CHARACTERIZATION OF THE NONLINEAR RATE DEPENDENT RESPONSE OF SHAPE MEMORY POLYMERS

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ABSTRACT

Shape Memory Polymers (SMPs) are a class of polymers, which can undergo deformation in a flexible state at elevated temperatures, and when cooled below the glass transition temperature, while retaining their deformed shape, will enter and remain in a rigid state. Upon heating above the glass transition temperature, the shape memory polymer will return to its original, unaltered shape. SMPs have been reported to recover strains of over 400%. It is important to understand the stress and strain recovery behavior of SMPs to better develop constitutive models which predict material behavior. Initial modeling efforts did not account for large deformations beyond 25% strain. However, a model under current development is capable of describing large deformations of the material. This model considers the coexisting active (rubber) and frozen (glass) phases of the polymer, as well as the transitions between the material phases. The constitutive equations at the continuum level are established with internal state variables to describe the microstructural changes associated with the phase transitions. For small deformations, the model reduces to a linear model that agrees with those reported in the literature.

Thermomechanical characterization is necessary for the development, calibration, and validation of a constitutive model. The experimental data reported in this paper will assist in model development by providing a better understanding of the stress and strain recovery behavior of the material. This paper presents the testing techniques used to characterize the thermomechanical material properties of a shape memory polymer (SMP) and also presents the resulting data. An innovative visual-photographic apparatus, known as a Vision Image Correlation (VIC) system was used to measure the strain. The details of this technique will also be presented in this paper. A series of tensile tests were performed on specimens such that strain levels of 10, 25, 50, and

100% were applied to the material while it was above its glass transition temperature. After deforming the material to a specified applied strain, the material was then cooled to below the glass transition temperature (T_g) while retaining the deformed shape. Finally, the specimen was heated again to above the transition temperature, and the resulting shape recovery profile was measured. Results show that strain recovery occurs at a nonlinear rate with respect to time. Results also indicate that the ratio of recoverable strain/applied strain increases as the applied strain increases.

INTRODUCTION

Intelligent systems, or systems that can sense and react to their environment autonomously, represent a rapidly growing sector of technology. These systems often exploit the properties of active materials to accomplish the desired sensing or actuation response Shape Memory Alloys (SMAs), shape memory ceramics, and piezoelectrics are a few examples of active materials that have been heavily researched and have been developed and utilized in a wide range of applications, such as oil exploration, medical, and aerospace industries [1,2]. Another such type of material is Shape Memory Polymers (SMPs). While both SMPs and the more widely researched SMAs have the ability to recover an apparently permanent deformation due to thermal manipulation, SMPs have the unique ability to recover strains up to 400% [3]. In addition, SMPs have a lower density and lower manufacturing and processing costs than SMAs. Recent research efforts exemplify the heightened interest in the use of SMP in modern applications. For instance, Lockheed Martin and Hypercomp/NextGen are developing and testing morphing wings using smart materials. These wings are expected to adjust the surface area based on the current flying conditions, with possible area increases of 300%. In this project, funded by the Defense Advanced Research Projects Agency (DARPA), SMPs are being considered as a possible choice for the skin of the wing [4]. Furthermore, in an effort to boost the naturally low stiffness and low recovery stress of SMPs, efforts are underway to create composites using a shape memory polymer matrix material [5, 6].

The material response allowing for strain recovery in SMPs is known as a shape memory effect. This phenomenon includes the transition between two material phases – glass and rubber. Materials in the glass phase possess a higher elastic modulus and will not deform easily. Conversely, materials above the glass transition temperature, and thus in the rubber phase, are much softer and can be deformed to large values of applied strain. The thermomechanical cycle for recovering a seemingly irrecoverable deformation, discussed in detail in references [7, 8], is summarized in the following steps:

1. Heat the material to above the glass transition temperature, T_g while maintaining a zero-stress.
2. Deform the material at the elevated temperature to the desired strain level.
3. At a constant applied strain on the SMP, cool to below T_g.
4. Release the load on the specimen.
5. Heat the material a second time to above T_g to recover original shape.

Using the knowledge of the shape memory mechanism employed by SMPs, predictive models are created to accurately depict the material response. Such models require thorough experimental characterization. Initial modeling efforts have represented SMPs as a discrete spring-dashpot system [7, 9]. Additional models have been created to capture the small deformation material response. At small levels of deformation, the strain recovery behavior can be approximated as linear behavior [8]. While advances have been made in SMP modeling, existing models still cannot adequately capture the unique large-deformation recovery. Chen and Lagoudas recently developed an SMP model which accounts for the nonlinear material response due to large deformations. [10, 11] The purpose for the study presented in this paper is to provide shape recovery test data to support current SMP model development and calibration. Shape memory polymer specimens were stretched to specific levels of applied strain, and upon removing any residual load, the specimen returned to its original shape. The degree to which the polymer returned to its original shape is measured by observing the recovered strain. Specimen preparation techniques and details of the experimental set up will be presented in this paper, followed by a discussion of the fundamental experimental properties of the SMP and the methodology for testing such material.

