ABSTRACT

SISKIND, RYAN D. Model Development for Shape Memory Polymers. (Under the direction of Professor Ralph C. Smith).

Shape memory polymers (SMPs) have garnered a considerable amount of attention in recent years due to their flexible, lightweight, and biodegradable nature. At high temperatures, SMPs share attributes with compliant elastomers and exhibit long-range reversibility. In contrast, at low temperatures they become very rigid and are susceptible to plastic, although recoverable, deformations. Their ability to withstand large, nonlinear deformations coupled with their ability to completely recover their original shape is of particular interest for biomedical, aerospace, and automotive applications. Whereas the scope of existing models involving isothermal nonlinear deformations at both high and low temperatures is broad, there is a noted lack of models which specifically deal with the transition process. This process cannot be overlooked as it is the driving factor for all thermomechanical shape memory effects in shape memory polymers.

The scope of this dissertation focusses on the strain storage and release for shape memory polymers as they transition from a rubbery state to a rigid state and back. The proposed homogenized model directly addresses the so-called glass transition process at a macroscopic level using small, linear deformations and is validated against experimental data. The dependence of the glass transition phenomenon on the frozen volume fraction requires the development of a constitutive model based on material properties for the frozen fraction. This is developed in concert with the homogenized model. An industrial application of shape memory polymers in a rod system is proposed, and the accompanying evolution equation is developed and solved numerically using a semi-implicit 2-stage L-stable Rosenbrock method. To admit future implementation of isothermal nonlinear deformations in the homogenized model, existing nonlinear models are summarized.

Model Development for Shape Memory Polymers

by
Ryan David Siskind

A dissertation submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the Degree of
Doctor of Philosophy

Applied Mathematics

Raleigh, North Carolina

2008

APPROVED BY:

Dr. Stefan Seelecke

Dr. Hien Tran

Dr. Ralph C. Smith
Chair of Advisory Committee

Dr. Mansoor Haider

DEDICATION

Dedicated to my family, friends and colleagues; all whom have undoubtedly impacted my academic career.

BIOGRAPHY

Ryan David Siskind is the youngest of Harry and Claudia Siskind's three children. He was born on November 22, 1980 and was raised in Willoughby, Ohio. While attending Willoughby South High School, he discovered his penchant for music and the sciences. After graduating high school in 1999, he attended Youngstown State University with an undeclared major and the desire to explore his musical and scientific talents further. After only one term, it was clear that mathematics came naturally and he declared it his major in early spring. He spent the remaining three-and-a-half years taking as many math classes as possible, exhausting the undergraduate catalog before his senior year.

Ryan earned his bachelors in Mathematics in 2003 and, because he didn't spend enough time thinking about what he was going to do with a degree in mathematics, he decided to pursue his PhD and was accepted at North Carolina State University. It was there that he grew a love for the practical applications of Applied Mathematics and began researching shape memory polymers in the summer of 2006 under the direction of Dr. Ralph Smith.

While at North Carolina State University, he met the love of his life, Anna Hart. She was a fellow graduate student in the Department of Mathematics and they will be married on August 2, 2008.

ACKNOWLEDGMENTS

I cannot begin without expressing the amount of gratitude I have for my adviser, Dr. Ralph C. Smith. I thought he was crazy when he promised I could earn a diploma within two years of starting research under him, but he kept that promise. He had the unenviable job of keeping me on task, encouraging me when I hit the doldrums, and inventing stories to tell my girlfriend about why I would be out of town for no good reason (even though that reason was to ask her parents for permission to marry her). For this and much more, I will be eternally grateful.

I also extend my deepest gratitude to Dr. Mansoor Haider, Dr. Stefan Seelecke, Dr. Kazufumi Ito, and Dr. Hien Tran, all who served in some capacity on my committee.

The faculty and (most importantly) the staff of the Mathematics department are truly top-notch. Whether I was a student, a subordinate, a colleague, or an absolute annoyance, their wisdom and support helped me through hard times; both personal and secretarial.

To my family: Whether you are a Siskind, Pasiechnik, Dingledein, Braund, Hart, Morgan, McDerment, Sweetapple, Pim, Cirnski (and more), you have always been the most important part of my life and will continue to be for the rest of it. Thank you not only for your love and support, but for your time and patience.

To my family members whom I dearly miss, Grampa Honey, Auntie Kris and Grampa Siskind: I know you are watching and guiding me from the cloud tops...I only wish I could see your smiles and feel your hugs one last time.

To all of my friends...there are too many to name, so I will just say one giant thank you. I couldn't have survived the agony of school without your compassion, humor, or livers.

Which brings me to the two loves of my life, Anna and Mc. Owning a dog was the second smartest thing I've ever done. I cannot imagine my life without Mc being there. From pushing me over so he can fit on the couch, to pushing me off the bed, to making me a push-over when he gives me "the face," he's taken the brunt of my neglect and still won't

stop loving me. And I will never stop loving him.

The smartest thing that I've ever done was to ask Anna Kathleen Hart out to dinner. She was in the last place that I thought to look for love but, once I opened my eyes, she was impossible to ignore. Whether it is her insight, patience, or (above all) beauty, she is my zen and has helped me along this journey more than she will ever know. I thank God every day for bringing us together and I cannot wait for the rest of our lives to start together as husband and wife.

TABLE OF CONTENTS

LIST OF TABLES.....	viii
LIST OF FIGURES	ix
1 Introduction.....	1
1.1 SMA shape recovery process	6
1.2 SMP shape recovery process	7
1.3 Comparison of SMPs with SMAs	9
1.4 Modeling Techniques	10
2 A Homogenized Model for Deformations in SMPs	11
2.1 Introduction	11
2.2 Thermal Strain	15
2.3 Polymer Network	16
2.4 Cooling a Polymer Network	18
2.4.1 Homogenized Cooling Thermal Strain	18
2.4.2 Homogenized Cooling Mechanical Strain	19
2.4.3 Homogenized Cooling Stored Strain	20
2.4.4 Homogenized Model for Cooling a Polymer Network	24
2.4.5 Cooling with Constant Strain	24
2.5 Heating a Polymer Network	26
2.5.1 Homogenized Heating Thermal Strain	26
2.5.2 Homogenized Heating Mechanical Strain	27
2.5.3 Homogenized Heating Stored Strain	27
2.5.4 Recovered Strain	29
2.5.5 Homogenized Model for Heating a Polymer Network	32
2.6 Glass Transition Phenomenon	33
2.6.1 Polydispersity	33
2.6.2 Tan δ	35
2.6.3 Modeling tan δ	37
2.7 Thermodynamic Considerations	43
2.8 Model Properties	46
2.8.1 Unconstrained Thermocycle	47
2.8.2 Cooling with Static Applied Force	47
2.8.3 Unconstrained Heating	48
2.8.4 Predicted Thermomechanical Cycle	48
2.9 Thermomechanical Experimental Validation	50
2.9.1 Fully Constrained Cooling	51
2.9.2 Recovery Heating.	54
2.10 Conclusion	57

3	Shape Memory Polymers in a Rod System.....	59
3.1	Introduction	59
3.2	Rod Model Setup	60
3.3	Homogenized SMP Model	62
3.4	Weak Formulation using Constitutive SMP Model	64
3.5	Numerical Methods	65
3.5.1	Gaussian Quadratures	66
3.5.2	Trapezoid methods	66
3.5.3	Rosenbrock-Type Methods	69
3.6	Model Implementation	70
3.6.1	Stability concerns	71
3.6.2	Implementation using Rosenbrock Method	73
3.7	Experimental Procedure	76
3.7.1	Isothermal tension and compression	76
3.7.2	Unconstrained cooling and heating	77
3.7.3	Glass transition	77
3.7.4	Constrained heating.	79
3.8	Homogenized rod model prediction	80
3.8.1	Model Validation	80
3.9	Model Properties	81
3.10	Conclusion	82
4	Models for Large Strain in Polymers.....	84
4.1	Models for Large Strain in Active Polymers	85
4.1.1	Mathematics of a Single Chain	85
4.1.2	Linearization for Small Strains	89
4.2	Network Models	90
4.2.1	3-Chain Model	91
4.2.2	8-Chain Model	91
4.2.3	Model Validation using Tension Tests	92
4.2.4	Full Network Model	96
4.3	Models for Large Strain in Frozen Polymers	99
4.3.1	Intermolecular Resistance to Flow	100
4.3.2	Molecular Alignment	100
4.3.3	Finite Strain Kinematics	101
4.3.4	Phenomenological exponential model	102
5	Conclusion	105
	Bibliography	107

LIST OF TABLES

Table 2.1 Initial and optimized values for a single distribution along with respective errors.....	40
Table 2.2 Initial and optimized values for a Galerkin approximation along with respective errors.....	41
Table 3.1 Nodes and weights for Gauss-Legendre quadrature on the interval $[x_{i-1}, x_1]$..	67

LIST OF FIGURES

Figure 1.1	Photoresponsive crosslinking agent azo-dye	2
Figure 1.2	SMP foam in a compact form	2
Figure 1.3	SMP temperature-dependent modulus	3
Figure 1.4	SMP stent	4
Figure 1.5	SMP suture	5
Figure 1.6	Cornerstone Research Group SMP wing	5
Figure 1.7	Possible SMP space applications	6
Figure 1.8	SMA cellular configurations	7
Figure 1.9	Thermomechanical cycle of a smart materials	7
Figure 1.10	Coexisting frozen and active portions of a polymer	9
Figure 2.1	Typical thermomechanical cycle of a shape memory polymer.	13
Figure 2.2	Thermal strain via curve fitting	15
Figure 2.3	Thermal strain of a single SMP element	16
Figure 2.4	A polymer network composed of N homogenous elements.	17
Figure 2.5	Cooling a single SMP element	21
Figure 2.6	Thermal recovery strain of a single SMP element	30
Figure 2.7	Mechanical recovery strain of a single SMP element	31
Figure 2.8	Total recovery strain of a single SMP element	32
Figure 2.9	Polydispersity relation for polymers	34
Figure 2.10	Tan δ data	36
Figure 2.11	Tan δ data from different rates of temperature change	37

Figure 2.12	Single distribution initial estimate of $\tan \delta$	38
Figure 2.13	Adjusted $\tan \delta$ data	39
Figure 2.14	Approximations of adjusted $\tan \delta$ data	41
Figure 2.15	Decomposed Galerkin approximation of adjusted $\tan \delta$ data	42
Figure 2.16	Frozen fraction during cooling and heating	43
Figure 2.17	$\tan \delta$ approximations with corresponding frozen fractions	44
Figure 2.18	Homogenized model's prediction of thermal strain	48
Figure 2.19	Homogenized model's prediction of constrained cooling	49
Figure 2.20	Homogenized model's prediction of unconstrained heating	49
Figure 2.21	Typical observed thermomechanical cycle	50
Figure 2.22	Liu's thermomechanical experiments	52
Figure 2.23	Isothermal stress-strain relation	53
Figure 2.24	Unconstrained cooling experiment	53
Figure 2.25	Model's prediction of the constrained cooling	54
Figure 2.26	Comparison of Liu's model with the homogenized model	55
Figure 2.27	Model's prediction of unconstrained and constrained heating	56
Figure 2.28	Constrained heating with dynamic α_f	56
Figure 2.29	Liu model prediction of unconstrained and constrained heating	57
Figure 3.1	Space boom	60
Figure 3.2	Rod model structure	60
Figure 3.3	Region of stability for explicit trapezoid method	69
Figure 3.4	Comparing implicit and explicit trapezoid method	73
Figure 3.5	Isothermal stress-strain experiments	77
Figure 3.6	Unconstrained heating experiment	78

Figure 3.7	Tan δ experiments	78
Figure 3.8	Partially constrained recovery	79
Figure 3.9	Model prediction of partially constrained recovery	80
Figure 3.10	Theoretical cooling strain	82
Figure 3.11	Theoretical heating strain	83
Figure 4.1	Single chain based on the assumptions of Kuhn and Gr $\ddot{u}$ n	86
Figure 4.2	Chain orientation for the (a) 3-chain and (b) 8-chain models.	92
Figure 4.3	Uniaxial and Biaxial data collected by Treloar	93
Figure 4.4	Data comparison with the 3-Chain model	95
Figure 4.5	Uniaxial and Biaxial model comparison for 3-Chain model	95
Figure 4.6	Data comparison with the 8-Chain model	96
Figure 4.7	Uniaxial and Biaxial model comparison for 8-Chain model	97
Figure 4.8	Plastic deformation of an SMP under compression	99
Figure 4.9	Model prediction of SMP plastic deformation	103

Chapter 1

Introduction

Shape memory polymers (SMPs) are a class of smart materials that have recently garnered a large amount of interest for their possible use in mechanical systems due to their lightweight, flexible, cost-effective, and highly deformable nature. They are non-metallic in nature and each SMP can be classified by the stimulus which creates a shape memory response.

Photoresponsive and chemoresponsive polymers are materials which change shape due to exposure to light or chemicals respectively. The most basic photoresponsive polymer contains the crosslinking agent azo-dye ($N=N$ group) which gives each crosslink a cis-trans isomerism property [26]. The trans form of the isomer has a molecular length of approximately $9\text{\AA}$ (Figure 1.1(a)) and the cis form of the isomer has a molecular length of approximately $5.5\text{\AA}$ (Figure 1.1(b)). When left unexposed to light, the cis and trans forms coexist. When irradiated with ultraviolet light, the cis form becomes dominant causing the polymer to contract. Upon irradiation with visible light, the trans form is dominant causing the polymer to expand. Figure 1.1 illustrates how utilizing the cis-trans isomerism of the azo-dye crosslinking agent can create displacement in a polymer.

Chemoresponsive polymers contain a reactive pendant group which cause the polymer to dissociate into ions when the pH of the surrounding medium is changed [26]. When crosslinked, these polymer networks comprise a gel or a film which, when submerged in water, changes shape when an acid or alkali is introduced into the water due to the ionic forces created between the polymer chains.

The most common form of shape memory polymer involves the class of polymers which change shape due to temperature-induced shifts in material properties. Polymer

Figure 1.1: The crosslinking agent azo-dye as (a) the trans isomer with a molecular length of 9Å and, (b) the cis isomer with a molecular length of 5.5Å .

foams and gels comprise a group of thermally-induced shape memory polymers which drastically change volume. Some gels can swell or shrink by up to a factor of three [45]. When heated, polymer foams can be compacted into very small volumes relative to their original size and subsequently cooled to retain the compact shape. Upon reheating, the foam will return to its original volume and shape. Figure 1.2 illustrates the ability of a polymer foam developed by Cornerstone Research Group to sustain a considerable decrease in volume. The ability of foams to retain their compact shape illustrates the phenomenon known as glass transition in polymers.

One of the most prominent features shape memory polymers exhibit is a dramatic change in modulus as a result of temperature change. At high temperatures, polymers exist

Figure 1.2: Shape memory polymer foam has the ability to be stored in a compact shape before returning to its original volume through heating. This sample was developed by Cornerstone Research Group (www.crgroup.net).

in a very compliant, malleable state. Conversely at low temperatures, polymers exist in a rigid state. The modulus of the polymer can increase between 100 and 1000 times when cooled and it is due to this change in modulus that deformations, much like the polymer foam's compacted state, can be locked into place when the polymer is cooled. Figure 1.3 shows the modulus of a typical shape memory polymer over a wide temperature range. There are three distinct regions: a high modulus plateau below the glass transition, the glass transition region, and a low modulus plateau above the glass transition. As a point of reference, it is common to describe the glass transition region by a point termed the glass transition temperature T_g which exists somewhere in the transition region (the definition of which varies widely in the literature). Temperatures termed “high” and “low” are always material-dependent based on the glass transition region. A temperature of 273°K (0°C) is considered a high temperature for polyethylene whose glass transition temperature is 168°K but is considered low for polycarbonate whose glass transition temperature is 418°K.

Two types of thermomechanical polymers are of particular interest due to their solid structures; thermoplastic and thermoset polymers. Thermoplastic polymers are solid polymers that possess drastically different properties depending on the operating temperature, but also possess the ability to melt at high temperatures. While in the melted state, the polymer exhibits a cohesive nature due to crosslinking and physical entanglements of polymer chains, is easily remolded into different shapes, and has the ability to be welded

Figure 1.3: Modulus of a shape memory polymer over a temperature range which includes the glass transition region.

with other thermoplastic polymers. Some examples of thermoplastic polymers are polyethylene, polypropylene, poly(methyl methacrylate) (PMMA, more commonly known as Plexiglas), and polycarbonates.

Thermoset polymers, unlike thermoplastics, cannot melt to be remolded or welded with other polymers; however, thermoset polymers tend to be much stronger than thermoplastic polymers. It is this classification of polymer which constitutes the bulk of research conducted for this dissertation. Biomedical applications involving thermoset SMPs already exist due to their biodegradability and their ability to be temporarily stored in a compact shape, implanted with minimally invasive surgery, and subsequently reheated *in vivo* in a controlled process to return to its original shape. Figure 1.4 illustrates how a stent made from a shape memory polymer [49] can be deployed in a compact shape and, through a slow and controlled release, recovers to its original shape. Shape memory polymers can also be implemented as sutures to aid in surgical procedures where working room is at a premium. Figure 1.5 shows how a shape memory polymer wire can be implemented as pre-stretched sutures [30]. After closing a wound, the suture can be slowly heated to contract to its original length and as a result, the wound is closed tighter.

Thermoset shape memory polymers are also being investigated for larger structural purposes. Aerospace industries are investigating the use of shape memory polymers as moldable skin for adaptable wings that can dynamically change their shape in order to optimize the aerodynamic properties of the wing during flight. Military applications involve the compact deployment of large structures such as bridges and drone planes (www.crgrp.com). Figure 1.6 shows how a wing can be compactly stored and subsequently heated to return

Figure 1.4: Proposed configuration for polymer stent deployment [49].

to its original, aerodynamic state. The concept for this wing was developed by Cornerstone Research Group using their high-performance suite of shape memory polymers including the polymer Veriflex, dynamic composite Veritex, and syntactic foam Verilyte.

The weightlessness of space can easily support enormous manmade structures, however the fabrication of such structures is still a terrestrial task. The ability to transport these structures is problematic due to the weight and size. Using shape memory polymers, the feasibility to construct large, lightweight structures that possess the ability to be compacted into small volumes is currently being explored. Deployable systems such as satellite dishes, solar sails, or solar arrays can be folded or rolled into compact sizes for shipment and, once in space, can recover their full size and shape. Figure 1.7(a) illustrates the deployment of a shape memory polymer membrane developed by Cornerstone Research Group. Booms and antennas are also necessary structures for space applications, however their size limits the usefulness of their application. Figure 1.7(b) shows a standard triangular layout for an antenna which can integrate shape memory polymers into its longerons, battens and cross

Figure 1.5: A prestretched suture can be used to loosely close a wound, and when subsequently heated it will return to its original length, tightly closing the wound [30].

Figure 1.6: Compactly stored wing structures can return to their original, rigid shape after heating (Cornerstone Research Group).

Figure 1.7: Possible space applications for shape memory polymers including (a) a membrane for satellites or solar sails (Cornerstone Research Group), and (b) an antenna or boom.

members. Doing so could allow folding and rolling to minimize the volume necessary to transport such a structure.

Before applications of shape memory polymers becomes commonplace, it is necessary to characterize the thermomechanical properties in order to accurately predict how a polymer will respond to stimulus. It is impossible to ignore the correlation between shape memory alloys (SMAs) and shape memory polymers, and with the wealth of information on their thermomechanical behavior, we will begin by summarizing the shape recovery process of SMAs.

1.1 SMA shape recovery process

Shape memory alloys are smart materials that are metallic in nature and whose shape recovery processes are enthalpy driven. The behavior of shape memory alloys is dictated by transformations from a high symmetry austenite phase to lower symmetry martensite phases. Figure 1.8 illustrates these cellular configurations.

The typical shape recovery process shown in Figure 1.9(a) [39] begins at a temperature above the transition temperature, T_{tr} . In this state, the austenite cellular configuration is dominant and stable. The alloy is then cooled below T_{tr} . During the cooling process, the austenite configuration becomes unstable (this happens around T_{tr}) and the cellular configuration transitions to twinned martensite.

Figure 1.8: (a) Austenite, (b) twinned martensite and (c) detwinned martensite cellular configurations of a shape memory alloy.

Figure 1.9: Comparison of thermomechanical cycles for (a) shape memory alloys [39] and (b) shape memory polymers [31].

Once the alloy is below T_{tr} , it is deformed with an applied stress (or strain). This applied deformation causes a strain (or stress) on the alloy which grows linearly until a critical stress is reached at which point the twinned martensite transitions to the detwinned martensite cell configuration. After the transition to the detwinned state, the applied deformation is released but a residual strain remains because of the detwinned martensite cellular configuration. In the final step of the shape recovery process, the alloy is heated above T_{tr} at which point the martensite configuration returns to the stable austenite configuration.

1.2 SMP shape recovery process

The shape memory effect of shape memory polymers is highly affected by its microstructure created during synthesis. Some factors include entanglement of polymer

chains, cross-linking, crystallization and the formation of domain structures. These inherent physical interactions give each SMP unique properties but, due to their polymeric nature, the overall shape recovery process is similar. When a deformation is applied to a polymer, the molecular chains move to accommodate the new configuration. Because the deformation creates an ordered motion of molecules, the number of possible configurations a single chain can attain decreases. The result is a decrease in configurational entropy and the force in the chain is not caused by a change in energy, but a change in entropy. Because of this distinction, shape memory polymers are considered to be entropy driven.

The typical shape recovery process for small deformations, shown in Figure 1.9(b), begins at a temperature above the glass transition temperature, T_g . At this temperature, the polymer is in a rubbery elastic (active) state. The polymer is then deformed with an applied stress (or strain) which creates a strain (or stress) in the polymer.

Once the polymer is deformed, it is cooled below T_g at which point the active polymer becomes inelastic (frozen or glassy). The applied deformation is removed; however, the polymer does not return to its original configuration because a portion of the deformation becomes “locked” in place below T_g . The resulting deformation creates a residual strain which remains present until the shape recovery process is completed when the polymer is heated above T_g .

