Nitinol-Reinforced Shape-Memory Polymers

by

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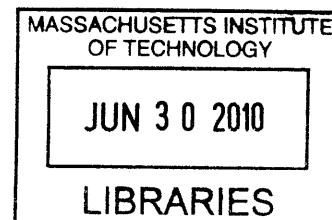MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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Abstract

Reinforced shape-memory polymers have been developed from an acrylate based thermoset shape-memory polymer and nitinol wires. A rectangular shape-memory polymer measuring approximately 1 by 2 by 0.1 inches has a ten fold increase in actuation force under three-point bending when reinforced with two 0.02 inch diameter nitinol wires. A constitutive model for shape-memory polymers and nitinol has been used to predict with good correlation the actuation-versus-time and displacement-versus-time behavior of the reinforced shape-memory polymer composites. It is possible then, using finite-element modeling, to design and manufacture reinforced shape-memory polymers tailored for use as thermally-activated actuators of specific force.

Thesis Supervisor: Lallit Anand
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Acknowledgments

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Chapter 1

Introduction

Shape-memory polymers can be deformed and fixed into a temporary shape which can then be recovered by heating the material above its glass transition temperature. When the polymer recovers from its temporary shape it returns stored energy and serves as a thermally-activated actuator. Due to the low rubbery modulus of the polymer above the glass transition temperature its actuation force is limited and the material is thus restricted form numerous applications where high actuation forces are required.

Shape-memory polymers have found applications in biomedicine (Baer et al., 2007a,b; Buckley et al., 2006), microsystems (Gall et al., 2004), and high desnity re-writable media for data storage (Vettiger et al., 2002), where the actuation forces required are low. They have also been used in high actuation force applications such as self-deployable space structures (Campbell et al., 2005) where a reinforced shape memory composite, using carbon fiber as the reinforcing material, is used to increase the actuation force of the polymer.

The focus of this thesis is the development, testing, and simulation of a reinforced shape-memory polymer composite using superelastic nitinol wires. Specifically, with the aim of developing a reinforced shape-memory polymer with high actuation force, I have

(i) developed a repeatable process and processing parameters for the manufacturing of thermoset shape-memory polymers based on a ulatraviolet curable liquid composed of a monomer and crosslinker;

(ii) conducted thermo-mechanical cyclic three-point bend experiments on samples with and without nitinol wires. In these experiments the recovery deformation is constrained so as to measure the actuation force;

(iii) conducted video-extensometer measurements of the free recovery of the shape-memory composites with and without nitinol wires to measure the displacement-time response of the composite; and

(iv) numerically simulated the thermo-mechanical response of the shape-memory polymer composite in the aforementioned conditions of constrained and free recovery.

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The plan of this paper is as follows. In chapter 2 the chemical composition and experimental procedures for the manufacturing of shape-memory polymer composites is presented. Chapter 3 is divided into two sections. In the first the experimental procedures and results of the three-point bending under kinematic constrains are presented. In the second the experimental procedures and results are presented for the free recovery experiments. Finally, chapter 4 closes with conclusions and future work.

Chapter 2

Manufacturing of Shape-Memory Polymer Composites

The shape-memory polymer chosen for experimentation in this work is a chemically-crosslinked thermoset polymer based on an acrylate network as has been studied recently (Safranski and Gall, 2008; Yakacki et al., 2007). The procedure described in the literature was modified slightly until a polymer of consistent quality and reproduction was achieved. The polymer composition chosen for this study was:

(i) tert-Butyl acrylate (tBA, 90% by weight, molecular weight: 128 g/mol) crosslinked with Poly(ethylene glycol) dimethacrylate (PEGDMA, 10% by weight, molecular weight: 550 g/mold) and 2,2-Dimethoxy-2-phenylacetophenone photoinitiator (0.2% by weight, molecular weight: 256 g/mol.

The tBA-PEGDMA polymer was chosen for these experiments because of its lower glass transition temperature, $\vartheta_g \approx 38°C$, and my ability to repeatedly produce a polymer of consistent mechanical behavior. The preparation of the polymer for UV curing follows the following procedure

1. Mix PEGDMA onto tBA in a glass beaker, followed by the addition of the photoinitiator powder.

2. Stir mixture for two minutes using magnetic stirrer. Remove stirrer when done.

3. Degas the mixture at vacuum for ten minutes.

4. Pour mixture onto casting structure and UV cure for ten minutes.

5. Anneal specimens at 90 °C for one hour.

The development of the casting structure was especially difficult. Shown in this work is the final result after several iterations of casting experimentation. The main problem associated with casting the shape-memory polymer was that it shrinks substantially during UV curing. If the polymer sticks to the casting structure, cracks will form in the polymer.

A cross-section of the structure used for casting nitinol reinforced shape-memory polymers is shown in Figure 2-1. The nitinol wires were glued between two aluminum spacers using a cyanoacrylate glue. This structure was then placed than placed inside a petri dish and covered with a glass slide. All glass surfaces were coated with Rain-X, a commercially available product that adds a hydrophobic coating to the glass.
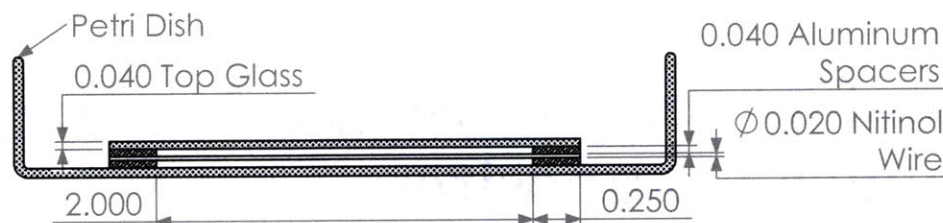

Figure 2-1: Cross-sectional view of the casting set up.

