Thermomechanical characterization of a shape memory polymer based syntactic foam

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THERMOMECHANICAL CHARACTERIZATION OF
A SHAPE MEMORY POLYMER BASED SYNTACTIC FOAM

A Thesis

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Louisiana State University and
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Abstract

Shape memory polymers (SMPs) are a type of smart material capable of “remembering” multiple shapes and transitioning between them in response to an external stimulus. They offer the potential to self-seal macro-length scale damage in a nearly autonomous fashion. Syntactic foams are lightweight structural materials currently used in the marine and aerospace industries. This study seeks to bring syntactic foams and SMPs together, retaining characteristics of both components, to create a low-density smart composite. The SMP based syntactic foam is used as the core of a grid stiffened sandwich structure capable of healing impact damage multiple times.

In order to better understand the sealing efficiency and the effect different programming and recovery conditions have on it, the current research is concerned with characterizing the SMP based syntactic foam using $T_g$ determination by DMA, isothermal uniaxial compressive behavior at three temperatures and three strain levels, quasi strain-controlled programming followed by free recovery, volume change, and through thermomechanical cycles using stress-controlled programming (at two different stresses) followed by free, strain-controlled, and stress-controlled recovery.

Compression above the $T_g$, at 79°C, revealed that the stiffness and strength were significantly lowered, with the foam being less affected. At 121°C, all compositions behaved like a rubber.

Creep effects were observed after the initial loading during stress-controlled programming. Additional deformation occurred during cooling due to thermal contractions, viscoelasticity around the $T_g$, and viscoplasticity below the $T_g$.

Stress-controlled programming offers the best results and allows for the most control. However, quasi strain-controlled compressive programming can be used to achieve reasonable shape fixities.
Shape fixity values were close to 100% for all compositions using stress-controlled programming. Free shape recovery was near 100% for non-foam and around 86% for the foam. The majority of the recovery occurred in the T_g region.

Strain-controlled recovery can be used to recover all of the programming stress, during which time there was an initial build up of thermal stress followed by a decrease and then a plateau.

Confined recovery is effective at sealing damage by either controlling the strain or stress and allowing the shape memory effect to recover into the internal free volume.
Chapter 1. Introduction

As our knowledge advances, we are often reminded of the limitations of our understanding and of the resulting output from its application to design, process, and product. Overcoming these barriers has been, essentially, the main focus of engineering. We are tasked not only with the implementation of viable solutions to problems, but also with the creation of new processes and technology which broaden our collective toolbox. Historically, the advancement of a society’s materials was accompanied by a significant step forward in their evolution. Indeed, we have assigned names to particular periods of time based on civilization’s access to certain materials and the tools created from them (e.g., The Stone Age, The Bronze Age, The Iron Age). Material science, in particular, constantly seeks to push our capabilities forward through improvements to existing methods, combinations of materials, or by new materials and systems which can be used as building blocks for larger projects. As we engage in these grander efforts, we require more from components, and the materials they are made of. The idea that a material can serve more than one function is a relatively new concept, and one that often requires the cooperation of multiple disciplines to realize. When properly conceived and implemented, these advanced materials become powerful vehicles by which all manner of progress is propelled.

Shape memory polymers (SMPs) are of recent interest as a smart functional material. They can provide a self-healing option through the invocation of the shape memory effect. Existing self-healing schemes are limited by their repeatability and the extent of damage they can effectively heal. Since the shape changing capability in SMPs is driven by conformational entropy, they can provide repeatable healing. Also, they are not limited to micro-length scale damage. Li and Nettles have demonstrated the capability to seal macro-length scale damage [1]. When coupled with other components in a composite, they become even more useful, offering several desirable properties. In conjunction with one of the existing healing schemes, a SMP
based composite can be used to effectively self-heal structural damage, while providing a lightweight, non-reactive, low cost material.

The research presented here is a corollary to, and in support of, the work done by Li and John [2,3] on SMP based grid stiffened sandwich structures (shown in Fig. 1). In particular, they explore the potential for using the SMP as the basis for a syntactic foam which can absorb and seal impact damage. This application reduces the density of the material while still retaining the majority of the unique shape memory characteristics. Incorporation of the SMP based syntactic foam as the core of a grid stiffened sandwich structure further increases its usefulness as the fiberglass grid provides reinforcement, thus enhancing its mechanical properties.

In order to utilize the shape memory properties, the material must be properly programmed and recovered. It is therefore critical to understand its response to thermal and mechanical circumstances. The current research is concerned with characterizing the SMP based syntactic foam through thermomechanical cycles based on uniaxial compression. Considerations are given to stress-controlled and quasi strain-controlled programming followed by free, strain-controlled, and stress-controlled recovery conditions. Additionally, the volume change after programming is briefly evaluated.

Figure 1: Grid stiffened sandwich structure developed by Li and John with the SMP based syntactic foam used as the core material.
Chapter 2. Review

2.1 Shape Memory Polymers

SMPs are part of a wider group of smart materials including piezoelectrics, shape memory alloys (SMAs) and ceramics. The first SMP, polynorbornene, was developed by CdF Chimie and commercialized by Nippon Zeon Co. [4,5]. They have garnered attention in recent times due to several characteristics which make them attractive candidates for a range of applications. The ability to perform the shape memory effect is their most notable feature, which provides a possible self-healing mechanism. Compared to other smart materials, SMPs are able to withstand much higher deformations. The unconstrained recoverable strain limits in shape memory ceramics and SMAs are on the order of 1% and 10% respectively, whereas SMPs can recover up to 100% for compression and several hundred percent in the case of tension [6,7]. Polymers are inherently less dense than metals, which allows SMPs to be many times lighter than SMAs. Additionally, their formability is cheaper and more versatile since high temperatures and forces are not required. SMPs are biocompatible, making them desirable for use in the biomedical field [8,9].

2.2 Shape Memory Effect

The unique feature of shape memory materials which makes them interesting is their ability to remember two different shapes and transition between them upon application of a stimulus. This is known as the shape memory effect. Fig. 2 shows the change from a permanent (original) to a temporary (or intermediate) shape through a programming process involving heat and an applied force. Later, heating during a recovery step causes the material to return back to its permanent shape. In SMPs the traditional thermally induced shape memory effect is triggered by direct heating, however, depending on the polymer structure or additional components (in the case of composites) other stimuli such as light, electrical current (applied or induced with a magnetic field), and solvents are possible and have been suggested [10-13].
2.2.1 Background

The discovery of the shape memory effect was born out of research into the martensite phase in steel, which was discovered in the 1890s by Adolf Martens. In steel, martensite is formed by a diffusionless phase transformation when austenite is rapidly cooled, trapping interstitial carbon atoms [15]. It is an irreversible process in the Fe-C system, but not necessarily in other alloys. Greninger and Mooradian observed thermally reversible martensite in CuZn alloy in 1938 [16]. This type of thermoelastic martensistic transformation was explained by Kurdjumov and Khandros in 1949 [17].

Eventually, a NiTi alloy named “NiTiNOL” was developed in 1963 by the U.S. Naval Ordnance Laboratory. It had desirable mechanical properties and exhibited shape recovery capabilities, which were dubbed the shape memory effect [18,19].

2.2.2 Mechanism: Two Phase Conformational Entropy Viewpoint

The shape memory effect in SMPs works by a different mechanism from that in SMAs. SMAs use a martensitic phase transformation to change shape, while SMPs utilize an entropic elasticity to achieve the shape memory effect. SMPs must contain at least two separated phases (so called soft and hard phases) related to the temporary and permanent shapes. The hard phase serves as netpoints (or anchor points) and deals with the permanent shape. The soft phase deals with the temporary shape and functions as molecular switches. Cross linking in these phases exists as either chemical bonds or as physical entanglements (which serve a similar role as they
are stabilized by the chemical links). Each phase is tied to a transition temperature, above which links in the phase can break down. The transition temperature \( T_{\text{perm}} \) is associated with the hard phase and is higher than the soft phase’s transition temperature, \( T_{\text{trans}} \). Changes in these phases allow the shape memory effect to progress. At a temperature below \( T_{\text{perm}} \), but above \( T_{\text{trans}} \), the molecular switches are open which allows soft segment elements to be manipulated while the hard segment (with its higher transition temperature) maintains an overall integrity. By working in this temperature range, the temporary shape can be formed by applying suitable external forces, which the ductile soft phase is able to accommodate. If the deformation is held while cooling to a temperature less than \( T_{\text{trans}} \), reversible netpoints in the soft phase fix the temporary shape even after the external constraints are removed. Depending on the specific chain segments, the reversible netpoints can be either physical or chemical in nature. Physical reversible netpoints form as domains undergo vitrification or crystallization, which provide a mechanically resistive element to overall chain movement. Chemical switching is possible if suitable functional groups are attached to the chains which participate in reversible covalent cross-linking \([11,14,20]\). Fig. 3 first shows the change from the permanent to temporary shape as a force is applied above \( T_{\text{trans}} \) and held until below the transition temperature, fixing the temporary shape. Later, reheating restores the permanent shape as the netpoints spring back to their original positions.

Randomly oriented polymer chains undergo a reduction in entropy upon stretching them. As they move from a coiled conformation to a more straightened form, the number of available rotational states decreases. With this ordering also comes a reduction in entropy. This change in entropy is the driving mechanism for the shape memory effect.

In order to better flesh out this effect, consider the following. We examine the case of a polymer chain in a Cartesian coordinate system with one end at \((0,0,0)\) and the other end stretched along the y-axis at \((0,y,0)\). The entropy of the polymer chain, \( S_p \), is \([21]\)

\[
S_p = k \ln Z_p(y)
\]  

(1)
where $k$ is Boltzmann’s constant and the partition function $Z_p$ is regulated by the number of available conformations at that distance. For a free end, that is, one at $(x,y,z)$, the probability distribution is the Gaussian function

$$p(x,y,z) = \left(\frac{3}{2\pi R_0^2}\right)^{3/2} \exp\left(-\frac{3(x^2 + y^2 + z^2)}{2R_0^2}\right)$$

(2)

where $R_0^2$ is the mean squared distance between the polymer chain ends.

$$R_0^2 = \langle x^2 + y^2 + z^2 \rangle$$

(3)

Figure 3: A graphic representation of the shape memory effect in polymers. Netpoints of the hard phase set the permanent shape. Deformation and cooling fixes the temporary shape. Subsequent reheating recovers the original shape. Adapted from [14].