EXPERIMENTAL DETERMINATION OF THERMOMECHANICAL PROPERTIES

To thoroughly quantify the shape memory polymer material response, a variety of thermomechanical experiments is necessary. The origin and preparation of the specimens are described in detail in this section. In addition, the components of the experimental setup as well as the experiments performed are explained.

Specimen Preparation

The material used for testing was received from Cornerstone Research Group, Inc. (CRG) in Dayton, Ohio. The styrene-based shape memory polymer was manufactured in 305 x 305 x 3.18 mm sheets. With the first experimental focus strictly on tension tests, the experimental specimens were prepared and tested according to the ASTM standard D638 *Standard Test Method for the Tensile Properties of Plastics* [12]. The resulting samples were a dog-bone shape with a 57-mm gage length and a 12.7-mm gage width. The portions of the sample where the grips attached were 25.4-mm x 25.4-mm. The complete length of the specimens was 114-mm. A water jet cutting procedure was used to cut the experimental specimens. The water jet technique resulted in fewer variations in dimensions from specimen to specimen, and significantly reduced the likelihood of the material being damaged or developing cracks during specimen preparation. The specimens were cut at NASA Langley Research Center.

Experimental Setup

All experiments on the shape memory polymers were performed in the Materials Research Laboratory at NASA Langley Research Center. The tests were conducted on an electromechanical, screw-driven MTS Alliance RT-1 test frame equipped with a MTS 1000 N load cell and a pair of MTS 2000 N pneumatic grips. To control the temperature

of the material, the specimen was heated in a Thermcraft oven and cooled via convection using liquid nitrogen introduced near the bottom of the furnace. Figure 1 depicts the entire experimental setup while Figure 2 presents a closer view of the specimen being held within the pneumatic grips. It is worth noting that, while the pneumatic grips are lightweight and exceptional at maintaining a constant clamp pressure, the pressure must carefully be considered. During preliminary testing, a force of 100-kPa was used and resulted in specimen failure within the grips during testing. The pressure was reduced to 50-kPa and the failures were eliminated.

The technique used to measure the strain of the material required further specimen preparation. The 3-D VIC system uses two cameras to monitor the change in position of many fine markings to determine the full field displacement measurements. Due to the transparency of the SMP, a base layer of white paint was applied, followed by a black "speckled" pattern. This yielded a highly contrasted image, as required by the VIC system. During preliminary large strain experiments, the original paint cracked and the VIC system experienced problems correlating the motion of the speckled pattern. As a result, a more compliant paint was used for tests when the total applied strain was greater than 50%. Figure 3 depicts the gauge length of a test specimen prepared for thermomechanical characterization.

Measurement of Glass Transition Temperature

Before configuring the hardware for any thermomechanical experiments, the glass transition temperature (T_g) of the material must be determined. The glass transition temperature is defined as the temperature at which, during heating, a glass transforms from an elastic to a viscoelastic material [13], was determined by two different methods.

The first method utilized a Perkin-Elmer ThermoMechanical Analyzer (TMA). In the TMA experiment, a material sample was placed under a probe that exerts a 5-gram applied load. As the temperature increases, the material becomes softer, and the movement of the probe detects the change in material thickness with respect to the temperature change. From this data, it is possible to determine the temperature at which the material softens. This is said to be T_g. Figure 4 presents the TMA test results which indicate a T_g of 57.82°C and a coefficient of thermal expansion (α) of 8.6E-07/°C.

The second method used to determine the T_g was performed using a Perkin-Elmer Differential Scanning Calorimeter (DSC). The DSC allows determination of the T_g by monitoring the change of internal energy of a specimen during heating and cooling. As the temperature increases, an inflection point can be observed in the internal energy curve at the glass transition temperature. Figure 5 provides the results of the DSC test, from which the T_g was determined to be 51.33°C.

While the results from the two methods indicate a disparity in the glass transition temperature, the more conservative result is utilized. Consequently, T_g is taken to be 58°C for the experiments performed.

Measurement of Young's Modulus

The elastic modulus of the material is beneficial in determining the stress-strain response of the SMP. For experiments in which force is specified, this relationship will provide a means of determining the subsequent strain resulting in the specimen during elastic loading. Figure 6 presents the nominal stress-strain data of a specimen loaded to failure at room temperature ($T < T_g$). The *nominal stress* is defined as the force applied per the original cross sectional area. This definition of stress is used for all experiments and results reported in this paper. Examining the linear portion of the loading curve, the Young's Modulus, E, was determined to be 1.4 GPa for the SMP glass phase. This modulus value agrees with typical values for lightly cross-linked polymers in the glass phase.

Methodology for SMP Testing

The thermomechanical method for initiating and then observing shape recovery in SMP requires a multi-step procedure. Initially, the material begins at room temperature ($T < T_g$) in a stress-free and strain-free state. Maintaining a zero stress constraint on the material, the temperature is raised to well above T_g (T_{max} = 90℃) at 2℃ per minute. The specimen is heated to a temperature significantly higher than the glass transition temperature to ensure that the material can be easily deformed. During the heating process, specimen extension is observed due to the axial thermal expansion.