When the casting structure is complete and coated, Figure 2-2 (a), the polymer is poured, UV cured, and annealed. Following the anneal the polymer is removed from the petri dish, Figure 2-2 (b), and then cut to its final geometry, Figure 2-2 (c).Experience has shown that demolding is best done when the polymer is above it's glass transition temperature. The final specimen geometries for a reinforce shape-memory polymer with one and two nitinol wires are show in Figure 2-3. Samples with no nitinol wires were also produced with the same geometry as the one wire specimen shown.

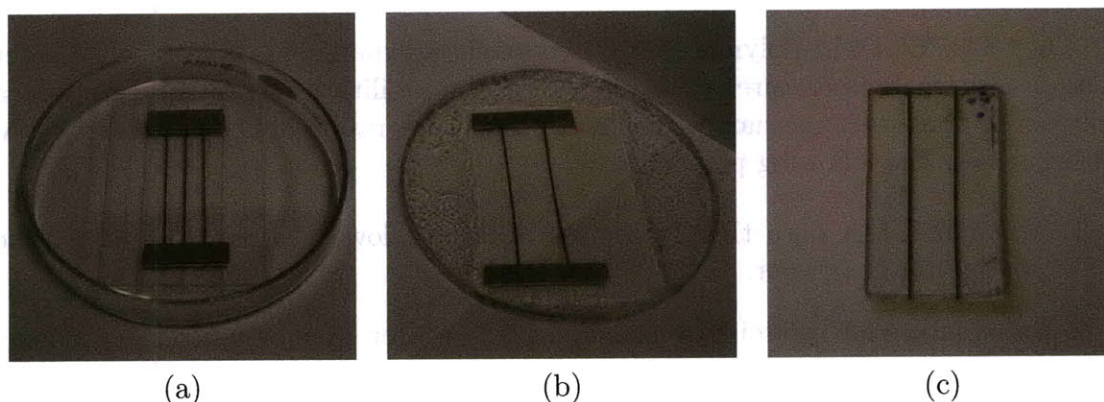(a)   (b)   (c)

Figure 2-2: Process for casting reinforced shape-memory polymers. (a) Casting set-up prior to pouring the polymer mixture and UV curing. (b) Shape-memory polymer after being UV cured and glass removed. (c) Final specimen after being cut from the bulk shape-memory polymer.
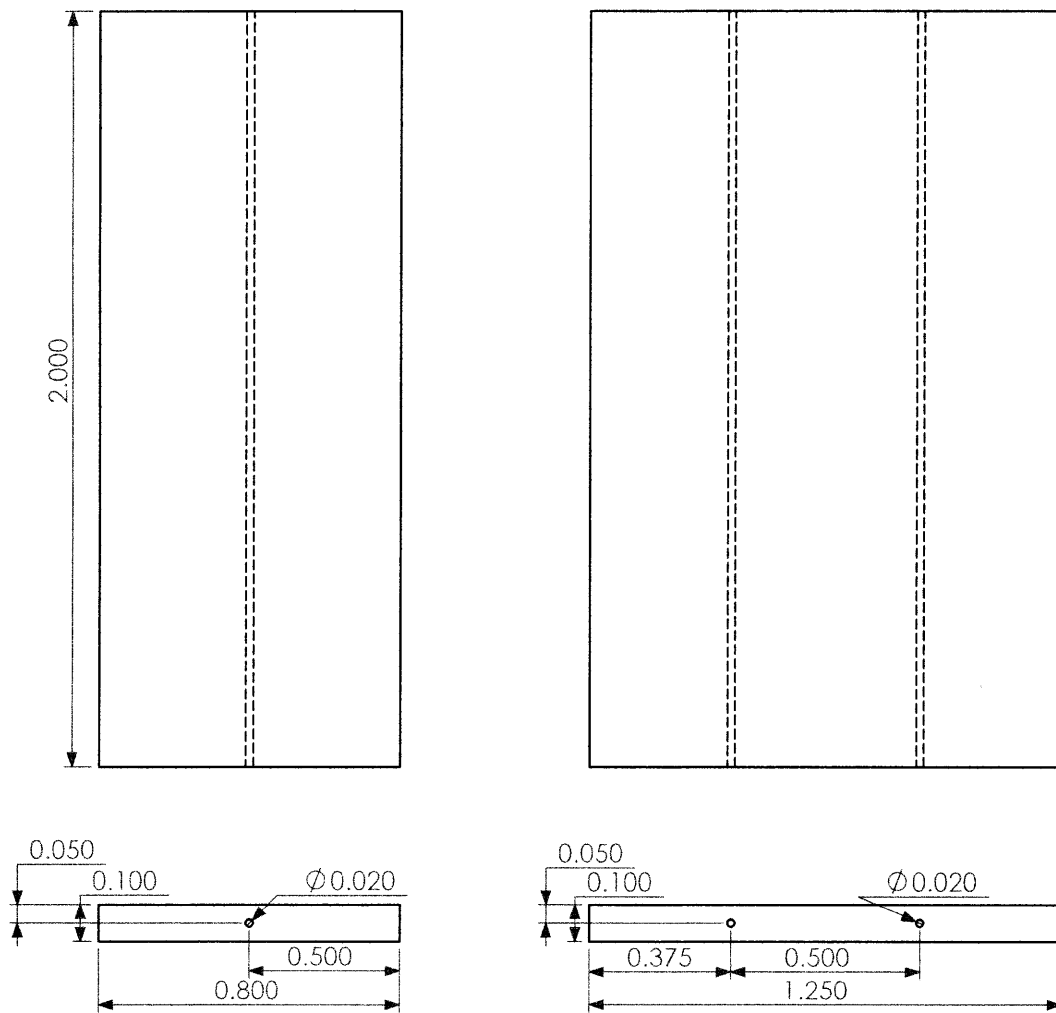
Figure 2-3: Specimen dimensions.