For our case at $(0,y,0)$, the partition function is proportional to Eqn. 2 at $p(0,y,0)$, or

$$Z_p(y) \propto p(0,y,0) \propto \exp\left(-\frac{3y^2}{2R_0^2}\right)$$

(4)

Eqn. 1 then becomes
Using the fixed junction model, a chain $i$ in an undeformed state has a distance vector, $r_i'$, between its ends given by

$$r_i' = \begin{pmatrix} x_i' \\ y_i' \\ z_i' \end{pmatrix}$$

If the chain was then deformed, its distance vector correspondingly becomes

$$r_i = \begin{pmatrix} x_i = \lambda_1 x_i' \\ y_i = \lambda_2 y_i' \\ z_i = \lambda_3 z_i' \end{pmatrix}$$

where $\lambda_{1,2,3}$ are the extension ratios.

To obtain the change in entropy upon deforming a chain, we first need to find the entropy in the undeformed state.

$$S_i' = S_p(0,0,0) - \frac{3k}{2R_0^2} r_i'^2$$

In order to calculate the total entropy in this state, we must include all of the chain lengths. For a volume, $V$, and a chain density, $c_p$, the total entropy, $S'$, is

$$S' = \sum_i S_i' = V c_p \int S_p'(x',y',z') p(x',y',z') dx' dy' dz'$$

$$= V c_p \int \frac{3}{2\pi R_0^3} \left( S_p(0,0,0) - \frac{3k}{2R_0^2} (x'^2 + y'^2 + z'^2) \right) \exp\left( -\frac{3k}{2R_0^2} (x'^2 + y'^2 + z'^2) \right) dx' dy' dz'$$

$$= V c_p \left( S_p(0,0,0) - \frac{3k}{2} \right)$$

The derivation for the total entropy in the deformed state yields a similar result with the extension ratios, $\lambda_i$, included.
\[
S = V_c \int \left( S_p(0,0,0) - \frac{3k}{2R_0^2} \left( \lambda_1^2 x'^2 + \lambda_2^2 y'^2 + \lambda_3^2 z'^2 \right) \right) \left( \frac{3}{2\pi R_0^2} \right)^{3/2} \exp \left( -\frac{3}{2R_0^2} \left( x'^2 + y'^2 + z'^2 \right) \right) dx'dy'dz' \tag{10}
\]

The entropy change is just the difference between the results of Eqns. 10 and 9.

\[
\Delta S = S - S' = V_c \left( S_p(0,0,0) - \frac{1}{2} k \left( \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \right) \right)
\tag{11}
\]

The extension ratio for a direction \( i \) is

\[
\lambda_i = \frac{L_i - \Delta L_i}{L_i}
\tag{12}
\]

where \( L \) denotes the length. For a chain extension, the \( \lambda \) s in Eqn. 11 will be greater than one and the term inside the parentheses will always be positive. Therefore, the entropy change will be negative, meaning a reduction in entropy. Fixing the temporary shape locks in this state. However, since it is not a thermodynamically favored state, the system will attempt to restore the lost entropy. During recovery it is able to do so when the temporary bonds which fix the temporary shape are broken, thereby reclaiming the lost entropy.

It should be noted that some assumptions have been made about uniformity in polymerization, transfer of deformation, and chain distribution in order to simplify the calculations. The intent, though, is to give a conceptual model in a thermodynamic framework for the basis of the shape memory effect.

### 2.2.3 Mechanism: Time Dependent Relaxation Viewpoint

A newer and somewhat different explanation for the driving mechanism behind the shape memory effect has been published by Nguyen et al. [22]. They propose that the polymer chain mobility governs the shape memory effect, with the system attempting to return to an equilibrium state. Additionally, they suggest that the rate of the effect is highly influenced by structural and stress relaxation.
The structural relaxation time, $\tau_R$, can be written as

$$\tau_R(T, T_f) = \tau_R^{ref} \exp \left[-\frac{C_1}{\log e} \left(\frac{C_2(T - T_f) + T(T_f - T_g^{ref})}{T(C_2 + T_f - T_g^{ref})}\right)\right]$$

(13)

where $\tau_R^{ref}$ is a reference time, $T$ is the temperature, $T_g^{ref}$ is a reference glass transition temperature, $C_1$ and $C_2$ are constants determined from thermomechanical experiments, and $T_f$ is a fictive temperature at which a nonequilibrium structure at $T$ is in equilibrium.

The Cauchy stress response is

$$\sigma = s + p1$$

(14)

with $s$ given by

$$s = \frac{1}{J} \mu^{eq}\left(\bar{b}_M - \frac{1}{3} \bar{I}_M, 1\right) + \frac{1}{J} \mu^{neq}\left(\bar{b}_M^e - \frac{1}{3} \bar{I}_M^e, 1\right), \quad \mu^{eq} = \mu_N \frac{\lambda_L}{\lambda_{eff}} L^{-1}\left(\frac{\lambda_{eff}}{\lambda_L}\right)$$

(15)

where $J$ is the Jacobian determinant of the deformation gradient, $\bar{b}_M$ and $\bar{b}_M^e$ are the total and volumetric (or elastic) Cauchy-Green deformation tensors, $\bar{I}_M$ and $\bar{I}_M^e$ are the total and volumetric first invariants, $\mu_N$ is the characteristic stiffness of the polymer network, $\lambda_L$ is the locking stretch, $\lambda_{eff}$ is the effective chain stretch, and $L^{-1}$ is the inverse Langevin function.

Finally, $p$ is given by

$$p = \frac{1}{J} \kappa(\Theta_M - 1)$$

(16)

where $\kappa$ is the characteristic bulk modulus and $\Theta_M$ is the mechanical component of the volumetric deformation.

When deformed during programming, the system is forced into a non-equilibrium state. By holding the deformation, it will be prevented from returning to an equilibrium condition. After cooling, the restricted chain mobility below the $T_g$ region serves to lock in the non-equilibrium state since the relaxation time is drastically increased at the lower temperature.
During recovery, the mobility is restored once the $T_g$ has been reached and the system can then return to an equilibrium state.

2.3 Shape Memory Parameters: Shape Fixity and Shape Recovery

Shape fixity and shape recovery are two important shape memory parameters commonly used as metrics to quantify shape memory performance. Shape fixity is related to a material’s ability to store a temporary shape, while shape recovery is a measure of how well the permanent shape can be restored. They are both ratios of various key strain points in the thermomechanical cycle and are dimensionless.

The shape fixity is defined as

$$R_f(N) = \frac{\varepsilon_u(N)}{\varepsilon_m}$$

(17)

where $\varepsilon_u$ is the temporary shape strain for $N$ cycles and $\varepsilon_m$ is the ideal mechanical deformation strain (i.e., before springback) [20]. They are given by

$$\varepsilon_u = \frac{l_0 - l_2}{l_0} \quad \text{and} \quad \varepsilon_m = \frac{l_0 - l_1}{l_0}$$

(18)

where $l_0$ is the initial length, $l_1$ is the length after compression but before springback, and $l_2$ is the actual length after springback. Therefore, for one cycle ($N=1$), the shape fixity can be written as

$$R_f = \frac{l_0 - l_2}{l_0 - l_1}$$

(19)

$l_0$ and $l_2$ are measured quantities, while $l_1$ is calculated as the length at maximum compression (based on the predefined strain level) from

$$l_1 = l_0\left(1 - \frac{\%\text{strain}}{100}\right)$$

(20)

For $N$ cycles, the shape recovery is defined as

$$R_r(N) = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N - 1)}$$

(21)
where $\varepsilon_p$ is the strain associated with the permanent shape given by

$$
\varepsilon_p = \frac{l_0 - l_3}{l_0}
$$

(22)

where $l_3$ is the measured length after recovery. For one cycle, the $\varepsilon_p$ in the denominator goes to zero and the shape recovery is

$$
R_r = \frac{l_3 - l_1}{l_0 - l_1}
$$

(23)

### 2.4 Thermomechanical Cycle

Shape memory polymers go through multiple phases as they transition between permanent $\rightarrow$ temporary $\rightarrow$ permanent shapes. Traditionally, the process is broken into four steps: 1) Loading; 2) Cooling; 3) Unloading; 4) Recovery [23]. During these steps the temperature and stress-strain response are considered. The procedure can be presented as a two or three dimensional plot, like the ones shown in Fig. 4 [14].

In step 1, a sample is loaded at some constant temperature higher than its glass transition temperature. It will deform to a strain value $\varepsilon_m$ (the ideal strain with no springback) with an ultimate stress $\sigma_m$. In step 2, the load (or alternately the strain) is held and the sample is cooled below its transition temperature, fixing the temporary shape. Step 3 is an unloading step where the sample experiences a springback (if the strain was held constant in step 2 then step 3 instead would involve reducing the strain until a stress free state is achieved), putting the strain value at the temporary shape strain $\varepsilon_u$. Free recovery (i.e., no external confinement) occurs in step 4 as the sample is heated. There is a drastic strain change around the $T_g$ as the temperature passes through this region. Finally, the sample stabilizes $\varepsilon_p$, which is at (or near) the starting strain value.
Figure 4: General two and three-dimensional representations of the four-step thermomechanical cycle. Step 1: High temperature loading; Step 2: Cooling while stress or strain is maintained; Step 3: Low temperature unloading; Step 4: Recovery of strain through heating. [14]

2.5 Syntactic Foams

Syntactic foams are a type of composite structural material created by forming a matrix around hollow particles, thus creating a closed-cell structure. A syntactic polymer foam is one in which the matrix consists of a polymer. Fig. 5 shows the microstructure of a closed-cell syntactic foam which uses a SMP as the binder and glass microspheres as the filler. Glass microspheres are a common filler choice due to their low cost, established manufacturing procedures, mechanical strength, surface uniformity, and good wetting characteristics [24]. By contrast, other foams are made by injecting gas into a matrix material and then stabilizing the state. The volume is expanded (and the density lowered) due to the creation of gas pockets. In syntactic foams, the density is still reduced, but gas pockets are enclosed by the walls of the hollow particles [25,26]. They are commonly used in marine and aerospace applications due to their low weight, ease of formability, and high compressive strength [26]. In general, the type of filler used and the interaction between the filler and binder strongly influence the mechanical properties of syntactic foams [24].
The addition of fillers serves to reinforce the matrix and, thereby, increase the overall strength. Polymer matrix composites are commonly used due to their high strength to weight ratio, low conductivity, corrosion resistance, and low moisture adsorption [27]. Glass microspheres are commonly used as fillers because of their strength, difference in elastic properties compared to polymers, and established processing technology. Other filler materials, such as carbon microspheres, can improve the mechanical and water resistance even more [25].