After a short dwell period to allow thermal equilibrium, the material is deformed to the desired value, which is corrected for thermal strain. The tests performed included applied strain values of 10, 25, 50, and 100%. After reaching the desired level of applied strain, the deformation is held constant, and the material-temperature is cooled to below the transition temperature (T_{min} = 20℃). This process is commonly referred to as "freezing" the material. Due to the constraint imposed on the material, a thermal stress is observed during the cooling process.

After the cooling process is complete and the thermal stress has reached a constant value, the material is unloaded to zero-stress. This process results in an almost undetectable elastic strain decrease. The material is then held at a constant stress and again heated to T_{max} at 2℃/min to initiate shape recovery. As the material temperature exceeds T_g, the material begins to recover its original, un-deformed shape.

RESULTS AND DISSCUSSION

SMP specimens were subjected to tensile loading at 90℃ to applied strain levels of 10, 25, 50, and 100%. The resultant loads were measured, and upon unloading the specimen, the resulting shape-recovery was measured as the specimens returned to the original shape. Figures 7, 8, 9, and 10 are representative data of the strain-stress-temperature profiles versus time for the 10, 25, 50, and 100% strain tests, respectively. The values of strain are calculated from measuring the change in length normalized by the original length of the material elements, which is actually the elongation of the

material elements. In each figure, it is shown that the temperature increases from room temperature to 90℃ at 2℃/minute, and the temperat ure is held at 90℃ while the strain increases. The temperature is then quickly decreased back to room temperature, and the resultant thermal load is removed. The temperature is increased to 90℃ again, allowing the specimen to recover its shape. At this temperature, the strain increases as the specimen is extended to the target value. Note that the actual strain values obtained are larger than the previously mentioned target values, more-so for the 100% experiment. This discrepancy is due to the limitations of the VIC system. A restraint of the system is that it cannot provide real-time values and the loading procedure must rely on the less accurate crosshead displacement.

The strain recovery profiles in Figures 7-10 also show that the majority of the recovery occurred shortly after heating above the glass transition temperature (during the second heating phase). In addition, little residual strain is present upon the completion of recovery. For instance, Figure 7 indicates the final plastic strain after shape recovery to be 1.5% for the 10% applied strain experiment. Figure 11 presents a comparison of the 10, 25, and 50% experiments. These data represent the ratio of recoverable strain/applied strain versus the applied strain for each test. These results demonstrate that the strain recovery ratio is a nonlinear function of applied strain, and that this ratio increases as the applied strain increases. The 10% tests recovered 72-86% of the applied strain, whereas the 50% experiments recovered 95% of the applied strain The one test performed at 100% strain recovered 96% suggesting that beyond a certain applied strain, the percentage of recoverable strain approaches a limit.

This observation initially seems counterintuitive; as one would expect the more the specimen is stretched, the more unrecoverable strain would be induced. Further research and investigation will be performed to determine the cause of this phenomenon as well as the effects of different thermal and mechanical loading rates.

CONCLUDING REMARKS

To provide input data for modeling the nonlinear recovery behavior of shape memory polymers, specimens were subjected to thermomechanical loading profiles with applied strain values of 10, 25, 50, and 100%. After removing the induced thermal load, the specimens were heated to return to their original shape. The subsequent strain recovery was measured as a function of time. Observations showed that the recovery occurred in a nonlinear manner. The nonlinear rate data that was generated in this study is essential for the development of an accurate constitutive model that predicts the material behavior. Analysis of the results indicates the ratio of recoverable strain/applied strain increases as the value of applied strain increases, which may be a significant consideration when facilitating future exploration of application possibilities, including morphing wings and similar aerospace structures. Furthermore, the experimental results demonstrate the unique ability to perform complex thermomechanical characterization for large values of strain.

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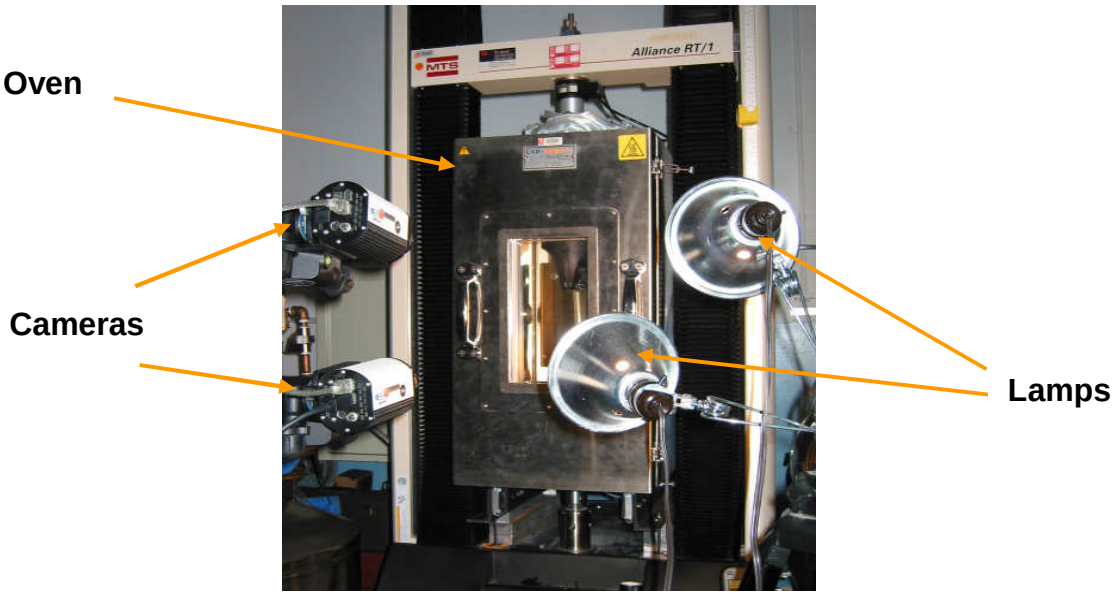

