Thermomechanical Characterization and Modeling of Shape Memory Polymers

Master of Science Thesis Defense

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Texas A&M University, College Station, TX
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Presentation Outline

- Motivation and research objectives
- Experimental investigation
  - Experimental setup
  - Thermomechanical load path
  - Results
- Small deformation model
  - 1-D calibration
  - Model predictions
- Large deformation model
  - 1-D calibration
  - Model predictions
- Conclusions
Motivation and Research Objectives
Motivation – Comparison of Active Materials

![Diagram illustrating the comparison of different active materials based on actuation stress and strain. The diagram includes categories such as Shape Memory Alloys (SMAs), Piezoelectric ceramics, Magnetostrictive ceramics, Ionic electroactive polymers, and Magnetic SMAs (MSMAs). Each category is represented by a rectangular bar, and the diagram also includes lines indicating energy densities such as 100 MJ/m³ and 10 kJ/m³.](image-url)
Motivation – Applications of SMPs


Ref: Liu, Qin, Mather. 2006.
Literature Review – Experimental Efforts

• **Small deformation experiments:**
  - Tensile strains of 2.4% to 10% on thin film specimens. [Tobushi.1997]
  - Tensile & compressive strains up to 9.1% on dogbone specimens. Captured non-linear strain versus temperature recovery profile. [Liu.2006]

• **Large deformation experiments:**
  - Tensile strains of 20% to 100% on thin film specimens. Effects of loading at various temperatures investigated. [Tobushi.1998]
  - Tensile strains of 20% and 100% on dogbone, polyurethane specimens. Stabilization of material response observed due to cyclic deformation. [Baer.2006]
  - Tensile strains up to 75% on dogbone specimens. Complete strain recovery profile not captured due to system limitations. [Atli.2008]
Literature Review – Modeling Efforts

• **Small deformation models:**
  - Phenomenological models:
    - Focused on formation of crystalline phase. [Rao.2002]
    - Used two internal state variables – frozen volume fraction & stored strain. [Liu.2006]

• **Large deformation model:**
  - Three dimensional constitutive model based on theory of nonlinear thermoelasticity. [Chen & Lagoudas.2007]
Research Objectives

• **Experimental efforts:**
  - Capture shape memory effect for large deformations (uniaxial extensions up to approximately 100%)
  - Determine influence on shape memory effect with respect to variations in experimental parameters
    - Applied deformation (uniaxial extension)
    - Temperature rate

• **Modeling efforts:**
  - Use experimental data to calibrate Chen and Lagoudas constitutive model
    - Linearized for small deformations
    - Large deformations
  - Compare model predictions to experimental results
Experimental Efforts
Experimental Setup

- Electromechanical, screw-driven test frame
- Forced convection heating and cooling
- Visual Image Correlation (VIC-3D) strain measurement
Thermomechanical Load Path

Shape memory effect (SME) thermomechanical cycle:
1. Load at high temperature
2. Cool at fixed deformation
3. Unload at low temperature
4. Heat at zero stress

Adapted From: Liu, et al. 2006.
Experimental Results – 10% Extension

![Graph showing temperature, extension, and stress over time.]

- **Motivation**
- **Experimental Efforts**
- **Model Background**
- **Small Deformations**
- **Large Deformations**
- **Supplemental**
Experimental Results – 25% Extension

Temperature (°C)

Extension (%)

Stress (MPa)

Time (min)

Length

Axial Strain (%)
Experimental Results – 50% and 100% Extension

Motivation
Experimental Efforts
Model Background
Small Deformations
Large Deformations
Supplemental

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Stress-Extension Relationship During Loading

![Graph showing the relationship between stress (MPa) and extension (%) for different levels of deformation.](graph)

- **Motivation**
- **Experimental Efforts**
- **Model Background**
- **Small Deformations**
- **Large Deformations**
- **Supplemental**

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Extension Recovery – Influence of Temperature Rate

![Graph showing extension recovery percentages at different temperature rates.](image-url)

- **Motivation**
- **Experimental Efforts**
- **Model Background**
- **Small Deformations**
- **Large Deformations**
- **Supplemental**

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Chen and Lagoudas
Constitutive Model
Chen and Lagoudas Model – Background

- Developed on basis of theory of thermoelasticity.
- Formulated in terms of general deformation gradients – allows for large deformation manipulations.