2.6 Current Self-Healing Schemes

Self-healing schemes exist based on a range of mechanisms and with varying degrees of effectiveness depending on the situation. Generally, however, they are limited in that repeatable healing is not possible and also by the extent of damage they can effectively heal.

Early self-healing efforts were based on chemical reactions between a two-part system. A monomeric fluid was encapsulated in either hollow microparticles or fibers dispersed in a matrix which contained a catalyst. When damage occurred, the hollow members would rupture and
encounter catalyst in the vicinity. A *in-situ* polymerization reaction would ensue and repair damage [28-30]. The main limitation to this healing scheme is that after the two reaction components are combined, the process cannot be repeated. Additionally, the hollow components may themselves become a source of defects once they are broken and leave behind an empty volume.

Other schemes seek to mimic biological systems by creating microvascular networks which can deliver healing agents to a damaged region [31]. The advantage over encapsulated schemes is that healing can be done repeatedly since the reaction components are not locally depleted after a single healing event. However, the complexity of the system introduces additional challenges.

Thermoplastic particles have been used as an alternative repair mechanism [32,33]. Heat is used to melt the thermoplastic particles. The molten plastic bonds the sides of fractured surfaces when cooled down. While this technique could potentially be used multiple times to heal, it may compromise the dimensional stability, in particular when a large amount of thermoplastic particles is involved.

Thermally reversible cross-linked polymers offer another healing option. In cross-linked polyamides, the toughness is increased and the links can be recycled to provide a degree of self-healing capability [34].

Finally, ionomer systems have been proposed for self-healing purposes [35]. Ionomers are polymers which contain mostly nonionic repeating units with a small amount of repeating units containing ions [36]. Surfaces which are brought in contact with each other will attract and bond due to the charge interaction. The drawback to this type of system is that some mechanism must be devised to reassociate damaged surfaces which have become physically separated.
The scale of damage presents a significant hurdle for these healing schemes. They are, generally, effective at healing micro-length scale damage. However, they are unable to heal macro-length scale or structural damage.

2.7 Research

Despite their impressive geometric capabilities, one potential drawback to SMPs is their relatively low load carrying capability. Shape memory polymer based composites are interesting because properties of both the SMP and additive components can be leveraged. For example, the addition of fibers to a SMP matrix can increase the mechanical properties. Liang et al. embedded woven and chopped fiberglass in a SMP matrix and subjected the material to tension. Both the strength and stiffness were significantly increased due to the higher modulus of the fiberglass [37].

As mentioned above, the shape memory effect in SMPs can be triggered in multiple ways. Cho report on using MWCNTs embedded in segmented polyurethane block copolymers having shape memory properties. An applied voltage was used for heating. MWCNTs were preprocessed in a solvent-acid mixture intended to modify the surface so that better interfacial bonding between the nanotubes and polymer was achieved. With a modified MWCNT content of 5 wt.%, application of 60V could raise the sample temperature above the transition temperature (35°C) in a short period of time (8 sec.) with a conversion efficiency of 10.4%. Surface treatment lowered the conductivity somewhat, but increased the strength [38].

Mohr used a magnetic field to induce a current and trigger the shape memory effect in a shape memory polyetherurethane (TFX) matrix embedded with spherical shaped nanoparticle fillers consisting of an iron (III) oxide core surrounded by silica. They were able to quickly raise the temperature to the necessary 88°C. They obtained fixity values of around 100% and recovery values of approximately 80%. They concluded that the results were comparable to using the normal thermally induced method [12].
Biercuk loaded industrial epoxy with single walled carbon nanotubes and vapor grown carbon fibers in an attempt to increase the thermal conductivity. The authors report that loading with as low as 1 wt.% single walled carbon nanotubes or vapor grown carbon fibers increased the conductivity by 125% and 45% respectively [39].

Li have used conducting carbon black as the filler in a polyurethane matrix. At a content of approximately 20 wt.%, a dramatic increase in conductivity was observed. The increase corresponds to the percolation threshold, a concentration at which a continuous conducting network forms, and the electrical conductivity drastically increases [40].

Thermal or electromagnetic activation are not the only methods to trigger the shape memory effect. Light may also be used. In the case of a photoresponsive polymer, irradiation with certain wavelengths of light can cleave photosensitive cross links. Lendlein have used this method to induce the shape memory effect, using a cinnamic acid type molecule as the molecular switch. The general concept is similar to that used for thermal activation, but ultraviolet light is used instead. One difference is that the strain fixation is due to the creation of a new netpoint rather than a “freezing” of stretched chains. The authors report a recovered strain similar to that of thermoresponsive materials, but lower strain fixity. They attribute this to an elastic contraction of the stretched chain segments. Nevertheless, the light-induced technique may have advantages in some cases where thermal constraints are an issue [10].

Equally important to triggering the shape memory effect is how a material will behave during the necessary programming and resulting recovery. Liu et al. have developed a constitutive model to predict the thermomechanical behavior of shape memory polymers and performed experiments to compare the results [41]. For unconstrained cases, they find most of the strain recovery occurs in the $T_g$ region. For uniaxial recovery tests under a strain constraint, the evolution of the stress is governed by thermal expansion. They conclude that the energy
released during recovery is the same as that stored during cooling, with a small mechanical dissipation.

Others have reported on work done using the same Veriflex resin system as our research group. Schmidt et al. found a very similar T_g value and observed thermomechanical responses over multiple cycles. They found a small mount of irreversible strain in the initial cycles, followed by a consistent shape fixity and shape recovery in later cycles [42].

Lan et al. explored the use of a reinforced Veriflex SMP composite as a deployable hinge [43]. Similar to the work of Schmidt et al., they find a dependence of the shape recovery on the number of thermomechanical cycles, with the value stabilizing after a few cycles. They conclude that the shape memory effect, realized in the form of microbuckling, can be used to deploy other structures (e.g., solar arrays).

Relatively recently, Atli et al. have performed thermomechanical characterization tests on the Veriflex SMP [44].

One of the larger areas of interest for use of SMPs is the biomedical field. Specifically, they are being considered as part of a treatment for stroke patients. Existing chemical dissolution methods are limited in their effectiveness because of the narrow time window around the onset of symptoms (about 3 hours) and the time involved in restoring blood flow. Outside of this time frame, the medication is ineffective at clot removal and the risk of death is increased. The window has been extended up to 8 hours using a mechanical clot removal procedure, which employs the shape memory alloy NiTiNOL. A wire in a straight temporary shape is navigated to the area of interest and pushed through the blockage. The shape memory effect is used to restore the wire to its permanent shape (a helical coil), wrapping it around the thrombus. It can then be mechanically retracted, restoring blood flow in minutes rather than hours (as with chemical therapies) [45]. More recently, this treatment has been adapted using a SMP instead of a SMA. Ward and Maitland report on a similar SMP based device which transitions between a straight
rod and a tapered corkscrew [8,9]. A laser is used to provide the energy necessary to initiate the shape memory effect.

Another application under review is the use of SMPs for the deployment of space systems. The reduced size and weight make them an economically attractive alternative for the aerospace industry. Gall et al. report on the compactibility of carbon fiber reinforced shape memory polymers [46]. They conclude that these materials are viable options and were able to recover nearly 100% of a permanent shape using bend radii as small as 1.6mm.
Chapter 3. Manufacturing

3.1 Raw Materials

We chose a commercially available SMP marketed under the name “Veriflex” from CRG Industries due to its availability and potentially adjustable $T_g$. It is a styrene based thermoset resin system with a nominal $T_g$ of 62°C. It’s comprised of ~50% stabilized styrene monomer, <50% styrene block copolymer, and <20% of a proprietary mixture. A curing agent comprised of ~52% dibenzoyl peroxide, <48% tricresyl phosphate, and <4% silane is also used [47,48]. Mechanical properties for cured samples below the $T_g$, as reported by the manufacturer, are shown in Table 1 [49].

Table 1: Mechanical properties of the cured pure SMP.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
<td>23.0</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>1240</td>
</tr>
<tr>
<td>Flexural Strength</td>
<td>37.1</td>
</tr>
<tr>
<td>Flexural Modulus</td>
<td>1240</td>
</tr>
<tr>
<td>Compressive Strength</td>
<td>32.4</td>
</tr>
<tr>
<td>Compressive Modulus</td>
<td>1450</td>
</tr>
</tbody>
</table>

Inorganic glass microspheres (Q-CEL 6014) from Potters Industries were used as the cell material. Physical properties of the microspheres are listed in Table 2 [50].

Table 2: Physical properties of the glass microspheres.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer Diameter</td>
<td>85μm</td>
</tr>
<tr>
<td>Wall Thickness</td>
<td>0.8μm</td>
</tr>
<tr>
<td>$\rho_{bulk}$</td>
<td>0.08 g/cm$^3$</td>
</tr>
<tr>
<td>$\rho_{effective}$</td>
<td>0.14 g/cm$^3$</td>
</tr>
</tbody>
</table>

The MWCNTs were purchased from Cheap Tubes Inc. Properties of the nanotubes are given in Table 3 [51].
Table 3: Properties of the MWCNTs.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer Diameter</td>
<td>20-30nm</td>
</tr>
<tr>
<td>Inner Diameter</td>
<td>5-10nm</td>
</tr>
<tr>
<td>Length</td>
<td>10-30µm</td>
</tr>
<tr>
<td>MWNT Purity</td>
<td>&gt;95 wt%</td>
</tr>
<tr>
<td>( \rho_{\text{bulk}} )</td>
<td>0.28 g/cm(^3)</td>
</tr>
<tr>
<td>( \rho_{\text{true}} )</td>
<td>2.1 g/cm(^3)</td>
</tr>
</tbody>
</table>

3.2 Fabrication

All material compositions were fabricated using a similar mixing/curing procedure with some variations to account for the difference in components. Compositions containing MWCNTs were blended by hand and also with ultrasonic and shear methods in order to better disperse the nanoparticles. Batches without nanotubes could adequately be mixed using just hand techniques. Foam compositions (ones containing microspheres) required longer curing times and higher temperatures to properly set. Curing cycles were correspondingly adjusted to compensate for these differences.