Figure 1 - Test Apparatus

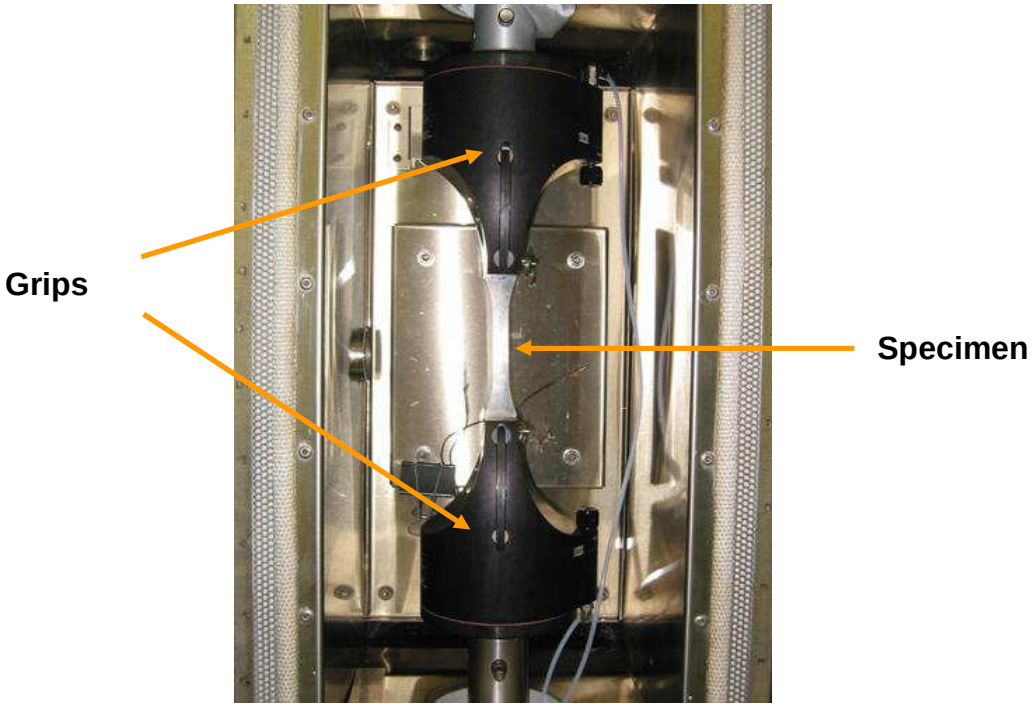

Figure 2 - Furnace Interior with Specimen

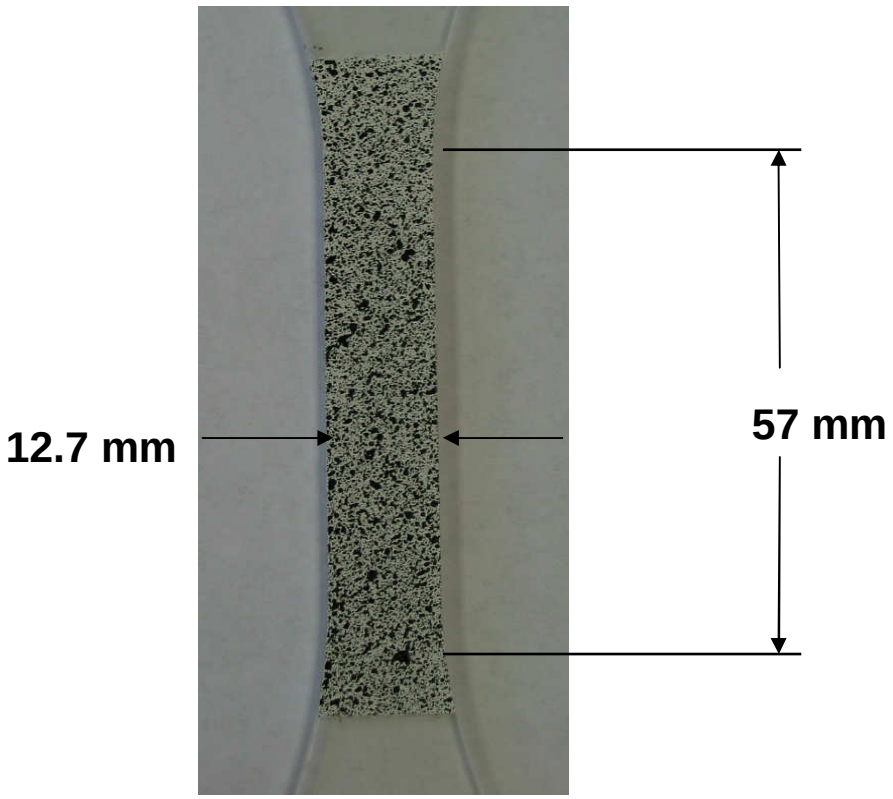

Figure 3 - Shape Memory Polymer Test Specimen with Speckled Pattern

