Published in final edited form as:

Smart Mater Struct. 2011 September ; 20(9): 094004-1–094004-18. doi:10.1088/0964-1726/20/9/094004.

Characterizing and modeling the free recovery and constrained recovery behavior of a polyurethane shape memory polymer

Brent L Volk^{1,2}, Dimitris C Lagoudas^{1,3}, and Duncan J Maitland^{1,2}

Duncan J Maitland: djmaitland@tamu.edu

¹Materials Science and Engineering Program, Texas A&M University, College Station, TX 77843, USA

²Department of Biomedical Engineering, Texas A&M University, College Station, TX 77843, USA

³Department of Aerospace Engineering, Texas A&M University, College Station, TX 77843, USA

Abstract

In this work, tensile tests and one-dimensional constitutive modeling are performed on a high recovery force polyurethane shape memory polymer that is being considered for biomedical applications. The tensile tests investigate the free recovery (zero load) response as well as the constrained displacement recovery (stress recovery) response at extension values up to 25%, and two consecutive cycles are performed during each test. The material is observed to recover 100% of the applied deformation when heated at zero load in the second thermomechanical cycle, and a stress recovery of 1.5 MPa to 4.2 MPa is observed for the constrained displacement recovery experiments.

After performing the experiments, the Chen and Lagoudas model is used to simulate and predict the experimental results. The material properties used in the constitutive model – namely the coefficients of thermal expansion, shear moduli, and frozen volume fraction – are calibrated from a single 10% extension free recovery experiment. The model is then used to predict the material response for the remaining free recovery and constrained displacement recovery experiments. The model predictions match well with the experimental data.

1. Introduction

Applications in the medical device industry, such as vascular stents, clot removal devices, and tissue scaffolds, often necessitate self-expansion, tunable material properties, biocompatibility, and/or biodegradability. Shape memory polymers (SMPs) are a class of active materials that, under an appropriate thermomechanical cycle, will recover a thermodynamically stable applied deformation [1-5]. The ability to address the aforementioned needs combined with inherent low density, relatively low cost, and excellent manufacturability has resulted in significant interest in using SMPs for biomedical applications [6-11].

To better understand the behavior of shape memory polymers, experimental investigations have been performed on SMPs subjected to complex thermomechanical loading conditions. Many of the initial studies focused on the SMP response when subjected to small deformations (<10% extension) [12-14]. In particular, Tobushi et al. tested polyurethane films to extensions of up to 10% [12, 14] and Liu et al. tested the small deformation response for an epoxy-based SMP [13]. In addition to performing free recovery experiments, Liu et al. also tested the SMP under constrained displacement recovery conditions [13]. Recent experimental efforts have investigated in more depth the finite deformation response of SMPs, with Atli et al. [15] and Volk et al. [16] testing a styrene-based SMP, Wilson et al.

[17] and Baer et al. [18] investigating polyurethane SMPs, and Voit et al. studying acrylate-based SMPs [19, 20] to large values of extension ($>10\%$). Additional efforts have studied the influence of manufacturing composites using a SMP matrix [21-25] as well as the influence of exposing styrene- and epoxy-based SMPs and SMP composites to potentially degrading conditions [26, 27].

In steps toward developing effective methods for designing, analyzing, and optimizing devices, there have also been efforts to more accurately describe and predict the material behavior of SMPs. While numerous models have assumed infinitesimal deformations [12, 13, 28, 29], models proposed by Chen and Lagoudas [30] as well as Qi, et al. [31] have been based on finite deformations. In addition, the works of Nguyen, et al. [32, 33] have considered viscoelasticity in a finite deformation framework, and the works of Reese et al. [34] and Srivastava et al. [35] have included thermo-mechanical coupling in models that have been implemented in finite element analysis packages.

The objectives of this work are two-fold and aim to characterize a previously untested high recovery force polyurethane shape memory polymer with a known composition [17] that is being considered for biomedical applications and to assess the predictions of a finite deformation model that had previously only been applied to styrene-based shape memory polymers [36] and, using a linearized version of the model for small deformations, epoxy-based SMPs [37]. While the shape recovery of the polyurethane SMP is expected to occur in a similar qualitative manner to the styrene- and epoxy-based SMPs, this work aims to provide a more accurate assessment of the model predictions by altering the load path to isolate the material response during constrained recovery and by using the deformation in the gage length, as measured by a laser extensometer, as input. The objectives in this work will serve to increase the capability for device design by validating the model predictions against the experimental results of a SMP with a known and controllable composition.

Specifically, the first objective of this work is to perform an experimental evaluation of the shape memory characteristics of a polyurethane (PU) SMP first proposed by Wilson et al. [17]. This experimental effort characterizes both the free recovery and the constrained displacement recovery conditions at applied extensions of 10%, 15%, 20%, and 25%. While the tests with free recovery (zero load) conditions provide a measure of the maximum shape recovery, the tests with constrained displacement recovery conditions, although relatively sparse in the literature, provide information about the blocking stress – the stress above which no shape recovery would be observed. The blocking stress is important in the design of SMP devices. Specifically, to achieve shape change in the device, the material and/or thermomechanical load path be selected such that the blocking stress is sufficiently higher than the stress imposed by the boundary conditions. It is important to note that *extension* is defined and used hereafter as the change in the gauge length of the material divided by the initial gauge length and *stress* is the applied load divided by the initial cross-sectional area. In 1-D, these are often referred to as engineering strain and engineering stress, respectively.

The second objective of this work is to use a subset of the experimental data to calibrate the finite deformation model proposed by Chen and Lagoudas [30] and implemented in 1-D by Volk, et al. [36]. After the material properties are calibrated, the model is used to predict the remaining free recovery experiments and constrained displacement recovery experiments and the predictions are then validated through comparison to the experimental data.

The outline of this work is as follows: first, the details of the fabrication of the polymer, the experimental setup used to perform the tests, and the experimental parameters for the tests are presented in section 2. Then, the experimental results for both the free recovery and constrained displacement recovery experiments are presented in section 3. A brief summary

of the Chen and Lagoudas model as well as the method used to calibrate the necessary parameters is presented in section 4, and the results of the model predictions, compared to the experimental results obtained in section 3, are presented in section 5.