It is important to note that polymers at low deformation levels (compared to what they are capable of sustaining) exhibit a fully recoverable linear elastic behavior. If an undeformed polymer is cooled below T_g and then stressed, it will return to its previous undeformed state upon removal of the stress. The yield in SMAs as a result of cellular reconfiguration (illustrated in part 2 of Figure 1.9(a)) does not occur in SMPs until molecular reconfiguration is achieved. Typically this does not happen until a strain of 20% or more is applied.

While the shape recovery process of shape memory alloys is a result of different cellular configurations in which they can exist, the recovery in SMP is governed by the transition from an active state to a frozen state (and back again). It is widely accepted that both the active and frozen states can coexist during the glass transition process resulting in a temperature range, rather than a point, where a polymer’s properties transition. This is illustrated in Figure 1.3 where the modulus of the polymer transitions for almost 30° before stabilizing. Figure 1.10 illustrates a representative volume that contains both frozen and active parts of the polymer.

Figure 1.10: Coexisting frozen and active portions of a polymer [31].

1.3 Comparison of SMPs with SMAs

Shape memory alloys are widely used and known to have large recovery pressures (as much as 500 MPa). When thermomechanically driven, they are able to conduct heat very well. They are also able to dissipate energy effectively when going through the shape recovery process. However, SMAs are only able to recover from deformations up to 10%, above which plastic deformation with unrecoverable shape change can occur. Also, they are subject to internal heating and metal fatigue, both of which degrade the reliability of SMAs.

On the other hand, SMPs can recover from deformations well over 100% and can go through a high number of repetitions without any significant material degradation. Below T_g , SMPs do sustain plastic deformations; however, these deformations are fully recoverable through stress relaxation or stress annihilation by heating above T_g [19]. Unlike alloys, polymers are unable to conduct heat well, disallowing fast thermomechanical cycles. The recovery pressure of SMPs is several orders of magnitude below that of SMAs (around 1-3 MPa) when transitioned through a thermomechanical cycle. These two features can be compensated for by including carbon fiber reinforcement which increases both thermal conductivity and recovery pressure; however, the research for this thesis does not explore polymer inclusions.

1.4 Modeling Techniques

Currently, the thermomechanical modeling of shape memory polymers can be classified into four categories: isothermal nonlinear plastic deformations for large strains at temperatures below T_g , isothermal nonlinear elastic deformations for large strains at temperatures above T_g , the strain storage process of linear deformations which bridge the glass transition gap, and the strain storage process of nonlinear deformations which bridge the glass transition gap.

Due to their ability to fully recover from large deformations, a considerable amount of research has been conducted on large strain, isothermal deformations in shape memory polymers. Applications which involve folding or rolling polymers requires strains above 20%, well within the nonlinear range of deformations; however, the amount of research involving the strain storage and recovery characteristics is notably lacking. The glass transition process is not well understood and, as a result, quantifying how a deformation is locked into place is difficult. In the following chapters, we explore these and other open questions regarding the thermomechanical shape recovery process of shape memory polymers.

A homogenized constitutive model is developed for the thermomechanical shape recovery process in Chapter 2. We restrict the model development to small, linear stress-strain relations; however, noting that large, nonlinear stress-strain relations can be applied in a similar manner. Accompanying the homogenized model is a phenomenological model to quantify the glass transition in Section 2.6. Chapter 3 uses the homogenized model to develop a model which quantifies the one-dimensional displacement of a polymer rod mechanical system. Data collected by C. Yakacki is used to verify the model's accuracy and possible, untested applications are presented. Chapter 4 identifies isothermal models for large deformations which can be implemented into the homogenized model in future work.

Chapter 2

A Homogenized Model for Temperature-induced Deformations in Shape Memory Polymers

2.1 Introduction

Whereas the research involving shape memory polymers (SMPs) is less mature than that of shape memory alloys (SMAs), the proposed uses for these materials demonstrate significant potential. Polymer medical sutures that are stretched and locked in an elongated state utilize a temperature-controlled release to return to their original length [30]. If this recovery process is implemented after the suture is used to close a skin laceration, a tighter stitch is possible. Polymer sutures can also be used where the parent shape is a loose knot [30]. Locking the suture in a straightened state prior to use allows for wound closure in tight areas where tying a finishing knot is difficult or impossible. Once the suture is made, again through a temperature-controlled release, the free end wraps around itself into a loose knot.

Morphing wing structures have long been an aeronautical area of research. Optimal wing characteristics shift from a triangular shape at low speeds to a cigar shape at high speeds. Whereas the internal components need to be a very rigid material, the skin of the

each wing needs to be a very pliable yet rigid material and SMPs exhibit both characteristics when transformed through different temperature regimes.

Space systems necessarily need to utilize smart materials due to their immense size once fully operational. The lightweight, flexible, cost effective, and highly deformable nature of SMPs make them a leading candidate in the development of space systems[45]. For example, deployable antenna booms with rigid battens can be constructed with SMP joints. These joints can be bent prior to deployment in order to minimize the fully assembled volume necessary for transport. Once in space, the polymer joints are returned to their parent shape, allowing the antenna to reach its fully deployed shape.

The scope of models that focus directly on temperature-induced deformations is much smaller than their isothermal counterparts. Several existing phenomenological models define the total strain ε as the sum of the thermal, mechanical and stored strains, respectively denoted by ε_T , ε_m and ε_s , so that

$$\varepsilon = \varepsilon_T + \varepsilon_m + \varepsilon_s. \quad (2.1)$$

It is the constitutive definitions of these strains that are addressed. A typical thermomechanical cycle for a shape memory polymer is shown in Figure 2.1. Beginning at a high temperature where the polymer exhibits rubbery elastic properties, the polymer is deformed (1). Once a desired deformation is achieved, it is held constant while the temperature is decreased. As the temperature decreases, the modulus of the polymer markedly increases (between two and three orders of magnitude) and the polymer becomes rigid. Once the entire polymer has reached a low temperature, the deformation is released and a fixed deformation is observed as a result of the increased modulus (3). The polymer is then heated to the original high temperature, releasing the fixed deformation and allowing the polymer to return to its original shape (4).

The recent model developed by Liu et al. [31, 32] is a three-dimensional phenomenological model that is based on experimental observations in combination with molecular interactions and distinctly divides the polymer into frozen and active volumes, both of which can occur simultaneously. The frozen and active volume fractions are quantified as ϕ_f and ϕ_a , respectively, where $\phi_f + \phi_a = 1$. The thermal and mechanical strains are quantified via the law of mixtures, and the stored strain is given as the solution to a differential equation.

Figure 2.1: Typical thermomechanical cycle of a shape memory polymer.

Therefore, the model defined by Liu is given as

$$\begin{aligned}
 \varepsilon_T(T) &= (1 - \phi_f(T))\varepsilon_T^a(T) + \phi_f(T)\varepsilon_T^f(T), \\
 \varepsilon_m(T, \sigma) &= (1 - \phi_f(T))\varepsilon_m^a(T, \sigma) + \phi_f(T)\varepsilon_m^f(T, \sigma), \\
 \frac{d\varepsilon_s}{dT}(T, \sigma) &= \frac{Y(T)}{Y_a(T)}(\varepsilon - \varepsilon_s(T, \sigma) - \varepsilon_T(T))\frac{d\phi_f}{dT}(T)(T), \\
 \varepsilon_s(T_0) &= 0,
 \end{aligned}$$

where T is the absolute temperature, ε is the constant strain during cooling, and $Y(T)$ and $Y_a(T)$ are the temperature-dependent moduli of the bulk polymer and active portion of the bulk polymer respectively. The internal state variable $\phi_f(T)$ defines the frozen fraction and is essential in the strain storage process.

More recently, Chen and Lagoudas [10, 11] have developed a three-dimensional model for large deformations, defining the deformation gradient for the active and frozen states independently, but ensuring that the total deformation gradient remains continuous throughout the thermomechanical process. The deformation gradient is then used to define the infinitesimal strain tensor, and assuming a uniaxial deformation the one-dimensional

model is given as

$$\begin{aligned}
\varepsilon_T(T(t)) &= [1 - \phi_f(T(t))] \varepsilon_T^a(T(t)) + \phi_f(T(t)) \varepsilon_T^f(T(t)) \\
&\quad + \int_{T_0}^{T(t)} (\varepsilon_T^a(\theta) - \varepsilon_T^f(\theta)) \phi_f'(\theta) d\theta, \\
\varepsilon_m(T(t)) &= \left(\frac{1 - \phi_f(T(t))}{Y_a(T(t))} - \frac{\phi_f(T(t))}{Y_f(T(t))} \right) \sigma(t), \\
\varepsilon_s(T(t)) &= \int_0^t \left(\frac{1}{Y_a(T(\tau))} - \frac{1}{Y_f(T(\tau))} \right) \sigma(\tau) \frac{d\phi_f}{dT}(T(\tau)) \tilde{T}'(\tau) d\tau,
\end{aligned}$$

where T is the absolute temperature, ε_T^a and ε_T^f are the respective thermal strains of the active and frozen volumes, Y_a and Y_f are the respective moduli of the active and frozen volumes, ϕ_f is the frozen volume fraction, and $\tilde{T}'$ is the change in the temperature history with respect to time (see [10] for details).

The Chen-Lagoudas model is similar to the Liu model and differences can be attributed to Liu's simplification of part of the freezing processes. Whereas these models predict the overall thermomechanics of a shape memory polymer's shape recovery process, both models rely on curve fitting to define several of their key elements. Because the glass transition does not necessarily overlap during cooling and heating [34], the process of strain storage and release may exhibit some hysteresis. Underlying physical properties, including strain relaxation and shifts in the glass transition due to pressure, are nominalized when curve fitting is applied universally. The goal of defining a model that relies on data strictly for parameter estimation and model calibration is the basis of this chapter.

In Section 2.2, an illustrative example is offered to describe a key feature of the polymer freezing process. The homogenization principles that will be used throughout the model development are described in Section 2.3. Because the strain storage process only occurs during cooling, it stands to reason that the cooling and heating processes need to be defined independently. In Sections 2.4 and 2.5, we develop the constitutive equations for the cooling and heating processes, respectively. A method of defining the internal state variable $\phi_f(T)$ is proposed in Section 2.6 which is the preferred method for this paper. For completeness, thermodynamic considerations are presented in Section 2.7 where it is shown the proposed model satisfies the second law of thermodynamics. Finally, in Sections 2.8 and 2.9, we provide model capabilities with illustrative examples and validation results where it is shown the homogenized model qualitatively and quantitatively agrees with the data. Any qualitative error is discussed in detail.

2.2 Thermal Strain

The total thermal strain ε_T is constitutively defined in [32] as

$$\varepsilon_T(T) = (1 - \phi_f(T))\varepsilon_T^a(T) + \phi_f(T)\varepsilon_T^f(T) = \int_{T_0}^T [(1 - \phi_f(\theta))\alpha_a(\theta) + \phi_f(\theta)\alpha_f(\theta)] d\theta.$$

An unconstrained cooling experiment was conducted where it was assumed the sole internal straining mechanism was thermal strain. This led to a simplified definition of thermal strain

$$\varepsilon_T = \int_{T_0}^T \alpha(\theta) d\theta,$$

where the thermal expansion was found via curve fitting to have the functional relation

$$\alpha(T) = -3.16 \times 10^{-4} + 1.42 \times 10^{-6}T$$

as shown in Figure 2.2. This relation, however, does not take into account the storage process which occurs upon cooling through the glass transition.

To illustrate, consider a single polymer element with total strain as given in (2.1) which is being cooled with no externally applied forces (thus $\varepsilon_m = \varepsilon_m^a = \varepsilon_m^f = 0$) as shown in Figure 2.3(a). The single polymer element is defined to have a glass transition point at T_g so that $\phi_f = 1$ for $T < T_g$ and $\phi_f = 0$ for $T > T_g$. The element begins in a reference configuration (I) at the reference temperature T_r . As thermal strain is created by

Figure 2.2: Thermal strain obtained via curve fitting for an unconstrained cooling experiment [31].

Figure 2.3: A single homogenous polymer element during a cooling process showing the deformation due to thermal strain given (a) at discrete values of T and (b) for continuous values of T .

the decreasing temperature, the polymer contracts (II) and the strain is $\epsilon = \epsilon_T^a$. At $T = T_g$ (III) the evolution of ϵ_T^a halts since this is the lowest temperature for which the polymer is active. At a temperature $T = T_g - \Delta T$, (2.1) simplifies to $\epsilon = \epsilon_T^f + \epsilon_s$; however, the thermal strain ϵ_T^a created while in the active phase is not lost. It is instantaneously frozen as stored strain ϵ_s at the glass transition point and the thermal strain, defined as $\epsilon_T = \epsilon_T^f$ when $T < T_g$, is again zero at $T = T_g - \Delta T$. While the temperature continues to decrease (IV), the stored strain remains constant as the frozen thermal strain develops.

Figure 2.3(b) shows the continuous temperature-induced response for the single homogenous polymer element during a cooling cycle. As previously argued, the thermal strain develops in both the active and frozen states; however the thermal strain instantaneously returns to zero at the glass transition point. The thermal strain that is ‘lost’ is locked into place in the stored strain allowing a continuous deformation. If each polymer network is considered to be the sum of polymer elements, each with unique properties, the entire network deformation can be considered the average of the elemental deformation.

2.3 Polymer Network

Consider a polymer network of size ℓ with N polymer elements of size ℓ_i , where $i = 1, \dots, N$ so that $\sum \ell_i = \ell$ shown in Figure 2.4. Each element i has a (possibly) unique

Figure 2.4: A polymer network composed of N homogenous elements.

glass transition point T_{g_i} with the elemental frozen fraction defined as

$$\phi_{f_i}(T) = \begin{cases} 0 & \text{when } T \geq T_{g_i}, \\ 1 & \text{when } T < T_{g_i}. \end{cases}$$

The weighted average of these ϕ_{f_i} defines the total frozen fraction of the polymer network so that

$$\phi_f = \sum_{i=1}^N \phi_{f_i} \frac{\ell_i}{\ell}. \quad (2.2)$$

The strain value of each element ε_i is unique in its description since it pertains to the deformation of the specific element. These strain values are defined as

$$\varepsilon = \frac{\Delta \ell}{\ell}, \quad \varepsilon_1 = \frac{\Delta \ell_1}{\ell_1}, \dots, \quad \varepsilon_N = \frac{\Delta \ell_N}{\ell_N}.$$

To consider each element's strain contribution to the overall network (i.e., $\Delta \ell_i / \ell$), we note that the total strain can be expressed as

$$\varepsilon = \sum_{i=1}^N \varepsilon_i \frac{\ell_i}{\ell}. \quad (2.3)$$

Since ε_i denotes the local strain, then

$$\varepsilon_i \frac{\ell_i}{\ell} = \frac{\Delta \ell_i}{\ell_i} \frac{\ell_i}{\ell} = \frac{\Delta \ell_i}{\ell}$$

designates how the locally generated strain affects the entire network. This interpretation of strain can be extended to any type of strain generated during a thermomechanical cycle of a shape memory polymer.

An important observation regarding the transition of thermal strain between the active and frozen states has its basis in the reference configuration of the polymer at reference temperature T_r . Previous work in [31], [32], [10] and [11] assume that $T_r > T_g$ since a shape memory polymer is typically considered in the reference configuration at a temperature well above T_g . This convention does not hold for $T_r < T_g$ since the reference configuration is considered to have no applied deformation and to contain zero stored strain.

Since it is assumed that all active thermal strain is completely stored at the glass transition point, it is not possible to have zero stored strain at a reference temperature below the glass transition point. Also, the frozen and active thermal strains are always considered to be continuous while the total thermal strain is not necessarily continuous.

2.4 Cooling a Polymer Network

To indicate the cooling portion of a thermomechanical cycle, all strain values, glass transition temperatures, and frozen fractions occurring during cooling will be denoted with a '-' in the exponent.

2.4.1 Homogenized Cooling Thermal Strain

Consider the thermal strains generated during a cooling cycle along with the previously defined convention that thermal strain is stored at the glass transition point. The active and frozen thermal strains of the entire network, as previously defined in (2.3), are given respectively as

$$\begin{aligned}\varepsilon_T^{a-} &= \sum_{i=1}^N \varepsilon_{T_i}^{a-} \frac{\ell_i}{\ell}, \\ \varepsilon_T^{f-} &= \sum_{i=1}^N \varepsilon_{T_i}^{f-} \frac{\ell_i}{\ell}.\end{aligned}\tag{2.4}$$

Assuming a heterogeneous polymer, it can be assumed that the thermal expansion coefficients $\alpha_f(\theta)$ and $\alpha_a(\theta)$ are equivalent throughout the network and thus each element's thermal strain can be defined as

$$\varepsilon_{T_i}^- = \int_{T_{g_i}^-}^T \alpha(\theta) d\theta.$$

To unify the notation for each element in the network, and considering the fact that the network will be uniformly thermally activated, the active and stored thermal strains can be respectively defined as

$$\begin{aligned}\varepsilon_{T_i}^{a-}(T) &= \int_{T_{g_i}^-}^T \alpha_a(\theta) d\theta = \int_{T_0}^T \alpha_a(\theta)(1 - \phi_{f_i}^-(\theta)) d\theta, \\ \varepsilon_{T_i}^{f-}(T) &= \int_{T_{g_i}^-}^T \alpha_f(\theta) d\theta = \int_{T_0}^T \alpha_f(\theta)\phi_{f_i}^-(\theta) d\theta.\end{aligned}$$

Considering only the active thermal strains (however, the similar treatment can be applied to the frozen thermal strains), (2.4) can be rewritten as

$$\begin{aligned}\varepsilon_T^{a-} &= \sum_{i=1}^N \int_{T_0}^T \alpha_a(\theta) (1 - \phi_{f_i}^-(\theta)) d\theta \frac{\ell_i}{\ell} \\ &= \int_{T_0}^T \alpha_a(\theta) \left[\sum_{i=1}^N (1 - \phi_{f_i}^-(\theta)) \frac{\ell_i}{\ell} \right] d\theta.\end{aligned}\tag{2.5}$$

Examination of the bracketed term in (2.5) reveals that it represents the active volume fraction of the entire network and can be rewritten as such. Therefore, (2.5) simplifies to

$$\varepsilon_T^{a-}(T) = \int_{T_0}^T \alpha_a(\theta) (1 - \phi_f^-(\theta)) d\theta.\tag{2.6}$$

Equation (2.6), along with the frozen thermal strain treated in the same manner, combine via (2.1) to define the total thermal strain of the polymer network as

$$\begin{aligned}\varepsilon_T^-(T) &= (1 - \phi_f^-(T)) \varepsilon_T^{a-} + \phi_f^-(T) \varepsilon_T^{f-} \\ &= (1 - \phi_f^-(T)) \int_{T_0}^T \alpha_a(\theta) (1 - \phi_f^-(\theta)) d\theta + \phi_f^-(T) \int_{T_0}^T \alpha_f(\theta) \phi_f^-(\theta) d\theta.\end{aligned}$$

2.4.2 Homogenized Cooling Mechanical Strain

Mechanical strain, as defined in [32] and [11], is

$$\varepsilon_m^-(T, \sigma) = (1 - \phi_f(T)) \varepsilon_m^a(T, \sigma) + \phi_f(T) \varepsilon_m^f(T, \sigma).$$

It is here that the overall stress-strain relationship is defined. In a general sense, it can be stated that $\sigma = F(T, \varepsilon_m)$ where F is the standard linear or nonlinear and (possibly) non-invertible stress relation determined by the operating temperature T and the applied mechanical stress ε_m . Since the basis of this chapter relies on a polymer network reacting in a linear-elastic manner due to relatively small values of strain, the mechanical strain acting on each polymer element can be defined via Hooke's Law as

$$\begin{aligned}\varepsilon_{m_i}^{a-}(T, \sigma) &= \frac{\sigma}{Y_a(T)} \\ \varepsilon_{m_i}^{f-}(T, \sigma) &= \frac{\sigma}{Y_f(T)}\end{aligned}$$

where Y_a and Y_f are the active and frozen moduli of the polymer respectively. Applying (2.3), the mechanical strains are given by

$$\begin{aligned}\varepsilon_m^{a-}(T, \sigma) &= \sum_{i=1}^N \frac{\sigma}{Y_a(T)} \frac{\ell_i}{\ell} = \frac{\sigma}{Y_a(T)} \\ \varepsilon_m^{f-}(T, \sigma) &= \sum_{i=1}^N \frac{\sigma}{Y_f(T)} \frac{\ell_i}{\ell} = \frac{\sigma}{Y_f(T)},\end{aligned}$$

and the total mechanical strain during cooling is

$$\varepsilon_m^-(T, \sigma) = \left(\frac{1 - \phi_f^-(T)}{Y_a(T)} + \frac{\phi_f(T)^-}{Y_f(T)} \right) \sigma.$$

2.4.3 Homogenized Cooling Stored Strain

Consider the cooling portion of a thermomechanical cycle on a single element as depicted in Figure 2.5. Beginning with the element in its reference configuration at reference temperature T_r (I), a force is applied (II). The only strain present is the mechanical strain caused by the applied force, $\varepsilon_m^a(T, \sigma)$. As the element cools towards its glass transition temperature (III), an active thermal strain develops and the strain is

$$\varepsilon(T, \sigma) = \varepsilon_m^a(T, \sigma) + \varepsilon_T^a(T).$$

At $T = T_g$, (IV), the polymer has a total strain of

$$\varepsilon(T_g, \sigma) = \varepsilon_m^a(T_g, \sigma) + \varepsilon_T^a(T_g);$$

however, this amount of strain is not the total strain that is stored during cooling. To properly identify the stored strain, the applied load σ must be removed. This causes the element to “spring-back” towards its original configuration, but its magnitude is exactly equal to the magnitude of the frozen mechanical strain $\varepsilon_m^f(T_g, \sigma)$. Therefore, the stored strain can be defined as

$$\varepsilon_s(T_g, \sigma) = \varepsilon_T^a(T_g) + \varepsilon_m^a(T_g, \sigma) - \varepsilon_m^f(T_g, \sigma).$$

In the manner that thermal strain is defined here during a cooling cycle, the frozen strain will always equal zero at the glass transition point. However, for symmetry and for comparative purposes with the stored strain developed in [11], the stored strain can be defined without loss of generality as

$$\varepsilon_s^-(T_g^-, \sigma) = \varepsilon_T^{a-}(T_g^-) - \varepsilon_T^{f-}(T_g^-) + \varepsilon_m^{a-}(T_g^-, \sigma) - \varepsilon_m^{f-}(T_g^-, \sigma). \quad (2.7)$$

Figure 2.5: Cooling portion of a thermomechanical cycle with both a compressive and tensile force

To evaluate the network stored strain properly, consider (2.7) to be the elemental stored strain, $\varepsilon_{s_i}^-(T_g^-, \sigma)$. To admit the possibility of a hysteretic glass transition (as is experimentally observed), as well as to differentiate between the cooling and heating portions of the thermomechanical cycle, the glass transition point for strain storage will be denoted T_g^- .