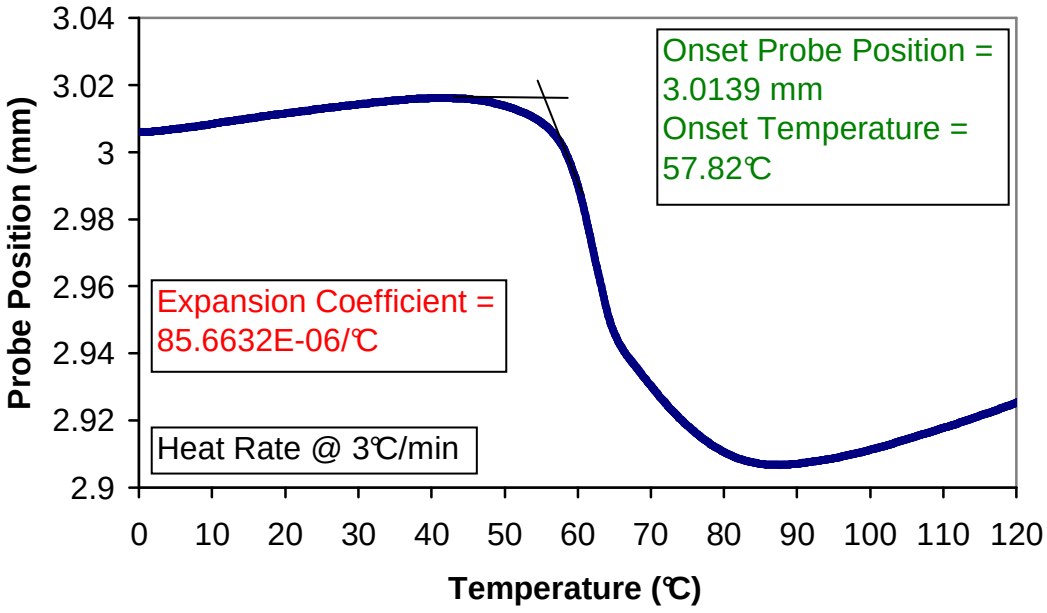

Figure 4 - ThermoMechanical Analyzer Results

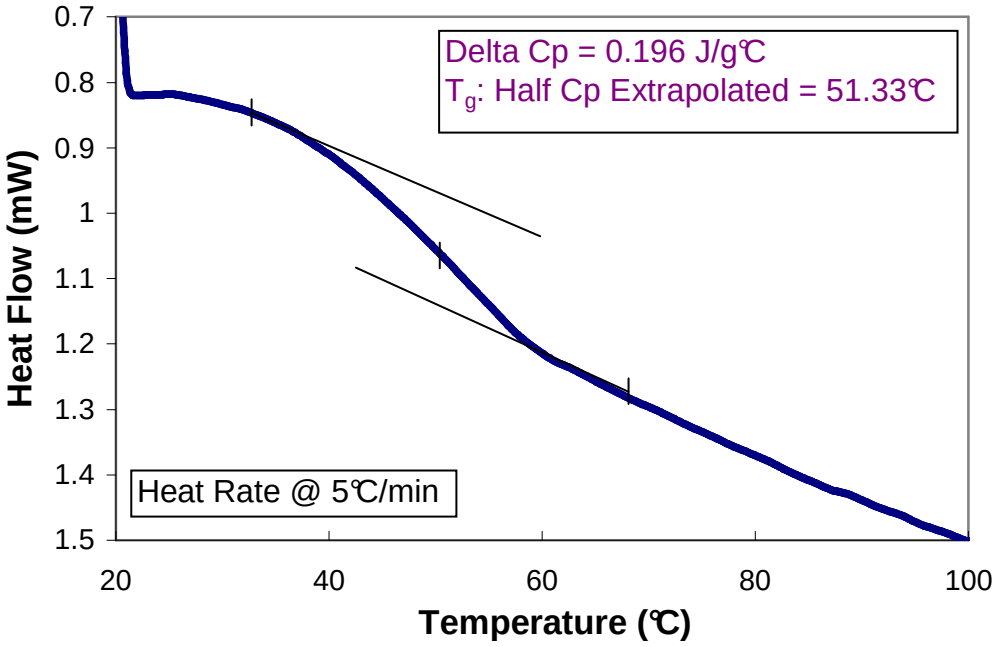

Figure 5 - Differential Scanning Calorimetry Results