2. Materials and methods

2.1. Specimen type and preparation

The shape memory polymer used for this study was a polyurethane SMP proposed by Wilson et al. [17], which consisted of 1,6-hexamethylene diisocyanate (HDI), N,N,N',N'-tetrakis(2-hydroxypropyl) ethylenediamine (HPED), and triethanolamine (TEA), of which the molar amounts were equal to 1.00, 0.40, and 0.133, respectively.

The method for fabricating the thermoset polyurethane SMP was adapted from [17]. The monomers were first decanted from source containers to 60mL glass containers and then subsequently vacuum degassed for 24 hours at 45°C. The monomers were weighed and combined in a glove box to reduce exposure to moisture. After removing the combination from the glove box, the monomers were mixed using a vortex mixer for 2 minutes. The mixture was sonicated for 2 minutes and vacuum degassed for 6.5 minutes. The mixture was then sonicated again for 3 minutes and then vacuum degassed again for 3 minutes.

The mixture was then cast into an aluminum mold coated with a polytetrafluoroethylene (PTFE) spray, which was sintered on the mold and served as a mold release. The mold was sealed using a silicone gasket between the two pieces, and then was positioned vertically in a clamp and stopcocks were placed into the tapered ports of the mold. The tips of the stopcocks were wrapped with a PTFE tape to provide a better seal, and quick-setting epoxy was used to hold the stopcocks in place during the casting process. Figure 1(a) presents the mold setup ready for casting the polymer. The polymer mixture was injected into the bottom port of the mold using a syringe and tubing which attached to the stopcock via a Luer connection. The mold and clamp setup was then placed in a programmable temperature chamber. The temperature profile was programmed to heat at 30°C/hour to 120°C at which the chamber was held constant for an hour before slowly cooling to room temperature. The fabrication process resulted in sheets of polymer material that measured 6in. × 4in. × 1mm thick. Differential scanning calorimetry (DSC) was performed on each sheet of material using a TA Instruments Q200, and the glass transition temperature (T_g) was measured to be 67°C with a standard deviation of 0.7°C at a temperature rate of 1°C/min. A GravoGraph[®] LS100 CO₂ laser cutter was used to cut nine ASTM D-638 Type V specimens from each sheet of material. A sheet of material and a resulting Type V specimen are shown in figure 1(b) and (c), respectively.

2.2. Experimental setup

The experiments in this work were performed in the Materials and Structures Lab at Texas A&M University. The tests were performed on a MTS[®] Insight 30kN electromechanical, screw-driven test frame equipped with a Thermcraft[®] temperature chamber that uses forced convection for heating and liquid nitrogen for cooling. The test frame was equipped with MTS[®] Advantage 2kN pneumatic grips and a Honeywell[®] 222 N (50 lbf) load cell. In addition, to avoid undesirable effects of a contact based measurement technique [15, 16, 38], a MTS[®] LX1500 laser extensometer was used to measure the extension of the material. Figure 2 presents the test frame, temperature chamber, and laser extensometer used for testing the shape memory polymers. To prepare the specimens for use with the laser extensometer, two pieces of reflective tape were attached, at the ends of the gauge region, to the surface of the specimen. The extension of the material was calculated as the change in the distance between the reflective tapes divided by their initial separation.

2.3. Experimental parameters

The experiments performed in this work evaluated both the free recovery (extension recovery at zero load) and the constrained displacement recovery (stress recovery at constant extension) of the SMP. The free recovery experiments were performed to determine the maximum shape recovery, and the constrained displacement recovery tests were performed to provide information (e.g., blocking stress) about the response of the SMP while subjected to external constraints. This constrained recovery response will be important for developing devices in constrained environments, such as the human body. The tests followed the thermomechanical path schematically presented in previous investigations [13, 15, 16] for free and constrained recovery conditions. First, the specimens were held at zero load and the temperature was increased to 90°C, which was higher than the glass transition temperature of 67°C that was measured by DSC with a temperature rate of 1°C/min. The temperature was held at 90°C for 25 minutes to allow the system to reach thermal equilibrium. This dwell time was selected by monitoring the time necessary for one of the pneumatic grips to reach 90°C, as measured by a thermocouple attached to the surface of the grip. The material was then deformed at 50mm/min – the displacement rate recommended for nonrigid materials by the ASTM D638 standard for testing tensile properties of plastics [39]. Although larger values of extension may be possible by deforming at temperatures near T_g [19, 40], this loading temperature was selected to evaluate the material response of the rubbery phase at temperatures above the glass transition region. The temperature was then decreased to 25°C. During the cooling step, the laser extensometer measurements were used as feedback to the proportional-integral-derivative (PID) controller in the MTS® Testworks® software to adjust the crosshead to minimize the extension induced in the specimen by the thermal contraction of the grips and extension rods. The temperature was held at 25°C for 25 minutes to allow the system to reach thermal equilibrium, and then the displacement was decreased at 5 mm/min – the rate recommended by ASTM D638 for rigid materials [39] – until the load equaled zero. After unloading, the specimen was heated to 90°C and the recovery was measured. At the end of the recovery heating, the thermomechanical cycle was repeated such that each specimen was subjected to two cycles under the same parameters. Additional cycles were not performed after observing negligible change in the shape memory response from the first to the second cycle and based on isothermal results [17] that indicate the largest hysteresis may occur as a result of loading in the first cycle with stable material response beginning in the second cycle.

The polyurethane SMP was tested at extensions of 10%, 15%, 20%, and 25% for each of the free recovery and constrained recovery conditions. The 25% extension upper limit was observed to be the largest value for which shape memory tests could be repeatably performed, and ongoing work is investigating whether larger extensions may be possible by further optimization of the fabrication and processing conditions. This value of extension, although lower than recently developed high-strain SMPs [19, 20], is a result of the trade-off for developing a high recovery force SMP with a rubbery modulus greater than 20 MPa [17] and is considered appropriate for the devices under consideration. The temperature rate, the rate of heating and cooling, was 1°C/min for all tests to minimize the temperature rate effects [16]. A pristine specimen was used for each experiment, and the tests were repeated twice for a total of three specimens per test condition.