3.2.1 Pure SMP

The pure SMP composition consists of the SMP resin (part A) and a cream hardening agent (part B). They were mixed by hand using an A:B weight ratio of 24:1. The mixture was poured into the 229×229×12.7mm steel frame mold shown in Fig. 7. Teflon sheets were used on the faces to aid in demolding, and two sided vacuum bag tape was used in joining areas to prevent loss of material from leaks. Hand clamps were used to hold pieces together, keeping the face plates and tape in place. In later fabrication sessions, 19mm thick glass plates, treated with a compatible mold release agent, were substituted for the steel face plates with Teflon (Fig. 7a). This change was made in order to obtain a final slab of material that had even parallel surfaces.
Figure 6: SMP resin being measured out.

Figure 7: Molds used for bulk sample fabrication. a) Steel frame with Teflon covered steel bottom plate. b) Steel frame with glass bottom plate.

The open mold was placed in a vacuum chamber (Fig. 8) at 40kPa for 20 minutes in order to remove any air pockets that may have been introduced during the mixing process. The mold was then closed and placed in the forced convection oven shown in Fig. 9 (Grieve model NB-350) for
curing. The SMP resin manufacturer suggests using a closed mold to avoid material bake-off during curing.

Figure 8: Vacuum chamber used for degassing.

Figure 9: Closed mold placed in the oven for curing.
We used the curing procedure shown in Table 4, which was originally developed in house by Manu John and later modified by Damon Nettles and Naveen Uppu based on post curing stress-strain tests.

Table 4: Curing procedure used.

<table>
<thead>
<tr>
<th>Composition</th>
<th>79°C</th>
<th>107°C</th>
<th>121°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure SMP</td>
<td>24 hrs.</td>
<td>6 hrs.</td>
<td>-----</td>
</tr>
<tr>
<td>SMP+CNT</td>
<td>24 hrs.</td>
<td>3 hrs.</td>
<td>3 hrs.</td>
</tr>
<tr>
<td>Foam (no CNT)</td>
<td>24 hrs.</td>
<td>3 hrs.</td>
<td>9 hrs.</td>
</tr>
<tr>
<td>Foam (with CNT)</td>
<td>24 hrs.</td>
<td>3 hrs.</td>
<td>9 hrs.</td>
</tr>
</tbody>
</table>

3.2.2 SMP with CNTs

The SMP with CNTs composition was fabricated by adding 0.15 vol.% of MWCNTs to the pure resin. Mixing consisted of a combination of hand, ultrasonic, and shear techniques as discussed below in section 3.2.4. The remaining steps followed the same procedure as for the pure SMP as outlined above in section 3.2.1.

3.2.3 Syntactic Foam (no CNTs)

The SMP based syntactic foam was fabricated by incrementally dispersing hollow glass microspheres into the SMP resin to a concentration of 40 vol.%. Several minutes of hand mixing was performed between additions. The hardening agent was then added. After pouring into the mold, degassing was done at 40kPa for 20 minutes. The mold was placed in an oven for curing following the cycle shown in Table 4.

Figure 10: The syntactic foam without CNTs after curing; after curing; left: cut specimen, right: specimen after compression.
3.2.4 Syntactic Foam (with CNTs)

The syntactic foam with CNTs (carbon nanotubes) contains the same ingredients as the non-CNT foam but includes a small amount of MWCNTs (multi-walled carbon nanotubes). The nanotubes were placed in a glass dish and heated on a hot plate for several minutes while stirring in order to evaporate accumulated moisture and break up any large clumps. They were added to the SMP resin at a resin:nanotube weight ratio of 159:1. Hand mixing was then done for approximately 20 minutes. In order to better disperse the nanotubes and deagglomerate particles, ultrasonic and shear techniques were employed after hand mixing. An ultrasonic mixer (Sonics & Materials Inc. model VC 750) was programmed to pulse on for 25 seconds at an amplitude of 40% followed by a 5 second rest. This process was repeated for 30 minutes. Finally, the solution was passed through a three-roll mill (NETZSCH type 272.50) to provide shear mixing (Fig. 11). The remaining steps are the same as those for the non-CNT foam; the microspheres and hardener are mixed in by hand (Fig. 12a), the mixture is poured into the mold (Figs. 12b and 12c), degassed, and placed into the oven for curing.

Figure 11: SMP-MWCNT solution being run through the three-roll mill.
Figure 12: a) Glass microspheres being mixed into the SMP/MWCNT solution. b) c) Pouring the mixture into a mold.
Figure 13: The syntactic foam with MWCNTs after curing; left: cut specimen, right: specimen after compression.
Chapter 4. Experimentation

4.1 DMA Testing

In order to perform programming and recovery effectively, we must first determine the $T_g$ for our material, as the shape memory effect revolves around this activation temperature. Below this temperature region the material is in a hard glassy state, while above it is in a rubbery elastic state. Programming should be done above the $T_g$, when the switching phase is open, in order to fully utilize its linkages. Similarly, recovery should be performed above the $T_g$ when complete activation of the switching phase has occurred. Any closed regions of the switching phase would not be able to participate in the storage/recovery process, and consequently the shape fixity and shape recovery performance would be reduced.

DMA (Dynamic Mechanical Analysis) was used to determine the $T_g$ for the pure SMP and pure foam. A single cantilever beam testing method was used on a DMA 2980 machine from TA Instruments. The temperature range was from room temperature to 120°C with a ramp rate of 3°C/min. The displacement amplitude used was 15µm with a frequency of 1Hz. Samples were prepared by cutting thin slices from larger blocks with a rectangular cross section. The sample dimensions are given below in Table 5.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Length (mm) ±0.01</th>
<th>Width (mm) ±0.01</th>
<th>Thickness (mm) ±0.01</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure SMP</td>
<td>17.50</td>
<td>11.87</td>
<td>1.20</td>
</tr>
<tr>
<td>Pure Foam</td>
<td>17.50</td>
<td>12.11</td>
<td>1.73</td>
</tr>
</tbody>
</table>

4.2 Stress-Strain Behavior

Isothermal, uniaxial, flat-wise compression was performed for all sample compositions using a QTEST/150 electromechanical frame MTS machine. Stress-strain responses were generated for room temperature and two temperatures above the $T_g$ (79°C and 121°C). For the higher temperatures, the fixture and furnace shown in Fig. 14 was used. The furnace and fixture were first preheated. Specimens of size 30×30×12.7mm were mounted atop the fixture’s lower
half in the furnace, the fixture’s upper half was brought in contact with the specimen, and the system was zeroed. At least 30 minutes was allowed for temperature equilibration. Compression was then performed at a constant rate of 1.3mm/min to a strain level of 60%.

Figure 14: Setup used for stress-strain testing.

4.3 Stress-Controlled Programming

For stress-controlled programming, the stress is held constant during steps one and two of the four-step thermomechanical cycle. Due to the sizing of the load cell (150kN) on our MTS machine, a static weight method, similar to that used by John [2], was adopted.

In order to determine the effect that stress and strain levels have on shape memory performance and to observe how microstructural changes influence thermomechanical behavior, two stress levels were chosen: 47kPa and 263kPa. These values were initially chosen such that the resulting strain levels would fall in regions 1 and 2 respectively of the foam’s room temperature stress-strain curve (see Fig. 26). The programming, however, is typically done at an elevated temperature (>\(T_g\)) where the stiffness has been greatly reduced. Therefore, there is not
as much microsphere damage produced at moderate to high strain levels compared to at room temperature. A third, higher, stress value corresponding with region 3 was not used because the required force could not be safely handled without constructing an additional test frame.

The experimental setup shown in Fig. 15 was used to conduct the stress-controlled programming. Additional weight was added as necessary to reach the desired stress level. The top half of the fixture and the load were suspended and preheated in an insulated forced convection environmental chamber to 79°C. The specimen was introduced into the system and 45 minutes were allowed for it to come to a uniform temperature. A rigid lightweight aluminum plate was situated on top the specimen so that its motion could be tracked. A linear variable differential transformer (LVDT) (Cooper Instruments & Systems model LDT 200) was independently mounted with an adjustable arm and magnetic base and used to record the displacement. The load was then gently lowered onto the specimen and the system was soaked at 79°C for approximately 25-30 minutes in order for the deformation to stabilize, allowing for creep effects. The system was then allowed to cool to room temperature over the course of...
several hours (usually overnight) while maintaining the stress level. The load was then removed, leaving the specimen in a working shape, and thus completing the programming process.

4.4 Quasi Strain-Controlled Programming

Utilizing the MTS machine, fixture, and removable furnace, the same setup shown in Fig. 14 was also used for quasi strain-controlled programming. The furnace and fixture were first preheated to a temperature above the $T_g$ of the material (either 79°C or 121°C). Specimens of size $30 \times 30 \times 12.7$mm were mounted atop the fixture’s lower half in the furnace, the fixture’s upper half was brought in contact with the specimen, and the system was zeroed. At least 30 minutes was allowed for temperature equilibration. Compression was then performed at a constant rate of 1.3mm/min to the desired strain level (5, 30, or 60%). At this point the compression was halted, while maintaining the specimen and fixture positions (in other words maintaining the strain). Without disturbing the rest of the system, the furnace was removed and the specimen cooled to room temperature. The programming and recovery procedure used for the quasi strain-controlled programming is shown in Fig. 16.