Chapter 3

Experimental Measurements and Theoretical Predictions

In order to characterize the behavior of reinforce shape-memory polymers and assess their improved actuation force two experiments were conducted. The experiment were conducted on specimens having one, two, or no nitinol wires as prescribed in chapter 2. The experiments conducted are:

(i) Measurement of the actuation force through thermo-mechanical cyclic three-point bend testing of a beam specimen under kinematic constraints. The specimen was subjected to the following thermo-mechanical history: the specimen was heated to a temperature above it's glass transition temperature, the specimen was then bent. The bent specimen was then cooled to a temperature below its glass transition temperature under constraints. With the fixture being held at the bend configuration the specimen was re-heated to a temperature above it's glass transition temperature and the recovery force measured.

(ii) Measurement of the displacement-versus-time behavior through video-extensometer measurements of the recovery of the shape-memory polymer under no kinematic constraints. The specimen was subjected to the following thermo-mechanical history: the specimen was heated to a temperature above it's glass transition temperature, the specimen was then bent. The bent specimen was then cooled to a temperature below its glass transition temperature under kinematic constraints. The specimen was then unloaded and re-heated to a temperature above it's glass transition temperature and the deformation was measured using a video-extensometer.

The temperature of the polymer was measured by using a thermo-couple embedded onto a separate shape-memory polymer specimen. This allowed for the thermo-couple to be covered by a material with equivalent thermal properties without interfering with the experimental measurements.

Both the recovery force and free recovery experiments were simulated on ABAQUS Standard using the constitutive model and material parameters for shape-memory polymers proposed by Srivastava et al. (2009). The nitinol wires were modeled using

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the ABAQUS built-in implicit user subroutine for nitinol with the default material parameters. The symmetry of the problem was used to reduce the number of elements needed in the simulation.

Referring to Figure 3-1 (a), (c), and (e), the nodes on the AB face extending in the 2-direction were prescribed a displacement boundary condition of symmetry in the 3-direction. The nodes in the BC face extending in the 2-direction were prescribed a displacement boundary condition of symmetry in the 1-direction. For all simulations ABAQUS-C3D8HT thermo-mechanically-coupled elements were used. The no nitinol simulation, Figure 3-1 (a), has 1802 elements, the 1 wire nitinol simulation, Figure 3-1 (c), has 3602 elements, and the 2 wire nitinol simulation, Figure 3-1 (e), has 5002 elements. Figure 3-1 (b), (d), and (f) shows the full model when mirrored above the symmetry boundary conditions.

The loading was applied through the use of two rigid analytical surfaces modeling the rollers used in the experiment. Figure 3-2 (a) shows the undeformed, mirrored, finite element mesh and the outline of the analytical rigid surfaces which extend in the 1-direction. Figure 3-2 (b) shows the same simulation in the deformed configuration where the top roller has traveled a distance of 10 millimeters in the negative 2-direction.
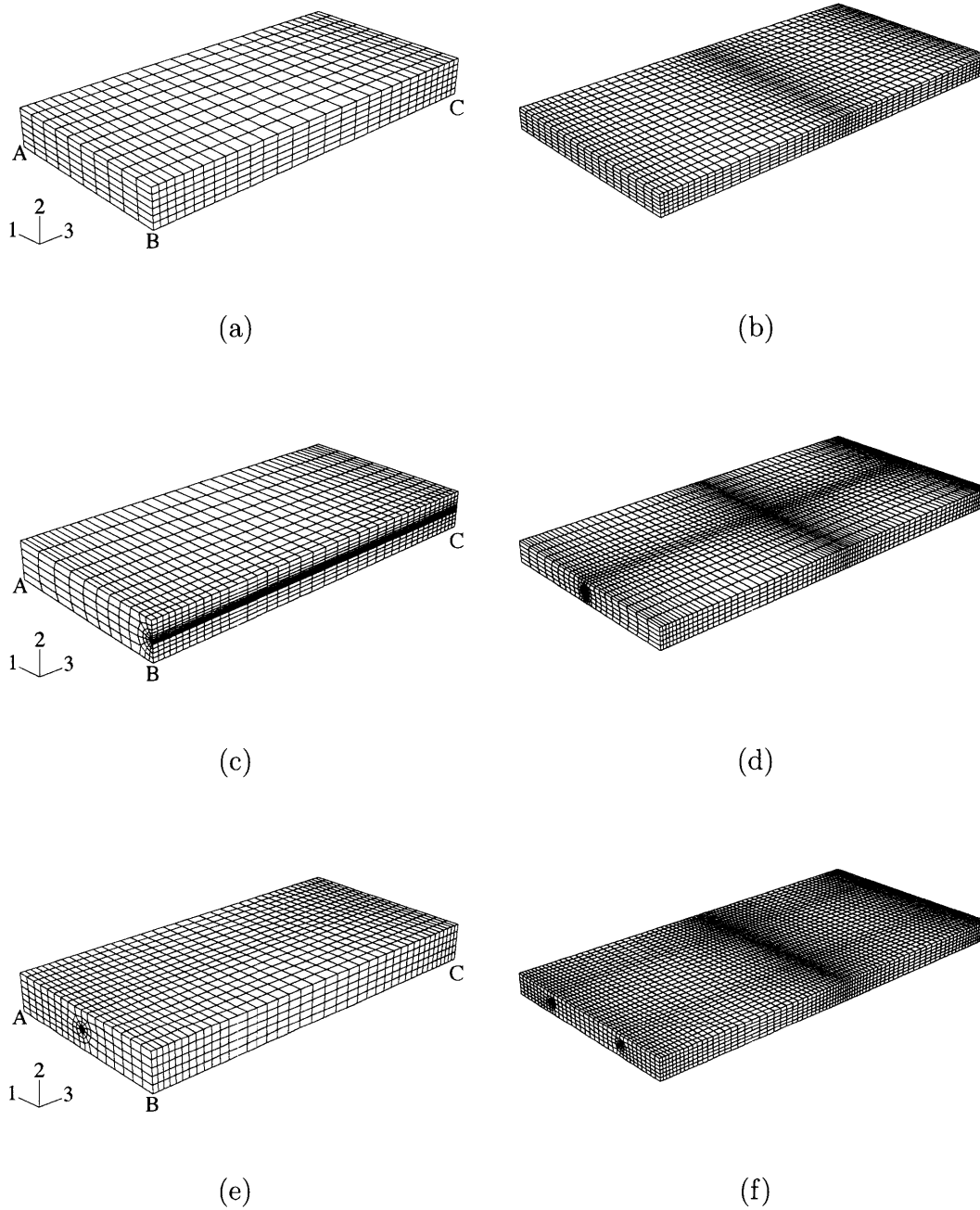
Figure 3-1: (a), (b), and (c) One-quarter symmetry finite element mesh for the no nitinol wire, 1 nitinol wire, and 2 nitinol wire simulations respectively. All the nodes on the surface formed by AB extending in the 2-direction were prescribed symmetry in the 3-direction, and all the nodes on the surface formed by BC extending in the 2-direction were prescribed symmetry in the 1-direction. (b), (d), and (f) Full finite-element mesh after mirroring about the symmetry boundary conditions for the no nitinol wire, 1 nitinol wire, and 2 nitinol wires simulations respectively.
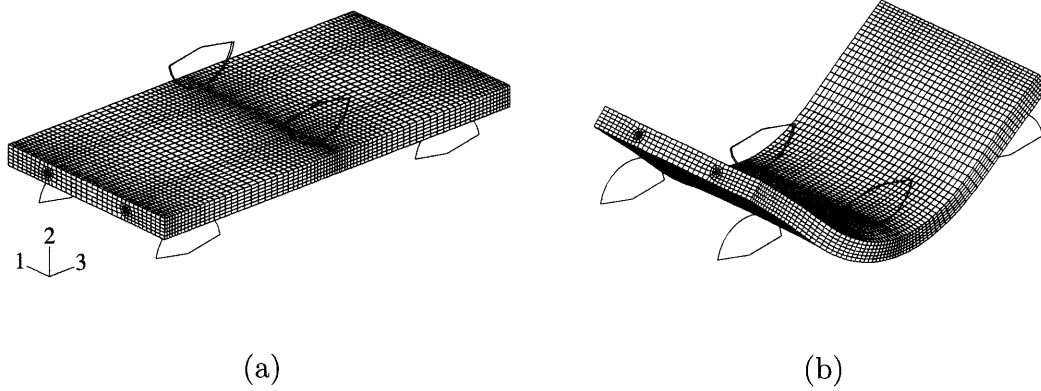
(a)   (b)