- **Assumptions:**
  - SMP is composed of individual material particles which may undergo phase transformation at different temperatures (phase transformation ‘nucleates’).
  - Deformation is continuous during cooling for a material particle with a reference configuration in active phase.
  - Stored deformation is released upon heating through the same temperature range.

- Integral technique used over entire volume to determine the average deformation gradient of the ‘composite’ material undergoing homogenous deformation.
## Chen and Lagoudas Model – Background

**State variables:**

- Piola-Kirchhoff Stress: \( S(X, t) \)
- Absolute Temperature: \( \theta(X, t) \)

**Deformation gradients:**

<table>
<thead>
<tr>
<th>Reference Configuration</th>
<th>Deformed Configuration</th>
<th>Deformation Gradient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active phase</td>
<td>Active phase</td>
<td>( \hat{F}_a(S, \theta) )</td>
</tr>
<tr>
<td>Frozen phase</td>
<td>Frozen phase</td>
<td>( \hat{F}_f(S, \theta) )</td>
</tr>
<tr>
<td>Active phase</td>
<td>Frozen phase</td>
<td>( \hat{F}_f(S, \theta)\hat{F} )</td>
</tr>
</tbody>
</table>
Chen and Lagoudas Model – Background

• Constitutive equations for an individual material particle undergoing deformation while in a pure active or pure frozen phase:

\[ F(X,t) = \begin{cases} 
\hat{F}_a(S(X,t), \theta(X,t)) & \text{if } X \text{ is in the active phase} \\
\hat{F}_f(S(X,t), \theta(X,t))\hat{F}_f^{-1}(S(X,\tau), \theta(X,\tau))\hat{F}_a(S(X,\tau), \theta(X,\tau)) & \text{if } X \text{ is in the frozen phase}
\end{cases} \]

where \( \tau \) is the last time when the material point \( X \) was frozen

• Average deformation gradient for the entire SMP undergoing homogenous deformation. Calculated via the volume integral of individual material particles in each phase (introducing frozen volume fraction and net cooling history):

\[ \bar{F}(t) = [1 - \phi(\theta(t))]\hat{F}_a(S(t), \theta(t)) + \int_0^t \hat{F}_f(S(t), \theta(t))\hat{F}_f^{-1}(S(\tau), \theta(\tau))\hat{F}_a(S(\tau), \theta(\tau))\phi'(\theta(\tau))\tilde{\theta}'(\tau)d\tau \]
Calibration of Small Deformation Model
Linearized Chen and Lagoudas Model

• Assumptions made during model development:
  
  ➢ **Infinitesimal strain tensor**
    \[ E \approx \frac{1}{2} (F + F^T) - I \]
  
  ➢ **Cauchy stress tensor**
    \[ S \approx \sigma \]
  
  ➢ **Thermoelastic material**
    \[ E = E'(\theta) + M(\theta) : \sigma \]

• **Constitutive equation in terms of infinitesimal strain tensor:**

\[
\bar{E}(t) = [1 - \phi(\theta(t))] \left\{ E'_a(\theta(t)) + M_a(\theta(t)) : \sigma(t) \right\} + \phi(\theta(t)) \left\{ E'_f(\theta(t)) + M_f(\theta(t)) : \sigma(t) \right\} \\
+ \int_0^t \left\{ E'_a(\theta(\tau)) + M_a(\theta(\tau)) : \sigma(\tau) - E'_f(\theta(\tau)) - M_f(\theta(\tau)) : \sigma(\tau) \right\} \phi'(\theta(\tau)) \tilde{\theta}'(\tau) d\tau
\]
Calibration of Linearized Model

- Assumptions made in model calibration:
  - Isotropic material behavior
  \[ E'(\theta) = \varepsilon' \mathbf{I} = \alpha \Delta \theta \mathbf{I} \]
  - Uniaxial tension
  \[ \sigma_{11} = \sigma(t) \]
  - Compliance tensor, assuming linear elastic behavior, independent of temperature
  \[ M_{11}(\theta) = \frac{1}{E} \]