3. Experimental results

This section presents the results for the free recovery and constrained displacement recovery experiments that were tested at extensions of 10%, 15%, 20%, and 25%. A single, complete result for each of the test cases is presented first, in figures 3 and 4. The data corresponding to the individual segments of the tests, including the samples tested for repeatability, are then presented in greater detail in sections 3.1 - 3.3. Note that sections 3.1 and 3.2 present

the data for segments that are common to all tests performed (loading at high temperature, constrained cooling, and unloading at low temperature). Section 3.3 presents the data for the two different types of recovery steps – free (zero load) recovery (Section 3.3.1) and constrained displacement recovery (Section 3.3.2).

To begin, consider the results presented in figures 3 and 4, where the temperature, extension, and stress are plotted with respect to time and the key steps of the thermomechanical load path are labeled as 'A', 'B', 'C', and 'D'. The reference temperature for each test was 90°C, at which the temperature was held constant for 25 minutes to allow the system to reach thermal equilibrium. During this dwell period, each specimen was allowed to hang freely from the top grip at zero load. At the end of the dwell period, denoted by point 'A', the load and extension readings were zeroed and the bottom of the specimens was gripped using the handheld pneumatic controls. The gripping procedure often resulted in a small, compressive force, and thus a non-zero extension at the beginning of loading on the specimen. The specimens were then stretched to a predetermined value of extension, specifically 10%, 15%, 20%, or 25%. After loading the extension was constrained and the temperature was lowered to 25°C. A stress increase was measured during this constrained cooling step from 'A' to 'B'. The temperature was then held at 25°C for 25 minutes to allow the system to reach thermal equilibrium, which coincides with the plateau in the stress profile. The additional increase in stress from 'B' to 'C' after cooling is complete is likely due to continued cooling of the grips and extension rods, which results in additional elastic stress imposed on the SMP. [16, 41] The load is then removed at time 'C' and the recovery step is initiated.

At the beginning of the recovery heating in the free recovery experiments (cf. figure 3), the bottom grip was released using the handheld pneumatic controls. By releasing the grip, zero load was maintained on the specimen, neglecting gravity. The temperature was then raised to 90°C, and the extension (shape) recovery was measured using the laser extensometer from 'C' to 'D'. After a 25 minute dwell period at 90°C, the bottom of the specimen was re-gripped, and the thermomechanical cycle was repeated.

In the constrained recovery experiments (cf. figure 4), the bottom grip was released at the beginning of the recovery step, denoted by time 'C'. Releasing the bottom grip ensured zero load during the beginning of the recovery heating; otherwise, the thermal expansion of the SMP combined with the thermal expansion of the grips and extension rods could have created a significant compressive stress and the potential for thermal buckling in the SMP [41]. At 60°C, before shape recovery would initiate, the bottom of the specimen was re-gripped. This gripping procedure resulted in a small, compressive force on the SMP. To offset this force, the crosshead was moved slightly up using the handheld control of the MTS® test frame. The crosshead was then held constant and a tensile stress increase was measured as the SMP attempted to return to its original shape. During the heating from 60°C to 90°C after re-gripping, the thermal expansion of the grips and extension rods imposed an elastic deformation on the specimen. At the end of the recovery heating (time 'D'), the system was allowed to dwell at 90°C for 25 minutes and then the thermomechanical cycle was repeated.

3.1. Loading at 90°C ($T > T_g$) and unloading at 25°C ($T < T_g$)

The stress-extension behavior during loading at 90°C and unloading at 25°C (cf. steps 'A' and 'C' in figures 3 and 4, respectively) for sample 10%, 15%, 20%, and 25% extension experiments is presented in figure 5(a) and (b), respectively, with the beginning (loading) and end (unloading) points offset to zero for comparison. It is observed that the stress-extension relationship is approximately linear during loading, even to extensions of 25%, and the behavior is consistent between specimens. The data for the loading and unloading

modulus for both cycles of all test cases is presented in table 1. Specifically, the average modulus value, calculated using a linear fit to the unloading data and initial loading data, and the range (maximum - minimum) of all three specimens tested at each test condition is presented. It is observed that the modulus during loading at 90°C, calculated up to an extension of 5%, is approximately 20 MPa in both the first and second cycles for all tests performed, and the unloading modulus at 25°C is approximately 1700 MPa. Further, there is a negligible change in the modulus values from the first cycle to the second cycle for the tests performed.

3.2. Constrained cooling from 90°C to 25°C

The stress-temperature and extension-temperature relationship during constrained cooling (cf. step 'A' to 'B' in figures 3 and 4) is presented in figure 6(a) and (b), respectively, for sample 10%, 15%, 20%, and 25% extension experiments. During this portion of the thermomechanical path, the laser extensometer measurements are used as feedback to the MTS® Testworks® PID control to offset the extension imposed by the thermal contraction of the grips and extension rods. Due to the resolution of the laser extensometer, which is 0.001 in. or 0.3% of the specimen gage length, the system is unable to completely offset the thermal contraction of the grips and rods without causing significant oscillations in the stress of the material. Therefore, the PID parameters were adjusted such that the SMP experienced a relatively smooth stress increase while minimizing the extension increase during the constrained cooling. As presented in table 2, the SMP specimens experienced a resulting increase in the extension of 1-1.5%, which was a combination of thermal contraction of the SMP and elastic deformation on the SMP due to the thermal contraction of the grips and rods. The stress increase during the cooling step was approximately 15 MPa. Further, no significant differences were observed in the material response from the first cycle to the second cycle.

3.3. Recovery during heating from 90°C to 25°C

The following sections present the recovery data for the free recovery (3.3.1) and constrained displacement recovery (3.3.2). This step of the load path starts at time 'D' in figures 3 and 4 and ends when the original temperature of 90°C is achieved.