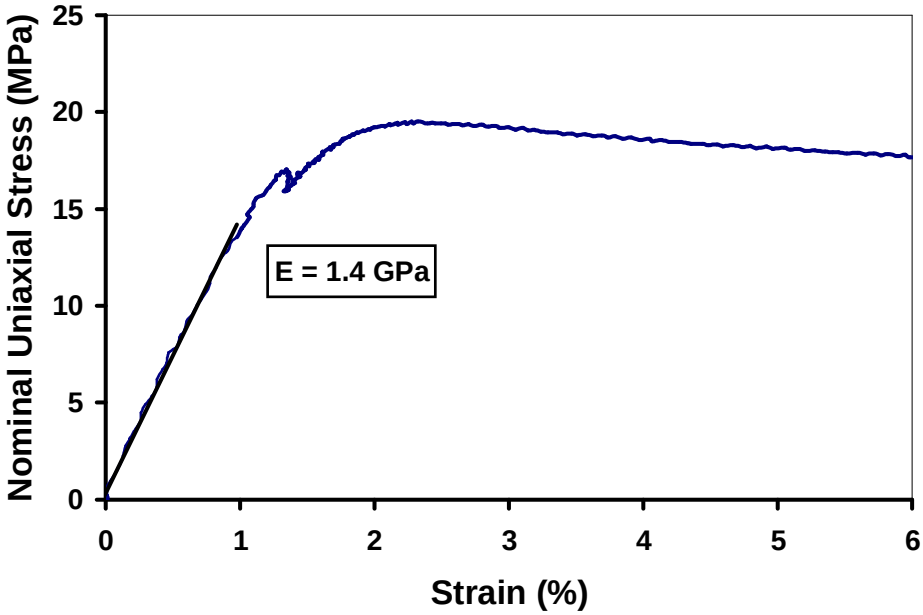

Figure 6 – Nominal Uniaxial Stress-Strain Plot of SMP at Room Temperature

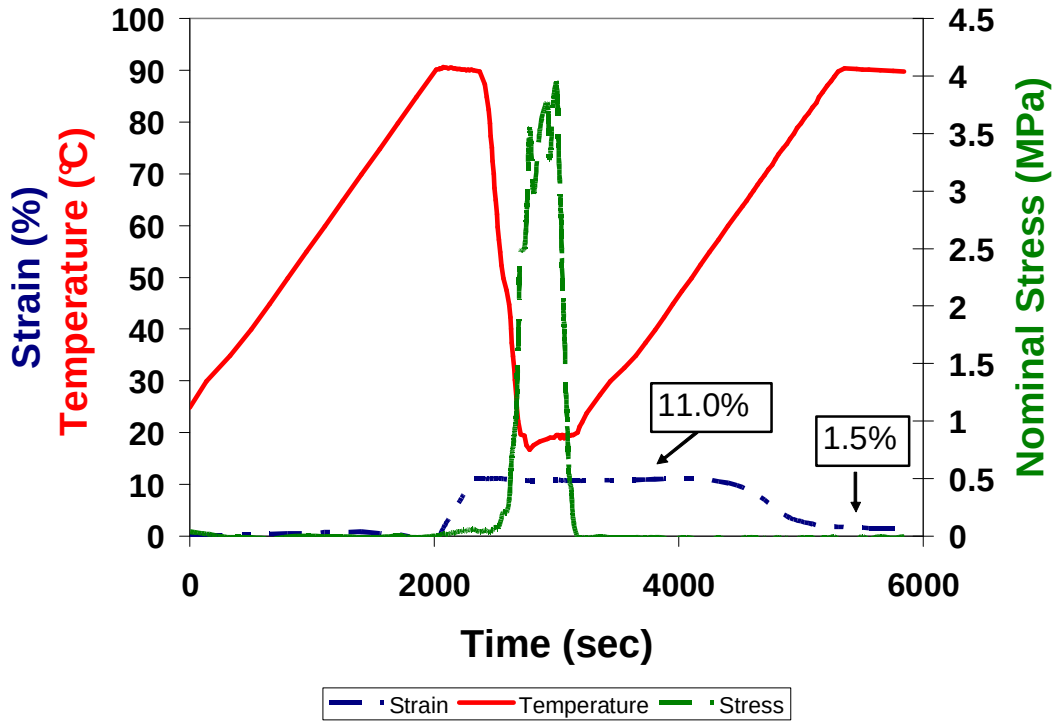

Figure 7 – Shape-Recovery Test - 10% Applied Strain