Figure 3-2: (a) Undeformed finite element mesh with outline of the rigid analytical rollers which extend in the 1-direction. (b) Deformed finite element mesh.

3.1 Actuation Force Experiments

There are two steps to this experiment. In the first step the shape-memory polymer was heated, deformed, and cooled while the deformation was being held. This part of the experiment was performed on an Instron with a heating chamber. The deformed specimen and test fixture where then placed on an EnduraTEC 3200 testing machine where the top fixture was placed in contact with the specimen and held at that position. At this point the EnduraTEC chamber was heated and the recovery force measured. Two separate machines where used in these experiments because the Instron can travel the full 10mm while the EnduraTEC testing machine can not. Inversely the EnduraTEC can measure smaller loads while the Instron can not. The following steps detail the experimental procedures:

On Instron

1. Test fixture and specimen where placed on the Instron testing machined and aligned using calipers.

2. Chamber was heated to 65 °C and specimen was allowed to heat for 30 minutes.

3. Top fixture was deflected 10mm to bend the specimen.

4. Heating was turned off and the chamber was opened allowing the specimen to cool for 30 minutes to a temperature of 25 °C. Figure 3-3 (a).

Transition between machines

5. Specimen and fixture were moved to the EnduraTEC testing machine.

On EnduraTEC

6. Specimen was brought back in contact with the top fixture and the fixture was secured at this position. Figure 3-3 (b).

7. Chamber was heated to 65 °C while the load on the fixture and the temperature were recorded.

The experimental actuation force measurements are shown in Figure 3-4 where the force in newtons is plotted as a function of temperature. Figure 3-5 shows the temperature profiles as recorded on the EnduraTEC testing machine. The introduction of just a single nitinol wire increases the actuation force from $\approx$ 0.4N to $\approx$ 2N, a five fold increase. With two nitinol wires the actuation force is increased to $\approx$ 4N, a ten fold increase from the actuation force of the shape-memory polymer without reinforcement.

Figure 3-6 compares the experimentally measured actuation force with the theoretical predictions. In order to account for the time delay between the temperature recorded through the thermo-couple and the actual specimen temperature a time shift of 25 seconds has been applied to the theoretical simulations. There is good
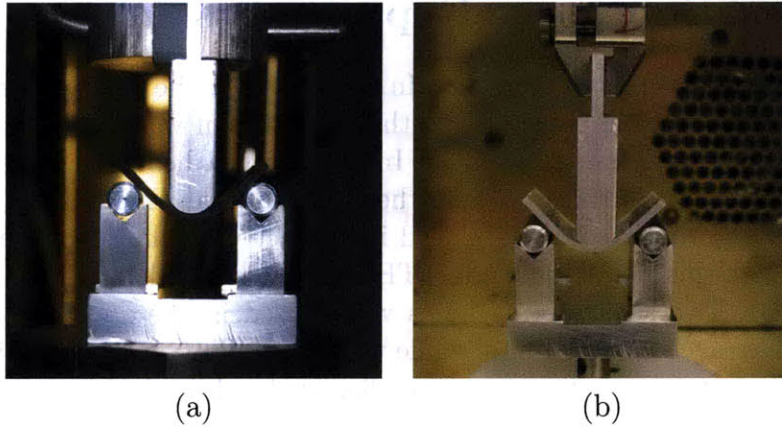
(a)   (b)

Figure 3-3: (a) Fixture on the Instron testing machine where specimen is heated, deformed, and cooled. (b) Fixture on the EnduraTEC testing machine where recovery fore and free recovery displacement are measured.