- Axial component of strain tensor:
  \[
  \bar{\varepsilon}(t) = \left[1 - \phi(\theta(t))\right] \left\{ \alpha_a \Delta \theta(t) + \frac{\sigma(t)}{E_a} \right\} + \phi(\theta(t)) \left\{ \alpha_f \Delta \theta(t) + \frac{\sigma(t)}{E_f} \right\} \\
  + \int_0^t \left\{ \alpha_a \Delta \theta(\tau) - \alpha_f \Delta \theta(\tau) + \frac{\sigma(\tau)}{E_a} - \frac{\sigma(\tau)}{E_f} \right\} \phi'(\theta(\tau)) \tilde{\theta}'(\tau) d\tau
  \]
Calibration of Linearized Model

- **Axial component of strain tensor:**

\[
\bar{\varepsilon}(t) = \left[1 - \phi(\theta(t))\right]\left\{\alpha_a \Delta \theta(t) + \frac{\sigma(t)}{E_a}\right\} + \phi(\theta(t))\left\{\alpha_f \Delta \theta(t) + \frac{\sigma(t)}{E_f}\right\} \\
+ \int_0^t \left\{\alpha_a \Delta \theta(\tau) - \alpha_f \Delta \theta(\tau) + \frac{\sigma(\tau)}{E_a} - \frac{\sigma(\tau)}{E_f}\right\} \phi'(\theta(\tau))\tilde{\theta}'(\tau)d\tau
\]

- **Necessary calibration functions:**
  - Frozen volume fraction \(\phi(\theta)\)
  - Thermal expansion coefficients
    - Active phase
    - Frozen phase
  - Elastic moduli
    - Active phase
    - Frozen phase

\[
\alpha_a = \frac{\varepsilon^t_a(\theta)}{\Delta \theta}, \quad \alpha_f = \frac{\varepsilon^t_f(\theta)}{\Delta \theta} \\
E_a, E_f
\]
Values of Calibration Functions – 10% Extension

- Coefficients of thermal expansion $\alpha_a$ and $\alpha_f$ calculated as slopes of linear regions in initial heating curve.

- Elastic moduli $E_a$ and $E_f$ calculated as slopes of stress-extension curves during loading at high temperature and unloading at low temperature, respectively.
Values of Calibration Functions – 10% Extension

- Frozen volume fraction is not capable of being measured directly.
- \( \phi(\theta) \) is thus assumed to take the shape of the extension recovery during heating \( \varepsilon(\theta) \) at zero load, which is normalized to values from 0 to 1.

Values of all calibration functions

\[
\alpha_a = 5.2 \times 10^{-4} / K \\
\alpha_f = 0.75 \times 10^{-4} / K \\
E_a = 0.33 \text{ MPa} \\
E_f = 1081 \text{ MPa} \\
\phi(\theta) = f(\varepsilon(\theta))
\]
Shape Memory Effect Predictions – 10% Strain

Motivation

Experimental Efforts

Model Background

Small Deformations

Large Deformations

Supplemental
Calibration of Large Deformation Model
Chen and Lagoudas Model – Large Deformations

- Recall the constitutive equation:

\[
\bar{F}(t) = \left[1 - \phi(\theta(t))\right]\hat{F}_a(S(t), \theta(t))
+ \int_0^t \hat{F}_f(S(t), \theta(t))\hat{F}^{-1}_f(S(\tau), \theta(\tau))\hat{F}_a(S(\tau), \theta(\tau))\phi'(\theta(\tau))\bar{\theta}'(\tau) d\tau
\]

- Assume the SMP behaves as a neo-Hookean material in each phase:

\[
S = -pF^{-T} + \mu(\theta)F
\]

\[
det(F) = \nu(\theta)
\]

- Where \(\mu(\theta), \nu(\theta)\) are the shear modulus and volume ratio, \(p\) is the pressure required by the incompressibility condition
Polar and Spectral Decompositions