The term “quasi” is used here to point out that this is not a strictly strain-controlled test. Due to the nature of a compression test, a specimen is merely brought in contact with the top and bottom halves of a fixture, not adhered or attached to them in any way (as is the case for tension where a specimen is clamped in place). For most uniaxial compression tests this isn’t an issue because during the test there is always a force from the top half ensuring contact, while gravity maintains contact on the bottom. However, in our case we are working at an elevated temperature and are concerned not just with the active compression part, but also post compression as the programming process continues. After compression is halted cooling begins. During this time there are thermal contractions of both the fixture and the specimen itself. Both of these produce an unloading effect on the specimen. Additionally, there is a competing effect in the specimen as it attempts to spring back. This elastic effect is much more pronounced above
the Tg and gradually falls off as the temperature is lowered. The end result is that contact between the specimen and fixture is maintained for most of the cooling step. However, near the end of cooling contact is sometimes lost creating a small gap between the top of the specimen and the top half of the fixture. The emergence and size of the gap depends on the ΔT (a higher testing temperature creates a larger gap since there is more thermal contraction), the strain level (a higher strain level creates a larger gap), and the amount of springback (less springback means a larger gap). We estimate that in the worst case scenarios, contact is maintained during cooling until approximately 40°C. This temperature is well below the glass transition regions of our foam and non-foam compositions. The majority of temporary shape should already be fixed by the time this temperature is reached. Therefore, we believe good shape fixity can be attained using quasi strain-controlled programming, which the results confirm.
Figure 16: Schematic of the programming and recovery process used for the quasi strain-controlled testing.

4.5 Recovery

Most of the specimens, except the quasi strain-controlled cases, were programmed under stress-controlled conditions using two stress levels (47kPa and 263kPa). The quasi strain-controlled ones underwent a free recovery as shown in Fig. 16. For the specimens which underwent stress-controlled programming, we also seek to evaluate how different recovery conditions affect the shape memory properties and sealing capability. We evaluated three
different types of recovery: free recovery, strain-controlled (fully confined), and stress-controlled (partially confined).

4.5.1 Free Recovery after Stress-Controlled Programming

The same setup which was used for the stress-controlled programming described in section 4.3 (Fig. 15) was also used for the subsequent free recovery. After programming, the temperature in the heating chamber was rapidly ramped from room temperature to 49°C and allowed to soak for 20-25 minutes. The controller used in this setup required the temperature to be changed manually. The quick ramp from room temperature was done in order to save testing time and to make the procedure easier. Several previous trials showed that negligible amounts of strain change occurred in this temperature range. Therefore, the ramping rate was justified. After soaking, the temperature was ramped from 49°C to 77°C at a rate of 0.16°C/min. A slower rate was used so that the temperature and strain change could be recorded. Finally, the temperature was set to 79°C for 30 minutes.

4.5.2 Free Recovery after Quasi Strain-Controlled Programming

Free recovery after quasi strain-controlled programming was carried out by placing specimens in a forced convection oven at 121°C for three hours. We later determined it was not necessary to heat to such a high temperature or soak for as long. Similar recovery results could be achieved using a temperature of 79°C for one hour. Fig. 16 shows the steps for programming and recovery of this kind.

4.5.3 Strain-Controlled Recovery

After undergoing stress-controlled programming, specimens of the pure SMP and pure foam were recovered under a fully confined (strain-controlled) condition using the setup shown in Fig. 14. As the shape memory effect attempts to return the specimen to its permanent shape, the confinement impedes this movement. The result is a building force as the process progresses.
Specimens were placed in the fixture such that the movement (or strain) was confined and the stress was initially zero. The furnace was used to heat the system from room temperature to 79°C at an average rate of 0.3°C/min. The system was then soaked for approximately 20 minutes. Some specimens were held for longer periods of time (up to 24 hours) to investigate stress relaxation behavior. During this time, the load cell on the MTS machine recorded the resulting force as a function of time and temperature.

**4.5.4 Stress-Controlled Recovery**

During stress-controlled programming, samples are subjected to a constant stress which causes a deformation into the temporary shape. Coupled with this stored strain is also an entropically stored stress as the structure is forced away from an equilibrium state. During recovery the material will exert an opposite force to that used during programming, driving it back to the permanent shape. The idea for stress-controlled recovery is to apply an equivalent stress to that used for programming (which should also be the stored stress) during the recovery step. When the stored stress encounters this equal but opposite stress, it will not be able to push the strain back to the permanent shape. However, any open volume (such as crack or damaged region) will become a candidate for strain to recover into.

Stress-controlled recovery was performed using the setup shown in Fig. 15, but without the LVDT. First, a specimen was programmed under stress-controlled conditions as described in section 4.3. The cross section was then exposed by clamping a small portion and breaking the sample by imparting an impulse to its side. Macroscopic damage was generated in several locations with a sharp blade (~0.2mm thick) along the cross section by cutting in a direction perpendicular to the programming axis. SEM images were taken in order to catalog the damage. Specimens were then recovered at 79°C for 3 hours while applying a constant stress as described above. Post recovery, SEM images of the damaged regions were again taken in order to show the sealing efficiency.
4.6 Volume Change

The change in volume upon fixing the temporary shape was obtained using a water displacement method given in ASTM D 792-00 [52]. Specimens consisting of the pure SMP, SMP with MWCNTs, and foam with MWCNTs were evaluated after undergoing quasi strain-controlled programming using 79°C and 121°C.
Chapter 5. Results

5.1 DMA Test Results

The results of DMA testing on the pure SMP and pure foam are shown in Fig. 17. The glass transition regions were determined using the storage modulus curve as suggested in ASTM E 1640-04 [53]. Upper and lower limits were placed on the region based on tangents to the curve. The $T_g$ value is taken as the average between endpoints. The transition values are summarized in Table 6. For the pure SMP, we find a $T_g = 67.7^\circ$C. The manufacturer provides a value of 62°C as determined by DSC (differential scanning calorimetry) [49]. They cite this value as approximately 4°C lower than values they have obtained via DMA, consistent with our results. For the pure foam, we observe a shift up 2.8°C in the transition region to a $T_g = 70.5^\circ$C. This shift is likely due to the addition of the glass microspheres. The mobility of the SMP may be restricted in the interaction layer between it and the microspheres through physical adsorption or chemical reactions. The reduced mobility would increase the $T_g$ of the SMP within this region, thereby increasing the overall $T_g$.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Lower $T_g$ Limit ($^\circ$C) $\pm 0.3$</th>
<th>Upper $T_g$ Limit ($^\circ$C) $\pm 0.3$</th>
<th>Average $T_g$ ($^\circ$C) $\pm 0.3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure SMP</td>
<td>60.7</td>
<td>73.0</td>
<td>67.7</td>
</tr>
<tr>
<td>Pure Foam</td>
<td>63.7</td>
<td>76.2</td>
<td>70.5</td>
</tr>
</tbody>
</table>

As mentioned previously in section 4.1, programming and recovery should be carried out at a temperature above the $T_g$. Our highest transition temperature is the upper limit for the pure foam at 76.2°C. Therefore, we chose a temperature of 79°C for testing since it is above the limit.
5.2 Stress-Strain Behavior

The stress-strain behavior of the pure SMP at room temperature, 79°C, and 121°C is shown in Figs. 18-20. Five specimens were run for each case, and three representative ones were chosen from each set (numbers in the legends correspond to the sample number). At both elevated temperatures there is a very large reduction in stiffness and in stress values (3 orders of magnitude lower) for equivalent strain levels when compared to room temperature. Both of the higher temperatures are above the SMP’s glass transition region, where it is in a rubbery state. Therefore, the modulus and necessary stress is greatly reduced. Additionally, the yield point is no longer discernable once the temperature has been increased past the $T_g$. 

Figure 17: Results of the DMA test to determine the $T_g$. 

- Stress-strain behavior of the pure SMP at room temperature, 79°C, and 121°C is shown in Figs. 18-20. Five specimens were run for each case, and three representative ones were chosen from each set (numbers in the legends correspond to the sample number). At both elevated temperatures there is a very large reduction in stiffness and in stress values (3 orders of magnitude lower) for equivalent strain levels when compared to room temperature. Both of the higher temperatures are above the SMP’s glass transition region, where it is in a rubbery state. Therefore, the modulus and necessary stress is greatly reduced. Additionally, the yield point is no longer discernable once the temperature has been increased past the $T_g$. 

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Figure 18: Compressive stress-strain response of the pure SMP at room temperature.

Figure 19: Compressive stress-strain response of the pure SMP at 79°C.
Figure 20: Compressive stress-strain response of the pure SMP at 121°C.

The stress-strain behavior of the SMP with nanotubes at room temperature and 79°C, and is shown in Figs. 21 and 22. These results are very similar to those for the pure SMP (see Figs. 19 and 20 for comparison). The addition of such a small amount of MWCNTs does not appear to alter the mechanical properties in any significant way at room temperature and 79°C. In order to create any macroscopically observable difference, it is likely that significantly more nanotubes would need to be added or the interaction between the nanotubes and the surrounding matrix/filler materials would need to be better.
Figure 21: Compressive stress-strain response of the SMP with nanotubes at room temperature.

Figure 22: Compressive stress-strain response of the SMP with nanotubes at 79°C.
The stress-strain behavior of the pure foam (i.e., no CNTs) is shown in Figs. 23 and 24 for room temperature and 79°C. Fig. 25 is a room temperature stress-strain comparison of the pure foam to the pure SMP. Additionally, the SEM insets display the increasing microsphere degradation as they are crushed and consolidated by the compressive stress. This type of response is typical of foams. Three distinct regions of the curve exist, which are related to the microstructural changes. Region 1 (up to 5% strain) represents the linear elastic portion governed by microsphere cell wall bending and stretching. A muted yield point occurs between regions 1 and 2. The curve plateaus in region 2 (5-40% strain) as the microsphere cell walls are irreversibly damaged from crushing and fracture. As the free volume is reduced, we move into region 3 (>40% strain) where the crushed microspheres are no longer visible and the material becomes consolidated. The increase in density leads to a rapid growth in stress as the compression continues [54].

The compressive stress-strain response of the foam with CNTs at room temperature, 79°C, and 121°C is shown in Figs. 26-28. The values are significantly different from the pure foam composition. These differences are discussed in more detail below.
Figure 23: Compressive stress-strain response of the foam without CNTs at room temperature.

Figure 24: Compressive stress-strain response of the foam without CNTs at 79°C.
Figure 25: Comparison of the stress-strain responses of the pure SMP and pure foam at room temperature. The inset SEM images show changes in the microspheres (at 5, 30, and 60%) as the strain increases.
Figure 26: Compressive stress-strain response of the foam with CNTs at room temperature.