correlation with the predicted values. As mentioned in Chapter 1, reinforced shape-memory polymers are especially useful in that their actuation force can be tailored to specific applications. It is clear from Figure 3-6 that the constitutive models used in this finite element simulation are capable of allowing one to design nitinol reinforced shape-memory polymers for a desired actuation force.
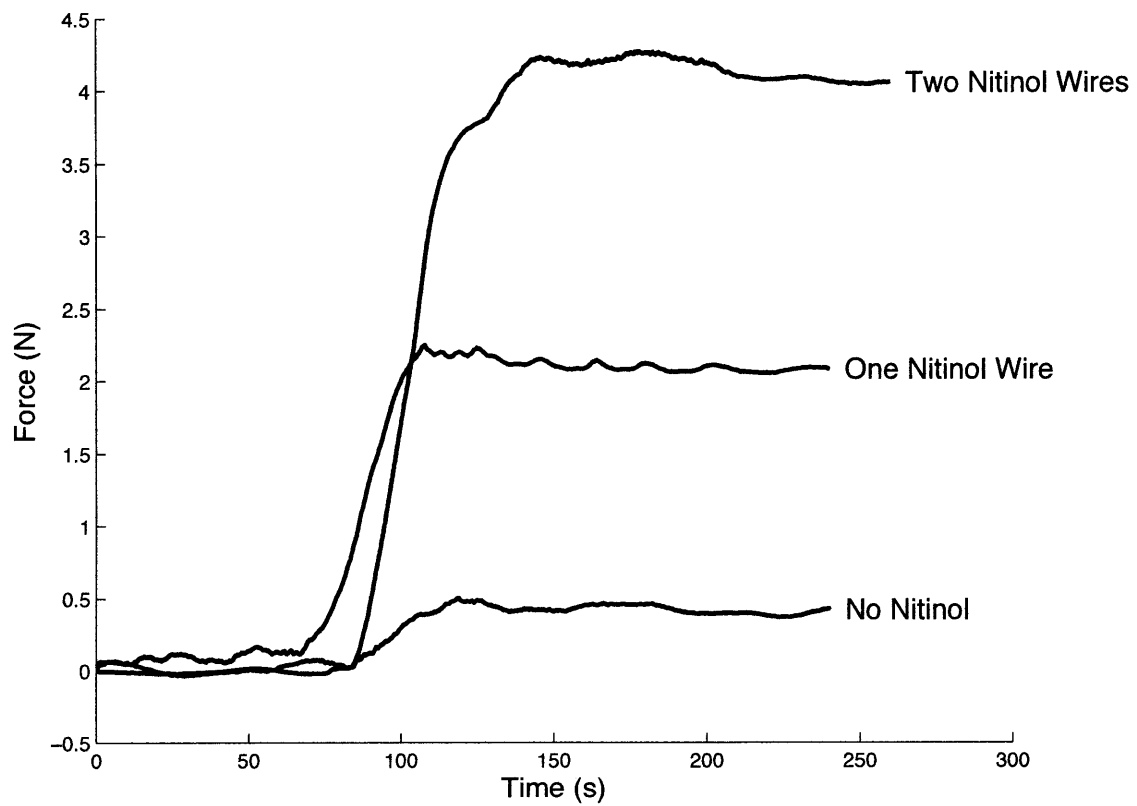
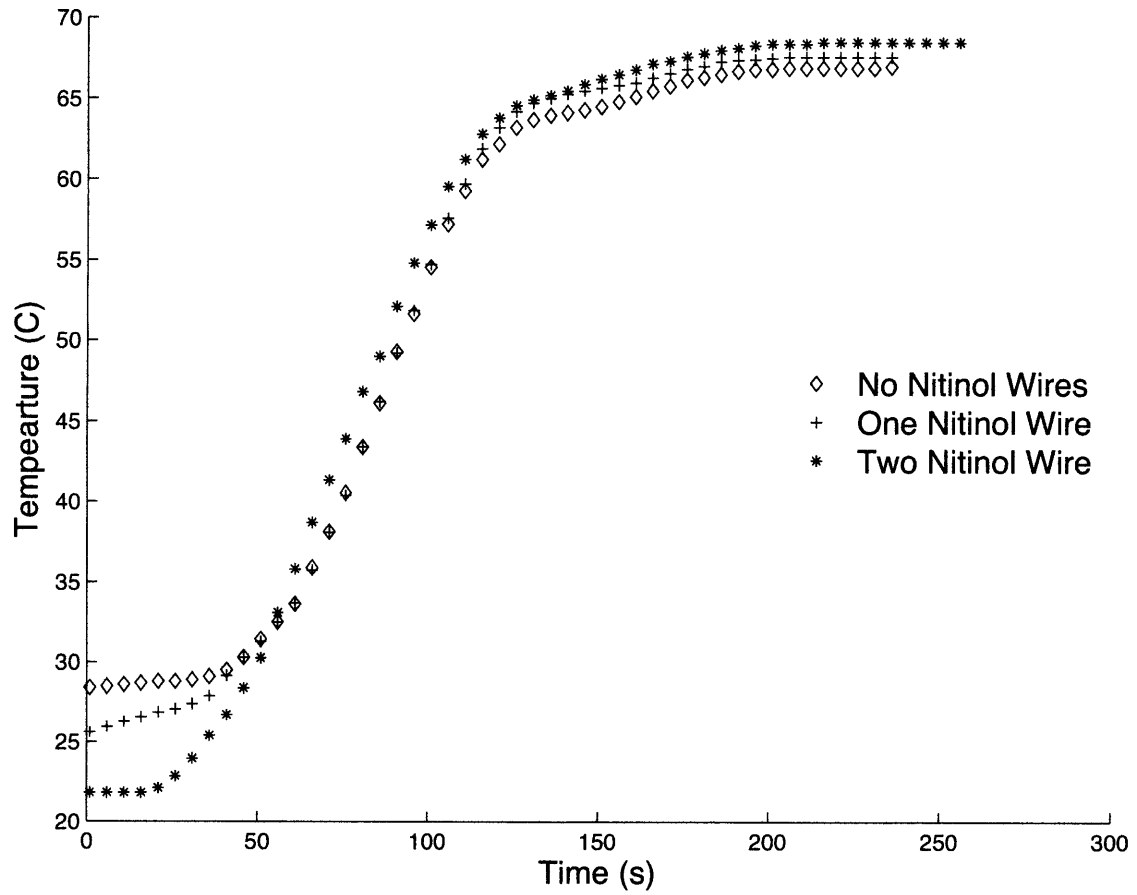Figure 3-4: Experimental actuation force measurements versus time.