• Polar decomposition of $F$ and $S$

$$\bar{F} = RU$$
$$S = QT$$

$$\Rightarrow QT = -pRU^{-T} + \mu(\theta)RU$$

• Assume $Q = R$ (stress aligned with deformation)

$$T = -pU^{-T} + \mu(\theta)U$$

• Spectral decomposition of $T$ and $U$

$$T = \sum_{i=1}^{3} s_i e_i \otimes e_i$$

$$s_i = -p\lambda_i^{-1} + \mu(\theta)\lambda_i, \quad i = 1, 2, 3$$

$$U = \sum_{i=1}^{3} \lambda_i e_i \otimes e_i$$

$$\lambda_1\lambda_2\lambda_3 = \nu(\theta)$$
Chen and Lagoudas Model – Uniaxial Tension

• Reducing for uniaxial tension:

\[ s_1 = s(t) \]
\[ s_2 = s_3 = 0 \]

\[ \mu(\theta) \left( \lambda - \frac{\nu(\theta)}{\lambda^2} \right) = s \]
\[ \lambda_1 = \lambda \]
\[ \lambda_2 = \lambda_3 = \sqrt{\frac{\nu(\theta)}{\lambda}} \]

• Let: \( Q = R = I \) (no rotation)

\[ F = RU = \begin{pmatrix} \lambda & 0 & 0 \\ 0 & \sqrt{\frac{\nu(\theta)}{\lambda}} & 0 \\ 0 & 0 & \sqrt{\frac{\nu(\theta)}{\lambda}} \end{pmatrix} \]
Calibration of Large Deformation Model

- Axial component of stretch tensor:

\[
\bar{\lambda}(t) = [1 - \phi(\theta(t))] \lambda_a(s(t), \theta(t)) + \int_0^t \frac{\lambda_f(s(t), \theta(t)) \lambda_a(s(\tau), \theta(\tau))}{\lambda_f(s(\tau), \theta(\tau))} \phi'(\theta(\tau)) \tilde{\theta}'(\tau) d\tau
\]

- Where the axial stretches are defined for each phase through:

\[
\mu_a(\theta)(\lambda_a - \frac{\nu_a(\theta)}{\lambda_a^2}) = s \\
\mu_f(\theta)(\lambda_f - \frac{\nu_f(\theta)}{\lambda_f^2}) = s
\]

- Necessary calibration functions:

- Frozen volume fraction
- Shear moduli
- Volume ratios

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Values of Calibration Functions – Volume Ratios

- Volume ratios \(\nu_a(\theta), \nu_f(\theta)\) assumed to have a value of unity (Poisson’s ratio = 0.5) due to incompressibility condition implied by neo-Hookean assumption (i.e. rubber-like material).

- Consistent with experimental results of a Poisson’s ratio in active phase of 0.5.

- A Poisson’s ratio of 0.4 in the frozen phase was calculated from experimental results, but incompressible assumption maintained for simplicity of model calibration.
Values of Calibration Functions – Shear Moduli

- Assume isotropic material

- Shear moduli related to elastic moduli \((E)\) and Poisson’s ratio \((\nu)\) through:

\[
\mu_a = \frac{E_a}{2(1+\nu_a)}
\]

\[
\mu_f = \frac{E_f}{2(1+\nu_f)}
\]

\[
\nu_a = \nu_f = 0.5
\]
Calibration Functions – Frozen Volume Fraction

- Approach in calibrating frozen volume fraction similar to that in the linearized model.

- $\phi(\theta)$ is recalibrated using the extension recovery from the 25% extension experiment

Values of all calibration functions:

\[ \nu_a = \nu_f = 1 \]
\[ \mu_a = 0.11 \text{ MPa} \]
\[ \mu_f = 360 \text{ MPa} \]
\[ \phi(\theta) = f(\varepsilon(\theta)) \]
SME Predictions – Stretches of 1.25, 1.5, 2.0
Comparison of Predictions – 10% Extension

- Small Def Model Prediction
- Large Def Model Prediction
- Experimental Data

Stress (MPa) vs. Extension (mm/mm) vs. Temperature (°C)
Conclusions and Significance of Work

- Captured complete shape recovery profile for large, uniaxial deformations.