Figure 27: Compressive stress-strain response of the foam with CNTs at 79°C.
Figure 28: Compressive stress-strain response of the foam with CNTs at 121°C.

Fig. 29 is a comparative summary of the stress-strain responses of the different sample compositions at 79°C. We observe two interesting features on this plot. As mentioned above, the addition of MWCNTs to the pure SMP does not affect the stress-strain response to a great extent. This is evidenced by the two curves marked with triangles in Fig. 29. They closely track each other over the entire range of strains used during testing. The two foam compositions, on the other hand, display large differences in their respective responses. As was expected, both generally maintain higher stress levels than the non-foam compositions. The glass microspheres increase the modulus and yield strength of the SMP at these higher temperatures (>T_g of SMP) since the microspheres are well below their glass transition temperature. However the pure foam has much higher values than its nanotube counterpart. This is also the case at room temperature (Fig. 31). Since both foams underwent the same curing cycle, we initially believed that the nanotubes were complicating the curing process, producing a CNT foam which was not fully cured. Partially cured samples were something we had seen before (indeed the curing cycle which was developed by Li and John [2] was done so through a trial and error process) and
would certainly lead to lower stress values. However, after reviewing the non-foam results this does not appear to be the case. Samples with MWCNTs added to the pure SMP were successfully cured as we can see from the two non-foam curves in Figs. 18 and 21. The pure SMP composition numbers at room temperature are in agreement with the manufacturer, and the SMP+CNT values are in agreement with the pure SMP. So, the CNTs do not appear to be the culprit for the reduced modulus and stresses we see. What about the glass microspheres? They are another candidate for reduced values, as they could retard the curing, and at least at room temperature the foam has a lower stiffness and yield point compared to the pure SMP. If the microspheres were to blame we should see similar trends for both foam compositions (as they both contain equal amounts of microspheres), even if they were lower than some optimal foam values we might imagine. This is not the case, as the foam stress-strain responses are not similar (Figs. 29 -31). What is left is some interaction (or lack of) between the microspheres and the MWCNTs which causes the CNT foam not fully cure. The surfaces of the microspheres and nanotubes were not treated during fabrication and no coupling agent was used. Coupling at interfaces can be chemical (covalent or non-covalent bonding) or physical (van der Waals interactions) in nature. Without the use of a coupling agent, weak nanotube interactions can cause decreased mechanical properties. Simulations have shown that matrix-filler interfacial stresses are significantly lower when non-chemical bonding is present [55]. The surface tension of normal polystyrene generally decreases with increasing temperature, in which case reasonable wetting between the matrix and microspheres (which are considered to have good wetting properties) can be expected during fabrication when the polymer melt and microspheres are in contact [56,57,24]. Polymer is likely to absorb into the microspheres with the wetting rate dependant on the movement of individual polymer segments [58]. However, the specifics of the cross linking in the Veriflex resin are unknown and may alter (or impede) the wetting properties. Additionally, nanotubes which are attracted to the microspheres may serve to weaken the
polymer-microsphere interaction by making the interfacial layer even more porous. FTIR (Fourier transform infrared spectroscopy) results from Li and Xu indicate that there is some activity at the interface, as the incorporation of microspheres changed the intensity ratio at two wavenumbers, implying that some hydrogen bonds may have been formed [59].

Fig. 30 summarizes the stress-strain responses of the various material compositions at 121°C. These results largely follow the lower temperature (79°C) trends with the exception of the foam compositions at lower strain levels. At 79°C there was a large discrepancy between the two foams at all strain levels. Here, there is a loose agreement at strain levels less than approximately 10%. This is likely due to the higher temperature obfuscating differences as it causes both compositions to behave like a rubber. At higher strain levels the discrepancy becomes apparent again as the partially cured CNT foam lags behind.

Figure 29: Mean stress-strain responses of the different material compositions at 79°C.
Figure 30: Mean stress-strain responses of different material compositions at 121°C.

Figure 31: Compressive stress-strain comparison of foam compositions at room temperature.
5.3 Stress-Controlled Programming and Recovery

We eventually determined that stress-controlled programming was our best option since we could entirely control the stress and contact, thus avoiding the potential gap introduced in the quasi strain-controlled case (as discussed in section 4.4). Additionally, using the stress-controlled method allows us to realize all four steps of the thermomechanical cycle since a manual unloading at room temperature distinctly separates the cooling and unloading steps. In the quasi strain-controlled case, steps 2 and 3 were blurred together because unloading occurred gradually during the cooling process (creating a sort of three-step thermomechanical cycle).

Stress-controlled programming (as discussed in section 4.3) was performed on pure SMP and pure foam compositions. Sets of specimens were selected to undergo either free recovery, strain-controlled recovery, or stress-controlled recovery. The results of these different recovery conditions are presented here.

5.3.1 Free Recovery

Free recovery was performed on four sets of specimens including two material compositions (pure SMP and pure foam) which had been programmed using two stress levels (47kPa and 263kPa). Figs. 32 and 33 show the three-step programming followed by free recovery for these specimens. These four steps constitute the thermomechanical cycle discussed previously.

The purpose of the programming is to fix a specimen in its temporary (or working) shape where it can be utilized. In step 1, the strain initially increases rapidly upon loading. Because the total load was applied all at once at 79°C and held, step 1 is represented by a stepped curve instead of a continuous function. Traditionally, step one looks more like the beginning of the curves shown above in Figs. 19 and 24. However, we have taken a slightly different approach because of our loading rate. An alternative representation is shown in Fig. 34 and 35, which plots strain vs. time. Since the applied prestress in step 1 is held over 30 minutes at a temperature
above the Tg, we observe some development of creep. This is why the compressive strain at the end of step 1 is higher than the strain at the same stress level from the isothermal compressive stress-strain curve shown in Figs. 19 and 24, which has no creep deformation. The subplot in Fig. 35 highlights the creep behavior for the foam at a constant stress of 263kPa. In step 2, we notice a gradual further increase in strain. This increase is partially attributed to thermal contraction, but also has a viscoelastic (creep) component in the Tg region and a viscoplastic component below the transition region. This behavior is best seen in Figs. 34 and 35. In the case of the foam, there may exist a thin layer at the boundary between the microspheres and matrix. There, polymer may be adsorbed by the microspheres. Any adsorbed SMP in this layer would have its mobility reduced, and thus its Tg increased. Berriot et al. observed similar behavior in CNT reinforced SMP composites [60]. If the Tg is higher in this layer, some of the deformation in the Tg region may be viscoplastic in nature, while deformation outside the layer proceeds in a viscoelastic manner. In step 3, the load is suddenly removed, which causes a springback in the specimen. The specimen is now in its temporary shape and the final strain at the end of step 3 is the strain stored due to programming. Step 4 encompasses a free recovery which is driven by conformational entropy. From Figs. 32-35, we see that the majority of the strain recovery occurs in the glass transition region once the switching phase has been activated.
Figure 32: Four-step thermomechanical cycle for the pure SMP and pure foam using a 47kPa programming stress and a free recovery.
Based on the thermomechanical cycles, shape fixity and shape recovery values were calculated using Eqns. 17 and 21. The results are summarized in Table 7. The shape fixity for both the pure foam and the pure SMP is near 100% for most of the stresses used, meaning there is very little springback in the room temperature unloading step. This is the case because of the relatively high stiffness and low stresses used during programming. The somewhat lower fixity value (and large error) for the pure foam programmed at 47kPa is attributed to the small deformation (only 3%) created by this stress. Any errors in length measurements or alignment have more of an impact on the final result than in cases where there was more deformation since the errors make up a greater percentage of the overall deformation for small deformation. We obtain slightly higher shape fixity values for specimens programmed with 263kPa. The higher prestress increases the density and stiffness, which results in a smaller springback, and,
consequently, a higher fixity. For the pure SMP, almost all of the stored strain is recovered. The shape recovery of the foam, however, has been reduced due to unrecoverable viscoplastic deformation below the T_g region. There may also be viscoplastic deformation within the T_g region for the interfacial transition zone confined by the glass microspheres. Additionally, the incorporation of microspheres may provide additional local intermolecular resistance to segmental rotation, and thus higher viscoplastic deformation, leading to a lower shape recovery value than the pure SMP. For the higher programming stress (263kPa), the unrecoverable viscoplastic deformation during step 2 is increased, resulting in a lower shape recovery than the 47kPa stress level.

Table 7: Shape fixity and recovery values for the pure SMP and pure foam using stress-controlled programming followed by free recovery at 79°C.

<table>
<thead>
<tr>
<th>Material</th>
<th>Stress (kPa)</th>
<th>Strain (%)</th>
<th>Shape Fixity (%)</th>
<th>Shape Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure SMP</td>
<td>47</td>
<td>11</td>
<td>98.5 ± 3.7</td>
<td>98.7 ± 3.8</td>
</tr>
<tr>
<td></td>
<td>263</td>
<td>30</td>
<td>99.6 ± 1.4</td>
<td>98.4 ± 1.4</td>
</tr>
<tr>
<td>Pure Foam</td>
<td>47</td>
<td>3</td>
<td>81.2 ± 11.8</td>
<td>87.6 ± 11.7</td>
</tr>
<tr>
<td></td>
<td>263</td>
<td>12</td>
<td>96.7 ± 3.5</td>
<td>83.9 ± 3.0</td>
</tr>
</tbody>
</table>

From the stress-controlled programming and free recovery results discussed above, we see that time is an important factor in at least some (if not all) parts of the thermomechanical cycle. In order to better understand the time dependence, we investigated the rate of change of strain. Figs. 34 and 35 are strain-time representations of the respective thermomechanical cycles shown in Figs. 32 and 33. Initially, there is a rapid development of strain once the specimen is loaded. The rate gradually tapers off as creep progresses. The creep effect from step 1 is highlighted in the insert of Fig. 35. During cooling in step 2, we can divide the rate of change into three parts. The conditions at the beginning of step 2 are nearly identical to those at the end of step 1. That is, the temperature is still above the T_g (though headed down) and the full load is present. Therefore, while still near the T_g region, the material continues to experience creep. As step 2 progresses and the temperature falls below the T_g region, the material becomes
increasingly more glassy. The strain change at this point is primarily due to thermal contractions, as is evidenced by the constant slope of the curve. Additionally, there is viscoplastic deformation below the T₉ region. Altogether, these effects increase the strain by a few percent over the range of step 2. The unloading in step 3 causes a small change in the strain from springback and is very short compared to the rest of the thermomechanical cycle. In step 4, we observe a rapid recovery of strain around the T₉ region as the shape memory effect returns the specimen to its permanent shape.