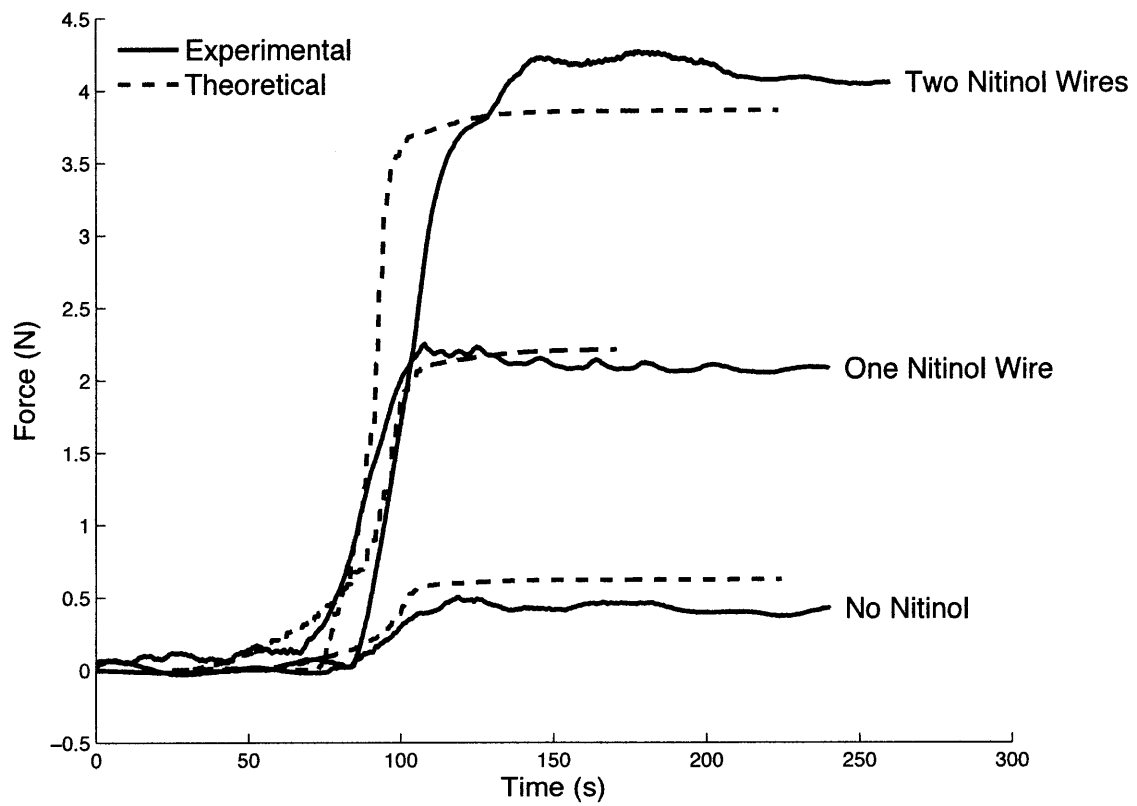Figure 3-5: Experimental temperature versus time profiles for actuation force measurements.

Figure 3-6: Experimental and theoretical actuation force versus time.

3.2 Free Recovery Experiments

Similar to the previous experiment this experiment is also separated into two parts. The first portion is done in the Instron following the same procedures as the actuation force experiments. The second portion of the experiment is performed on the EnduraTEC testing machine where the fixture is positioned without the top roller coming into contact and the recovery displacement-versus-time behavior is measured visually through a video extensometer. The detailed steps 1 through 5 are the same as above, the rest of the procedure differs as follows:

On EnduraTEC

6. Specimen and bottom fixture where brought into the EnduraTEC chamber and video camera was set up.

7. Chamber was heated to 65 °C while the temperature and visual displacement of the beam where recorded.

Figure 3-7 shows the experimentally measured displacements of the reinforced shape-memory polymers and regular shape-memory polymer specimens as s function of time. As expected the reinforced shape-memory polymer specimens display a faster recovery as the elastic energy stored in the nitinol wires helps the shape-memory polymer recover its original shape. Figures 3-8 (a), (b), and (c) show the experimentally measured free recovery displacement behavior compared with the theoretical predictions, as before to account for the time delay in temperature from the thermo-couple to the actual specimen a time shift has been applied to the theoretical curves. Figure 3-9 compares the recorded images during free recovery with the finite-element mesh at four distinct intervals for the one wire nitinol specimen.