3.3.1. Free recovery—The extension recovery during heating at zero load for each of the four extension values is presented in figure 7. Figure 7(a) presents the extension recovery as a function of temperature, and figure 7(b) presents the extension recovery normalized by the extension at the start of the heating. It is observed that the recovery occurs at the same temperature, regardless of the value of applied extension, with the midpoint of recovery occurring at approximately 75°C. Further, table 3 presents the average values for the extension at the start (25°C) and the end (90°C) of the heating procedure. In the first cycle, the 10% extension tests had a small irrecoverable deformation (0.4%) but the 15%, 20%, and 25% tests recovered 100% of the applied deformation as the final extension at 90°C was within the error range (+/- 0.3%) of the resolution of the laser extensometer. In the second cycle, the specimens recovered 100% of the applied deformation for all values of applied extension.

3.3.2. Constrained displacement recovery—The results for the stress-temperature and extension-temperature behavior during the constrained displacement recovery are presented in figure 8. In this heating step, the load is first maintained at zero by allowing the specimen to hang freely from the top grip. At approximately 60°C, the bottom of the specimen is re-gripped, the crosshead is adjusted to satisfy zero load conditions, and then the crosshead is held constant until the temperature reaches 90°C. In figure 8(a), the increase in stress is observed to initiate at approximately 65°C, with recovery complete by

approximately 75°C. In addition, the extension-temperature results in figure 8(b) indicate the bottom of the SMP was re-gripped before the onset of shape recovery, and then the thermal expansion of the grips and extension rods imposes an elastic deformation on the SMP from 60°C to 90°C. Table 4 presents the values for the stress recovery and the resulting decrease in the extension after re-gripping the bottom of the specimen that is caused by the thermal expansion of the extension rods and grips. The value of the stress at the end of recovery ranges approximately linearly from 1.5 MPa at 10% extension to 4.2 MPa at 25% extension, and the stress recovery is observed to be repeatable between the first and second cycles.

4. Modeling preliminaries

4.1. Model description

The model used in this work to simulate the material response is the finite deformation model proposed by Chen and Lagoudas [30] and numerically implemented in 1-D by Volk et al. [36]. The model is formulated on the basis of nonlinear thermoelasticity such that the deformation gradient is assumed to be a function of only the stress and temperature of the material. Further, the model assumes the glass transition occurs through a random nucleation process and that the stress is equal for portions of the material in either the glass (frozen) phase or the rubber (active) phase. In the reduction to 1-D and subsequent numerical implementation, the material is assumed to behave as a neo-Hookean material in each the pure active and pure frozen phases. The constitutive equation proposed by Chen and Lagoudas and reduced to 1-D is given in (1). [30]

$$\lambda(t) = [1 - \phi(\theta(t))] \lambda_a(s(t), \theta(t)) + \int_0^t \lambda_f(s(\tau), \theta(\tau)) \phi'(\theta(\tau)) \theta'(\tau) d\tau \quad (1)$$

where $\lambda(t)$, $\phi(\theta(t))$, $s(t)$, and $\theta(t)$ are the stretch ratio, frozen volume fraction, stress, and temperature, respectively. Additionally, the stretch ratios of the active and frozen phases are denoted $\lambda_a(t)$ and $\lambda_f(t)$, respectively, whose neo-Hookean constitutive equations are defined through (2).

$$\begin{aligned} \mu_a \left(\lambda_a - \frac{v_a(\theta)}{\lambda_a^2} \right) &= s(t) \\ \mu_f \left(\lambda_f - \frac{v_f(\theta)}{\lambda_f^2} \right) &= s(t) \end{aligned} \quad (2)$$

where μ_a , μ_f , $v_a(\theta)$, and $v_f(\theta)$ are the shear moduli in the active and frozen phases and the volume ratios in the active and frozen phases, respectively. These four parameters in addition to the frozen volume fraction $\phi(\theta(t))$ need to be calibrated and used as input to the constitutive model to simulate and predict the material response.

4.2. Calibration of material properties

In this work, the data from a single experimental result is used to calibrate the material properties and frozen volume fraction for the constitutive model. Because the elastic modulus is commonly defined at smaller values of extension and because the mechanism for shape recovery is observed to be independent of applied extension (cf. figure 7(b)), the material properties for the model are calibrated from the 10% free recovery experiment presented in figure 3(a). The model is then used to predict the temperature, stress, and extension for the remaining seven experiments presented in figures 3 and 4. Assuming the polyurethane SMP behaves as an isotropic material, the shear modulus in each the active and frozen phases is calculated from the elastic modulus in each phase and the assumption that the material behaves as an incompressible material in each phase (Poisson ratio = 0.5). As

such, the elastic moduli of the active phase and frozen phase are calculated from the loading segment at time 'A' and the unloading segment at time 'C,' respectively.

In the numerical implementation of [36], the volume ratios are assumed to be functions of the coefficients of thermal expansion (CTE) and the frozen volume fraction is assumed to take the form of a hyperbolic tangent function. The coefficient of thermal expansion in the active phase is calculated from the linear portion of the extension-temperature data after recovery has completed. Due to the low coefficient of thermal expansion in the frozen phase and the limitations on the laser extensometer resolution, however, the frozen phase coefficient of thermal expansion is manually adjusted such to fit the stress simulation during cooling to the experimental data. While the implementation of Volk et al. uses a single hyperbolic tangent to fit the frozen volume fraction to the extension recovery profile [36], it is observed in figure 8(b) that a single hyperbolic tangent is unable to precisely capture the initiation of the shape recovery observed in figure 8(a). As such, a piecewise function composed of two hyperbolic tangents is used in the current work, with one hyperbolic tangent dictating the curvature of the initiation of recovery and the second hyperbolic tangent dictating the rest of the recovery process. The switch temperature between the two functions is chosen to be the corner at the onset of shape recovery, and a least squares method is used to fit the parameters for the two hyperbolic tangents while enforcing continuity of the frozen volume fraction and its derivative at the switch temperature. The resulting, piecewise hyperbolic tangent is shown in figure 8(b) as fit to the normalized extension recovery data. It should be noted that the model predictions for the SMP are extremely sensitive to the fit for the frozen volume fraction. For instance, modeling the frozen volume fraction using the single hyperbolic tangent can be shown, in this system, to affect the stress at the end of cooling by more than 25%. Table 5 presents a summary of the material properties for a polyurethane SMP as calibrated from the 10% extension free recovery experiment of Figure 3(a).