The cooling in step 2 in these experiments was done naturally in that no effort was made to accelerate the process through some forced cooling mechanism. In order to capture the temperature data during this step, the heating chamber remained sealed. Consequently, the cooling rate was governed by the small heat leak through the walls of the insulated chamber. Step 2, then, in Figs. 34 and 35 spans multiple (overnight) hours (as can be seen from the x-axis). The change in strain during this time was due partly to viscoelasticity (creep) and partly to viscoplasticity. The viscoplastic contribution to the change in strain occurs below the T₉ region and is not recoverable. We speculate that a more rapid cooling would effectively reduce the viscoelastic contribution while increasing viscoplastic deformation since less time would be spent in the T₉ region and more time would be spent below it.
Figure 34: Four-step thermomechanical cycle strain-time representation of the pure SMP and pure foam for a programming stress of 47kPa followed by free recovery.

Figure 35: Four-step thermomechanical cycle strain-time representation of the pure SMP and pure foam for a programming stress of 263kPa followed by free recovery.
5.3.2 Strain-Controlled Recovery

We now turn our focus to a second type of recovery condition, strain-controlled recovery. It is a type of confined recovery in which a programmed strain is mechanically held while heating through a temperature range. The resulting force is measured as a function of the temperature and/or time.

The recovered stress results for the pure SMP and pure foam programmed using 47kPa and 263kPa are shown in Fig. 36. The basic trend for all compositions and stresses is an initial rise of stress to some peak value (which is larger than the programming stress) followed by a decline and finally a leveling off as the programming stress is reached. This general trend has been observed previously in shape memory polymers by others [41,61].

The overall recovered stress is composed of two parts: 1) stresses from thermal expansion (in both the specimen and the testing fixture) as heat is added to the system and 2) recovery of the entropically stored stress in the specimen. The thermal stress, $\sigma_T$, can be calculated using Eqn. 24 [62]

$$\sigma_T = E \alpha \Delta T$$

(24)

where $E$ is the modulus, $\alpha$ is the coefficient of thermal expansion, and $\Delta T$ is the change in temperature. During heating, stress builds up as the fixture and specimen expand in response to the rise in temperature. There is a maximum once the T_g region is reached because of the drastic decrease in the modulus as the material transitions from a glassy to rubbery state. Continued heating through the T_g region shows a stress relaxation, which eventually plateaus near the programming stress. The pure SMP has a shorter relaxation time than the pure foam, and reaches the programming stress sooner. The foam has a longer relaxation time due to the restricted mobility of chains in the locale of microspheres. We investigated the relaxation of the pure foam, maintained at 79°C, over a prolonged time period of almost 24 hours. These observations are
presented in Fig. 37. There is a further decrease in stress after the large drop after the peak that is small over the course of several hours.

Figure 36: Recovered stress during strain-controlled recovery for the pure SMP and pure foam after stress-controlled programming at 47kPa and 263kPa.

Figure 37: Stress relaxation of the pure foam during strain-controlled recovery after programming with a constant stress of 47kPa.
There does not exist a conventional definition for the stress recovery like the one for the shape recovery (Eqn. 21), so we simply define it here as the ratio of the final stress measured during fully confined recovery to the stress used during programming. That is

\[
\text{stress recovery} = \frac{\sigma_{\text{recovered}}}{\sigma_{\text{programming}}} 
\]  

(25)

The stress recovery results are summarized in Table 8. For a programming stress of 263kPa, we have stress recovery percentages similar to shape recovery ratios presented in section 5.3.1. However, for the lower programming stress the recovered stress values are much too high. We purpose two possible noncompeting explanations for these abnormal results. First, the test fixture experienced thermal expansion during the recovery process, which applied a compressive stress to the specimen. This stress can be viewed as a kind of additional programming stress, which may contribute to the recovered stress during recovery. The 263kPa specimens experienced a similar effect, but were less sensitive to it since the extra strain produced by the thermal expansion was a smaller percentage of the overall deformation. Secondly, the load cell on the MTS machine used to measure the recovered stress was not sensitive enough. Its capacity is 150kN. When the surface areas of specimens are taken into account, the 47kPa stress equates to approximately 40-45N of force. This is an extremely small percentage of the load cell’s capacity. The load cell operates as a transducer, converting mechanical movement to an electrical signal. For such a small force, the output voltage is very small. Therefore, the measured recovered stress values for the lower programming stress likely contain significant instrument error. Error estimates are not included in Table 8 because the load cell sensitivity could not be adequately determined as of the writing of this document.
Table 8: Stress recovery results for the pure SMP and pure foam during strain-controlled recovery.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Programming Stress (kPa)</th>
<th>Recovered Stress (kPa)</th>
<th>Stress Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure SMP</td>
<td>47</td>
<td>52</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td>263</td>
<td>259</td>
<td>98</td>
</tr>
<tr>
<td>Pure Foam</td>
<td>47</td>
<td>70</td>
<td>149</td>
</tr>
<tr>
<td></td>
<td>263</td>
<td>222</td>
<td>84</td>
</tr>
</tbody>
</table>

Comparing the recovery stress of the pure foam with the pure SMP, we can see that the foam has a higher peak stress than the pure SMP. This is because the foam has a higher modulus than the SMP at higher temperatures. The temperature corresponding to the peak stress is higher for the foam than for the SMP, which is in agreement with the Tg results from DMA tests. The peak stress in specimens programmed by a 263kPa prestress is higher than in specimens programmed by a 47kPa prestress. This is because the 263kPa prestress makes the specimens denser and stiffer producing a quicker build up of thermal stress during heating and ultimately a higher peak stress.

5.3.3 Stress-Controlled Recovery

As a final recovery method, we now look at another type of confined recovery: stress-controlled recovery. The results of the stress-controlled recovery on the foam are represented by direct SEM observation in Figs. 38 and 39. An equivalent stress to that used during programming was applied during recovery. Fig. 38 shows the damaged area before the recovery process. Distinct reference features were chosen to aid in location of the same area of the specimen after recovery. Fig. 39 shows the same region post stress-controlled recovery. They show effective sealing of the artificial crack, which was approximately 0.2mm wide. This result suggests that confined shape recovery of the SMP based syntactic foam can be used to seal structural-scale damage.
Figure 38: SEM image of a cross section of the foam showing an intentionally damaged portion after programming.

Figure 39: SEM image of the syntactic foam after a stress-confined recovery cycle. The sealing effect is apparent when compared to the image taken before recovery.
5.4 Quasi Strain-Controlled Programming and Recovery

The shape fixity and shape recovery for the quasi strain-controlled condition were evaluated for the loading direction at two temperatures and three strain levels (Figs. 40 and 41). Three material compositions, one foam and two non-foam, were considered. The general trend for all compositions was the same. Higher strains during programming produced higher shape fixity values. At lower strain values the elastic effect is more pronounced, leading to more springback and, consequently, lower fixity. At higher strain levels there is less springback because of the increased stiffness and density, which creates higher shape fixity. Additionally, the foam composition likely experienced some crushing of the microspheres with increasing strain even at these elevated temperatures. This type of damage may enhance the fixity, as any crushed cells would not be able to contribute to the springback and would also leave a partially empty volume into which other components could expand (further reducing the overall springback effect).

As the temperature is raised (79°C → 121°C), we obtain lower shape fixity values in the case of the non-foam compositions, but slightly higher fixity values in the case of the foam. Recall that during this type of programming, there is a continual unloading during the cooling step. Any elasticity in the specimens will serve to drive them back towards the permanent shape (even during programming) while above the T_g if not fully confined. For 79°C, the temperature passes through the T_g region relatively early in the cooling process. Consequently, the shape fixity is not terribly affected by this elastic recovery during programming. At 121°C, however, the specimens are well above their T_g. The cooling, then, takes longer, which subjects the material to more unloading, resulting in lower shape fixity values. The foam, on the other hand, does not experience this effect as much because 40% of it is microspheres, which have a much higher T_g, and do not contribute to the elasticity during cooling. Also, any damaged microspheres would contribute to higher fixity as mentioned above.
Shape recovery values for the SMP are high (at or near 100%) for both temperatures and most strain levels (Fig. 41). The foam displays lower shape recovery values since the microspheres do not possess any shape memory functionality. Also, the recovery in the foam drops with an increase in strain level. This isn’t surprising since we suspect there is some microsphere damage (which can’t be recovered).

![Shape Fixity Graph]

Figure 40: Shape fixity in the loading direction for specimens which have undergone quasi strain-controlled programming. Three strain levels (5, 30, 60%) and two temperatures (79°C and 121°C) were used for the programming.
Figure 41: Shape recovery in the loading direction for specimens which have undergone quasi strain-controlled programming. Three strain levels (5, 30, 60%) and two temperatures (79°C and 121°C) were used for the programming.

5.5 Volume Change

The change in volume after programming compared to the original volume is given in Tables 9 and 10 respectively for the pure SMP, SMP with MWCNTs, and the foam with MWCNTs.

For the pure SMP, the volume change after programming is fairly constant (~5%) across all strain levels and both temperatures. This implies a homogenous material that deforms uniformly.

The SMP with nanotubes displayed similar volume reduction to the pure SMP, which is not surprising considering the close composition.

The foam showed a small reduction in volume at the low strain level (comparable to the other compositions). However, there was much more volume change at the higher strain levels, indicating that at least some of the microspheres had been crushed, creating a denser specimen. This is supported by the smaller (but still larger than the other compositions) volume change for
the higher strain levels at 121°C. The higher temperature lowers the matrix modulus even more, which reduces (but does not eliminate) the amount of microsphere damage.

Table 9: Volume change after programming.