The network active thermal strain, frozen thermal strain, active mechanical strain, and frozen mechanical strain need to be found independent of one another. Applying (2.3) yields

$$\begin{aligned}\varepsilon_T^{a-}(T; T_g^-) &= \sum_{i=1}^N \varepsilon_{T_i}^{a-}(T_{g_i}^-) \frac{\ell_i}{\ell} = \sum_{i=1}^N \int_{T_0}^T \varepsilon_{T_i}^{a-}(\theta) \delta(T_{g_i}^- - \theta) d\theta \frac{\ell_i}{\ell}, \\ \varepsilon_T^{f-}(T; T_g^-) &= \sum_{i=1}^N \varepsilon_{T_i}^{f-}(T_{g_i}^-) \frac{\ell_i}{\ell} = \sum_{i=1}^N \int_{T_0}^T \varepsilon_{T_i}^{f-}(\theta) \delta(T_{g_i}^- - \theta) d\theta \frac{\ell_i}{\ell},\end{aligned}\tag{2.8}$$

for the stored thermal strain and

$$\begin{aligned}\varepsilon_m^{a-}(T, \sigma; T_g^-) &= \sum_{i=1}^N \varepsilon_{m_i}^{a-}(T_{g_i}^-, \sigma) \frac{\ell_i}{\ell} = \sum_{i=1}^N \int_{T_0}^T \varepsilon_{m_i}^{a-}(\theta, \sigma) \delta(T_{g_i}^- - \theta) d\theta \frac{\ell_i}{\ell}, \\ \varepsilon_m^{f-}(T, \sigma; T_g^-) &= \sum_{i=1}^N \varepsilon_{m_i}^{f-}(T_{g_i}^-, \sigma) \frac{\ell_i}{\ell} = \sum_{i=1}^N \int_{T_0}^T \varepsilon_{m_i}^{f-}(\theta, \sigma) \delta(T_{g_i}^- - \theta) d\theta \frac{\ell_i}{\ell}.\end{aligned}\tag{2.9}$$

for the stored mechanical strain. Note that the definitions for the thermal and mechanical strains at the glass transition point T_g^- are unequal to their generalized counterparts

(i.e., $\varepsilon_T^a(T) \neq \varepsilon_T^a(T; T_g^-)$, $\varepsilon_T^f(T) \neq \varepsilon_T^f(T; T_g^-)$, $\varepsilon_m^a(T, \sigma) \neq \varepsilon_m^a(T, \sigma; T_g^-)$, and $\varepsilon_m^f(T, \sigma) \neq \varepsilon_m^f(T, \sigma; T_g^-)$); however naming them in a comparable fashion is intentional to demonstrate both their similarities and differences. Recall the definition of $\phi_{f_i}(T)H(T_{g_i}^- - T)$ where H is the heaviside function. The proper definition of the derivative would then be

$$\phi'_{f_i}(T) = \delta(T_{g_i}^- - T).$$

Therefore, (2.8) can be rewritten as

$$\varepsilon_T^{a-}(T; T_g^-) = \sum_{i=1}^N \int_{T_0}^T \varepsilon_{T_i}^{a-}(\theta) \frac{d\phi_{f_i}^-}{dT}(\theta) d\theta \frac{\ell_i}{\ell} \quad (2.10a)$$

$$\begin{aligned} &= \int_{T_0}^T \sum_{i=1}^N \left(\left[\int_{T_0}^{\theta} \alpha_a(\theta)(1 - \phi_{f_i}^-(\tau)) d\tau \right] \frac{d\phi_{f_i}^-}{dT}(\theta) \frac{\ell_i}{\ell} \right) d\theta \\ \varepsilon_T^{f-}(T; T_g^-) &= \sum_{i=1}^N \int_{T_0}^T \varepsilon_{T_i}^{f-}(\theta) \frac{d\phi_{f_i}^-}{dT}(\theta) d\theta \frac{\ell_i}{\ell} \quad (2.10b) \\ &= \int_{T_0}^T \sum_{i=1}^N \left(\left[\int_{T_0}^{\theta} \alpha_f(\theta)\phi_{f_i}^-(\tau) d\tau \right] \frac{d\phi_{f_i}^-}{dT}(\theta) \frac{\ell_i}{\ell} \right) d\theta \end{aligned}$$

and (2.9) can be rewritten as

$$\begin{aligned} \varepsilon_m^{a-}(T, \sigma; T_g^-) &= \sum_{i=1}^N \int_{T_0}^T \varepsilon_{m_i}^{a-}(\theta, \sigma) \frac{d\phi_{f_i}^-}{dT}(\theta) d\theta \frac{\ell_i}{\ell} \quad (2.11a) \\ &= \int_{T_0}^T \frac{\sigma}{Y_a(\theta)} \sum_{i=1}^N \left(\frac{d\phi_{f_i}^-}{dT}(\theta) \frac{\ell_i}{\ell} \right) d\theta \end{aligned}$$

$$\begin{aligned} \varepsilon_m^{f-}(T, \sigma; T_g^-) &= \sum_{i=1}^N \int_{T_0}^T \varepsilon_{m_i}^{f-}(\theta, \sigma) \frac{d\phi_{f_i}^-}{dT}(\theta) d\theta \frac{\ell_i}{\ell} \quad (2.11b) \\ &= \int_{T_0}^T \frac{\sigma}{Y_f(\theta)} \sum_{i=1}^N \left(\frac{d\phi_{f_i}^-}{dT}(\theta) \frac{\ell_i}{\ell} \right) d\theta. \end{aligned}$$

The formula for the active thermal strain at the glass transition can be simplified through integration by parts. Doing so for (2.10a) yields

$$\begin{aligned} \varepsilon_T^{a-}(T; T_g^-) &= \sum_{i=1}^N \int_{T_0}^T \left(\left[\int_{T_0}^{\theta} \alpha_a(\theta)(1 - \phi_{f_i}^-(\tau)) d\tau \right] \frac{d\phi_{f_i}^-}{dT}(\theta) \right) d\theta \frac{\ell_i}{\ell} \\ &= \sum_{i=1}^N \left[\int_{T_0}^{\theta} \alpha_a(\theta)(1 - \phi_{f_i}^-(\tau)) d\tau \phi_{f_i}^-(\theta) \right]_{\theta=T_0}^T - \int_{T_0}^T \alpha_a(\theta)(1 - \phi_{f_i}^-(\theta)) \phi_{f_i}^-(\theta) d\theta \frac{\ell_i}{\ell}. \end{aligned}$$

As is evident, the second term in the sum is exactly zero since, for each polymer element, either $\phi_{f_i}(T) = 0$ or $(1 - \phi_{f_i}(T)) = 0$ for all T . The first term is evaluated at both $\theta = T_0$ and $\theta = T$. Since T_0 is the reference temperature at which the polymer is completely active (i.e., $\phi_{f_i}^- = 0$ for all i), what remains is

$$\varepsilon_T^{a-}(T; T_g^-) = \sum_{i=1}^N \left[\int_{T_0}^T \alpha_a(\theta) (1 - \phi_{f_i}^-(\theta)) d\theta \phi_{f_i}^-(T) \frac{\ell_i}{\ell} \right] = \sum_{i=1}^N \varepsilon_{T_i}^{a-}(T) \frac{\ell_i}{\ell} \phi_{f_i}^-(T). \quad (2.12a)$$

It is clear from this form of the active thermal strain at the glass transition that, during the storing process, only the accumulated active thermal strains from the elements which are frozen at temperature T are included in the summation (via the term $\phi_{f_i}^-(T)$), which agrees with the theoretical storage process. Further analysis of (2.12a) reveals that it is the weighted sum of each elements active thermal strain that is fully frozen at temperature T , which is equivalent to

$$\varepsilon_T^{a-}(T; T_g^-) = \sum_{i=1}^N \varepsilon_{T_i}^{a-}(T) \frac{\ell_i}{\ell} \phi_{f_i}^-(T) = \varepsilon_T^{a-}(T) \phi_f^-(T). \quad (2.12b)$$

The frozen thermal strain can be simplified in a similar manner via integration by parts. Doing so to (2.10b) yields

$$\begin{aligned} \varepsilon_T^{f-}(T; T_g^-) &= \sum_{i=1}^N \int_{T_0}^T \left(\left[\int_{T_0}^{\theta} \alpha_f(\theta) \phi_{f_i}^-(\tau) d\tau \right] \frac{d\phi_{f_i}^-(\theta)}{dT} \right) d\theta \frac{\ell_i}{\ell} \\ &= \sum_{i=1}^N \left[\int_{T_0}^{\theta} \alpha_f(\theta) \phi_{f_i}^-(\tau) d\tau \phi_{f_i}^-(\theta) \right]_{\theta=T_0}^T - \int_{T_0}^T \alpha_f(\theta) \phi_{f_i}^-(\theta) \phi_{f_i}^-(\theta) d\theta \frac{\ell_i}{\ell}. \end{aligned}$$

The first term is evaluated at both $\theta = T_0$ and $\theta = T$. Since T_0 is the reference temperature at which the polymer is completely active (i.e., $\phi_{f_i}^- = 0$ for all i), what remains is

$$\begin{aligned} \varepsilon_T^{f-}(T; T_g^-) &= \sum_{i=1}^N \left[\int_{T_0}^T \alpha_f(\theta) \phi_{f_i}^-(\theta) d\theta \phi_{f_i}^-(T) - \int_{T_0}^T \alpha_f(\theta) \phi_{f_i}^-(\theta) \phi_{f_i}^-(\theta) d\theta \right] \frac{\ell_i}{\ell} \\ &= \sum_{i=1}^N \left[\int_{T_0}^T \alpha_f(\theta) \phi_{f_i}^-(\theta) (\phi_{f_i}^-(T) - \phi_{f_i}^-(\theta)) d\theta \right] \frac{\ell_i}{\ell}. \end{aligned} \quad (2.13)$$

For any $T > T_{g_i}^-$, (2.13) is exactly zero since $\phi_{f_i}^- = 0$. Likewise, for any $T < T_{g_i}^-$, the term $(\phi_{f_i}^-(T) - \phi_{f_i}^-(\theta)) = (1 - \phi_{f_i}^-(\theta))$. Therefore, (2.13) can be equivalently rewritten as

$$\varepsilon_T^{f-}(T; T_g^-) = \sum_{i=1}^N \left[\int_{T_0}^T \alpha_f(\theta) \phi_{f_i}^-(\theta) (1 - \phi_{f_i}^-(\theta)) d\theta \right] \frac{\ell_i}{\ell} = 0$$

since either $\phi_{f_i}^- = 0$ or $(1 - \phi_{f_i}^-) = 0$ for all θ . As initially assumed, the frozen strain upon freezing plays no role in the strain storage process.

The formulas for the active and frozen mechanical strain at the glass transition in (2.11a) and (2.11b) respectively can be simplified even further. Since the term $\sum \phi'_{f_i}(\theta)\ell_i/\ell$ is the weighted average of the derivative of the frozen fractions, similar to (2.2), equations (2.11a) and (2.11b) can be written as

$$\begin{aligned}\varepsilon_m^{a-}(T, \sigma; T_g^-) &= \int_{T_0}^T \left(\frac{\sigma}{Y_a(\theta)} \frac{d\phi_f^-}{dT}(\theta) \right) d\theta \\ \varepsilon_m^{f-}(T, \sigma; T_g^-) &= \int_{T_0}^T \left(\frac{\sigma}{Y_f(\theta)} \frac{d\phi_f^-}{dT}(\theta) \right) d\theta.\end{aligned}$$

Therefore the total stored strain on the polymer network created during cooling is given by

$$\begin{aligned}\varepsilon_s^-(T, \sigma) &= \varepsilon_T^{a-}(T; T_g^-) + \varepsilon_m^{a-}(T, \sigma; T_g^-) - \varepsilon_m^{f-}(T, \sigma; T_g^-) \\ &= \varepsilon_T^{a-}(T)\phi_f^-(T) + \int_{T_0}^T \sigma \left(\frac{1}{Y_a(\theta)} - \frac{1}{Y_f(\theta)} \right) \frac{d\phi_f^-}{dT}(\theta) d\theta.\end{aligned}\tag{2.14}$$

2.4.4 Homogenized Model for Cooling a Polymer Network

The strain for the entire network now has been constitutively defined for a cooling process as

$$\varepsilon^-(T, \sigma) = \varepsilon_m^-(T, \sigma) + \varepsilon_T^-(T) + \varepsilon_s^-(T, \sigma),$$

where

$$\begin{aligned}\varepsilon_T^-(T) &= (1 - \phi_f^-(T)) \int_{T_0}^T \alpha_a(\theta)(1 - \phi_f^-(\theta))d\theta + \phi_f^-(T) \int_{T_0}^T \alpha_f(\theta)\phi_f^-(\theta)d\theta, \\ \varepsilon_m^-(T, \sigma) &= \left(\frac{1 - \phi_f^-(T)}{Y_a(T)} + \frac{\phi_f^-(T)}{Y_f(T)} \right) \sigma, \\ \varepsilon_s^-(T, \sigma) &= \varepsilon_T^{a-}(T)\phi_f^-(T) + \int_{T_0}^T \sigma \left(\frac{1}{Y_a(\theta)} - \frac{1}{Y_f(\theta)} \right) \frac{d\phi_f^-}{dT}(\theta) d\theta.\end{aligned}\tag{2.15}$$

2.4.5 Cooling with Constant Strain

Some experimentalists wish to cool a polymer with a predetermined deformed shape by dynamically adjusting the force in order to maintain this desired shape. In this manner, (2.15) must be solved for stress, σ . Starting with the equation for mechanical

strain, stress becomes a function of strain, and temperature

$$\sigma(T, \varepsilon) = Y(T) [\varepsilon - \varepsilon_s^-(T, \sigma) - \varepsilon_T^-(T)], \quad (2.16)$$

where

$$Y(T) = \frac{1}{\frac{1 - \phi_f^-(T)}{Y_a(T)} + \frac{\phi_f^-(T)}{Y_f(T)}}$$

is the bulk modulus of the polymer. Substituting (2.16) into the stored strain results in an implicit function where stored strain is a function of stored strain;

$$\varepsilon_s^-(T, \varepsilon) = \varepsilon_T^{a-}(T) \phi_f^-(T) + \int_{T_0}^T Y(\theta) [\varepsilon - \varepsilon_s^-(\theta, \varepsilon) - \varepsilon_T^-(\theta)] \left(\frac{1}{Y_a(\theta)} - \frac{1}{Y_f(\theta)} \right) \frac{d\phi_f^-}{dT}(\theta) d\theta.$$

Taking the derivative with respect to temperature results in the differential equation

$$\frac{d\varepsilon_s^-}{dT}(T, \varepsilon) = \frac{d}{dT} \left(\varepsilon_T^{a-}(T) \phi_f^-(T) \right) + Y(T) [\varepsilon - \varepsilon_s^-(T, \varepsilon) - \varepsilon_T^-(T)] \left(\frac{1}{Y_a(T)} - \frac{1}{Y_f(T)} \right) \frac{d\phi_f^-}{dT}(T)$$

with the initial condition

$$\varepsilon_s^-(T_0) = 0.$$

The constitutive model for cooling a polymer with constant deformation σ is then defined as

$$\sigma(T, \varepsilon) = Y(T)(\varepsilon - \varepsilon_s^-(T, \sigma) - \varepsilon_T^-(T)),$$

where

$$\begin{aligned} Y(T) &= \frac{1}{\frac{1 - \phi_f^-(T)}{Y_a(T)} + \frac{\phi_f^-(T)}{Y_f(T)}}, \\ \varepsilon_T^-(T) &= (1 - \phi_f^-(T)) \int_{T_0}^T \alpha_a(\theta) (1 - \phi_f^-(\theta)) d\theta + \phi_f^-(T) \int_{T_0}^T \alpha_f(\theta) \phi_f^-(\theta) d\theta, \\ \frac{d\varepsilon_s^-}{dT}(T, \varepsilon) &= \varepsilon_T^{a-}(T) \frac{d\phi_f^-}{dT}(T) + \frac{d\varepsilon_T^{a-}}{dT}(T) \phi_f^-(T) \\ &\quad + Y(T) [\varepsilon - \varepsilon_s^-(T, \varepsilon) - \varepsilon_T^-(T)] \left(\frac{1}{Y_a(T)} - \frac{1}{Y_f(T)} \right) \frac{d\phi_f^-}{dT}(T), \\ \varepsilon_s^-(T_0) &= 0. \end{aligned}$$

2.5 Heating a Polymer Network

In Section 2.4, we defined the thermal, mechanical and stored strain strictly for the cooling portion for a thermomechanical cycle. Consideration must be given to the heating process separately for three primary reasons. First, the thermal strain is assumed to be continuous in both the frozen and active states; however, is not necessarily continuous over the glass transition threshold. Second, the strain storage process is entirely dependent on the glass transition during cooling. It is assumed that all stored strain for each element is completely released upon reaching the glass transition point. For high rates of temperature change, the glass transition is a hysteretic process and therefore the stored strain is not necessarily released at the same temperature that it was created. To remedy the first point, the thermal strain needs to be uniquely defined for the heating process. The second point will be addressed later and a unique type of strain called the “recovered strain” will be defined. To indicate the heating portion of a thermomechanical cycle, all strain values, glass transition temperatures, and frozen fractions occurring during heating will be denoted with a ‘+’ in the exponent.

2.5.1 Homogenized Heating Thermal Strain

Suppose the cooling portion of the thermomechanical cycle began at $T = T_0$ and ended at $T = T_1$. Beginning with the same convention as the cooling thermal strain, both the active and frozen thermal strains during heating can initially be defined as

$$\begin{aligned}\varepsilon_{T_0}^{a+}(T) &= \int_{T_0}^T \alpha_a(\theta)(1 - \phi_f^+(\theta)) d\theta, \\ \varepsilon_{T_0}^{f+}(T) &= \int_{T_0}^T \alpha_f(\theta)\phi_f^+(\theta) d\theta,\end{aligned}$$

with the added constraints that $\varepsilon_T^{a+}(T_0) = \varepsilon_T^{a-}(T_0)$ for $T > T_g^+$ and $\varepsilon_T^{f+}(T_1) = \varepsilon_T^{f-}(T_1)$ for $T < T_g^-$. Since the active thermal strain is zero at T_0 by this convention, defining $\varepsilon_T^{a+}(T) = \varepsilon_{T_0}^{a+}(T)$ ensures the equality requirement at $T = T_0$.

To satisfy the equality constraint for the frozen thermal strain, $\varepsilon_{T_0}^{a+}(T)$ must be shifted to match ε_T^{f-} by subtracting the difference between $\varepsilon_T^{f-}(T_1)$ and $\varepsilon_{T_0}^{f+}(T_1)$. Therefore

the active and frozen thermal strains during heating can be defined as

$$\begin{aligned}\varepsilon_T^{a+}(T) &= \int_{T_0}^T \alpha_a(\theta)(1 - \phi_f^+(\theta)) d\theta \\ \varepsilon_T^{f+}(T) &= \int_{T_0}^T \alpha_f(\theta)\phi_f^+(\theta) d\theta - \left(\int_{T_0}^{T_1} \alpha_f(\theta)\phi_f^+(\theta) d\theta - \int_{T_0}^{T_1} \alpha_f(\theta)\phi_f^-(\theta) d\theta \right)\end{aligned}$$

and the total thermal strain during heating is

$$\begin{aligned}\varepsilon_T^+(T) &= (1 - \phi_f^+(T))\varepsilon_T^{a+}(T) + \phi_f^+(T)\varepsilon_T^{f+}(T) \\ &= (1 - \phi_f^+(T)) \int_{T_0}^T \alpha_a(\theta)(1 - \phi_f^+(\theta))d\theta + \phi_f^+(T) \int_{T_0}^T \alpha_f(\theta)\phi_f^+(\theta)d\theta \\ &\quad - \phi_f^+(T) \left(\int_{T_0}^{T_1} \alpha_f(\theta)\phi_f^+(\theta)d\theta - \int_{T_0}^{T_1} \alpha_f(\theta)\phi_f^-(\theta)d\theta \right).\end{aligned}$$

2.5.2 Homogenized Heating Mechanical Strain

Again assuming small deformations, the mechanical strain acting on each polymer element during heating can be defined as

$$\begin{aligned}\varepsilon_{m_i}^{a+}(T, \sigma) &= \frac{\sigma}{Y_a(T)} \\ \varepsilon_{m_i}^{f+}(T, \sigma) &= \frac{\sigma}{Y_f(T)}\end{aligned}$$

where Y_a and Y_f are the moduli of the active and frozen polymer volumes respectively. Applying (2.3), the mechanical strains are

$$\begin{aligned}\varepsilon_m^{a+}(T, \sigma) &= \sum_{i=1}^N \frac{\sigma}{Y_a(T)} \frac{\ell_i}{\ell} = \frac{\sigma}{Y_a(T)} \\ \varepsilon_m^{f+}(T, \sigma) &= \sum_{i=1}^N \frac{\sigma}{Y_f(T)} \frac{\ell_i}{\ell} = \frac{\sigma}{Y_f(T)},\end{aligned}$$

and the total mechanical strain during heating is

$$\varepsilon_m^+(T, \sigma) = \left(\frac{1 - \phi_f^+(T)}{Y_a(T)} + \frac{\phi_f(T)^+}{Y_f(T)} \right) \sigma.$$

2.5.3 Homogenized Heating Stored Strain

Once a thermomechanical cycle reaches its lowest temperature, the strain storage process is (usually) complete. The stored strain is completely released from each element

during heating once that element reaches the glass transition point. Therefore,

$$\varepsilon_{s_i}^+ = \varepsilon_{s_i}^- \phi_{f_i}^+(T).$$

The stored strain for the entire system is found to be

$$\varepsilon_s^+ = \sum_{i=1}^N \varepsilon_{s_i}^- \phi_{f_i}^+(T) \frac{\ell_i}{\ell}.$$

Assuming that each element becomes frozen in a specific order and subsequently becomes active in the reverse order (i.e., the last element to freeze is the first to become active), then the stored strain is not necessarily a decreasing function. Consider a polymer network loaded at a high temperature with an small applied tensile force that results in a strain smaller than the thermal strain expected to accumulate while cooling the network over a specific temperature range. As the network is cooled through the glass transition region, the first polymer elements to freeze may store a tensile strain while the last polymer elements to freeze may store a compressive strain since it is possible for the strain accumulated as a result of thermal expansion to overcome the mechanical tension. Therefore, at any value of the heating frozen fraction, the stored strain during heating must essentially “look-up” the stored strain during cooling related to the corresponding value of the cooling frozen fraction. As a function of temperature, this can be written as

$$\varepsilon_s^+(T) = \int_{T_0}^{T_1} \varepsilon_s^-(\theta) \delta(\phi_f^+(T) - \phi_f^-(\theta)) d\theta$$

where T_0 and T_1 are the initial and final temperatures of the cooling cycle and δ is the Dirac-delta density.