5. Modeling results

After calculating the parameters necessary to calibrate the constitutive model, the 10% extension free recovery experiment from which the material properties were calculated was first simulated and then the model was validated by comparing the model predictions to the experimental data for the 15%, 20%, and 25% extension free recovery experiments and the 10%, 15%, 20%, and 25% constrained displacement recovery experiments.

5.1. Free recovery

The simulation of the 10% extension free recovery experiment from which the material properties were calibrated is presented in figure 10. It is observed in not only the three-dimensional representation of figure 10(a), but also in the two-dimensional projections of (b), (c), and (d) that the simulation matches well with the experimental measurements. In this simulation, the extension increase during the constrained cooling (cf. section 3.4) is modeled as a linear increase on the SMP, as shown in figure 10(d). Using this linear input, the model simulates well the stress increase due to the constrained cooling, as shown in figure 10(c). Further, the model captures well the extension recovery behavior upon heating in figure 10(d), with the differences a result of the assumption in the model that the material recovers all of the applied deformation.

After simulating the 10% free recovery experiment, the model was used to predict the 15%, 20%, and 25% free recovery experiments that were presented in figure 3. Figure 11 presents the three-dimensional extension-temperature-stress predictions for the 15%, 20%, and 25% extension experiments, and figure 12 presents the two-dimensional projections in (a) stress-extension, (b) stress-temperature, and (c) extension-temperature space. It is observed that the

model, calibrated from a 10% free recovery extension experiment, is able to predict well the free recovery response for extensions of up to 25%. The small differences in both the extension recovery in figure 12(c) and the stress increase in figure 12(b) are likely primarily due to small differences in the material properties and/or the shape of the onset of shape recovery (cf. figure 7(b)), to which the frozen volume fraction is fit and is a critical calibration parameter in predicting the response of the SMP.

5.2. Constrained displacement recovery

In addition to predicting the free recovery experiments, the model was used to predict the constrained recovery experiments of figure 4. The results for the 10%, 15%, 20%, and 25% extension constrained recovery experiments are presented in figure 13. Specifically, the three-dimensional projections for the entire thermomechanical load path are presented in figure 13(a), and the model predictions are observed to have good agreement with the experimental results. In these model predictions, the extension change observed during the constrained cooling is input as a linear increase during the cooling step and the extension change during the constrained heating (after re-gripping) is input as a linear decrease from 62°C to 90°C. Although matching the qualitative trend well, there are deviations in the stress prediction during the constrained cooling step (~5-11% error in the value at the end of cooling). These deviations are likely a result of variations in the oscillations of the PID system attempting to maintain a constant extension during the constrained cooling. The model predictions, however, match well with the stress-extension response and the stress-temperature response during recovery, as presented in figure 13(d).

6. Conclusions

In this work, experiments were performed on a polyurethane shape memory polymer [17] to evaluate the free recovery and constrained displacement recovery response. In these experiments, the SMP specimens were loaded to 10%, 15%, 20%, and 25% extension at 90°C ($T > T_g$), cooled to 25°C ($T < T_g$) while using the laser extensometer measurements to minimize the change in extension, unloaded to zero load at 25°C, and then heated to 90°C for recovery. In the free recovery condition, the material was allowed to hang freely from the top grip and the extension (shape change) was measured. In the constrained recovery condition, the material was allowed to hang freely from the top grip – to avoid excessive compressive stress and potential buckling – until 60°C, at which temperature the bottom of the specimen was regripped and the resulting stress recovery was measured while heating to 90°C.

In analyzing the experimental results, it was observed that the stress-extension response during loading remains approximately linear at 90°C for all values of extension up to 25%. The tensile modulus was calculated to be approximately 20 MPa at 90°C and 1700 MPa at 25°C. During the constrained cooling step, the PID system in the MTS® Testworks® software was able to limit the extension imposed on the SMP by the thermal contraction of the grips and extension rods to approximately 1.5%. In the free recovery experiments, it was observed that the specimens tested to 10% extension recovered nearly all of the deformation in the first cycle and then 100% of the applied deformation in the second cycle. For the 15%, 20%, and 25% extensions, 100% recovery was observed in both cycles. In addition, the shape recovery occurred at the same temperatures, regardless of the value of applied deformation. In the constrained recovery experiments, it was observed that the value of the stress at the end of recovery, ranging from 1.5 MPa at 10% extension to 4.2 MPa at 25% extension, was approximately linear with respect to the value of the applied extension.

The results from a 10% extension free recovery experiment were then used to calibrate the parameters necessary for input to the Volk et al. 1-D implementation of the Chen and

Lagoudas model [30]. For this SMP system, however, it was necessary to split the single hyperbolic tangent of [36] into a piecewise hyperbolic tangent to precisely fit the onset of shape recovery, which is a key parameter affecting the stress predictions during constrained cooling. By using a single hyperbolic tangent, the model would have been unable to precisely capture the asymmetrical curvature in the onset and completion of recovery. Thus, the model would have resulted in large errors (>25%) in the stress at the end of constrained cooling. After calibrating the necessary parameters and observing good agreement of the model simulation with the experimental data, the model was then used to predict the 15%, 20%, and 25% extension free recovery experiments as well as the 10%, 15%, 20%, and 25% extension constrained displacement recovery experiments. The model predictions were observed to have good agreement with the experimental data, with minor differences likely due to variations in the material properties and phase transformation behavior between specimens.