- **Calibrated Chen and Lagoudas constitutive models for:**
  - Small uniaxial deformations (assumed infinitesimal strain)
  - Large uniaxial deformations (assumed neo-Hookean material behavior)

- Model predictions agreed well with experimental results.

- Represents first step toward implementing a finite deformation constitutive model for SMPs in finite element software such as ABAQUS to analyze and/or optimize complicated structures.
Questions?
Supplemental Slides
ThermoMechanical Analyzer (TMA) Results

Heat Rate = 3°C/min

$T_g \approx 60^\circ$C

Motivation Experimental Efforts Model Background Small Deformations Large Deformations Supplemental

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Stress Increase During Cooling

![Graph showing stress increase during cooling](image)

**Motivation**

**Experimental Efforts**

**Model Background**

**Small Deformations**

**Large Deformations**

**Supplemental**

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Stress-Extension At Low Temperature

\[ y = 543.24x - 51.604 \]
Glass Transition

- A polymeric material undergoes glass transition in a temperature range.
- A thermodynamic view: second order phase transition.
- A kinetic view: during cooling, glass phase (frozen phase) nucleates at some sites, and the region of glass phase grow continuously as temperature decreases.
Frozen Volume Fraction

Frozen region function $\Omega_f(\theta)$: Totality of the frozen region at temperature $\theta$.

$$\Omega_f(\theta_1) \subseteq \Omega_f(\theta_2) \quad \text{if} \quad \theta_1 > \theta_2.$$ 

$$\Omega_f(\theta_{\text{high}}) = \emptyset.$$ 

$$\Omega_f(\theta_{\text{low}}) = \Omega.$$ 

Volume fraction of the frozen phase:

$$\phi(\theta) = \frac{1}{V} \int_{\Omega_f(\theta)} dV,$$

$V$ being the volume of the entire body $\Omega$. 
Continuity Requirement

- Assume a material particle freezes at $t = \tau$. The deformation gradient immediately before freezing is:

\[
F(X, \tau-0) = \hat{F}_a (S(X, \tau), \theta(X, \tau))
\]

- Let $\tilde{F}$ be the deformation gradient from the active reference configuration to the frozen reference configuration. The deformation gradient immediately after freezing is then:

\[
F(X, \tau+0) = \hat{F}_f (S(X, \tau), \theta(X, \tau))\tilde{F}
\]

- Enforcing continuity at the time at which freezing occurs:

\[
\hat{F}_a (S(X, \tau), \theta(X, \tau)) = \hat{F}_f (S(X, \tau), \theta(X, \tau))\tilde{F}
\]

\[
\Rightarrow \tilde{F} = \hat{F}_f^{-1}(S(X, \tau), \theta(X, \tau))\hat{F}_a (S(X, \tau), \theta(X, \tau))
\]
Net Cooling History

\( \theta(\tau) \)

\( \tilde{\theta}(\tau) \)
Shape Memory Effect Predictions – 10% Strain

- Model Prediction
- Experimental Data
Shape Memory Effect Predictions – 10% Strain

![Graph showing stress vs. temperature for shape memory effect predictions with experimental data and model predictions.](image-url)
Shape Memory Effect Predictions – 10% Strain

![Temperature vs. Strain Graph](image-url)

- **Temperature (°C)**
- **Strain (mm/mm)**

- **Model Prediction**
- **Experimental Data**
SME Predictions – Stretch of 1.25

Model Prediction

Temperature (°C)

Stress (MPa)

Stretch (mm/mm)
SME Predictions – Stretch of 1.5

![Graph showing stress (MPa) vs. stretch (mm/mm) and temperature (°C). The graph has a model prediction line.](image)

- **Stress (MPa)**: 0.5 to 1.5
- **Stretch (mm/mm)**: 0 to 1.6
- **Temperature (°C)**: 0 to 100

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SME Predictions – Stretch of 2.0

- Stress (MPa)
- Temperature (°C)
- Stretch (mm/mm)
SME Predictions – Stretches of 1.25, 1.5, 2.0

Model Predictions

Stress (MPa) vs. Stretch (mm/mm) graph showing model predictions for stretches.
SME Predictions – Stretches of 1.25, 1.5, 2.0