Since the strain storage process typically occurs over a temperature range of about 30° where thermal expansion accounts for strain of approximately 0.5%, the stored strain can be approximated by

$$\varepsilon_s^+(T) = \varepsilon_s^-(T_1) \phi_f^+(T).$$

One facet of the strain storage process that has not been addressed is plastic deformations in the frozen state. Due to the general manner in which stress and strain have been defined, large scale deformations can be admitted using this model where plastic deformations are possible. At a temperature below the glass transition temperature, a polymer network can be deformed beyond its linear elastic capabilities at which point plastic

(although recoverable through heating) deformation can occur. It is here that the stored strain can be adjusted in terms of an applied load.

Suppose the polymer begins at a temperature below the glass transition and exhibits an unloaded strain $\varepsilon^- = \varepsilon_T^f + \varepsilon_s^-$. Deforming the polymer with an applied load creates the mechanical strain $\varepsilon_m^f(T, \sigma)$ and subsequent unloading reveals the polymer exhibits an unloaded strain $\varepsilon^{-*} = \varepsilon_T^f + \varepsilon_s^- + \varepsilon_m^*$ where ε_m^* is the mechanically induced plastic (stored) deformation. Upon heating the polymer beyond its glass transition, the plastic deformation will be recovered, much like the stored strain. Therefore, before the heating stored strain is calculated, the stored strain shall be redefined as

$$\varepsilon_s^* = \varepsilon_s^- + \varepsilon_m^*.$$

2.5.4 Recovered Strain

During an ideal thermomechanical process where the glass transition occurs identically during both heating and cooling with a constant deformation throughout, the thermally induced deformation will overlap exactly. However, experiments show that the glass transition rarely overlaps through the entire thermomechanical cycle. This discrepancy can be attributed to several phenomena including, but not solely due to, rate of temperature change, applied pressure, and specimen volume. The result is an effect referred to as “snap-back” where any stored strain is immediately released upon reaching the glass transition point; however, the resulting deformation may not be continuous with respect to temperature. Quantifying this snap-back, referred to as the recovered strain ε_r , is important for future work since the polymer’s inherent damping properties would physically disallow snap-back to occur.

As an example, consider a polymer element with no applied deformation ($\sigma = 0$) cooled and heated at a rate such that the glass transition point during cooling (T_g^-) and heating (T_g^+) satisfy $T_g^- < T_g^+$. During cooling, the total strain evolves as depicted in Figure 2.3(b) and the stored strain can be found from (2.14) as

$$\varepsilon_s^-(T, \sigma; T_g^-, 0) = \varepsilon_T^a(T_g^-).$$

During subsequent heating, the polymer remains in the frozen state beyond T_g^- and thermally expands as a frozen polymer until it reaches T_g^+ . At this point, the stored strain is

instantaneously released and the thermal strain transitions to the active state. The difference between the frozen and active thermal strains at T_g^+ can be termed the “thermal jump.” The recovered strain can be quantified as the difference between the stored strain created during cooling and the thermal jump during heating. Therefore, it follows that

$$\varepsilon_r = \varepsilon_s^- - (\varepsilon_T^a - \varepsilon_T^f) = \varepsilon_s^- - (\varepsilon_T^a(T_g^+) - \varepsilon_T^f(T_g^+)).$$

Figure 2.6(a) illustrates the thermal strain during a hysteretic thermocycle responsible for the overall strain and the inherent recovered strain; see Figure 2.6(b).

As a second example, consider a polymer element with an applied deformation which has zero thermal expansion in both the frozen and active states. Again, consider the element being cooled and heated at a rate such that the glass transition point during cooling (T_g^-) and heating (T_g^+) satisfy $T_g^- < T_g^+$. During cooling, the total strain is equal to the active mechanical strain in the active state and is equal to the sum of the stored and frozen mechanical strains in the frozen state; see Figure 2.7(a). The stored strain can be determined from (2.14) and is equal to

$$\varepsilon_s^-(T, \sigma; T_g^-) = \varepsilon_m^a(T, \sigma; T_g^-) - \varepsilon_m^f(T, \sigma; T_g^-).$$

Once the element is cooled below the glass transition point, the deformation is changed (or removed) which creates a changed frozen strain on the polymer. During subsequent heating,

Figure 2.6: The (a) thermal strain $\varepsilon_T(T)$ and (b) total strain $\varepsilon(T)$ for a hysteretic thermal cycle.

the polymer remains in the frozen state beyond T_g^- and finally releases the stored strain upon reaching T_g^+ as is illustrated in Figure 2.7(b). At this temperature, the frozen mechanical strain of the second deformation instantaneously transitions to its active mechanical counterpart, creating a mechanical jump. Again, the deformation is not continuous due to the recovered strain; however, it can be quantified as the difference between the stored strain created during cooling and the mechanical jump created during heating. Therefore, it follows that

$$\varepsilon_r = \varepsilon_s^- - (\varepsilon_m^a - \varepsilon_m^f) = \varepsilon_s^- - (\varepsilon_m^a(T, \sigma; T_g^+, \sigma_2) - \varepsilon_m^f(T, \sigma; T_g^+, \sigma_2)).$$

The total deformation of the mechanical thermocycle is shown in Figure 2.8.

Taking into consideration the previous two examples, the recovered strain for each element can be defined as

$$\varepsilon_{r_i}(T_g^+, \sigma_2) = \varepsilon_{s_i}^- - \left(\varepsilon_{T_i}^{a+}(T_g^+) - \varepsilon_{T_i}^{f+}(T_g^+) + \varepsilon_{m_i}^{a+}(T_g^+, \sigma_2) - \varepsilon_{m_i}^{f+}(T_g^+, \sigma_2) \right)$$

where $\varepsilon_{s_i}^-$ is the constant stored strain found during the cooling process. The total recovered

Figure 2.7: The (a) strain storage during cooling and (b) recovered strain during heating for a hysteric thermal cycle with zero thermal expansion.

Figure 2.8: An idealized hysteretic thermomechanical cycle showing recovered strain with zero thermal expansion.

strain is found by adding up each element, which yields

$$\begin{aligned}
 \varepsilon_r(T, \sigma) &= \sum_{i=1}^N \frac{\ell_i}{\ell} \int_{T_0}^T \left[\varepsilon_{s_i}^- - \left(\varepsilon_{T_i}^{a+}(\theta) - \varepsilon_{T_i}^{f+}(\theta) + \varepsilon_{m_i}^{a+}(\theta, \sigma) - \varepsilon_{m_i}^{f+}(\theta, \sigma) \right) \right] \frac{d\phi_{f_i}^+}{d\theta}(\theta) d\theta \\
 &= \varepsilon_s^- \phi_f^+(T) - \varepsilon_T^{a+}(T) \phi_f^+(T) + \left(\varepsilon_T^{f-}(T_1) - \int_{T_0}^{T_1} \alpha_f(\theta) \phi_f^+(\theta) \right) \\
 &\quad - \int_{T_0}^T \sigma \left(\frac{1}{Y_a(\theta)} - \frac{\sigma}{Y_f(\theta)} \right) \frac{d\phi_f^+}{dT}(\theta) d\theta.
 \end{aligned}$$

Note that T_1 is the temperature reached at the end of the cooling portion of the thermomechanical cycle. The final equality is found by using similar arguments as those found in evaluating the cooling stored strain.

2.5.5 Homogenized Model for Heating a Polymer Network

The strain for the entire network has now been constitutively defined for a heating process as

$$\varepsilon^+(T, \sigma) = \varepsilon_m^+(T, \sigma) + \varepsilon_T^+(T) + \varepsilon_s^+(T) + f(\varepsilon_r(T, \sigma; T_g^+))$$

where

$$\begin{aligned}
\varepsilon_T^+(T) &= \int_{T_0}^T \alpha_a(\theta)(1 - \phi_f^+(\theta))d\theta + \int_{T_0}^T \alpha_f(\theta)\phi_f^+(\theta)d\theta \\
&\quad - \left(\int_{T_0}^{T_1} \alpha_f(\theta)\phi_f^+(\theta)d\theta - \int_{T_0}^{T_1} \alpha_f(\theta)\phi_f^-(\theta)d\theta \right), \\
\varepsilon_m^+(T, \sigma) &= \left(\frac{1 - \phi_f^+(T)}{Y_a(T)} + \frac{\phi_f^+(T)}{Y_f(T)} \right) \sigma, \\
\varepsilon_s^+(T) &= \int_{T_0}^{T_1} \varepsilon_s^-(\theta)\delta(\phi_f^+(T) - \phi_f^-(\theta))d\theta \\
\varepsilon_r(T, \sigma) &= \varepsilon_s^-\phi_f^+(T) - \varepsilon_T^{a+}(T)\phi_f^+(T) + \left(\varepsilon_T^{f-}(T_1) - \int_{T_0}^{T_1} \alpha_f(\theta)\phi_f^+(\theta)d\theta \right) \\
&\quad - \int_{T_0}^T \sigma \left(\frac{1}{Y_a(\theta)} - \frac{1}{Y_f(\theta)} \right) \frac{d\phi_f^+}{dT}(\theta)d\theta,
\end{aligned} \tag{2.17}$$

and f is some function of the recovered strain to be quantified in future research.

2.6 Glass Transition Phenomenon

Equations (2.15) and (2.17) define the cooling and heating process of a typical thermomechanical cycle for shape memory polymers. The entire process is a function of temperature and stress, but most importantly, the state variable ϕ_f which defines the frozen fraction of the polymer network. Work done in [32] and [11] used a sigmoidal fit on normalized strain recovery data; however, the data was collected during a heating cycle. Under the assumption that the rate of temperature change affects the range of glass transition, the data does not provide an accurate account of the glass transition during cooling.

To this point, no restrictions have been made on the elements that define the polymer network. Both the glass transition points T_{g_i} and elemental sizes ℓ_i have been considered in a generic sense. To define the frozen fraction for the entire network, some assumptions are necessary.

2.6.1 Polydispersity

During the process of synthesizing a shape memory polymer, crosslinking occurs between polymer chains. The network that is produced contains polymer chains with a wide variety of lengths, called polydispersity. The hypothesized thermomechanical result

of polydispersity is a gradual glass transition because of the following property: shorter polymer chains have higher glass transition temperatures and conversely, longer polymer chains have lower glass transition temperatures. It follows that polymer chains with shorter lengths have a lower molecular weight than their longer counterparts. The typical shape of a polydispersity curve (molecular weight M_w versus number N) is shown in Figure 2.9. The number of small molecular weight polymer chains is typically larger than the number of high molecular weight polymer chains. This implies that the median molecular weight $\overline{M}_w$ will be lower than the mode molecular weight M_w^* .

Consider a finite number of molecular weights M_{w_i} . Polydispersity implies that each molecular weight M_{w_i} has a corresponding glass transition point T_{g_i} that satisfies $T_{g_i} > T_{g_k}$ when $M_{w_i} < M_{w_k}$ for all i, k . This implies that the glass transition points will have a similar distribution as the polydispersity curve, only reversed. As the molecular weight increases, the element's relative size to the entire network (ℓ_i) also increases, causing the relative weight of each glass transition temperature to increase. The weight of each element's glass transition point can be quantified as the glass transition point times the relative size of the element, $T_{g_i}\ell_i/\ell$. The result, as desired, is that the relative effect of each glass transition temperature on the entire network $T_{g_i}\ell_i/\ell$ is qualitatively similar to a normal distribution. This distribution can be considered the transition probability distribution.

Figure 2.9: Typical polydispersity relation for polymers with N chains of molecular weight M_w .

2.6.2 Tan δ .

The apparent strong correlation between the process of glass transition and the $\tan \delta$ curve in glassy thermoset polymers is impossible to ignore. With its peak roughly centered in the glass transition region and with a width that roughly spans the glass transition temperature range, useful information can be extracted from the $\tan \delta$ curve.

To help draw on the correlation assumption, it is helpful to state some essential preliminaries regarding $\tan \delta$. $\tan \delta$ is defined to be the ratio of the storage modulus (E'') to the loss modulus (E'). The storage and loss moduli are found by applying an oscillatory strain, defined as

$$\varepsilon(t) = \varepsilon_0 \sin(\omega t)$$

where ε_0 is the magnitude of the applied strain and ω is the period of strain oscillation. The associated stress is defined to be

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta)$$

where σ_0 is the magnitude of the stress, ω is the same period as the applied strain, and δ quantifies the phase lag in the stress response. The storage and loss moduli are then defined to be

$$\begin{aligned} E' &= \frac{\sigma_0}{\varepsilon_0} \cos \delta, \\ E'' &= \frac{\sigma_0}{\varepsilon_0} \sin \delta. \end{aligned}$$

As δ tends towards 0, the material exhibits a more elastic response since the stress response to the strain are closely in-phase, so the storage modulus, E' , represents the elastic/stored portion. Conversely, as δ tends towards $\pi/2$, the material exhibits a more viscous response since the stress response approaches a complete out-of-phase shift, so the loss modulus, E'' , represents the viscous/dissipative portion. The $\tan \delta$ curve (E''/E') represents the viscoelastic propensity of the polymer. Many experimentalists consider the peak of the curve to be the glass transition temperature, T_g .

Typically the $\tan \delta$ curve represents the mechanical damping capacity a material possesses. In ferroic materials, the damping capacity is directly related to the domain wall density [13]. To draw on this analogy, as a polymer is undergoing its glass transition, both frozen and active domains occur simultaneously. The expected maximum of domain wall density would occur when there is an equal amount of frozen and active domains and

gradually taper as one domain becomes dominant over the other. Thus, the peak of the $\tan \delta$ curve corresponds to the middle of the glass transition region.

Taking into account the hysteresis that is seen in the glass transition during high rates of temperature change, the $\tan \delta$ curve can only be useful if it too exhibits hysteresis. Figure 2.10(a) shows little hysteresis in the $\tan \delta$ data collected by Y. Liu [31] during a $1^\circ\text{C}/\text{min}$ thermocycle. Figure 2.10(b) illustrates a strong hysteresis in the $\tan \delta$ data during a $3^\circ\text{C}/\text{min}$ thermocycle. During heating and cooling, the $\tan \delta$ curves typically do not overlap. Overlap can occur, however, if the rate of temperature change is of the same magnitude of the material-dependent relaxation time. When the rate of temperature change is increased, the $\tan \delta$ peaks during cooling and heating migrate away from each other. Extensive research has been done regarding this peak-shift by G.B. McKenna and S.L. Simon in thermoplastic polymers [34] as a result of temperature rate, pressure, and volume, and analogous properties in polymer thermosets are experimentally seen. Figure 2.11 illustrates this phenomenon by comparing the $\tan \delta$ curves found during a thermocycle at $1^\circ\text{C}/\text{min}$, $3^\circ\text{C}/\text{min}$, and $5^\circ\text{C}/\text{min}$.

Not ignoring the shape of the $\tan \delta$ curve, it may be possible to treat it as a transition probability distribution to predict the glass transition during both heating and cooling.

Figure 2.10: $\tan \delta$ curves for (a) Y. Liu's experiment at $1^\circ\text{C}/\text{min}$ [31] and (b) C. Yakacki at $3^\circ\text{C}/\text{min}$ (www.medshapesolutions.com).

Figure 2.11: Comparison of $\tan \delta$ curves during thermocycle at $1^\circ\text{C}/\text{min}$, $3^\circ\text{C}/\text{min}$, and $5^\circ\text{C}/\text{min}$ using data collected by C. Yakacki (www.medshapesolutions.com).

2.6.3 Modeling $\tan \delta$.

To compare this idea with Liu's data (on which a considerable amount of modeling has been done) the apparent 'bias' that occurs in the data far from T_g needs to be addressed. Considering the the full data set shown in Figure 2.10(a), it can be assumed that the values of $\tan \delta$ do not converge asymptotically to zero and in order to approximate the data with a normal distribution, the bias needs to be removed. To do this, an initial approximation of the frozen fraction, ϕ_f , must be formulated from the raw $\tan \delta$ data. The approximation will ideally be modeled by a normal distribution, so an initial data fit using a normal distribution is appropriate.

The continuous probability density function of a normal distribution is given as

$$\varphi_{\mu,\sigma^2}(T) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(T-\mu)^2}{2\sigma^2}}, \quad T \in \mathbb{R}, \quad (2.18)$$

where μ is the mean and σ^2 is the variance ($\sigma > 0$ is the standard deviation). Since the integral of the data almost certainly will never achieve unity, we ignore the pre-exponential factor $1/\sigma\sqrt{2\pi}$ and instead replace this factor with K which is analogous the maximum value that the $\tan \delta$ data achieves. The mean value μ is assumed to be the glass transition temperature as this is where both the data and any normal distribution achieves their maximum values. The variance, in essence, quantifies the squared half-width of the bulk of the $\tan \delta$ data curve.

Using initial values of

$$\begin{aligned} K_0 &= \max(\tan \delta) = 0.757767 \\ \mu_0 &= T_g = 341.5 \\ \sigma_0^2 &= (\text{data width}/2)^2 = 10^2 \end{aligned}$$

and then optimizing using a least squares fit, Figure 2.12 shows an initial estimate of the $\tan \delta$ curve of the optimized distribution

$$\varphi(T) = 0.71925e^{-0.003314(T-340.958)^2}.$$

Using this initial estimate, the frozen fraction at temperature T_0 is considered to be the percentage of the area under the distribution for $T > T_0$; therefore,

$$\phi_0(T) = \frac{\int_T^\infty \varphi(\theta) d\theta}{\int_{\mathbb{R}} \varphi(\theta) d\theta}.$$

Noting that

$$\text{erf}(T) \equiv \frac{2}{\sqrt{\pi}} \int_0^T e^{-u^2} du$$

and applying a u -substitution to φ , the integral becomes

$$\begin{aligned} \int_T^\infty \varphi(\theta) d\theta &= \int_T^\infty K e^{-c(\theta-T_g)^2} d\theta \\ &= \frac{K\sqrt{\pi}}{2\sqrt{c}} \cdot \frac{2}{\sqrt{\pi}} \int_{\sqrt{c}(T-T_g)}^\infty e^{-u^2} du \\ &= \frac{K\sqrt{\pi}}{2\sqrt{c}} [1 - \text{erf}(\sqrt{c}(T - T_g))] \end{aligned}$$

Figure 2.12: Initial estimate of Liu's $\tan \delta$ curve using a single distribution.

and likewise,

$$\int_{\mathbb{R}} \varphi(\theta) d\theta = \frac{K\sqrt{\pi}}{\sqrt{c}}.$$

Therefore the frozen fraction can be simplified to be

$$\phi_0(T) = \frac{1 - \operatorname{erf}(\sqrt{c}(T - T_g))}{2}. \quad (2.19)$$

This frozen fraction will be used to subtract off the bias found in the frozen and active states, β_f and β_a , respectively. Ideally, β_f and β_a would be estimated with data sufficiently far away from T_g where the data flattens out; however, due to the incompleteness of the data, it is necessary to extrapolate the values to be approximately $\beta_f = 0.04$ and $\beta_a = 0.06$. Therefore the adjusted $\tan \delta$ data is found by

$$\tan \delta_{adj} = \tan \delta_{data} - \beta_f \phi_0(T) - \beta_a (1 - \phi_0(T)).$$

Figure 2.13 shows how the $\tan \delta$ curve is adjusted to remove the bias.

The first attempt at modeling the adjusted $\tan \delta$ curve again involves the modified distribution

$$\varphi(T) = K e^{-c(T-T_g)^2}$$

where initial estimates of K , c and T_g can be approximated as the maximum value, inverse of the squared half-width, and temperature at the maximum value, respectively. The fit is optimized using a least squares error, L . Table 2.1 shows the initial estimates and least

Figure 2.13: Adjusted $\tan \delta$ data to remove bias away at extremes.

Table 2.1: Initial and optimized values for a single distribution along with respective errors

Initial		Optimized	
K	= 0.6762	K	= 0.6559
c	= 0.0050	c	= 0.0044
T_g	= 340.9581	T_g	= 340.2762
L	= 0.6419	L	= 0.2452

squares error along with their optimized values. Figure 2.14(a) shows the approximation's fit to the adjusted $\tan \delta$ data.

As one can see, although the fit is not particularly poor, the adjusted $\tan \delta$ curve is clearly not normally distributed. To alleviate this disconnect, a Galerkin expansion

$$\tan \delta(T) \approx \varphi(T) = \sum_{i=1}^n w_i \varphi_i(T)$$

can be utilized where $\varphi_i(T)$ are basis functions that are normal distributions like (2.18). The motivation to do this is the fact that there is a clear relation of the data with a distribution with the desire to identify the underlying means and variances. The parameter N can be chosen to be as large as necessary; however, due to how close the data is to a single distribution, $N = 2$ is sufficient: one which addresses the peak values of the $\tan \delta$ curve, and another to address the more gradual dissipation away from the glass transition. Therefore, we take

$$\varphi^0(T) = K_1 e^{-c_1(T-T_{g1})^2} + K_2 e^{-c_2(T-T_{g2})^2}.$$

Initial values for this approximation can be determined by assuming the term which will directly estimate the $\tan \delta$ peak will have a larger pre-exponential and exponential factor, while the other term which will directly estimate the gradual dissipation away from the peak will have smaller pre-exponential and exponential factors. One such way is to choose

$$\varphi^0(T) = 0.8K e^{-0.8c(T-T_g)^2} + 0.2K e^{-0.2c(T-T_g)^2}$$

where K is the maximum value of $\tan \delta_{adj}$ and c is the approximate value for $1/2\sigma^2$. Table 2.2 shows the initial values for the Galerkin approximation and the least squares error along with the optimized values and accompanying error. Figure 2.14(b) shows how the Galerkin approximation fits the adjusted $\tan \delta$ data.