As can be seen through Figure 3-8, the constitutive model is also capable of predicting slower recovery forces in the regular shape-memory polymer simulation as compared to the reinforced shape-memory polymer simulations. It is important to note in Figure 3-8 (a) how the simulation predicted that the bent specimen would not recover fully.
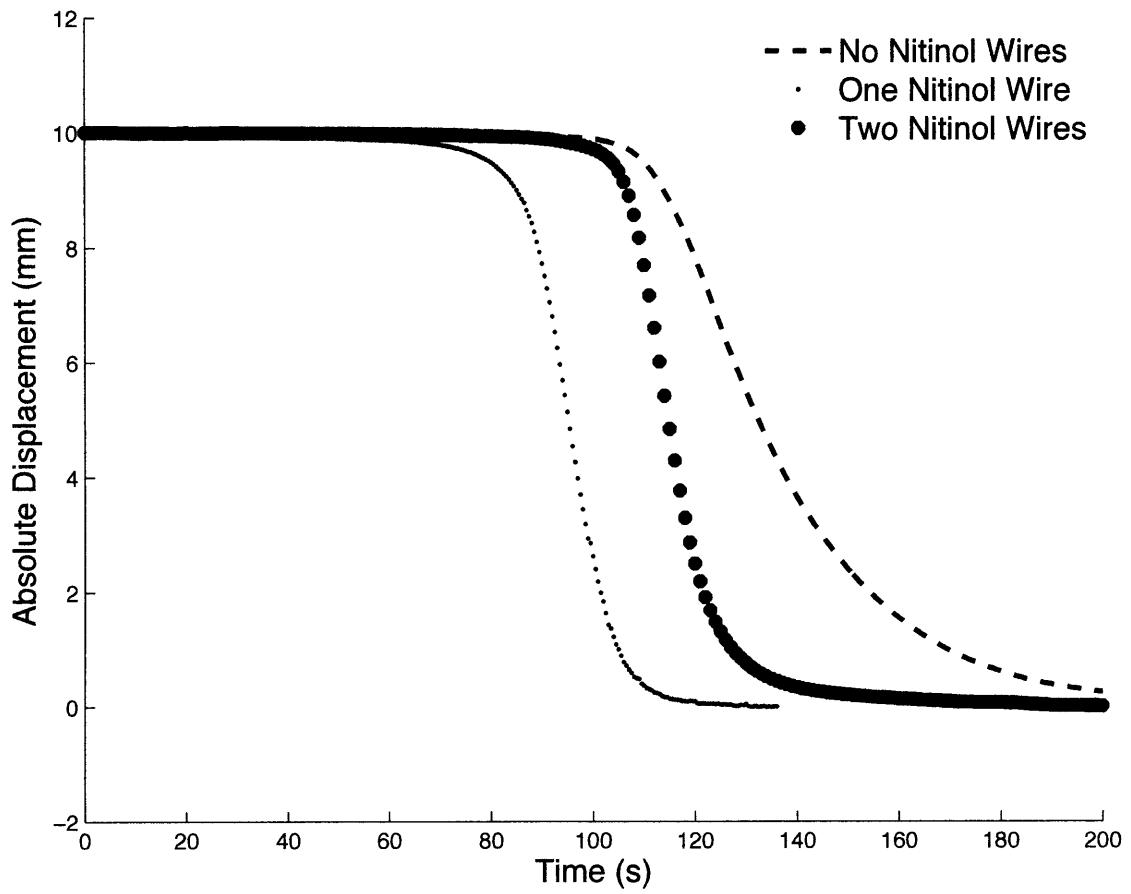
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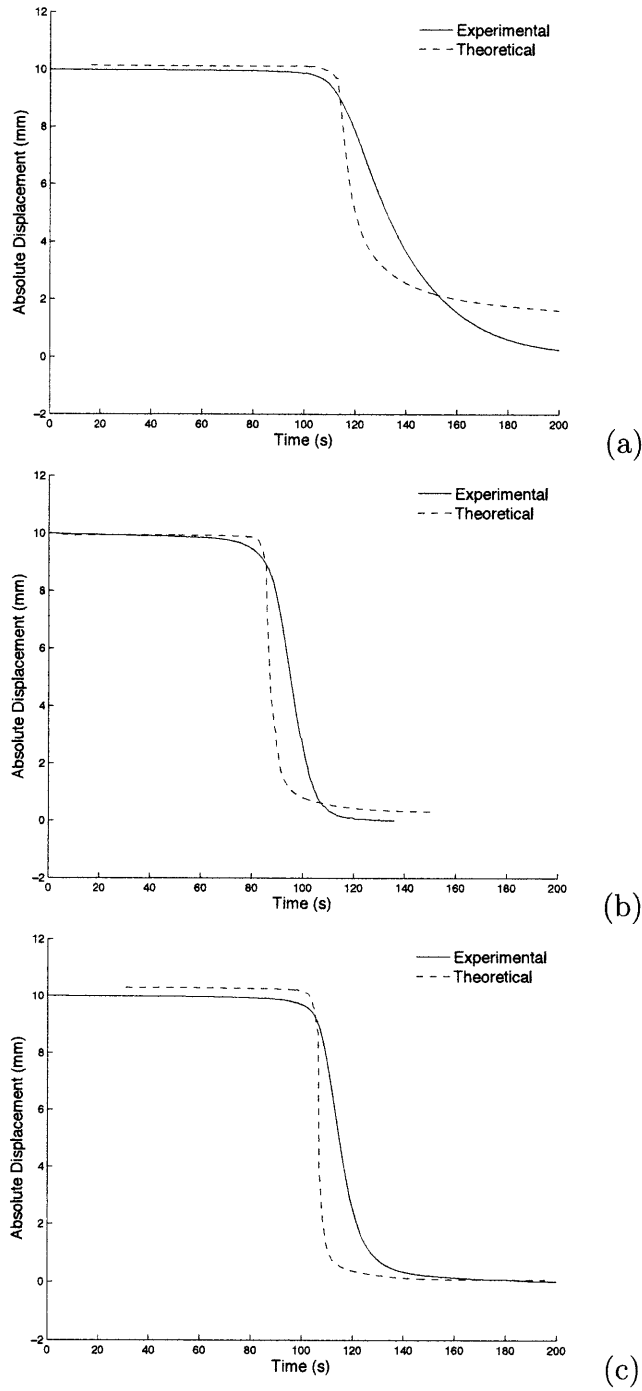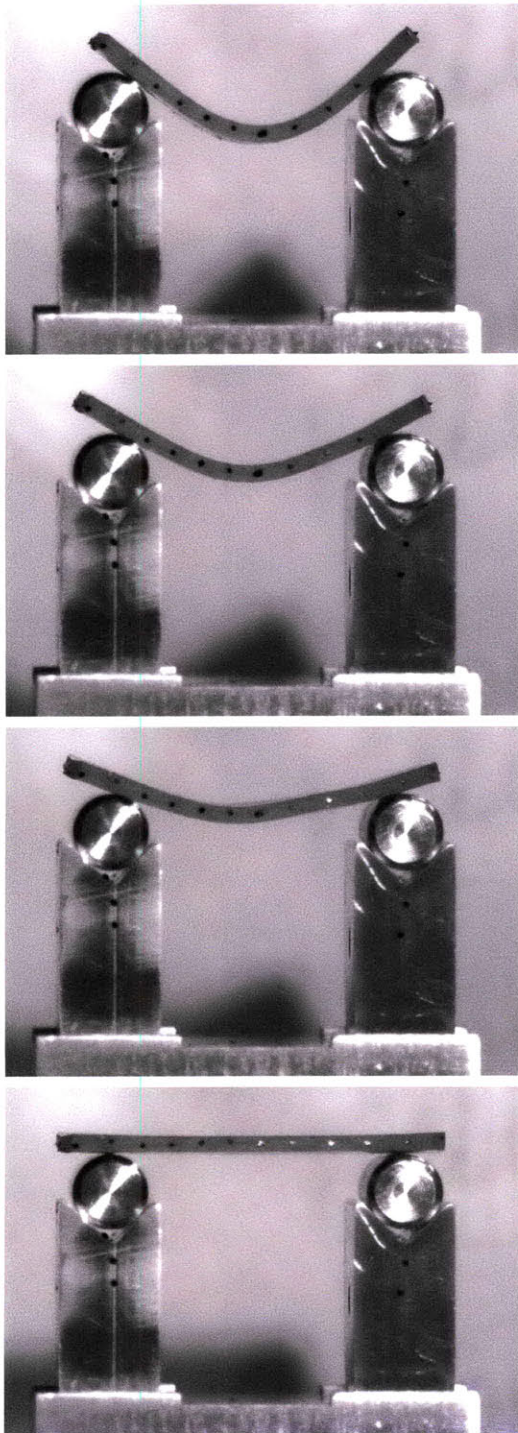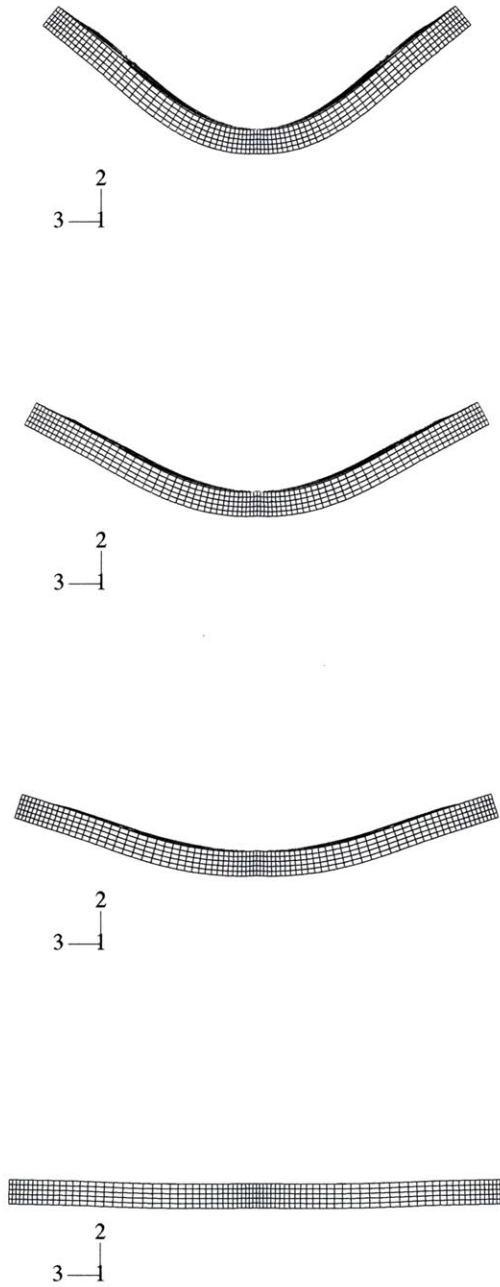Figure 3-7: Experimental free recovery displacement versus time.

