generally increases both the modulus and strain-to-failure.
Figure A1-3 Loading and unloading curves showing the elasticity of (a) a relatively low molecular weight POSS-TPU (synthesis 6) and (b) a relatively high molecular weight POSS-TPU (synthesis 11). The cycles are represented in black (100 % strain stretch), red (first 50 % strain stretch), green (second 50 % strain stretch), and blue (third 50 % strain stretch). The higher molecular weight POSS-TPU shows lightly improved elasticity as is seen by the greater recovery upon unloading.
Figure A1-4 (a) Elasticity and (b) recovery ratios as functions of number average molecular weight ($M_n$, left column) and weight average molecular weight ($M_w$, right column). The ratios are shown in black (100 % strain stretch), red (first 50 % strain stretch), green (second 50 % strain stretch), and blue (third 50 % strain stretch). It is noted that the recovery ratio does not have values indicated for the third stretch to 50 % strain, since a subsequent stretch is required for its calculation. The first cycle stretch to 100 % strain generally has an increasing elasticity and recovery ratio with increasing molecular weight. The subsequent stretches to 50 % strain have relatively constant ratios around 85 % (elasticity ratio) and 100 % (recovery ratio).
Vita

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EDUCATION

Syracuse University, L.C. Smith College of Engineering, Syracuse, NY
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BS, Chemical Engineering, Mathematics, GPA: 3.945, Summa Cum Laude, Syracuse University Scholar  May 2013

RESEARCH EXPERIENCE

Syracuse Biomaterials Institute, Research Assistant  Aug. 2012 – Present
Advisor: Patrick T. Mather (PhD), Syracuse University, Syracuse, NY
• Developed a fully thermoplastic, two polymer system capable of being simultaneously electrospun to form composites with low moduli and shape memory capabilities
• Synthesized thermoplastic polyurethanes for use in the composite system
• Characterized the thermal, mechanical, and microstructural properties of composites with varying composition
• Developed water-triggered origami using electrospun polymer fiber mats
• Characterized the curling behavior of laminated anisotropic shape memory elastomeric composites after mechanical stimulation

Supervisor: Larry R. Holmes, Aberdeen Proving Ground, MD
• Designed and developed microfluidic devices capable of self-sustained, reversible pumping
• Modified material composition (properties) and device design to optimize performance

University of Alabama REU in Fluid Mechanics, Undergraduate Researcher  May 2012 – July 2012
Advisor: Christopher S. Brazel (PhD), University of Alabama, Tuscaloosa, AL
• Determined the effects of protein concentration and a poly(ethylene glycol) coating on the capture of magnetic nanoparticles suspended in a flowing solution

PUBLICATIONS


Birjandi Nejad, H.; Robertson, J.M.; Mather, P.T. “Novel Interwoven Polymer Composites via Dual-Electrospinning with Shape Memory/Self-Healing Properties,” MRS Communications by invitation 2015, 5 (2) 211-221.


PATENT APPLICATION


TECHNICAL PRESENTATIONS