Table 2.2: Initial and optimized values for a Galerkin approximation along with respective errors

<i>Initial</i>	<i>Optimized</i>
$K_1 = 0.8(0.6762)$	$K_1 = 0.5205$
$c_1 = 0.8(0.0050)$	$c_1 = 0.0072$
$T_{g1} = 340.9581$	$T_{g1} = 340.8597$
$K_2 = 0.2(0.6762)$	$K_2 = 0.1967$
$c_2 = 0.2(0.0050)$	$c_2 = 0.0012$
$T_{g2} = 340.9581$	$T_{g2} = 341.2509$
$L = 0.3021$	$L = 0.0452$

(a) Single Distribution Approximation

(b) Galerkin Approximation

Figure 2.14: $\tan \delta$ approximation using (a) a single distribution, and (b) a dual distribution.

Since the analogy is proposed that the $\tan \delta$ curve indicates damping in the polymer as a result of domain walls, it can be extended to assume that there is still a sufficient amount of domain wall interaction from the smaller polymer chains that are in a different state than the surrounding larger chains at higher temperatures. However, the different state that these smaller chains are in contribute little to the polymer volume fraction. It can also be assumed that the medium the polymers exist in has some intrinsic damping which can lead to wider $\tan \delta$ curves. With this in mind, it can be assumed that the two exponentials defining Galerkin approximation define these phenomena simultaneously. Figure 2.15 shows the tendency of the two exponentials during heating and cooling.

The exponential which has a considerably larger variance and higher T_g (Figure 2.15) can be directly related to the small molecular chains while the other approximation can be used to describe the macroscopic glass transition. Therefore, the transition probability distribution is defined as

$$\varphi(T) = K_1 e^{-c_1(T-T_{g1})^2}$$

and the frozen fraction is defined via (2.19) as

$$\phi_f(T) = \frac{1 - \operatorname{erf}(\sqrt{c_1}(T - T_{g1}))}{2}.$$

As previously stated, it is assumed that the glass transition exhibits some hysteresis in a thermocycle due to the apparent lag in the $\tan \delta$ curve data. Figure 2.16 compares

Figure 2.15: Comparing the two exponentials created to make the approximation in Figure 2.14(b) along with the $\tan \delta$ curve during (a) cooling and (b) heating.

Figure 2.16: Frozen fraction found with Liu’s sigmoidal approximation versus with the adjusted $\tan \delta$ data during cooling and heating.

the frozen fraction found with the adjusted $\tan \delta$ curve while cooling, the frozen fraction found with the adjusted $\tan \delta$ curve while heating, and Liu’s sigmoidal approximation. There is some apparent hysteresis in the frozen fraction curves, however since the $\tan \delta$ data significantly overlapped, only a small amount is expected.

Applying this method to the data collected by C. Yakacki, Figure 2.17 shows the Galerkin approximation to both the heating and cooling adjusted $\tan \delta$ data and their corresponding glass transition predictions. As expected, the frozen fraction curves are very hysteretic as expected by the distance between the $\tan \delta$ data curves.

2.7 Thermodynamic Considerations

The idea of internal energy and entropy have been used to identify the underlying physical nature of shape memory polymers. Due to the importance of thermodynamic consistency, the proposed homogenized model must be thermodynamically admissible and, for completeness, the framework is given in this section.

A constitutive model for the isothermal and isotropic behavior of general compressible materials is given by Ogden [36] where it is shown that the strain-energy function $\psi(\epsilon, T)$ can be decoupled into its volumetric and isochoric parts

$$\psi = \psi_{\text{vol}} + \psi_{\text{iso}}. \quad (2.20)$$

Figure 2.17: $\tan \delta$ approximations during (a) heating and (b) cooling and (c) the corresponding frozen fraction approximations during a typical thermocycle at $3^\circ\text{C}/\text{min}$.

The volumetric portion encompasses the elastic response which includes the mechanical strain ε_m and phase fraction ϕ_f , both of which are functions of T . The isochoric portion encompasses the elastic response of the hyperelastic material which includes the stored strain ε_s which is a function of T . Therefore, the overall energy function is dependent on the variables $(\varepsilon_m, \varepsilon_s, \phi_f, T)$, but noting that

$$\varepsilon_m = \varepsilon - \varepsilon_s - \varepsilon_T, \quad (2.21)$$

it stands that ψ is also a function of $(\varepsilon, \varepsilon_T)$.

Following the approach of Liu [32], the frozen fraction can be considered analogous to the martensitic fraction in shape memory alloys. Work done by Helm and Haupt [23] formulated the free energies in the volumetric and isochoric portions of shape memory alloys and investigations by Holzapfel [25] extended the definition to rubber-like materials where ψ_{vol} is a sum including a quadratic of the mechanical strain, the initial free energy, and a purely thermal contribution and ψ_{iso} is strictly a quadratic of the stored strain. Therefore, (2.20) can be rewritten as

$$\psi(\varepsilon, \varepsilon_s, T, \phi_f) = \psi_{mT}(\varepsilon_m, T, \phi_f) + \psi_s(\varepsilon_s, T). \quad (2.22)$$

The Clausius-Duhem inequality is equivalent to the second law of thermodynamics and can be expressed as

$$\sigma \dot{\varepsilon} - \dot{e} + T \dot{\eta} - q \frac{\nabla T}{T} \geq 0 \quad (2.23)$$

where e is the internal energy, η is the entropy, and $-q \frac{\nabla T}{T}$ is the entropy production due to conduction of heat. However, since heat flows from hot to cold and entropy production by conduction of heat must be nonnegative, this implies that $q \frac{\nabla T}{T} \leq 0$. Also, since T is nonnegative, the heat conduction inequality is expressed as $q \cdot \nabla T \leq 0$ which implies that heat flows against the temperature gradient.

Employing the Legendre transformation for the free energy $\psi = e - T\eta$, where $\dot{\psi}$ is the temporal derivative, (2.23) can be rewritten in terms of entropy as

$$\sigma \dot{\varepsilon} - \dot{\psi} - \eta \dot{T} - q \frac{\nabla T}{T} \geq 0. \quad (2.24)$$

Using the decompositions for ε and ψ from (2.21) and (2.22), the Clausius-Duhem inequality becomes

$$\left[\left(\sigma - \frac{\partial \psi_{mT}}{\partial \varepsilon_m} \right) \dot{\varepsilon}_m \right] + \left[\sigma \dot{\varepsilon}_T - \left(\frac{\partial \psi}{\partial T} + \eta \right) \dot{T} \right] + \left[\left(\sigma - \frac{\partial \psi_s}{\partial \varepsilon_s} \right) \dot{\varepsilon}_s \right] - \frac{\partial \psi_{mT}}{\partial \phi_f} \dot{\phi}_f - q \frac{\nabla T}{T} \geq 0. \quad (2.25)$$

This definition yields the potential stress and entropy relations

$$\begin{aligned}\sigma &= \frac{\partial \psi_{mT}}{\partial \varepsilon_m} \\ \eta &= \frac{\partial \psi}{\partial T} + \sigma \frac{\partial \varepsilon_T}{\partial T}\end{aligned}\tag{2.26}$$

and internal stress field, which stores the entropic strain in the frozen phase,

$$\sigma_s = \frac{\partial \psi_s}{\partial \varepsilon_s}.\tag{2.27}$$

Since (2.25) holds for all admissible values, utilizing the potential relations for entropy and stress given in (2.26) and the internal stress field given in (2.27), the Clausius-Duhem inequality in (2.25) simplifies to

$$(\sigma - \sigma_s)\dot{\varepsilon}_s - \frac{\partial \psi_{mT}}{\partial \phi_f}\dot{\phi}_f - q\frac{\nabla T}{T} \geq 0.$$

The total dissipation can be considered the sum of the internal dissipation,

$$\mathcal{D}_i = (\sigma - \sigma_s)\dot{\varepsilon}_s - \frac{\partial \psi_{mT}}{\partial \phi_f}\dot{\phi}_f$$

and the thermal dissipation

$$\mathcal{D}_T = -q\frac{\nabla T}{T}$$

and each must be non-negative. Considering the fact that the homogenized model does not currently take strain rate into consideration for the actual strain storage process, the strain rate can be prescribed as $\dot{\varepsilon}_s = 0$. Helm and Haupt show that $-\frac{\partial \psi_{mT}}{\partial \phi_f} = \Delta\psi_0$, the difference of the initial free energy between the active and frozen phases, and in order for $\mathcal{D}_i \geq 0$, $\Delta\psi_0$ and $\dot{\phi}_f$ must have the same sign.

The law of heat conduction imposes the definition that $q = -k\nabla T$ with $k > 0$, and therefore $\mathcal{D}_T = k\frac{(\nabla T)^2}{T} \geq 0$ is always satisfied. As a result, the Clausius-Duhem inequality is satisfied and the proposed homogenized model is thermodynamically admissible.

2.8 Model Properties

Before fully implementing the model as defined in (2.15) and (2.17), the qualitative response of the model is illustrated. To do so, generic mechanical properties are assigned

including

$$\begin{aligned}
\alpha_f &= 1 \times 10^{-4} \text{K}^{-1}, \\
\alpha_a &= 2 \times 10^{-4} \text{K}^{-1}, \\
\tan\delta^- &= \exp\left(-\frac{(T-313)^2}{100}\right), \\
\tan\delta^+ &= \exp\left(-\frac{(T-333)^2}{100}\right), \\
Y_a(373) &= 10 \text{ MPa}, \\
Y_f(323) &= 1 \text{ GPa},
\end{aligned}$$

where $Y_a(T) = 3NkT$ and $Y_f(T) = 1 \text{ GPa}$ (similar to [31]), and theoretical thermomechanical tests are discussed.

2.8.1 Unconstrained Thermocycle

As a polymer with no applied deformation is cooled from its reference configuration at T_r below the glass transition region and back, the polymer will contract due to thermal strain. If the rate of temperature change is sufficiently high, the polymer will exhibit hysteresis where the glass transition regions do not overlap. The hysteresis is a result of the non-overlapping glass transition regions and the different thermal expansion coefficients for both states of the polymer. If the thermal expansion coefficients were the same in both the frozen and active states, there would be no apparent hysteresis due to thermal expansion. Figure 2.18 illustrates this hysteresis assuming the glass transition for heating occurred at a range 20°K higher than the glass transition for cooling.

2.8.2 Cooling with Static Applied Force

When a polymer is in its reference configuration at reference temperature T_r , a deformation is often applied using a static force. This force is then held constant while the polymer is cooled through its glass transition, resulting in stored strain. Figure 2.19 shows the model prediction of the strain a polymer will exhibit while cooling. As is expected, the curve pertaining to the cooling process with zero applied force will be exactly the same as in Figure 2.18; however, as the magnitude of force increases, the shape begins to change. Considering the assumption that the active modulus is equal to $Y_a(T) = 3NkT$, where N

Figure 2.18: Homogenized model's prediction of thermal strain during a deformation-free thermocycle.

is the crosslink density and k is Boltzmann's constant, it is not surprising that an applied force of 1 MPa results in an increase of strain prior to the glass transition. Once an applied tensile load is great enough to overcome the thermal contraction upon cooling, this increase in strain will be expected.

2.8.3 Unconstrained Heating

Once a polymer is cooled below its glass transition region and the previously applied deformation is removed and subsequently heated, the polymer will return to its undeformed reference configuration. Figure 2.20 illustrates how the polymer system releases its stored strain during an unconstrained heating cycle where all strains return to zero.

2.8.4 Predicted Thermomechanical Cycle

N. Choi and A. Lendlein have observed in [12] that shape memory polymers undergoing a elongation stress-controlled thermomechanical test exhibited a repeatable cyclic shape. Figure 2.21 shows both the observed path of Choi and Lendlein's experiments, as well as the model's prediction of such a thermomechanical cycle.

Figure 2.19: Homogenized model's prediction of cooling a polymer with static tensile and compressive applied forces.

Figure 2.20: Homogenized model's prediction of unconstrained heating after cooling with different static tensile and compressive applied forces.

Figure 2.21: Typical thermomechanical cycles as (a) observed by Choi and Lendlein and as (b) predicted by the homogenized model.

2.9 Thermomechanical Experimental Validation

The thermomechanical cycle for small deformations; e.g., see Figure 2.1, begins at a temperature above the glass transition region. At this temperature, the polymer is in a rubbery elastic (active) state. The polymer is then deformed with an applied stress (or strain) which creates a strain (or stress) in the polymer.

Once the polymer is deformed, it is cooled below T_g at which point the active polymer becomes rigid. The applied deformation is removed; however, the polymer remains almost fully in its deformed state because the deformation becomes stored. The resulting deformation creates a residual strain which remains present until the shape recovery process is completed when the polymer is heated above the glass transition region.

The proposed homogenized model in (2.15) and (2.17) is now tested against the linear elastic data collected by Liu et. al. [32] from small-strain uniaxial experiments on a commercial thermoset epoxy system intended for deployable composite space structure applications. The primary goal of the model is to predict the strain storage and release process during cooling and heating, respectively. It is the data from these experiments that the model will be validated.

Figure 2.22 shows the three portions of the thermomechanical cycle which are of interest. Figure 2.22(a) shows a polymer cooled from $T = 358^\circ\text{K}$ to $T = 273^\circ\text{K}$ while holding the strain constant at 9.1%, 0%, and -9.1% . Once cooled, the force required to

hold the strain is released, and the residual strain is a result of the strain storage process. Figure 2.22(b) shows the strain recovery of the polymer during an unconstrained heating process. Figure 2.22(c) shows the evolution of stress during a constrained heating process. The constraining values of strain corresponded to the amount of residual strain after cooling.

Experimental data is used to calibrate the model, including the assumed constant values for frozen modulus Y_f , active thermal expansion coefficient α_a , and frozen thermal expansion coefficient α_f , as well as the temperature dependent values for active modulus $Y_a(T) = 3NkT$ and frozen fraction, $\phi_f(T)$. The frozen and active moduli are found via isothermal stress response experiments at temperatures well above and well below the glass transition regions. Choosing temperatures $T_a = 358^\circ\text{K}$ and $T_f = 273^\circ\text{K}$, the response of the polymer is shown in Figure 2.23(a). From this, the bulk modulus of the polymer can be ascertained to be $Y(T_f) = 750 \text{ MPa}$ and $Y(T_a) = 8.8 \text{ MPa}$ and the calibrated model predicts the isothermal data very well as is seen in Figure 2.23(b). From the rubbery elasticity of a network polymer [47], the active modulus can be described as a linear function of absolute temperature

$$Y_a(T) = 3NkT$$

where N is the crosslink density and k is Boltzmann's constant. The crosslink density can be found assuming $Y_a(T_a) = 3Nk(358) = 8.8 \text{ MPa}$.

The thermal expansion coefficients are estimated using data from an unconstrained thermocycle, where the coefficients can be determined from the slope of the continuous strain in each region. Figure 2.24 shows the data from which the frozen and active thermal expansion coefficients were determined to be $\alpha_f = 0.9 \times 10^{-4} \text{ K}^{-1}$ and $\alpha_a = 1.8 \times 10^{-4} \text{ K}^{-1}$. The frozen fraction $\phi_f(T)$ is calibrated using the method previously outlined and the homogenized model is now completely calibrated for a set of thermomechanical experiments.

2.9.1 Fully Constrained Cooling

The thermomechanical cycle of a polymer begins at a reference temperature where the polymer network is forced to a constant deformation. As it cools through the glass transition point, much of the original strain generated is stored allowing the required force to keep the deformation to remain relatively constant. Once a substantial amount of the polymer becomes frozen, the thermal strain begins to contract the polymer, requiring a greater amount of force to maintain the desired deformation. Figure 2.25(a) shows the

(a) Constrained cooling

(b) Unconstrained heating

(c) Constrained heating

Figure 2.22: The three portions of interest for a shape memory polymer's thermomechanical cycle: (a) Constrained cooling data with 9.1%, 0% and -9.1% strain, (b) unconstrained heating data with zero stress, and (c) constrained heating data with 8.6%, 0% and -9.4% strain. Experimental data collected by Liu et. al. [31]

Figure 2.23: Polymer's isothermal stress response (a) data and (b) model prediction after calibration.

Figure 2.24: Unconstrained cooling experiment with estimated thermal expansion coefficients.

collected data as well as the calibrated model's prediction. As is evident, the model does not accurately predict the stress increase during cooling; however, this was using the assumption that there is no hysteresis in the glass transition. Although the $\tan \delta$ data used to calibrate the frozen fraction was collected at a rate of $1^\circ\text{K}/\text{min}$, most experiments were run at a rate of $5^\circ\text{K}/\text{min}$. Assuming there was a small amount of hysteresis, Figure 2.25(b) shows the data with a predicted shift in the $\tan \delta$ peak of -7°K .

Comparing the homogenized model with the model developed by Liu, Figure 2.26(a) compares the two models' prediction of the data directly while Figure 2.26(b) shows Liu's model with a suspected shift in the $\tan \delta$ data.

2.9.2 Recovery Heating.

Once the fully constrained cooling has occurred, there are two options. The first is to heat the polymer through the glass transition region and fully recover its stored strain. Figure 2.27(a) shows the polymer's response as well as its predicted response via the homogenized model.

The second option is to heat the polymer through the glass transition region while constraining it at its deformed, rigid state. By doing this, the stress will evolve due to both thermal expansion and stored strain release. Figure 2.27(b) shows the polymer's response

Figure 2.25: Model's prediction of the constrained cooling using (a) no shift in the $\tan \delta$ peak and (b) assuming a shift of -7°K .

Figure 2.26: (a) Comparison of Liu's model with the homogenized model and unconstrained cooling data. (b) Assuming the same shift in the glass transition region, Liu's model compared to unconstrained cooling data.

as well as its predicted response via the homogenized model.

The model's predicted response of the polymer is qualitatively accurate for both the constrained and unconstrained heating; however, is only quantitatively accurate for the unconstrained heating. Some improvement on the unconstrained heating can be made since the data seems to indicate there is some apparent strain relaxation well before the glass transition region. Since strain relaxation would tend to force the polymer towards its reference configuration, it seems reasonable that the pre-tensioned experiment exhibits lower magnitudes of stress because the strain relaxation would counteract the thermal expansion. At the other extreme, the pre-compressed experiment exhibits higher magnitudes of strain because strain relaxation would compliment the increasing thermal strain before.

Another possible improvement is to consider a non-constant frozen thermal expansion coefficient. Figure 2.28 shows the homogenized model's prediction with a frozen thermal expansion coefficient defined as

$$\alpha_f(T) = .4 \times 10^{-4} \left(\frac{273 - T}{27} \right) + .9 \times 10^{-4}$$

so that $\alpha_f(273) = 0.9 \times 10^{-4}$ and gradually decreases as the polymer approaches the glass transition region (similar to water). While quantitatively more accurate, the homogenized model does not yet capture the divergent paths the polymer data immediately takes upon heating.

Figure 2.27: (a) Unconstrained and (b) constrained heating of a polymer after cooling with different constraints with the homogenized model's prediction.

Figure 2.28: Model's prediction of a polymer's constrained heating with a non-constant α_f .

Figure 2.29: (a) Unconstrained and (b) constrained heating of a polymer after cooling with different constraints with both the homogenized model and Liu's model predictions.

Comparing the homogenized model with the model developed by Liu, Figure 2.29 illustrates how each model predicts the overall deformation of a polymer.

2.10 Conclusion

A phenomenological homogenized model for the deformation of shape memory polymers is proposed. Several unique features of the homogenized model include:

- the independent definitions of the active and frozen thermal strain,
- the unique definitions of the total thermal strain during cooling and heating that do not rely on curve fitting for simplification,
- the definition of stored strain by identifying which components of strain are stored and how,
- the definition of the frozen fraction by utilizing the $\tan \delta$ curve as a physical identifier of the glass transition phenomenon,
- and the homogenization principles which aided in construction of the constitutive equations.

The prediction of the thermomechanical cycle of SMPs while remaining in the linear elastic regime with small deformations ($< 10\%$) will be instrumental as a building block for the future research of system responses and development of models involving large deformations ($\gg 10\%$).

Chapter 3

Shape Memory Polymers in a Rod System

3.1 Introduction

Applications involving the one-dimensional displacement of rods using various smart materials have long been desired due to their lightweight, non-intrusive and repeatable natures. Stacked PZT actuators are used as x - and y - stages in atomic force microscopes to provide specimen positioning with nanometer accuracy [39]. Infrastructure applications includes outfitting connection points of bridges with shape memory alloy (SMA) rods for vibration isolation. The SMAs are designed to dissipate the maximum amount of energy while in their pseudoelastic phase. Magnetostrictive transducers employ Terfenol-D rods whose magnetic moments are controlled by solenoids surrounding the rod. The resulting displacement produces a significant amount of force and applications such as out-of-round milling can be achieved.

Shape memory polymers have more recently come into consideration for many applications due to their lightweight structure and large-deformation recovery capabilities. Aerospace applications are currently being explored where large, sturdy structures (such as space solar power system concepts) are needed. Shape memory polymers are a leading candidate for integration in longerons, battens, and cross members for constructing collapsible booms due to their high modulus below the glass transition region and their capability to recover from large strains. The booms are designed to be collapsed and rolled to decrease

the storage volume. Through any number of processes, the original triangular shape is to be completely recovered [14].

Figure 3.1 illustrates a standard triangular boom with longerons, battens and cross members. When collapsed, the stress exerted on the battens and cross members is uniaxial in nature and the interconnecting layout of the entire boom creates a spring-like force that decreases in magnitude during recovery. To consider shape memory polymers for use in such a mechanical system, one must explore their capabilities in a forced rod system.