Figure 3-8: Experimentally and theoretical free recovery displacement time behavior for (a) no nitinol wire specimen, (b) one nitinol wire specimen and (c) two nitinol wire specimen.

Figure 3-9: (a) Experimentally observed free recovery and (b) Numerically-predicted free recovery of a one nitinol wire shape-memory polymer beam.

Chapter 4

Conclusions and Future Work

Reinforced shape-memory polymers have been manufactured using an acrylate based thermoset shape-memory polymer and superelastic nitinol wires. It has been shown that inserting two 0.02 in diameter nitinol wires on a 1.25 by 2 by 0.1 in shape-memory polymer beam can increase its actuation force by ten times from $\approx$ 0.4 Newtons to $\approx$ 4 Newtons. The inclusion of the nitinol wires has also been shown to increase the speed of the free recovery of the polymer.

The constitutive model for shape-memory polymers proposed by Srivastava et al. (2009) can accurately predict the actuation force during thermal recovery of the shape-memory polymer. Using the built-in implicit ABAQUS subroutine for Nitinol wires good theoretical predictions have also been achieved for reinforced shape-memory polymers. With these tools it is possible to design reinforce shape-memory polymer composite with specific actuation force requirements.

In future work it would be of interest to characterize not just the actuation force of the reinforce shape-memory polymers under kinematical constrains, but rather the work output by measuring the force-displacement of the polymer composite. This measurements would more realistically mimic the use of such a thermally-activated actuator. It would also be of interest to use the theoretical model to predict the maximum possible recovery force given certain geometric constrains. That is to predict the maximum number of nitinol wires that can be used while still having the polymer maintain it's deformed configuration when cooled.

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