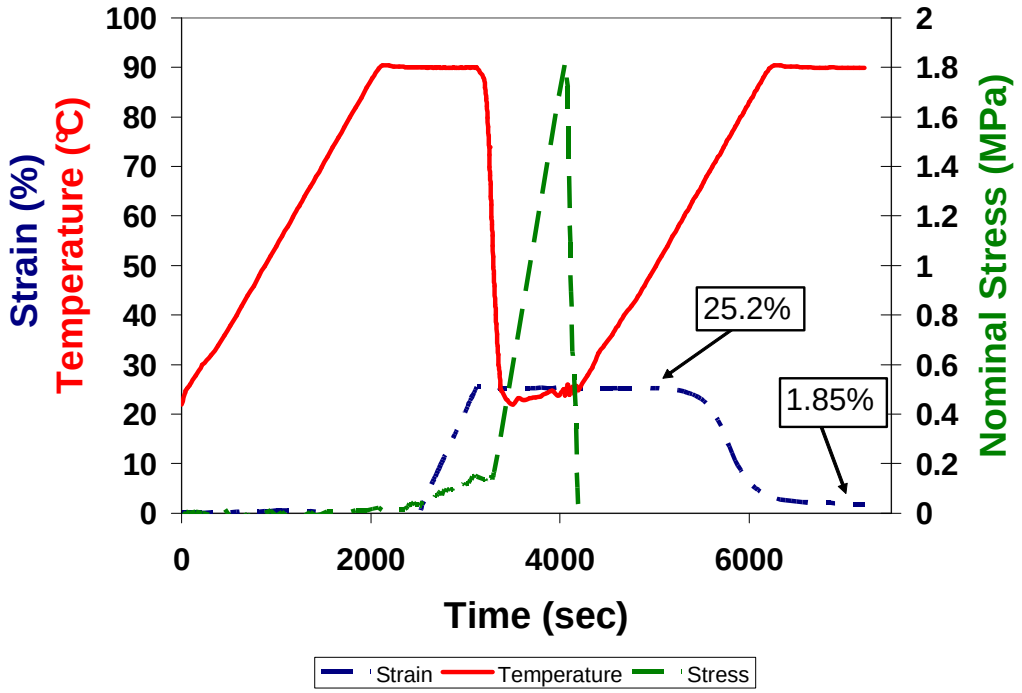

Figure 8 - Shape-Recovery Test - 25% Applied Strain

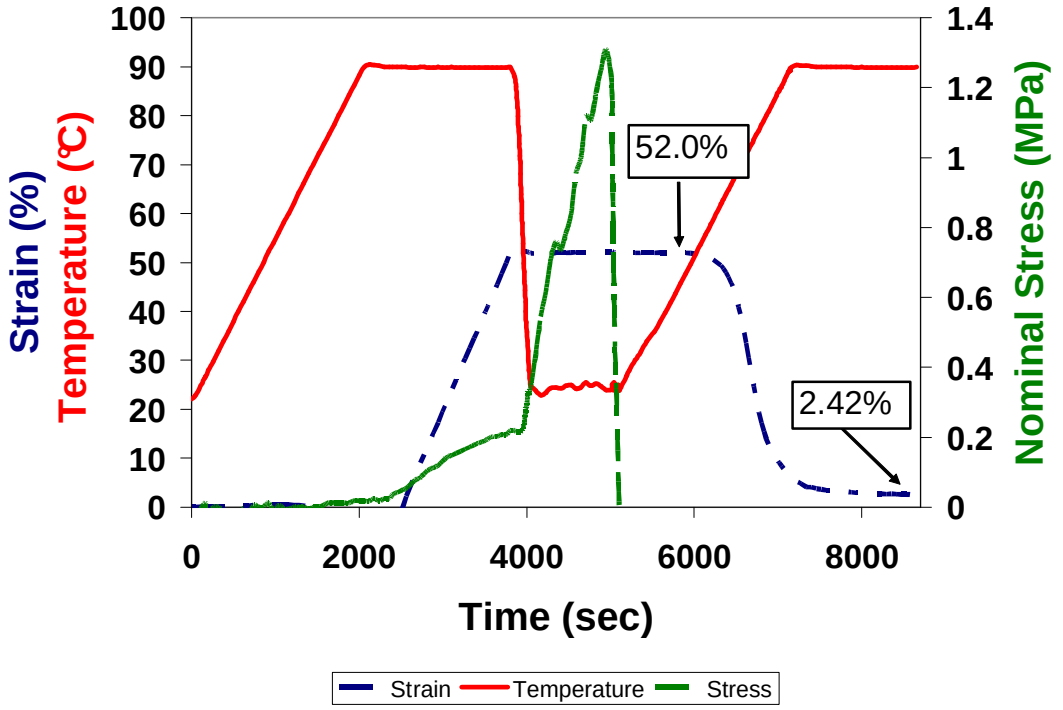

Figure 9 - Shape-Recovery Test - 50% Applied Strain