3.2 Rod Model Setup

To quantify the dynamics of a rod, consider the the shape memory rod mechanical system shown in Figure 3.2(a) and the corresponding infinitesimal element $[x, x + \Delta x]$ shown in Figure 3.2(b). The displacement of the rod at time t and position x on the rod is given

Figure 3.1: A standard layout for a boom intended for space applications with possibilities for shape memory polymer integration as longerons, battens, or cross members.

Figure 3.2: (a) Rod of length ℓ and cross-sectional area A with fixed end at $x = 0$ and energy dissipating boundary at $x = \ell$. (b) Infinitesimal element considered when balancing forces.

by $u(t, x)$. The dissipative boundary condition is characterized by the values for mass m_ℓ , damping c_ℓ , and spring constant k_ℓ . Any externally applied forces at time t and position x along the rod are lumped into $f(t, x)$. The in-plane force resultant is

$$N(t, x) = \int_A \sigma \, dA = \sigma(t, x, T)A,$$

where A denotes the cross-sectional area, since the rod is considered uniform and homogeneous.

The strong formulation of the rod model is found by balancing forces over the infinitesimal rod element. The balance of forces gives

$$\begin{aligned} \int_x^{x+\Delta x} \rho A \frac{\partial^2 u}{\partial t^2}(t, s) \, ds &= N(t, x + \Delta x) - N(t, x) + \int_x^{x+\Delta x} f(t, s) \, ds \\ \Rightarrow \lim_{\Delta x \rightarrow 0} \frac{1}{\Delta x} \int_x^{x+\Delta x} \rho A \frac{\partial^2 u}{\partial t^2}(t, s) \, ds &= \lim_{\Delta x \rightarrow 0} \frac{N(t, x + \Delta x) - N(t, x)}{\Delta x} \\ &\quad + \lim_{\Delta x \rightarrow 0} \frac{1}{\Delta x} \int_x^{x+\Delta x} f(t, s) \, ds \end{aligned}$$

which yields

$$\rho A \frac{\partial^2 u}{\partial t^2} = \frac{\partial N}{\partial x} + f \quad (3.1)$$

as the strong formulation of the rod model. Strain is defined as the ratio of the change in length and the original length, therefore the local strain defined in terms of the displacement is

$$\varepsilon = \lim_{\Delta x \rightarrow 0} \frac{\Delta u}{\Delta x} = \frac{\partial u}{\partial x}.$$

Spatial boundary conditions are imposed to both the fixed and free ends. By assuming a fixed end condition at $x = 0$, it follows that

$$u(t, 0) = 0.$$

The boundary condition at the free end results from the balance of forces between the rod at $x = \ell$ and the dissipative boundary and is expressed as

$$N(t, \ell) = -k_\ell u(t, \ell) - c_\ell \frac{\partial u}{\partial t}(t, \ell) - m_\ell \frac{\partial^2 u}{\partial t^2}(t, \ell).$$

The initial conditions are specified as

$$\begin{aligned} u(0, x) &= u_0(x) \\ \frac{\partial u}{\partial t}(0, x) &= v_0(x). \end{aligned}$$

3.3 Homogenized SMP Model

Consider the constitutive behavior of a shape memory polymer derived in Chapter 2 given as

$$\sigma(t, x, T) = Y(T) \left[\frac{\partial u}{\partial x}(t, x) - \varepsilon_T(T) - \varepsilon_s(x, T) \right].$$

Because the model is constitutively defined independently for cooling and heating, the rod model will have to be addressed in this manner, too. During cooling, the thermal and stored strains are defined as

$$\begin{aligned} \varepsilon_T^-(T) &= \phi_f^-(T) \int_{T_0}^T \alpha_f(\theta) \phi_f^-(\theta) d\theta + (1 - \phi_f^-(T)) \int_{T_0}^T \alpha_a(\theta) (1 - \phi_f^-(\theta)) d\theta \\ \frac{d\varepsilon_s^-}{dT}(t, x, T) &= \varepsilon_T^{a-}(T) \frac{d\phi_f^-}{dT}(T) + \frac{d\varepsilon_T^{a-}}{dT}(T) \phi_f^-(T) \\ &\quad + \left(\frac{Y(T)}{Y_a(T)} - \frac{Y(T)}{Y_f(T)} \right) \left[\frac{\partial u}{\partial x}(t, x) - \varepsilon_T^-(T) - \varepsilon_s^-(x, T) \right] \frac{d\phi_f^-}{dT}(T); \\ \varepsilon_s^-(t_0, x, T_0) &= \varepsilon_s^0(x). \end{aligned}$$

The state variable ϕ_f^- is the frozen fraction found during cooling. The coefficients of thermal expansion in the active and frozen states are given respectively as α_a and α_f . The thermal strain accumulated entirely in the active state is defined as ε_T^{a-} . Y , Y_a and Y_f are the Young's moduli of the bulk polymer, active and frozen states respectively.

During heating, the thermal and stored strains are defined as

$$\begin{aligned} \varepsilon_T^+(T) &= \phi_f^+(T) \int_{T_0}^T \alpha_f(\theta) \phi_f^+(\theta) d\theta + (1 - \phi_f^+(T)) \int_{T_0}^T \alpha_a(\theta) (1 - \phi_f^+(\theta)) d\theta \\ &\quad - \left(\int_{T_0}^{T_1} \alpha_f(\theta) \phi_f^+(\theta) d\theta - \int_{T_0}^{T_1} \alpha_f(\theta) \phi_f^-(\theta) d\theta \right) \\ \varepsilon_s^+(T) &= \int_{T_0}^{T_1} \varepsilon_s^-(\theta, x) \delta(\phi_f^+(T) - \phi_f^-(\theta)) d\theta \end{aligned} \tag{3.2}$$

where $\varepsilon_s^+(T)$ can be approximated by

$$\varepsilon_s^+(T) = \varepsilon_s^-(T_1) \phi_f^+(T).$$

The state variable ϕ_f^+ is the frozen fraction found during heating. The limits T_0 and T_1 are the initial and final temperatures during cooling and δ is the Dirac-delta. The stored strain in (3.2) can be approximated by

$$\varepsilon_s^+(t, x, T) = \varepsilon_s^-(\phi_f^+(T)).$$

Since the controlled input is T , define $T = T(t)$ and the constitutive equations during cooling and heating can be rewritten as functions solely in terms of time and space. Therefore,

$$\sigma(t, x) = Y(T(t)) \left[\frac{\partial u}{\partial x}(t, x) - \widehat{\varepsilon}_T(t) - \widehat{\varepsilon}_s(t, x) \right]$$

where $\widehat{\varepsilon}_T$ and $\widehat{\varepsilon}_s$ are the time-dependent thermal and stored strains respectively. During cooling, the thermal and stored strains are defined as

$$\begin{aligned} \widehat{\varepsilon}_T^-(t) &= \phi_f^-(T(t)) \int_0^t \alpha_f(T(\tau)) \phi_f^-(T(\tau)) T'(\tau) d\tau \\ &+ (1 - \phi_f^-(T(t))) \int_0^t \alpha_a(T(\tau)) (1 - \phi_f^-(T(\tau))) T'(\tau) d\tau \\ \frac{d\widehat{\varepsilon}_s^-}{dt}(t, x) &= \left(\varepsilon_T^{a-}(T(t)) \frac{d\phi_f^-}{dT}(T(t)) + \frac{d\varepsilon_T^{a-}}{dT}(T(t)) \phi_f^-(T(t)) \right) \dot{T}(t) \\ &+ \left(\frac{Y(T(t))}{Y_a(T(t))} - \frac{Y(T(t))}{Y_f(T(t))} \right) \left[\frac{\partial u}{\partial x}(t, x) - \varepsilon_T^-(T(t)) - \widehat{\varepsilon}_s^-(t, x) \right] \frac{d\phi_f^-}{dT}(T(t)) \dot{T}(t); \\ \widehat{\varepsilon}_s^-(t_0, x) &= \varepsilon_s^0(x). \end{aligned}$$

During heating, the thermal and stored strains are defined as

$$\begin{aligned} \widehat{\varepsilon}_T^+(t) &= \phi_f^-(T(t)) \int_0^t \alpha_f(T(\tau)) \phi_f^-(T(\tau)) T'(\tau) d\tau \\ &+ (1 - \phi_f^-(T(t))) \int_0^t \alpha_a(T(\tau)) (1 - \phi_f^-(T(\tau))) T'(\tau) d\tau \\ &- \left(\int_{T_0}^{T_1} \alpha_f(\theta) \phi_f^+(\theta) d\theta - \int_{T_0}^{T_1} \alpha_f(\theta) \phi_f^-(\theta) d\theta \right) \\ \widehat{\varepsilon}_s^+(t, x) &= \int_{T_0}^{T_1} \varepsilon_s^-(\theta, x) \delta(\phi_f^+(T(t)) - \phi_f^-(\theta)) d\theta. \end{aligned}$$

The superscripts ‘-’ and ‘+’ used to denote the constitutive equations for cooling and heating portions are dropped during model development due to the model’s generality.

3.4 Weak Formulation using Constitutive SMP Model

The weak formulation of the rod model is found by multiplying (3.1) by $\phi \in H_0^1(0, \ell)$ and using integration by parts:

$$\begin{aligned} & \int_0^\ell A\rho(T(t)) \frac{\partial^2 u}{\partial t^2} \phi \, dx + \int_0^\ell \left(AY(T(t)) \frac{\partial u}{\partial x} + Ac(T(t)) \frac{\partial^2 u}{\partial x \partial t} \right) \frac{d\phi}{dx} \, dx \\ = & \int_0^\ell f(t, x) \phi \, dx + AY(T(t)) \widehat{\varepsilon}_T(t) \int_0^\ell \frac{d\phi}{dx} \, dx + AY(T(t)) \int_0^\ell \widehat{\varepsilon}_s(t, x) \frac{d\phi}{dx} \, dx \\ & - \left[k_\ell u(t, \ell) - c_\ell \frac{\partial u}{\partial t}(t, \ell) - m_\ell \frac{\partial^2 u}{\partial t^2}(t, \ell) \right] \phi(\ell). \end{aligned} \quad (3.3)$$

Equation (3.3) must hold for all ϕ in the space of test functions

$$V = \{ \Phi = (\phi, \varphi) \in L^2(0, \ell) \times \mathbb{R} \mid \phi \in H^1(0, \ell), \phi(0) = 0, \phi(\ell) = \varphi \}.$$

Let $\{\phi_i\}$ be piecewise linear splines defined as

$$\begin{aligned} \phi_j(x) &= \frac{1}{h} \begin{cases} x - x_{j-1}, & x_{j-1} \leq x < x_j \\ x_{j+1} - x, & x_j \leq x < x_{j+1} \\ 0, & \text{otherwise} \end{cases} \quad , \quad j = 1, \dots, N-1 \\ \phi_N(x) &= \frac{1}{h} \begin{cases} x - x_{N-1}, & x_{N-1} \leq x < x_N \\ 0, & \text{otherwise} \end{cases} \end{aligned} \quad (3.4)$$

The solution to (3.3) can be approximated using these linear splines via the expansion

$$u^N(t, x) = \sum_{j=1}^N u_j(t) \phi_j(x) \quad (3.5)$$

and (3.3) becomes

$$\begin{aligned} & \sum_{j=1}^N \left[\ddot{u}_j(t) \int_0^\ell A\rho(T(t)) \phi_i \phi_j \, dx + \dot{u}_j(t) \int_0^\ell Ac(T(t)) \phi_i' \phi_j' \, dx + u_j(t) \int_0^\ell AY(T(t)) \phi_i' \phi_j' \, dx \right] \\ = & \int_0^\ell f(t, x) \phi_i \, dx + AY(T(t)) \widehat{\varepsilon}_T(t) \int_0^\ell \phi_i' \, dx + \int_0^\ell AY(T(t)) \widehat{\varepsilon}_s(t, x) \phi_i' \, dx \\ & - [k_\ell u_N(t) \phi_N(\ell) + c_\ell \dot{u}_N(t) \phi_N(\ell) + m_\ell \ddot{u}_N(t) \phi_N(\ell)] \phi_N(\ell). \end{aligned}$$

This can be written as a second order vector valued system

$$\mathbb{M}(t) \ddot{\mathbf{u}}(t) + \mathbb{Q}(t) \dot{\mathbf{u}}(t) + \mathbb{K}(t) \mathbf{u}(t) = \mathbf{f}(t) + AY(T(t)) \widehat{\varepsilon}_T(t) \mathbf{b} + AY(T(t)) \mathbf{e}_s(t) \quad (3.6)$$

where

$$\mathbf{u}(t) = [u_1(t), \dots, u_N(t)]^T.$$

The matrices $\mathbb{M}$, $\mathbb{Q}$, and $\mathbb{K}$ are defined as

$$\begin{aligned} [\mathbb{M}]_{ij}(t) &= \int_0^\ell A\rho(T(t))\phi_i\phi_j dx + \delta_{ijN}m_\ell, \\ [\mathbb{K}]_{ij}(t) &= \int_0^\ell AY(T(t))\phi'_i\phi'_j dx + \delta_{ijN}k_\ell, \\ [\mathbb{Q}]_{ij}(t) &= \int_0^\ell Ac(T(t))\phi'_i\phi'_j dx + \delta_{ijN}c_\ell, \end{aligned}$$

and the vectors $\mathbf{f}$, $\mathbf{b}$ and $\mathbf{e}_s$ are defined as

$$\begin{aligned} [\mathbf{f}]_i(t) &= \int_0^\ell f(t, x)\phi_i(x)dx, \\ [\mathbf{b}]_i &= \int_0^\ell \phi'_i(x)dx, \\ [\mathbf{e}_s]_i(t) &= \int_0^\ell \widehat{\varepsilon}_s(t, x)\phi'_i(x)dx. \end{aligned}$$

To formulate a first-order semi-discrete system, let $\mathbf{z} = [\mathbf{u}, \dot{\mathbf{u}}]^T$ and define the system matrix $\mathbb{A}$ as

$$\mathbb{A}(t) = \begin{bmatrix} 0 & \mathbb{I} \\ -\mathbb{M}^{-1}(t)\mathbb{K}(t) & -\mathbb{M}^{-1}(t)\mathbb{Q}(t) \end{bmatrix}, \quad (3.7)$$

and vectors $\mathbf{F}(t)$, $\mathbf{B}(t)$ and $\mathbf{E}_s(t)$ as

$$\mathbf{F}(t) = \begin{bmatrix} 0 \\ \mathbb{M}^{-1}(t)\mathbf{f}(t) \end{bmatrix}, \quad \mathbf{B}(t) = \begin{bmatrix} 0 \\ \mathbb{M}^{-1}(t)\mathbf{b} \end{bmatrix}, \quad \mathbf{E}_s(t) = \begin{bmatrix} 0 \\ \mathbb{M}^{-1}(t)\mathbf{e}_s(t) \end{bmatrix}.$$

The first-order system is therefore

$$\dot{\mathbf{z}} = \mathbb{A}(t)\mathbf{z} + \mathbb{V}(t) \quad (3.8)$$

where

$$\mathbb{V}(t) = \mathbf{F}(t) + AY(T(t))\widehat{\varepsilon}_T(t)\mathbf{B}(t) + AY(T(t))\mathbf{E}_s(t).$$

3.5 Numerical Methods

To evaluate the rod model, the use of numerical schemes is necessary. Subsequently outlined are the methods implemented in MATLAB codes created to evaluate the differential equation in (3.8).

3.5.1 Gaussian Quadratures

Consider the approximation of an integral of the function $f(x)$ on the interval $[-1, 1]$. An approximation found using an N_q point expansion can be written as

$$\int_{-1}^1 f(x) dx \approx \sum_{j=1}^{N_q} f(\xi_j) \eta_j$$

where ξ_j are the Gaussian nodes and η_j are the corresponding Gaussian weights. Nodes and weights are determined by solving the system of equations generated from the error term

$$E(x^i) = \int_{-1}^1 x^i dx - \sum_{j=1}^{N_q} \xi_j^i \eta_j, \quad i = 0, \dots, 2N_q - 1 \quad (3.9)$$

Since the determination of the $2N_q$ nodes and weights are found by evaluating exactly polynomials up to order $2N_q - 1$, Gaussian quadratures have order of exactness $2N_q - 1$.

Assuming exact evaluation so that $E(x^i) = 0$ for all i , solving the system of equations in (3.9) determines the weights η_i and nodes ξ_i on the interval $[-1, 1]$. However, to find the weights and nodes on any general subinterval $[a, b]$, a 1-to-1 map is used and is defined as

$$x_i = \frac{a+b}{2} + \frac{b-a}{2} \xi_i, \quad w_i = \frac{b-a}{2} \eta_i.$$

A composite quadrature technique can be implemented on any interval with N equal subintervals. To find the $N + 1$ nodes $\{x_i\}$, $i = 0, \dots, N$, which form a uniform partition of an interval of length ℓ , we first define $h = \ell/N$ and then

$$x_i = ih.$$

The 2- and 4-point Gauss-Legendre nodes $x_{i,j}$ and weights w_j are defined by mapping the nodes ξ_j and weights η_j found on the interval $[-1, 1]$ to the interval $[x_{i-1}, x_i]$ via the relations

$$x_{i,j} = \frac{x_i + x_{i-1}}{2} + \frac{h}{2} \xi_j, \quad w_j = \frac{h}{2} \eta_j.$$

The 2- and 4-point nodes and weights on the interval $[0, \ell]$ are given in Table 3.1.

3.5.2 Trapezoid methods

Implicit trapezoid

The implicit trapezoid (Crank-Nicholson) method is a one-step method that uses minimal storage and is second-order accurate (i.e., error = $\mathcal{O}(\Delta t^3)$). For a non-autonomous

Table 3.1: Nodes and weights for Gauss-Legendre quadrature on the interval $[x_{i-1}, x_1]$.

2-point Gauss-Legendre	
$x_{i,1} = x_{i-1} + h \left(\frac{1}{2} - \frac{1}{2\sqrt{3}} \right),$	$w_1 = \frac{h}{2}$
$x_{i,2} = x_{i-1} + h \left(\frac{1}{2} + \frac{1}{2\sqrt{3}} \right),$	$w_2 = \frac{h}{2}$

4-point Gauss-Legendre	
$x_{i,1} = x_{j-1} + h \left(\frac{1}{2} - \frac{\sqrt{15+2\sqrt{30}}}{2\sqrt{35}} \right),$	$w_1 = \frac{49h}{12(18+\sqrt{30})}$
$x_{i,2} = x_{j-1} + h \left(\frac{1}{2} - \frac{\sqrt{15-2\sqrt{30}}}{2\sqrt{35}} \right),$	$w_2 = \frac{49h}{12(18-\sqrt{30})}$
$x_{i,3} = x_{j-1} + h \left(\frac{1}{2} + \frac{\sqrt{15-2\sqrt{30}}}{2\sqrt{35}} \right),$	$w_3 = \frac{49h}{12(18-\sqrt{30})}$
$x_{i,4} = x_{j-1} + h \left(\frac{1}{2} + \frac{\sqrt{15+2\sqrt{30}}}{2\sqrt{35}} \right),$	$w_4 = \frac{49h}{12(18+\sqrt{30})}$

differential equation given as

$$\begin{aligned}\dot{u} &= f(t, u) \\ u(t_0) &= u_0,\end{aligned}$$

the implicit trapezoid method can be written as

$$\begin{aligned}u_k &= u_{k-1} + \frac{\Delta t}{2}(f_{k-1} + f_k), \\ u_0 &= u_0.\end{aligned}\tag{3.10}$$

The use of this method is preferred whenever possible due to its computational advantages. However, if u_k cannot be decoupled from the implicit evaluation of f_k , then an explicit method must be used.

Explicit trapezoid

The explicit trapezoid (Heun) method, like its implicit counterpart, is a one step method that uses minimal storage and is second-order accurate. The explicit modification is made through the use of an explicit method to approximate f_k (generally forward Euler). Therefore, the implicit trapezoid method given in (3.10) can be written as

$$\begin{aligned}u_k &= u_{k-1} + \frac{\Delta t}{2}(f_{k-1} + f(t_k, u_{k-1} + \Delta t f_{k-1})), \\ u_0 &= u_0.\end{aligned}$$

The implementation of the explicit trapezoid method is considered a predictor-corrector (PECE) method given as

$$\begin{aligned} u_k^{(0)} &= u_{k-1}^{(1)} + \Delta t f_{k-1}^{(1)}, \\ f_k^{(0)} &= f(t_k, u_k^{(0)}), \\ u_k^{(1)} &= u_{k-1}^{(1)} + \frac{\Delta t}{2} \left[f_{k-1}^{(1)} + f_k^{(0)} \right], \\ f_k^{(1)} &= f(t_k, u_k^{(1)}). \end{aligned}$$

Stability

The difference between the implicit and explicit trapezoid methods is found in their stability. The region of absolute stability of any numerical method can be found by applying the linear Cauchy problem (also known as the standard test problem) given as

$$\begin{aligned} \dot{u}(t) &= \lambda u(t), \quad t > 0, \\ y(0) &= 1 \end{aligned}$$

and determining the values of $\lambda \Delta t$ that allow

$$|u_n| \rightarrow 0 \quad \text{as} \quad t_n \rightarrow +\infty. \quad (3.11)$$

The resulting stability equation for the implicit method is

$$u_n = \left[\left(1 + \frac{1}{2} \lambda \Delta t \right) / \left(1 - \frac{1}{2} \lambda \Delta t \right) \right]^n, \quad n \geq 0 \quad (3.12)$$

while the stability equation for the explicit method is

$$u_n = \left[1 + \lambda \Delta t + \frac{(\lambda \Delta t)^2}{2} \right]^n, \quad n \geq 0.$$

It can be shown that (3.12) satisfies the absolute stability condition (3.11) for any $\lambda \Delta t \in \mathbb{C}^-$. In contrast, the explicit method is bounded inside of the region found in Figure 3.3.

The concern over stability of each of the trapezoid methods is relevant when dealing with a stiff differential equation. If an implicit method cannot be used, an explicit method may become computationally cumbersome if the time step required to remain in the stability region is extremely small.

Figure 3.3: Region of stability for explicit trapezoid method. Values of $\lambda\Delta t$ are part of the complex plane.