In conclusion, free recovery and constrained displacement recovery experiments were performed on a previously untested polyurethane SMP proposed by Wilson et al. [17]. The parameters used as input to the Chen and Lagoudas model were calibrated using a single free recovery experiment, and then the model was used to predict the remaining experiments. Good agreement of the model predictions and experimental data was observed. Not only did this work expand on the constrained displacement recovery data available in the literature, but the modeling efforts helped to validate the Chen and Lagoudas model for another shape memory polymer system.

Acknowledgments

The authors would like to thank Tom Wilson and Pooja Singhal for their discussions on the fabrication of the shape memory polymer as well as the analysis of the material response. Funding for the work of B.L. Volk was provided by the National Defense Science and Engineering Graduate (NDSEG) Fellowship. This work was supported by the National Institutes of Health/National Institute of Biomedical Imaging and Bioengineering Grant R01EB000462. The authors would also like to acknowledge the support of the Texas Institute for Intelligent Bio-Nano Materials and Structures for Aerospace Vehicles (TiiMS).

References

1. Mather PT, Luo X, Rousseau IA. Shape memory polymer research. *Annual Review of Materials Science*. 2009; 39:445–71.
2. Lendlein A, Kelch S. Shape-Memory Polymers. *Angew Andte Chemie-International Edition*. 2002; 41(12):2034–57.
3. Liu C, Qin H, Mather P. Review of progress in shape-memory polymers. *Journal of Materials Chemistry*. 2007; 17(16):1543–58.
4. Ratna D, Karger-Kocsis J. Recent advances in shape memory polymers and composites: a review. *Journal of Material Science*. 2008; 43:254–69.
5. Dietsch B, Tong T. A Review - Features and Benefits of Shape Memory Polymers (SMPs). *Journal of Advanced Materials*. 2007; 39(2):3–12.
6. Small W IV, Wilson TS, Buckley PR, Benett WJ, Loge JM, Hartman J, Maitland DJ. Prototype fabrication and preliminary *in vitro* testing of a shape memory endovascular thrombectomy device. *IEEE Trans Biomed Eng*. 2007; 54:1657–66. [PubMed: 17867358]
7. Small W IV, Wilson TS, Singhal P, Maitland DJ. Biomedical applications of thermally actuated shape memory polymers. *Journal of Materials Chemistry*. 2010; 20:3356–66. [PubMed: 21258605]
8. Lendlein A, Behl M, Hiebl B, Wischke C. Shape-memory polymers as a platform for biomedical applications. *Expert Reviews Medical Devices*. 2010; 7(3):357–79.
9. Lendlein A, Langer R. Biodegradable, elastic shape-memory polymers for potential biomedical applications. *Science*. 2002; 296(5573):1673–6. [PubMed: 11976407]

10. Yakacki CM, Shandas R, Lanning C, Rech B, Eckstein A, Gall K. Unconstrained recovery characterization of shape-memory polymer networks for cardiovascular applications. *Biomaterials*. 2007; 28:2255–63. [PubMed: 17296222]
11. Small W IV, Buckley PR, Wilson TS, Benett WJ, Hartman J, Saloner D, Maitland DJ. Shape memory polymer stent with expandable foam: a new concept for endovascular embolization of fusiform aneurysms. *IEEE Transactions on Biomedical Engineering*. 2007; 54:1157–60. [PubMed: 17549908]
12. Tobushi H, Hashimoto T, Hayashi S, Yamada E. Thermomechanical constitutive modeling in shape memory polymer of polyurethane series. *Journal of Intelligent Material Systems and Structures*. 1997; 8(8):711–8.
13. Liu Y, Gall K, Dunn ML, Greenberg AR, Diani J. Thermomechanics of shape memory polymers: Uniaxial experiments and constitutive modeling. *International Journal of Plasticity*. 2006; 22:279–313.
14. Tobushi H, Hara H, Yamada E, Hayashi S. Thermomechanical properties in a thin film of shape memory polymer of polyurethane series. *Smart Materials & Structures*. 1996; 5(4):483–91.
15. Atli B, Gandhi F, Karst G. Thermomechanical characterization of shape memory polymers. *Journal of Intelligent Material Systems and Structures*. 2009; 20:87–95.
16. Volk BL, Lagoudas DC, Chen Y-C, Whitley KS. Analysis of the finite deformation response of shape memory polymers: I. Thermomechanical characterization. *Smart Materials and Structures*. 2010; 19
17. Wilson TS, Bearinger JP, Herberg JL, M JE III, Wright WJ, Evans CL, Maitland DJ. Shape memory polymers based on uniform aliphatic urethane networks. *Journal of Applied Polymer Science*. 2007; 106:540–51.
18. Baer G, Wilson TS, Matthews DL, Maitland DJ. Shape-memory behavior of thermally stimulated polyurethane for medical applications. *Journal of Applied Polymer Science*. 2006; 103:3882–92.
19. Voit W, Ware T, Dasari RR, Smith P, Danz L, Simon D, Barlow S, Marder SR, Gall K. High-Strain Shape-Memory Polymers. *Advanced functional materials*. 2010; 20:162–71.
20. Voit W, Ware T, Gall K. Radiation crosslinked shape-memory polymers. *Polymer*. 2010; 51:3551–9.
21. Gall K, Dunn ML, Liu Y, Finch D, Lake M, Munshi NA. Shape memory polymer nanocomposites. *Acta Materialia*. 2002; 50(20):5115–26.
22. Gall K, Mikulas M, Munshi NA, Beavers F, Tupper M. Carbon fiber reinforced shape memory polymer composites. *Journal of Intelligent Material Systems and Structures*. 2000; 11(11):877–86.
23. Liu YP, Gall K, Dunn ML, McCluskey P. Thermomechanics of shape memory polymer nanocomposites. *Mechanics of Materials*. 2004; 36(10):929–40.
24. Ni Q, Zhang C, Fu Y, Dai G, Kimura T. Shape memory effect and mechanical properties of carbon nanotube/shape memory polymer nanocomposites. *Composite Structures*. 2007; 81(2):176–84.
25. Madbouly SA, Lendlein A. Shape-memory polymer composites. *Advanced Polymer Science*. 2010; 226:41–95.
26. Tandon GP, Goecke K, Cable K, Baur J. Durability assessment of styrene- and epoxy-based shape-memory polymer resins. *Journal of Intelligent Material Systems and Structures*. 2009; 20(17): 2127–43.
27. Tandon GP, Goecke K, Cable K, Baur J. Environmental Durability of Fabric-Reinforced Shape-Memory Polymer Composites. *Journal of Intelligent Material Systems and Structures*. 2010; 21:1365–81.
28. Tobushi H, Okumura K, Hayashi S, Ito N. Thermomechanical constitutive model of shape memory polymer. *Mechanics of Materials*. 2001; 33(10):545–54.
29. Bhattacharyya A, Tobushi H. Analysis of the isothermal mechanical response of a shape memory polymer rheological model. *Polymer Engineering and Science*. 2000; 40(12):2498–510.
30. Chen Y-C, Lagoudas DC. A constitutive theory for shape memory polymers. Part I: Large deformations. *Journal of the Mechanics and Physics of Solids*. 2008; 56(5):1752–65.
31. Qi HJ, Nguyen TD, Castroa F, Yakacki CM, Shandas R. Finite deformation thermo-mechanical behavior of thermally induced shape memory polymers. *Journal of the Mechanics and Physics of Solids*. 2008; 56:1730–51.