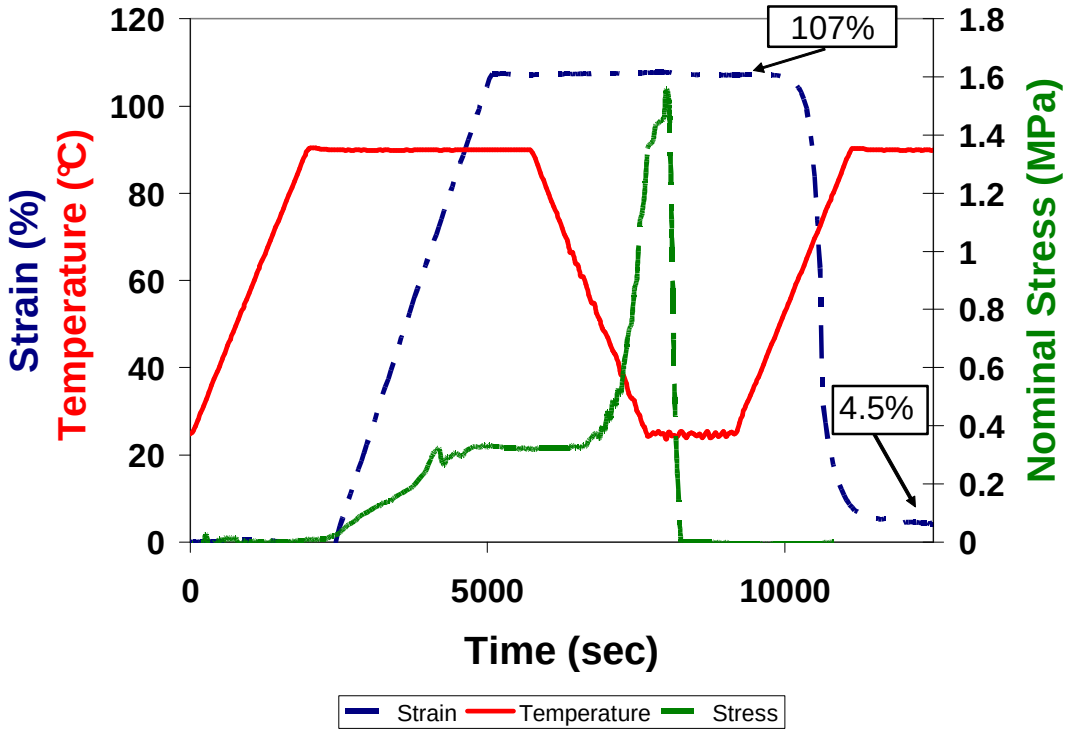

Figure 10- Shape-Recovery Test - 100% Applied Strain

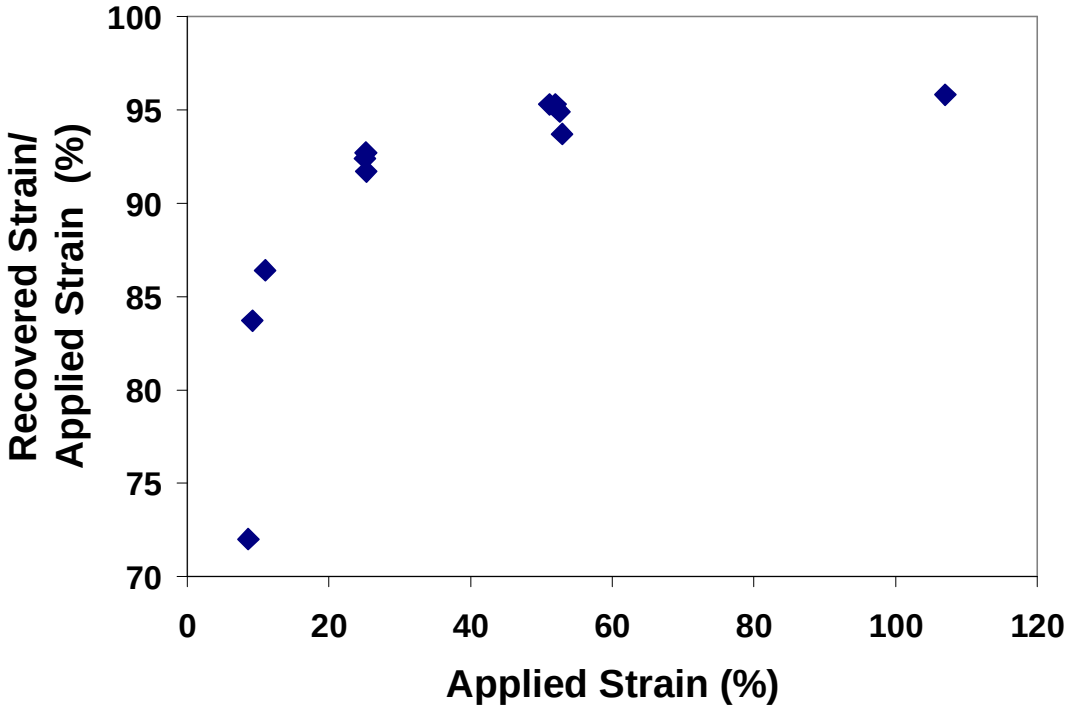

Figure 11 - Percentage of Recovered Strain versus Applied Strain