3.5.3 Rosenbrock-Type Methods

Rosenbrock-type methods are considered “semi-implicit” methods that use a sequence of linear systems applied to differential equations. They are considered semi-implicit because they start with a diagonally implicit Runge-Kutta method generalized as

$$K_i = \Delta t f \left(t_0 + \alpha_i \Delta t, u_0 + \sum_{j=1}^{i-1} a_{ij} K_j + a_{ii} K_i \right), \quad i = 1, \dots, s$$

$$u_1 = u_0 + \sum_{i=1}^s b_i K_i.$$

Through linearization about $(t_0, u_0 + \sum_{j=1}^{i-1} a_{ij} K_j)$, replacing the Jacobian $J = \partial f / \partial u(t, u)$ with the initial Jacobian $J_0 = \partial f / \partial u(t_0, u_0)$ for computational advantage, and introducing additional linear combinations of terms $J_0 K_j$, the Rosenbrock-type method is generally given as

$$K_i = \Delta t f \left(t_0 + \alpha_i \Delta t, u_0 + \sum_{j=1}^{i-1} a_{ij} K_j \right) + \gamma_i \Delta t^2 \frac{\partial f}{\partial t}(t_0, u_0) + \Delta t J_0 \sum_{j=1}^i \gamma_{ij} K_j$$

$$u_1 = u_0 + \sum_{i=1}^s b_i K_i$$

where $\alpha_{ij}, \gamma_{ij}, b_i$ are the determining coefficients for the scheme with necessary conditions $\alpha_i = \sum_{j=1}^{i-1} \alpha_{ij}$ and $\gamma_i = \sum_{j=1}^i \gamma_{ij}$.

Consider the two-stage Rosenbrock method given as

$$\begin{aligned} K_1 &= \Delta t f(t_0, u_0) + \gamma \Delta t^2 \dot{f}(t_0, u_0) + \gamma \Delta t J_0 K_1 \quad , \\ K_2 &= \Delta t f\left(t_0 + \frac{\Delta t}{2}, u_0 + \frac{1}{2} K_1\right) + \gamma \Delta t J_0 (K_2 - K_1) \quad , \\ u(t_0 + \Delta t) &= u_0 + K_2, \end{aligned}$$

where $\gamma = 1 - 1/\sqrt{2}$. As written, this numerical scheme is second-order and, more importantly, is L -stable. This means the method is A-stable and has an asymptotic amplification factor of zero. The stability function is given as

$$u_n = \left[\frac{1 - (1 - 2\gamma)\lambda\Delta t}{(1 - \gamma\lambda\Delta t)^2} \right]^n, \quad n \geq 0.$$

3.6 Model Implementation

To evaluate $[\mathbf{f}]_i$ and $[\mathbf{e}_s]_i$, the use of an N_q -point composite Gaussian quadrature technique is necessary. To implement this composite quadrature technique, it is required that $f(t, x)$ and $\varepsilon_s^*(t, s)$ have discrete values at nodes

$$\{x_{i,j}\}_{j=1}^{N_q} \in [x_{i-1}, x_i].$$

Thus it follows that

$$\begin{aligned} [\mathbf{f}]_i(t) &= \int_0^\ell f(t, x) \phi_i(x) dx = \sum_{k=1}^N \sum_{j=1}^{N_q} f(t, x_{k,j}) \phi_i(x_{k,j}) w_j, \\ [\mathbf{e}_s]_i(t) &= \int_0^\ell \widehat{\varepsilon}_s(t, x) \phi'_i(x) dx = \sum_{k=1}^N \sum_{j=1}^{N_q} \widehat{\varepsilon}_s(t, x_{k,j}) \phi'_i(x_{k,j}) w_j. \end{aligned} \tag{3.13}$$

Both $[\mathbf{f}]_i$ and $[\mathbf{e}_s]_i$ can be simplified by the definition of $\phi_i(x)$ in (3.4). Since $\phi_i(x) \neq 0$ and $\phi'_i(x) \neq 0$ strictly on the interval (x_{i-1}, x_{i+1}) , each value of $[\mathbf{f}]_i$ and $[\mathbf{e}_s]_i$ only require the Gaussian nodes $x_{i,j}$ and $x_{i+1,j}$, $j = 1, \dots, N_q$, for evaluation. Therefore, (3.13) can be rewritten as

$$\begin{aligned} [\mathbf{f}]_i(t) &= \frac{1}{h} \sum_{j=1}^{N_q} f(t, x_{i,j}) (x_{i,j} - x_{i-1}) w_j + \frac{1}{h} \sum_{j=1}^{N_q} f(t, x_{i+1,j}) (x_{i+1} - x_{i+1,j}) w_j, \\ [\mathbf{e}_s]_i(t) &= \frac{1}{h} \sum_{j=1}^{N_q} \widehat{\varepsilon}_s(t, x_{i,j}) w_j - \frac{1}{h} \sum_{j=1}^{N_q} \widehat{\varepsilon}_s(t, x_{i+1,j}) w_j. \end{aligned} \tag{3.14}$$

Assuming the force $f(t, x)$ is continuously defined, the discrete values $f(t_k, x_{i,j})$ involve simple evaluation. In contrast, $\widehat{\varepsilon}_s(t, x)$ is the solution to a differential equation involving spacial components $\widehat{\varepsilon}_s(t, x)$ and $\frac{\partial u}{\partial x}(t, x)$. Therefore, in order to have the discrete values at $x_{i,j}$, it is necessary to have the values of $\frac{\partial u}{\partial x}(t, x_{i,j})$ and $\widehat{\varepsilon}_s(t, x_{i,j})$.

Since the value of strain will be found at each node x_i , we can implement the expansion in (3.5) so that

$$\frac{\partial u}{\partial x}(t, x_{i,j}) = \sum_{k=1}^N u_k(t) \phi'_k(x_{i,j}). \quad (3.15)$$

However, since $x_{i,j} \in [x_{i-1}, x_i]$, $\phi'_k(x_{i,j}) \neq 0$ only when $k = i - 1$, or $k = i$ and (3.15) simplifies to

$$\frac{\partial u}{\partial x}(t, x_{i,j}) = \frac{1}{h} [u_i(t) - u_{i-1}(t)]. \quad (3.16)$$

3.6.1 Stability concerns

Applying the implicit trapezoid method to (3.8) is not possible due to the coupling of implicit strain values in the evaluation of $\mathbf{e}_s$. However, applying the explicit trapezoid method causes instability and the need to decrease Δt creates a computationally prohibitive method. To explore this instability, we consider the work done by [39] on smart materials rod model. Similar to the SMP rod equation, the first order equation that describes the motion of a ferroelectric rod can be expressed as

$$\dot{\mathbf{z}} = \mathbb{A}(t)\mathbf{z} + \mathbb{V}(t) \quad (3.17)$$

where $\mathbb{A}$ is identically defined as in (3.7),

$$\mathbb{V}(t) = \begin{bmatrix} 0 \\ \mathbb{M}^{-1} (\mathbf{f}(t) + A[a_1(P(E(t)) - P_R) + a_2(P(E(t)) - P_R)^2]\mathbf{b}) \end{bmatrix}$$

and

$$\begin{aligned} [\mathbf{f}]_i(t) &= \int_0^\ell f(t, x) \phi_i(x) \, dx, \\ [\mathbf{b}]_i &= \int_0^\ell \phi'_i(x) \, dx. \end{aligned}$$

Ignoring $\mathbf{f}(t)$ for this illustration (the rod model with no applied force), it can be shown that

$$A[a_1(P(E(t)) - P_R) + a_2(P(E(t)) - P_R)^2] \approx 10^5$$

and, during model implementation, $\|\mathbf{b}\| \approx 10^{-2}$ where $\|*\|$ is the standard 2-norm. The norm of $\mathbb{M}^{-1}$ can be given as the largest singular value, and is approximately

$$\|\mathbb{M}^{-1}\| = 10^2$$

for any reasonable number of nodes along the rod. Therefore the norm of vector $\mathbb{V}(t)$ can be approximated as

$$\|\mathbb{V}\| \approx 10^5$$

and similar values are expected for SMP rods.

Substituting (3.17) into Heun's method previously outlined (letting $\mathbf{z}(t_k) = \mathbf{z}_k$ and similarly for all functions of time), we arrive at the following formulation:

$$\begin{aligned} \mathbf{z}_k^{(0)} &= \mathbf{z}_{k-1}^{(1)} + \Delta t f_{k-1}^{(1)}, \\ &= \mathbf{z}_{k-1}^{(1)} + \Delta t (\mathbb{A}_{k-1} \mathbf{z}_{k-1}^{(1)} + \mathbb{V}_{k-1}), \\ &= (\mathbb{I} + \Delta t \mathbb{A}_{k-1}) \mathbf{z}_{k-1}^{(1)} + \Delta t \mathbb{V}_{k-1} \\ f_k^{(0)} &= f(t_k, \mathbf{z}_k^{(0)}), \\ &= \mathbb{A}_k \mathbf{z}_k^{(0)} + \mathbb{V}_k \\ &= \mathbb{A}_k (\mathbb{I} + \Delta t \mathbb{A}_{k-1}) \mathbf{z}_{k-1}^{(1)} + \Delta t \mathbb{A}_k \mathbb{V}_{k-1} + \mathbb{V}_k \\ \mathbf{z}_k^{(1)} &= \mathbf{z}_{k-1}^{(1)} + \frac{\Delta t}{2} \left[f_{k-1}^{(1)} + f_k^{(0)} \right], \\ &= \mathbf{z}_{k-1}^{(1)} + \frac{\Delta t}{2} \left[\mathbb{A}_{k-1} \mathbf{z}_{k-1}^{(1)} + \mathbb{V}_{k-1} + \mathbb{A}_k (\mathbb{I} + \Delta t \mathbb{A}_{k-1}) \mathbf{z}_{k-1}^{(1)} + \Delta t \mathbb{A}_k \mathbb{V}_{k-1} + \mathbb{V}_k \right], \\ &= \left[\mathbb{I} + \frac{\Delta t}{2} (\mathbb{A}_{k-1} + \mathbb{A}_k) + \frac{\Delta t^2}{2} \mathbb{A}_k \mathbb{A}_{k-1} \right] \mathbf{z}_{k-1}^{(1)} + \left[\frac{\Delta t}{2} \mathbb{I} + \frac{\Delta t^2}{2} \mathbb{A}_k \right] \mathbb{V}_{k-1} + \frac{\Delta t}{2} \mathbb{V}_k \end{aligned}$$

The instability in this (and expectedly any other explicit method) is apparent where the vector $\mathbb{V}$ is multiplied by Δt . The rod is known to have a maximum displacement of approximately 10^{-4}m ; however, for insufficiently small values of Δt ,

$$\Delta t \mathbb{V} \gg 10^{-4}$$

and thus the differential equation (3.17) is stiff. In order for the explicit trapezoid method to generate useful results, this requires stepsizes on the order of $\Delta t \approx 10^{-7}$.

The ferroelectric rod equation can be accurately solved using the implicit trapezoid method against which, as a matter of verification, the explicit trapezoid method results are

compared. Figure (3.4) shows the comparison of ferroelectric rod equations evaluated using the implicit trapezoid rule with $\Delta t = 10^{-2}$ and explicit Heun's method with $\Delta t = 10^{-7}$. Hence Heun's method (which takes approximately 240 seconds to run versus one second of data) is visually as accurate as the trapezoid rule (which takes approximately 0.02 seconds on the same machine), but requires runtimes that are prohibitive.

3.6.2 Implementation using Rosenbrock Method

Due to the stiff nature of (3.8), the 2-stage Rosenbrock method shall be used to solve the rod model equation. Consider the differential equation as a function of t and $\mathbf{z} = [\mathbf{u}, \dot{\mathbf{u}}]$ so that

$$\begin{aligned} f(t, \mathbf{z}) &= \mathbb{A}(t)\mathbf{z} + \mathbb{V}(t), \\ \dot{f}(t, \mathbf{z}) &= \dot{\mathbb{A}}(t)\mathbf{z} + \dot{\mathbb{V}}(t), \end{aligned}$$

and

$$J = \mathbb{A}(t).$$

Consider the dynamic equation (3.6) rewritten as [37]

$$\mathbb{M}(t)\ddot{\mathbf{u}} + r(t, \mathbf{u}, \dot{\mathbf{u}}) = p(t)$$

Figure 3.4: Evaluation of the SMA rod model using the implicit trapezoid method and explicit Heun's method.

where

$$r(t, \mathbf{u}, \dot{\mathbf{u}}) = \mathbb{C}(t)\dot{\mathbf{u}} + \mathbb{K}(t)\mathbf{u}, \quad p(t) = \mathbf{f}(t) + AY(T(t))\widehat{\varepsilon}_T(t)\mathbf{b} + AY(T(t))\mathbf{e}_s(t).$$

The following steps will find the value of $\mathbf{z}$ at $t = t_{k+1}$. For all components dependent on the time step t_k , this dependence will be denoted by the subscript $\mathbf{z}_k$. The first stage of the Rosenbrock method is

$$k_1 = \Delta t f(t_k, z_k) + \gamma \Delta t J_k k_1 + \gamma \Delta t^2 \dot{f}(t_k, z_k)$$

where k_1 is a vector of length $2N$. Now consider $k_1 = [\hat{d}, \hat{e}]^T$ where $\hat{d}$ and $\hat{e}$ are vectors of length N . Then

$$\hat{d} = \Delta t \dot{\mathbf{u}}_k + \gamma \Delta t \hat{e} \tag{3.18a}$$

$$\hat{e} = \Delta t \mathbb{M}_k^{-1}(p_k - r_k) - \gamma \Delta t \mathbb{M}_k^{-1}(\mathbb{K}_k \hat{d} + \mathbb{C}_k \hat{e}) + \gamma \Delta t^2 [\dot{\mathbb{M}}_k^{-1}(p_k - r_k) + \mathbb{M}_k^{-1}(\dot{p}_k - \dot{r}_k)] \tag{3.18b}$$

and substituting (3.18a) into (3.18b), multiplying by $\mathbb{M}_k$ and solving for $\hat{e}$ yields

$$\hat{e} = \widehat{\mathbb{M}}_k^{-1} \left[\Delta t(p_k - r_k) - \gamma \Delta t^2 \mathbb{K}_k \dot{\mathbf{u}}_k + \gamma \Delta t^2 \mathbb{M}_k \dot{\mathbb{M}}_k^{-1}(p_k - r_k) + \gamma \Delta t^2(\dot{p}_k - \dot{r}_k) \right]$$

where

$$\widehat{\mathbb{M}}_k = \mathbb{M}_k + \gamma \Delta t \mathbb{C}_k + \gamma^2 \Delta t^2 \mathbb{K}_k. \tag{3.19}$$

The derivatives $\dot{p}$ and $\dot{r}$ are given as

$$\begin{aligned} \dot{p}(t) &= \dot{\mathbf{f}}(t) + A \left(\dot{Y}(T(t))\widehat{\varepsilon}_T(t) + Y(T(t))\dot{\widehat{\varepsilon}}_T(t) \right) \mathbf{b} + A \left(\dot{Y}(T(t))\mathbf{e}_s(t, x) + Y(T(t))\dot{\mathbf{e}}_s(t, x) \right), \\ \dot{r}(t) &= - \left(\dot{\mathbb{M}}^{-1}(t)\mathbb{K}(t) + \mathbb{M}^{-1}(t)\dot{\mathbb{K}}(t) \right) \mathbf{u} - \left(\dot{\mathbb{M}}^{-1}(t)\mathbb{C}(t) + \mathbb{M}^{-1}(t)\dot{\mathbb{C}}(t) \right) \dot{\mathbf{u}} \end{aligned}$$

where

$$\begin{aligned} [\dot{\mathbf{f}}]_i(t) &= \int_0^\ell \dot{f}(t, x) \phi_i(x) \, dx, \\ [\dot{\mathbf{e}}_s]_i(t) &= \int_0^\ell \dot{\widehat{\varepsilon}}_s(t, x) \phi'_i(x) \, dx \end{aligned}$$

are found using the identical quadrature technique used to find $\mathbf{f}$ and $\mathbf{e}_s$. Attention must be paid to $\dot{\mathbb{M}}_k^{-1}$ which is the temporal derivative of the inverse. To calculate this, one can use the relation

$$\frac{d\mathbb{M}_k^{-1}}{dt} = -\mathbb{M}_k^{-1} \frac{d\mathbb{M}_k}{dt} \mathbb{M}_k^{-1}$$

which is found simply by taking the temporal derivative of $\mathbb{M}(t)\mathbb{M}^{-1}(t) = \mathbb{I}$ and solving for $\frac{d\mathbb{M}^{-1}}{dt}$.

The second stage of the Rosenbrock method is

$$k_2 = \Delta t f\left(t_k + \frac{\Delta t}{2}, \mathbf{z}_k + \frac{1}{2}k_1\right) + \gamma \Delta t J_k(k_2 - k_1)$$

where the values of $t_k + \Delta t/2$ and $\mathbf{z}_k + k_1/2$ are denoted by

$$t_{1/2} = t_k + \Delta t/2,$$

$$\mathbf{u}_{1/2} = \mathbf{u}_k + \hat{d}/2,$$

$$\dot{\mathbf{u}}_{1/2} = \dot{\mathbf{u}}_k + \hat{e}/2.$$

For all vector and scalar values dependent on $t_{1/2}$, $u_{1/2}$ and $\dot{u}_{1/2}$ this dependence will be denoted by the subscript $\mathbf{z}_{1/2}$

Similarly to the first stage of the Rosenbrock method, consider $k_2 = [d, e]^T$ where d and e are vectors of length N . Then

$$d = \Delta t \left(\dot{\mathbf{u}}_k + \frac{1}{2}\hat{e} \right) + \gamma \Delta t (e - \hat{e}) \quad (3.20a)$$

$$e = \Delta t \mathbb{M}_{1/2}^{-1}(p_{1/2} - r_{1/2}) - \gamma \Delta t \mathbb{M}_k^{-1} \left(\mathbb{K}_k(d - \hat{d}) + \mathbb{C}_k(e - \hat{e}) \right) \quad (3.20b)$$

and substituting (3.20a) into (3.20b), multiplying by $\mathbb{M}_k$ and solving for e yields

$$e = \hat{\mathbb{M}}_k^{-1} \left[\Delta t \mathbb{M}_k \mathbb{M}_{1/2}^{-1}(p_{1/2} - r_{1/2}) - \gamma \Delta t^2 \left(\frac{1}{2} - 2\gamma \right) \mathbb{K}_k \hat{e} + \gamma \Delta t \mathbb{C}_k \hat{e} \right]$$

where $\hat{\mathbb{M}}_k$ is previously defined in (3.19).

Special consideration must be paid to $p_{1/2}$ when evaluating $\mathbf{e}_s(t_{1/2})$. Since

$$[\mathbf{e}_s]_i(t) = \int_0^\ell \hat{\varepsilon}_s(t, x) \phi'_i(x) dx$$

we will need the Gaussian nodal values of $\frac{\partial u}{\partial x}$ and $\hat{\varepsilon}_s$ at time $t = t_{1/2}$. For the values of strain, we will again employ (3.5) so that

$$\frac{\partial u^N}{\partial x}(t_{1/2}, x) = \sum_{j=1}^N u_j(t_{1/2}) \phi'_j(x)$$

where $\mathbf{u}(t_{1/2})$ is found from the first step of Rosenbrock's method.

The stored strain $\hat{\varepsilon}_s(t_{1/2}, x)$ can be found using the implicit trapezoid method where

$$\hat{\varepsilon}_s(t_{1/2}, x) = \hat{\varepsilon}_s(t_k, x) + \frac{\Delta t}{4} \left[\dot{\hat{\varepsilon}}_s(t_k, x) + \dot{\hat{\varepsilon}}_s(t_{1/2}, x) \right].$$

The final step in Rosenbrock's method is to update the new values of $\mathbf{u}$ and $\dot{\mathbf{u}}$ by

$$\mathbf{u}_{k+1} = \mathbf{u}_k + d,$$

$$\dot{\mathbf{u}}_{k+1} = \dot{\mathbf{u}}_k + e.$$

3.7 Experimental Procedure

Unlike their PZT, SMA, and magnetostrictive transducer counterparts, shape memory polymers in a rod system have few existing industrial applications and available data is lacking. To test the rod model, experimental data was collected from a shape memory polymer developed by Christopher Yakacki. A tert-butyl acrylate (tBA) monomer, poly(ethylene glycol) dimethacrylate (PEG550) crosslinker, and the photoinitiator 2,2-dimethoxy-2-phenylacetophenone were used. A monomer solution was created by combining tBA, PGE550 and initiator with a 79.9:20.0:0.1 weight ratio. The solution was mixed manually in a glass vial and then injected between two glass slides using a pipette. The glass slides were separated with 1 mm spacers and coated with Rain-X, which acted as a nonreactive releasing agent. Photopolymerization was then achieved by placing the solutions under a UVP CL-1000 Ultraviolet Crosslinker for 10 minutes. Samples for thermo-mechanical testing were laser cut from the polymer to dimensions of 20 mm×2 mm×1 mm. The edges of the samples were polished using 600-grit silicon carbide sandpaper to remove any edge effects caused by the laser cutting. The polymer samples were tested using a PerkinElmer Dynamic Mechanical Analyzer (DMA-7). Experimental results are shown in Figures 3.5 to 3.8.

3.7.1 Isothermal tension and compression

To determine the polymer's modulus when fully frozen and fully active, uniaxial tensile stress-strain experiments were conducted. Since the model assumes small deformations resulting in a linear stress-strain relation, the modulus of the polymer is determined to be the slope of the loading curve prior to yield. Each subsequent experiment is run

on a temperature range from 273°K to 373°K, so isothermal stress-strain tests were run accordingly and the results are shown in Figure 3.5.

3.7.2 Unconstrained cooling and heating

A polymer left in a stress-free state will deform during cooling and heating as a result of thermal expansion. By cooling a polymer from $T = 373^\circ\text{K}$ to $T = 273^\circ\text{K}$ and then subsequently heating it back to $T = 373^\circ\text{K}$, the thermal expansion coefficients can be approximated for both the frozen and active states. Figure 3.6 illustrates the data during heating after the polymer was cooled with no applied forces at a rate of $1^\circ\text{K}/\text{min}$. The near-linear deformation leads to the assumption that the thermal expansion coefficients in both the frozen and active states are constant.