32. Nguyen TD, Qi HJ, Castro F, Long KN. A thermoviscoelastic model for amorphous shape memory polymers: Incorporating structural and stress relaxation. *Journal of the Mechanics and Physics of Solids*. 2008; 56:2792–814.
33. Nguyen TD, Chen X. Influence of Thermoviscoelastic Properties and Loading Conditions on the Recovery Performance of Shape Memory Polymers. *Mechanics of Materials*. 2011
34. Reese S, Bol M, Christ D. Finite element-based multi-phase modelling of shape memory polymer stents. *Comput Methods Appl Mech Engrg*. 2010; 199:1276–86.
35. Srivastava V, Chester SA, Anand L. Thermally actuated shape-memory polymers: Experiments, theory, and numerical simulations. *Journal of the Mechanics and Physics of Solids*. 2010; 58:1100–24.
36. Volk BL, Lagoudas DC, Chen Y-C. Analysis of the finite deformation response of shape memory polymers: II. 1D calibration and numerical implementation of a finite deformation, thermoelastic model. *Smart Materials and Structures*. 2010; 19
37. Chen Y-C, Lagoudas DC. A constitutive theory for shape memory polymers. Part II: A linearized model for small deformations. *Journal of the Mechanics and Physics of Solids*. 2008; 56(5):1766–78.
38. McClung AJW, Tandon GP, Goecke KE, Baur JW. Non-contact technique for characterizing full-field surface deformation of shape memory polymers at elevated and room temperatures. *Polymer Testing*. 2011; 30:140–9.
39. American Society for Testing Materials (ASTM). D638-08: Standard test method for tensile properties of plastics. 2003
40. Safranski DL, Gall K. Effect of chemical structure and crosslinking density on the thermo-mechanical properties and toughness of (meth)acrylate shape memory polymer networks. *Polymer*. 2008; 49:4446–55.
41. Volk, BL.; Lagoudas, DC.; Maitland, DJ. Characterizing and modeling the free recovery and constrained recovery behavior of a polyurethane shape memory polymer. *ASME 2010 Conference on Smart Materials, Adaptive Structures, and Intelligent Systems*; Philadelphia, PA. 2010. p. 1-8.

Figure 1.

(a) Mold setup used to fabricate the polyurethane SMPs. The SMP resin is injected through the bottom port. (b) A resulting sheet of shape memory polymer, after curing in an oven. (c) An ASTM Type V dogbone sample, which was laser cut.

Figure 2.
Experimental setup used for testing the shape memory polymers.

Figure 3.

(a) 10%, (b) 15%, (c) 20%, and (d) 25% free recovery experiments performed with a temperature rate of 1°C/min. Two shape memory cycles per test were performed, and the data for both cycles is presented with respect to time.

Figure 4.

(a) 10%, (b) 15%, (c) 20%, and (d) 25% constrained displacement recovery experiments performed with a temperature rate of 1°C/min. Two shape memory cycles per test were performed, and the data for both cycles is presented with respect to time.

Figure 5. Stress-extension results during (a) loading at 90°C and (b) unloading at 25°C for 10%, 15%, 20%, and 25% extension experiments.

Figure 6.

(a) Stress-temperature and (b) extension-temperature results during constrained cooling from 90°C to 25°C for 10%, 15%, 20%, and 25% extension experiments.

Figure 7.

(a) Extension-temperature and (b) normalized extension-temperature results during the first cycle recovery heating at zero load from 25°C to 90°C for 10%, 15%, 20%, and 25% extension experiments.

Figure 8.

(a) Stress-temperature and (b) extension-temperature results during the first cycle constrained displacement recovery heating from 25°C to 90°C for 10%, 15%, 20%, and 25% extension experiments. The specimen is allowed to hang freely from the top grip until 60°C, at which temperature the bottom is re-gripped and the crosshead is manually adjusted to offset the compressive stress, denoted by the points near the asterisk * in (a), caused by the gripping procedure.

Figure 9.

(a) 10% extension-temperature free recovery profile and (b) a piecewise hyperbolic tangent function fit to the normalized extension-temperature data. A single hyperbolic tangent is unable to precisely capture the onset of shape recovery and is presented for comparison.

Figure 10.

Simulation of the 10% free recovery extension experiment from which the material properties were calibrated. The 3-D stress-temperature-extension results are shown in (a) and the corresponding 2-D projections of (b) stress-extension, (c) stress-temperature, and (d) extension-temperature. The asterisk * in (b) and (d) denote an example of oscillations in the experimental data as the PID system attempts to maintain a constant extension during cooling through the glass transition.