<table>
<thead>
<tr>
<th>Composition, Strain Level</th>
<th>Volume Change (%) for 79°C Programming</th>
<th>Volume Change (%) for 121°C Programming</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure SMP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5%</td>
<td>-5.56 ± 0.84</td>
<td>-3.58 ± 0.66</td>
</tr>
<tr>
<td>30%</td>
<td>-5.88 ± 1.3</td>
<td>-5.20 ± 0.84</td>
</tr>
<tr>
<td>60%</td>
<td>-5.81 ± 0.93</td>
<td>-5.57 ± 0.74</td>
</tr>
<tr>
<td>SMP + CNT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5%</td>
<td>-5.38 ± 1.1</td>
<td>-3.84 ± 0.60</td>
</tr>
<tr>
<td>30%</td>
<td>-3.77 ± 0.64</td>
<td>-3.23 ± 0.50</td>
</tr>
<tr>
<td>60%</td>
<td>-4.12 ± 0.68</td>
<td>----</td>
</tr>
<tr>
<td>Foam (with CNT)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5%</td>
<td>-3.63 ± 0.38</td>
<td>-4.11 ± 1.0</td>
</tr>
<tr>
<td>30%</td>
<td>-14.8 ± 0.4</td>
<td>-9.97 ± 0.71</td>
</tr>
<tr>
<td>60%</td>
<td>-28.5 ± 0.7</td>
<td>-12.4 ± 1.0</td>
</tr>
</tbody>
</table>
Chapter 6. Conclusion

DMA results were used to determine the T_g of the pure SMP and pure foam. The pure SMP has an average T_g = 67.7°C, in agreement with the manufacturer. Addition of the microspheres, in the case of the pure foam, shifts the glass transition region up slightly to a T_g = 70.5°C. The higher T_g may be due to the existence of a thin layer between the microspheres and surrounding SMP where the chain mobility has been restricted due to polymer adsorption by the microspheres.

Foam compositions which have undergone compressive stress-strain testing at room temperature display three regions (with increasing strain level) on their stress-strain curves relating to microstructural changes. The second region entails irreversible damage to the glass microspheres.

For all sample compositions, increasing the temperature reduces the stresses during compression. At temperatures above the T_g, the values are significantly reduced. At 79°C, the foam compositions still have trends reminiscent of those at room temperature, while the non-foam compositions do not, having the yield points flattened and obscured. At 121°C all compositions behave like a rubber.

The pure foam (SMP+microspheres) composition and the SMP with nanotubes (SMP+CNT) composition can be fully cured. However, the combination of microspheres and MWCNTs in the SMP matrix complicates the curing procedure and produces undesirable mechanical performance. Either the curing procedure needs to be changed or, more likely, the interaction needs to be enhanced through surface treatment of the microspheres and carbon nanotubes.

Very small additions of MWCNTs to the SMP do not appear to enhance the mechanical or shape memory properties, and actually causes a slight reduction in the shape fixity values compared to the pure SMP. It is possible that much higher concentrations could provide
alternative ways to trigger the shape memory effect (e.g., a percolating network could allow for much faster and cleaner triggering using a supplied electrical current or one induced with a magnetic field). Additionally, if there is a good interaction between nanotubes and the surrounding material (chemical compatibility), it may be possible to leverage the mechanical properties of CNTs and provide increased strength and stiffness. Issues with the compatibility between components and the interfacial bonding strength need to be addressed.

Free recovery was performed at 79°C on pure SMP and foam specimens after having undergone stress-controlled programming using 47kPa and 263kPa. Four-step thermomechanical cycles (high temperature loading → cooling → unloading → recovery) were generated as 3-D stress-strain-temperature and 2-D strain-time plots. Because of the elevated temperature (>\(T_g\)) and timescale (30 min.), creep was observed during the loading step. During the cooling step further deformation occurred due to a combination of thermal contractions, viscoelasticity (in the \(T_g\) region), and viscoplasticity (below the \(T_g\)). A small springback in step 3 due to high stiffness and low stress levels yields shape fixity values near 100% for both material compositions. Higher programming stresses yield slightly higher fixity values because of increased density and stiffness. We observe almost full recovery of the stored strain for the pure SMP. The foam, however, has somewhat lower shape recovery values due to unrecoverable viscoplastic deformation during the later part of the cooling step or crushed microspheres. The majority of the strain recovery occurs in the \(T_g\) region during step 4 once the switching phase is activated.

Strain-controlled recovery was performed on specimens which underwent stress-controlled programming at 47kPa and 263kPa by mechanically confining movement during the heating process. All trials experienced a similar trend of a build up to a peak stress (greater than the programming stress) followed by a decline once the \(T_g\) region is reached, and finally a plateauing near the programming stress. Thermal expansion primarily contributes to the initial increase. Around the \(T_g\) the material has a stress relaxation. Stress recovery percentages for the
263kPa programming stress were similar to those for shape recovery. Values for the 47kPa programming stress, however, were artificially high due to additional programming stress introduced during recovery (from thermal expansion of the test fixture) and from a lack of instrument sensitivity. Peak stresses during strain-controlled recovery were higher for the foam because of its higher modulus at higher temperatures, which lead to a more rapid build up of thermal stress during the early heating phases.

After programming specimens in a stress-controlled manner, intentional damage (of macroscopic size) was generated in order to evaluate the sealing capability during confined recovery. The specimens were then recovered under a stress-controlled condition. SEM observations were made at each stage to evaluate the extent of the damage. After the confined recovery the damaged region displayed significant sealing, leaving next to no visible damage left. The images convincingly show that confined recovery can be used to seal macro-length scale damage.

Shape fixity and shape recovery in the loading direction for the quasi strain-controlled condition were evaluated for three material compositions at two temperatures (79°C and 121°C) and three strain levels (5, 30, and 60%). The general trend was that higher strains during programming produced higher fixity values. A higher temperature caused similar (or slightly higher) shape fixity values for the foam, but lower values for the non-foam compositions. Continual unloading during the cooling step in this type of test allowed elasticity in the specimens to work against the programming, thus lowering the fixity in more elastic compositions. The higher T_g of the microspheres in the foam shields it in a way from these effects, thereby maintaining similar fixity levels to the lower temperature test. The quasi strain-controlled method can be used to program foam, but loses some of its effectiveness when applied to non-foam compositions. Shape recovery for the non-foam compositions is near 100%. The foam, on the other hand, displays lower shape recovery values since the microspheres do not
possess any shape memory capability. Also, the foam shows a decrease in recovery with increasing strain, indicating that some microsphere damage has occurred.

The volume change after programming was low and consistent around 5% for the pure SMP and SMP with MWCTs, consistent with a highly elastic homogenous material. For the foam, the values were higher, indicating damage to the microspheres.
Chapter 7. Recommendations/Future Work

From the study presented here, it is clear that the SMP based syntactic foam can effectively seal damage while reducing weight by approximately 40%. However, by adding glass microspheres in the manner we have done, the modulus and strength have been negatively affected (Fig. 25). By incorporating the SMP based syntactic foam into the grid structure (Fig. 1), some of the loss is mitigated by the reinforcement. Nevertheless, the core itself could still benefit from increasing its mechanical properties. A good avenue to pursue in this regard is working to improve the chemical compatibility between the microspheres and the polymer matrix. Surface treatment of the microspheres or addition of a chemical compound that acts as an intermediary (coupling agent) may strengthen the interfacial gap. Another option is to use microspheres with thicker walls or ones made of other materials (there can be weight tradeoffs however).

The incorporation of CNTs offers two potential benefits. The nanotubes could act as reinforcement by way of their good mechanical properties. Secondly, a conducting nanotube network would provide other ways to trigger the shape memory effect. These benefits are not realized at the low nanotube concentration discussed here. As was mentioned previously, however, there were problems in the curing process using higher concentrations. Since we would like to add significantly more nanotubes, understanding their effect on the curing is important. It may be instructive to explore the use of block copolymers to obtain better nanotube dispersion. Additionally, the combination of MWCNTs and glass microspheres caused undesirable mechanical performance (Figs. 29-31). Surface treatment of the filler particles and/or the use of coupling agents should be explored in order to enhance the compatibility between the constituent ingredients.

Quality and consistency of fabrication is very important, as it affects all measurements made afterwards. The uniformity of dimensions in a prepared specimen greatly influenced the
ease of testing and the results obtained. In particular, surfaces where load is applied must be as close to parallel as is possible. Any deviation creates a non-uniform loading situation and complicates the analysis. For the work presented here, a large number of tests had to be redone due to misalignment or uneven loading. The glass plate shown in Fig. 7b was an attempt to avoid some of these issues (which largely worked). Loss of material due to leaks or bake-off during the curing process also reduces the quality of the final specimen. If a large amount of fabrication were to be done in the future, it would be worthwhile to rethink the molds and fabrication process. Specifically, a frame made from Teflon with glass plates may aid in de-molding while keeping top and bottom surfaces flat and parallel. Also recommended is a good cutting procedure so that edges can be kept straight and parallel.

Finally, the next big step to take would be to combine the sealing capability of the SMP based composite with one of the current healing schemes. While any of them would provide additional functionality to some degree, ionomers may be the best match. Their main drawback is lack of a mechanism to reassociate damaged surfaces, a problem which the shape memory effect nicely solves. Additionally, they are also polymer chains. Without the addition of another component, SMP chains could possibly be further functionalized by adding ionic segments to create a SMP-ionomer.
References


Appendix. Supplementary Notes

All data plots were generated as encapsulated postscript files in MATLAB with the exception of Figure 17, which was made using the TA Instruments software.

Most plots were resized using Adobe Illustrator.

Figure 25 was prepared using a combination of MATLAB and Adobe Photoshop.

Figure 15a was created using AutoCAD.

All other original illustrations were created using Adobe Illustrator.

This document was written in OS X with Microsoft Word 2008 and was later converted to the PDF format.
Vita

Damon Nettles was born in New Orleans, Louisiana. He attended Northshore High School in Slidell, Louisiana. He enrolled at Louisiana State University, receiving a Bachelor of Science in physics in 2002. During his sophomore year he participated in the national student exchange, studying in the bay area at California State University Hayward. After graduation, he worked for several years as a research associate on the ALLEGRO project at the Gravitational Wave Laboratory in the Department of Physics and Astronomy at LSU. He then pursued a Master of Science degree in mechanical engineering at Louisiana State University, working with Dr. Guoqiang Li and the NASA-EPSCoR group, focusing on smart composite materials.