Figure 11. Model predictions for the the (a) 15%, (b) 20%, and (c) 25% extension free recovery experiments.

Figure 12.

(a) Stress-extension, (b) stress-temperature, and (c) extension-temperature predictions for the 15%, 20%, and 25% extension free recovery experiments.

Figure 13.

(a) Extension-stress-temperature, (b) extension-temperature, (c) stress-temperature, and (d) recovery stress-temperature predictions for the 10%, 15%, 20%, and 25% extension free recovery experiments.

Table 1

Tensile modulus during loading at 90°C and unloading at 25°C.

	Loading at 90°C				Unloading at 25°C			
	Cycle 1		Cycle 2		Cycle 1		Cycle 2	
	Tensile Modulus (MPa)	Range ^a (MPa)	Tensile Modulus (MPa)	Range (MPa)	Tensile Modulus (MPa)	Range (MPa)	Tensile Modulus (MPa)	Range (MPa)
FR 10%	20.2	2.3	20.8	2.0	1794	312	1802	90
FR 15%	19.7	2.6	20.3	2.3	1700	154	1734	141
FR 20%	20.1	0.8	20.4	1.0	1567	182	1613	60
FR 25%	18.8	1.1	19.6	1.7	1520	115	1497	266
FR Avg.	19.7	1.7	20.3	1.8	1645	191	1661	139
CR 10%	20.8	1.4	21.6	1.5	1799	149	2113	563
CR 15%	20.0	0.7	21.0	1.4	1814	359	1778	92
CR 20%	20.8	1.2	19.5	1.5	1634	283	1658	413
CR 25%	20.6	0.3	21.1	2.8	1555	350	1614	334
CR Avg.	20.6	0.9	20.8	1.8	1701	285	1791	351

^a Range is the maximum value minus the minimum value of the three specimens tested in each case.

Table 2

Stress and extension increases^a during constrained cooling from 90°C to 25°C.

	Cycle 1				Cycle 2			
	Stress Increase	Range ^b	Extension Increase	Range	Stress Increase	Range	Extension Increase	Range
	(MPa)	(MPa)	(%)	(%)	(MPa)	(MPa)	(%)	(%)
FR 10%	16.0	0.8	1.4	0.1	15.8	0.2	1.3	0.7
FR 15%	14.1	0.1	0.8	0.7	14.3	1.0	1.7	0.4
FR 20%	14.5	0.9	1.8	0.6	14.2	1.3	1.5	0.6
FR 25%	13.7	0.5	1.8	0.6	14.3	0.3	1.5	0.9
FR Avg.	14.6	0.6	1.5	0.5	14.7	0.7	1.5	0.6
CR 10%	15.7	0.5	1.3	0.5	15.7	1.3	0.8	0.5
CR 15%	15.1	0.8	1.3	0.1	14.3	1.3	0.6	0.9
CR 20%	15.2	2.6	1.8	0.5	14.2	1.4	0.7	0.7
CR 25%	15.1	1.1	2.1	0.7	14.0	1.5	1.4	1.8
CR Avg.	15.3	1.3	1.6	0.5	14.6	1.4	0.9	1.0

^a Stress increase and extension increase are the stress and extension values, respectively, measured at the end of cooling (25°C) minus the stress and extension values measured at the beginning of cooling (90°C).

^b Range is the maximum value minus the minimum value of the three specimens tested in each case.

Table 3

Extension recovery at zero load.

	Cycle 1				Cycle 2			
	Extension at 25°C		Extension at 90°C		Extension at 25°C		Extension at 90°C	
	Range ^a	Range ^a	Range	Range	Range	Range	Range	Range
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
10%	10.2	0.5	0.4	0.3	10.2	0.4	0.1	0.1
15%	15.5	0.6	-0.2	0.8	15.3	0.4	0.1	0.8
20%	20.2	0.9	-0.1	0.6	25.0	0.2	0.0	0.8
25%	25.0	0.2	0.0	0.8	24.9	0.1	0.3	0.2

^aRange is the maximum value minus the minimum value of the three specimens tested in each case.

Table 4

Stress recovery at constant crosshead displacement.

Cycle 1				Cycle 2			
Stress at End of Recovery	Range ^a	Extension Decrease after Re-gripping	Range	Stress at End of Recovery	Range	Extension Decrease after Re-Gripping	Range
(MPa)	(MPa)	(%)	(%)	(MPa)	(MPa)	(%)	(%)
10%	1.5	0.5	-1.8	0.5	1.4	0.2	-1.8
15%	2.4	0.1	-1.7	1.0	2.4	0.3	-1.8
20%	3.3	0.0	-1.6	0.9	3.4	0.1	-1.8
25%	4.2	0.1	-1.8	1.2	4.1	0.5	-1.7

^aRange is the maximum value minus the minimum value of the three specimens tested in each case.

Table 5

Material properties calculated from a 10% free recovery experiment and used as input to the 1-D Chen and Lagoudas model.

Parameter	Value
Active phase volume ratio	$v_a = [1 + \alpha_a (\theta - \theta_0)]^3$ $\alpha_a = 5.1 \cdot 10^{-4} / \text{K}$
Frozen phase volume ratio	$v_f = [1 + \alpha_f (\theta - \theta_0)]^3$ $\alpha_f = 2.0 \cdot 10^{-5} / \text{K}$
Active phase shear modulus	$\mu_a = 7.03 \text{ MPa}$
Frozen phase shear modulus	$\mu_f = 606 \text{ MPa}$
Frozen volume fraction	$\phi(\theta) = C \frac{\tanh\left(\frac{\theta_{\max} - A}{B}\right) - \tanh\left(\frac{\theta - A}{B}\right)}{\tanh\left(\frac{\theta_{\max} - A}{B}\right) - \tanh\left(\frac{\theta_{\min} - A}{B}\right)}$ $\theta_{\min} = 323, \theta_{\max} = 363$ $A = 508.44, B = 18.71, C = 1.00 \quad \theta < 341.1$ $A = 347.25, B = 3.05, C = 0.94 \quad \theta \geq 341.1$