3.7.3 Glass transition

To approximate the glass transition process, $\tan \delta$ tests were run at 1°K min^{-1} and 3°K min^{-1} as these were the rates at which all experiments were run. The results are shown in Figure 3.7. The affect rate of change in temperature has on the polymer is very apparent as the $\tan \delta$ peaks for heating and cooling are further away for higher rates of change.

Figure 3.5: Isothermal stress-strain experiments used to determine the elastic modulus in both the frozen and active states.

Figure 3.6: Unconstrained heating at $1^{\circ}\text{K}/\text{min}$ immediately following a cooling cycle with no applied forces.

Figure 3.7: $\text{Tan } \delta$ tests on polymer samples conducted at $1^{\circ}\text{K min}^{-1}$ and $3^{\circ}\text{K min}^{-1}$.

3.7.4 Constrained heating.

The response of a shape memory polymer rod during the shape recovery process is highly dependent on the applied constraining forces. Figure 3.8(a) shows the response of the polymer with static applied forces of 0, 10, 30, 50, and 100 kPa while heating the polymer from $T = 273^\circ\text{K}$ to $T = 373^\circ\text{K}$. The polymer was previously cooled from its reference temperature of $T_r = 373^\circ\text{K}$ to $T = 273^\circ\text{K}$ with no applied forces so that no mechanical strain was stored.

Figure 3.8(b) shows the normalized response of the polymer with static applied forces of 0, 100, 200, 300, 400, 450, and 500 kPa while heating the polymer from $T = 273^\circ\text{K}$ to $T = 373^\circ\text{K}$. The polymer was previously cooled from its reference temperature of $T_r = 333^\circ\text{K}$ to $T = 273^\circ\text{K}$ with a static force of 500 kPa so that active mechanical strain was stored. The data has been normalized due to the expected “spring back” that will occur when releasing the static force before heating. Several of the data sets gathered during heating are incomplete due to sample failure attributed to large values of applied stress during heating. As the sample begins to fail, the strain increases since the integrity of the sample is compromised. This is seen in the data for the 300, 400, and 450 kPa experiments.

Figure 3.8: Recovery of a polymer with different values of static applied force during heating. The samples were previously cooled with (a) no applied force and (b) a static force of 500 kPa.

3.8 Homogenized rod model prediction

To implement the rod model as presented in Section 3.6.2, the parameters for the polymer need to be estimated. The isothermal stress-strain relations in Figure 3.5 indicate the modulus of the frozen and active states can be defined respectively as $Y_f(273) = 526$ MPa and $Y_a(373) = 1.84$ MPa. Similar to [32], the frozen modulus is assumed to be constant while the active modulus is defined as $Y_a(T) = 3NkT$ where N is the crosslink density, k is Boltzmann's constant and T is absolute temperature. The unconstrained heating data in Figure 3.6 allow the assumption that the thermal expansion in both the frozen and active states is linear and the thermal expansion coefficients are $\alpha_f = 1.19 \times 10^{-4} \text{ K}^{-1}$ and $\alpha_a = 2.38 \times 10^{-4} \text{ K}^{-1}$.

3.8.1 Model Validation

Using the physical parameters of the polymer found from the previous tests, as well as the glass transition defined by the $\tan \delta$ data using the method defined in Section 2.6, Figure 3.9 shows the homogenized rod model's prediction of the partially constrained recovery following different constraints during cooling.

Figure 3.9(a) shows the quantitative similarities the model has with the data after the polymer was cooled with no applied forces. Below the glass transition, the rod model

Figure 3.9: Homogenized rod model prediction of constrained recovery of a polymer that was previously cooled with (a) no applied force and (b) a static force of 500 kPa.

is linear in nature (as expected with a constant thermal expansion coefficient); however, the data exhibits a quadratic nature below the glass transition. This can be attributed to thermal effects due to the speed that the test was run, $3^\circ\text{K}/\text{min}$. After being cooled at such a high rate, “thermal inertia” causes the polymer to continue to contract even though the ambient temperature is increasing. For experiments run sufficiently slow and over sufficiently broad temperature ranges, this inertial effect becomes negligible (as is seen in Figure 3.6) and the data should quantitatively resemble the model’s predicted strain. Even with this thermal effect present, the overall behavior is captured well by the homogenized rod model.

Figure 3.9(b) shows the qualitative and quantitative similarities between the data and the model’s prediction of the normalized strain recovery. The model predicts the magnitude of deformation and the overall stored strain release accurately. Differences between the data and model occur at the glass transition where the data seems to indicate the onset of the glass transition happens at a lower temperature than what the model predicts. Similar to the constrained recovery data in [32], apparent strain relaxation can be attributed to the early onset of strain recovery. After the glass transition and strain recovery processes are complete, the model predicts the response of stress against the increasing value of thermal strain.

3.9 Model Properties

Whereas data is easily collected for a rod with a static applied force applied, experiments are currently being designed to collect data from a polymer rod/mechanical spring system. Because the rod model qualitatively and quantitatively predicts the polymer rod with a static force, we now wish to use the model in a predictive manner for future experiments.

Consider a polymer rod system where the externally applied force $\mathbf{f} = 0$ but where the dissipative element at the end of the rod ($x = \ell$) is present. If the rod and spring begin at equilibrium, a change in temperature creates thermal expansion in the polymer which will cause a displacement. The spring will act to prevent this displacement by working against the thermal expansion. Figure 3.10 illustrates how the polymer rod system would react during cooling.

Now consider heating a rod from $T = T_1$ to T_0 that has been previously cooled

Figure 3.10: Theoretical strain while cooling a polymer with different values of spring constants k_ℓ for the attached spring assuming no end mass or damping.

in an unforced manner. If the dissipative element with different spring constants k_ℓ are assumed on the system, the polymer displacement is largely affected. Figure 3.11 compares the model's prediction of the rod with different values of k_ℓ during this heating process.

For both predictive tests, it is apparent that, due to the high modulus at temperatures below the glass transition region, the polymer is able to resist the spring's restorative force. While the temperature is above the glass transition, the polymer is very susceptible to the spring's force, almost eliminating any displacement for sufficiently large values of k_ℓ .

3.10 Conclusion

A rod model for shape memory polymers implementing the homogenized constitutive equations developed in Chapter 2 is developed. The predictive capabilities of the model is illustrated in Section 3.8.1 as compared to data collected by C. Yakacki. Theoretical experiments are predicted with the model in Section 3.9 in order to illustrate more of the model's capabilities. Future research and experiments are necessary to verify these predictions.

As the need for lightweight and high performance smart materials continues to grow, the need to properly predict the deformation characteristics grows also. The continued improvement of predictive models such as the homogenized rod model is tantamount in the development of structures which implement these smart materials.

Figure 3.11: Theoretical strain while heating a polymer with different values of spring constants k_ℓ for the attached spring.

Chapter 4

Models for Large Strain in Polymers

Whereas the homogenized model developed in Chapter 2 relies on the assumption that deformations are small and the stress-strain relation is linear in nature, we wish to examine the integration of the nonlinear stress-strain relation for large deformations. There has been a considerable amount of research and modeling done for isothermal deformations of polymers both in the active and frozen states; however, the amount of research on thermomechanical cycles is lacking. A linear model developed by Tobushi et. al. [41] uses the standard linear viscoelastic model to define the stress-strain relation. The stress-strain relation is later redefined in [42] as nonlinear by adding power terms of stress. The temperature dependence of the stress-strain relation that Tobushi implements is the necessary feature for temperature-induced deformations.

Isothermal models that incorporate large-strain dynamics can be lumped into two categories: deformation in the active, elastic state and deformation in the frozen, inelastic state. Section 4.1 outlines existing models that predict the large deformation characteristics of active polymers above the glass transition temperature. Models that incorporate the large deformation characteristics of frozen polymers below the glass transition temperature are outlined in Section 4.3. Finally, a phenomenological model is presented in Section 4.3.4 due to its simplicity and efficiency in simulations.

Chapter 2 defines the stress-strain relations in terms of engineering stress σ_E and engineering strain ε_E , both very accurate based on the assumption of small deformations

because the cross-sectional area changes little due to the deformation. In this chapter, large deformations are assumed and, in order to account for the possible change in cross-sectional area (seen when the polymer sample “necks”), the stress-strain relations will be in terms of true stress and true strain. The true strain is defined as $\varepsilon = \ln(1 + \varepsilon_E)$ and true stress is defined as $\sigma = \sigma_E(1 + \varepsilon_E)$. Because both the true strain and true stress are in terms of $1 + \varepsilon_E$, it is common to define this as the stretch $\lambda = 1 + \varepsilon_E$.

4.1 Models for Large Strain in Active Polymers

The classical experiments by Treloar [43] on natural rubber discuss the non-linear, neo-Hookean nature of rubber elasticity and work done by Kuhn and Gr $\ddot{u}$ n [28] as well as James and Guth [27] attempt to model these polymer networks. James and Guth discuss dividing a polymer network into equal parts of three oriented polymers which lay on the principle axes of a cube. Work done by Flory and Rehner [17] proposed a four-chain, tetrahedral geometry for a polymer network. Most recently, work by Arruda and Boyce [3] proposed an eight-chain, cubic geometry. A full-network model was proposed by Treloar [44] where the orientation of an unoriented polymer network was taken to be spherically symmetric, however computation of this sort was prohibitive until more recently.

4.1.1 Mathematics of a Single Chain

Consider a polymer chain described by a vector in spherical coordinates as shown in Figure 4.1 (To simplify notation, all values of the reference state will contain a subscript 0 while all deformed configurations will not). The initial end-to-end vector $\mathbf{r}_0$ is described by angles $0 \leq \phi_0 \leq \pi$ and $0 \leq \theta_0 \leq 2\pi$. As the chain is deformed, the strained state of the chain $\mathbf{r}$ is defined by length r and angles ϕ and θ . Both the initial and deformed states are oriented according to some orthonormal bases $\{e_i^0\}$ and $\{e_i\}$, respectively.

The stretch of a single chain λ is considered to be the ratio of the deformed chain length and the reference chain length. In any base, we can assume that $|\lambda|^2 = \lambda^2$ is the sum of the squared values of the principle directions of stretch.

Kuhn and Gr $\ddot{u}$ n [28] originated the theory of rubber elasticity based on several fundamental assumptions. The first assumption made in Kuhn and Gr $\ddot{u}$ n’s theory regarded the definition of a polymer chain. Each network contains N chains per unit volume, where a chain is defined as the molecular segment between adjacent chemical cross-links. A cross-

link is a point on the chain that is connected to either another molecular chain or with another section of itself, thus creating a non-independent mechanical network. Between each cross-link exist n molecules of length ℓ that create the chain (n can range anywhere from 10^2 to 10^9), each with a single rotational degree of flexibility. This causes the chain to take on a randomly kinked shape (Figure 4.1).

The second assumption of Kuhn and Grn defined the length of a single chain in its undeformed state. To do this, a probability of chain lengths is necessary. Using a random walk model, the probability distribution of the end-to-end length of a chain can be written as

$$p(r) = \left(\frac{3}{2\pi n\ell^2} \right)^{3/2} \exp \left(\frac{-3r^2}{2n\ell^2} \right) \quad (4.1)$$

and the probability density of a chain having length between r and $r + dr$ is

$$P(r) = 4\pi r^2 p(r).$$

The average initial squared chain length is then found by

$$r_0^2 = \frac{\int_0^\infty r^2 P(r) dr}{\int_0^\infty P(r) dr} = n\ell^2$$

and therefore $r_0 = \sqrt{n\ell}$.

Using Boltzmann's entropy which is defined as the number of microscopic configurations that result in an observed macroscopic system, we can define the entropy for a single chain in a volume element $d\tau$ as

$$s = k \ln(p(r)d\tau) \quad (4.2)$$

Figure 4.1: Single chain based on the assumptions of Kuhn and Grn [28]

where k is Boltzmann's constant. Substituting (4.1) into (4.2), the entropy can be rewritten as

$$s = k \ln \left[\left(\frac{3}{2\pi nl^2} \right)^{3/2} \exp \left(\frac{-3r^2}{2nl^2} \right) d\tau \right] = k \left[\frac{3}{2} \ln \left(\frac{3}{2\pi nl^2} \right) - \frac{3r^2}{2nl^2} + \ln(d\tau) \right]. \quad (4.3)$$

As a reference for future use, we will condense (4.3) in terms of the stretch λ ,

$$s(\lambda, T) = c - kn \left[\frac{3}{2} \left(\frac{\lambda}{\sqrt{n}} \right)^2 \right] \quad (4.4)$$

where c is a constant that incorporates the two terms independent of λ .

As noted by Treloar [43] as well as Kuhn and Grn, long molecular chains follow Gaussian chain statistics only for small deformations much less than the limiting deformation. However, large deformations approaching the limiting cases are expected. To this end, the use of Langevin statistics is introduced which incorporates a locking stretch.

The logarithm of the probability density for the chain length r using non-Gaussian statistics is given as

$$\ln(p(r)) = c - n \left[\frac{r}{nl} \beta + \ln \frac{\beta}{\sinh \beta} \right]$$

where c is a constant and $\beta = \mathcal{L}^{-1}(r/nl)$ is the inverse Langevin function where

$$\mathcal{L}(\beta) = \coth \beta - 1/\beta = r/nl.$$

Again using Boltzmann's entropy, the entropy using non-Gaussian statistics can be written as

$$s = c - kn \left[\frac{r}{nl} \beta + \ln \frac{\beta}{\sinh \beta} \right], \quad \beta = \mathcal{L}^{-1}(r/nl). \quad (4.5a)$$

Rewritten in terms of the stretch $\lambda = r/r_0$, equation (4.5a) is

$$s(\lambda, T) = c - kn \left[\frac{\lambda}{\sqrt{n}} \beta + \ln \frac{\beta}{\sinh \beta} \right], \quad \beta = \mathcal{L}^{-1}(\lambda/\sqrt{n}). \quad (4.5b)$$

Although dissimilar in presentation, the Gaussian and Langevin statistical derivations of entropy have similar Taylor expansions. Consider the series expansion of the bracketed term of (4.5b) and restate the entropy as

$$s(\lambda) = c - kn \left[\frac{3}{2} \left(\frac{\lambda}{\sqrt{n}} \right)^2 + \frac{9}{20} \left(\frac{\lambda}{\sqrt{n}} \right)^4 + \frac{99}{350} \left(\frac{\lambda}{\sqrt{n}} \right)^6 + \dots \right]. \quad (4.6)$$

Recalling (4.4), we note that the entropy terms are identical through the second order term where the higher order terms in (4.6) deal with the non-Gaussian nature of the molecular chain.

The Helmholtz free energy for a single chain at stretch λ is given by $\psi = -Ts$; therefore, the Helmholtz energy using Gaussian statistics is

$$\psi = nkT \left(\frac{3\lambda^2}{2n} \right) - c^*$$

and the Helmholtz energy using non-Gaussian statistics is

$$\psi = nkT \left(\frac{\lambda}{\sqrt{n}} \beta + \ln \frac{\beta}{\sinh \beta} \right) - c^*; \quad \beta = \mathcal{L}^{-1} \left(\frac{\lambda}{\sqrt{n}} \right). \quad (4.7)$$

We know that stress can be defined as

$$\sigma = \frac{\partial \psi}{\partial \varepsilon} \quad (4.8)$$

however, our definition of the Helmholtz energy is in terms of stretch λ and not strain ε . This is easy to correct, since true strain is considered the logarithm of one-plus-engineering strain ($\varepsilon = \ln(1 + \varepsilon^{\text{eng}})$), and engineering strain is considered to be stretch-minus-one ($\varepsilon^{\text{eng}} = \lambda - 1$). Therefore, the relation between strain and stretch is given as

$$\varepsilon = \ln \lambda$$

and (4.8) becomes

$$\sigma = \frac{\partial \psi}{\partial \lambda} \frac{d\lambda}{d\varepsilon} = \lambda \frac{\partial \psi}{\partial \lambda}. \quad (4.9)$$

To find the derivative of $\mathcal{L}^{-1}(\lambda/\sqrt{n})$, first consider

$$\mathcal{L}^{-1} \left(\frac{\lambda}{\sqrt{n}} \right) = \beta$$

and thus

$$\mathcal{L}(\beta) = \mathcal{L} \left(\mathcal{L}^{-1} \left(\frac{\lambda}{\sqrt{n}} \right) \right). \quad (4.10)$$

Implementing the chain rule on (4.10) yields

$$\frac{d}{d\lambda}(\mathcal{L}(\beta)) = \frac{d}{d\beta}(\mathcal{L}(\beta)) \frac{d\beta}{d\lambda} = \frac{1}{\sqrt{n}}$$

and solving for $\frac{d\beta}{d\lambda}$ yields

$$\frac{d\beta}{d\lambda} = \frac{1}{\sqrt{n}} \left(\frac{d\mathcal{L}}{d\beta} \right)^{-1} = \frac{1}{\sqrt{n}} \left(-\frac{1}{\sinh^2 \beta} + \frac{1}{\beta^2} \right). \quad (4.11)$$

To find the stress on a single stretched chain using Langevin statistics, the derivative of β becomes necessary. Therefore, recalling (4.7), it follows that

$$\begin{aligned}\frac{\partial\psi}{\partial\lambda} &= nkT \left[\frac{\beta}{\sqrt{n}} + \frac{\lambda}{\sqrt{n}} \frac{\partial\beta}{\partial\lambda} + \frac{\sinh\beta}{\beta} \left(\frac{\sinh\beta - \beta \cosh\beta}{\beta^2} \right) \frac{\partial\beta}{\partial\lambda} \right] \\ &= \sqrt{n}kT\beta + nkT \left[\frac{\lambda}{\sqrt{n}} + \underbrace{\frac{1}{\beta} - \frac{\cosh\beta}{\sinh\beta}} \right] \frac{d\beta}{d\lambda} \\ &= \sqrt{n}kT\beta + nkT [\mathcal{L}(\beta) - \mathcal{L}(\beta)] \frac{d\beta}{d\lambda} \\ &= \sqrt{n}kT \mathcal{L}^{-1} \left(\frac{\lambda}{\sqrt{n}} \right).\end{aligned}$$

The stresses for the Gaussian and non-Gaussian chains can now be written as

$$\sigma = 3kT\lambda^2 \quad (4.12a)$$

and

$$\sigma = \sqrt{n}kT\lambda \mathcal{L}^{-1} \left(\frac{\lambda}{\sqrt{n}} \right). \quad (4.12b)$$

Again, to observe the similarity between the Gaussian and Langevin derivations of stress, the Taylor expansion of $\mathcal{L}^{-1}$ replaced in (4.12b) yields

$$\sigma = \sqrt{n}kT\lambda \left[3\frac{\lambda}{\sqrt{n}} + \frac{9}{5} \left(\frac{\lambda}{\sqrt{n}} \right)^3 + \dots \right]$$

which is leading-order equivalent with the Gaussian stress in (4.12a).

The principle values of the Cauchy stress is defined by proper differentiation of the energy function

$$\sigma_i = \lambda_i \frac{\partial\psi}{\partial\lambda_i} - p$$

where p is an additional pressure term.

4.1.2 Linearization for Small Strains

Consider the definition of stress using Langevin statistics given as

$$\sigma(\lambda, T) = NkT\sqrt{n}\lambda \mathcal{L}^{-1} \left(\frac{\lambda}{\sqrt{n}} \right). \quad (4.13)$$

The Taylor expansion of the inverse Langevin equation is given as

$$\mathcal{L}^{-1} \left(\frac{\lambda}{\sqrt{n}} \right) = 3\frac{\lambda}{\sqrt{n}} + \frac{9}{5} \left(\frac{\lambda}{\sqrt{n}} \right)^3 + \dots$$

and (4.13) can be rewritten as

$$\begin{aligned}\sigma(\lambda, T) &= NkT\sqrt{n}\lambda \left[3\frac{\lambda}{\sqrt{n}} + \frac{9}{5} \left(\frac{\lambda}{\sqrt{n}} \right)^3 + \dots \right] \\ &= 3NkT\lambda^2 \left[1 + \frac{3}{5} \left(\frac{\lambda}{\sqrt{n}} \right)^2 + \dots \right]\end{aligned}\tag{4.14}$$

If we assume the models for large strain are accurate, then they necessarily should predict the polymer response for small strain. Recall the definition of stress given under the assumption of small deformations in Chapter 2 as the linear relation

$$\sigma_E = Y(T)\varepsilon_E,$$

where $Y(T)$ is the temperature-dependent bulk modulus and ε_E is the engineering strain which is equivalent to the mechanical strain ε_m for isothermal processes. The engineering stress from the derivation of stress using Langevin statistics in (4.14) is then

$$\begin{aligned}\lambda\sigma_E &= 3NkT\lambda^2 \left[1 + \frac{3}{5} \left(\frac{\lambda}{\sqrt{n}} \right)^2 + \dots \right] \\ \Rightarrow \sigma_E &= 3NkT\lambda \left[1 + \frac{3}{5} \left(\frac{\lambda}{\sqrt{n}} \right)^2 + \dots \right].\end{aligned}$$

Noting that n can range anywhere from 10^2 to 10^9 and for small values of stretch ($|\lambda - 1| \ll 1$), the engineering stress can be further simplified to be

$$\sigma_E = 3NkT\lambda$$

as the linear approximation of stress. It is widely accepted for active polymers that $Y(T) = 3NkT$ represents the bulk modulus of the polymer [48, 31] and noting that $\lambda = 1 + \varepsilon_e$, the engineering stress in terms of engineering strain is defined as

$$\sigma_E = Y(T)\varepsilon_E - p^*.\tag{4.15}$$

4.2 Network Models

The last assumption that Kuhn and Grn made is the entropy/energy/stress of the network is equal to the sum of the entropy/energy/stress of every individual chain. To find the energy and stress of an entire network of molecular chains, one must take into account all

possible orientations of each individual chain and the response to applied stretch. Several models have been proposed which lump the total number of chains N in a unit volume into a finite number of groups including a 3-chain and 8-chain cubic group and a 4-chain tetrahedral group.

4.2.1 3-Chain Model

The geometry of a 3-chain network model as proposed by [27] is given as follows:

1. The N chains of a network are divided into 3 independent groups, each containing $N/3$ chains.
2. Each independent group lays on the principle axes defined by the basis $\{e_i^0\}$ and one chain triad is contained in a cube with length $r_0 = \sqrt{n}l$.

The principle values of the Cauchy stress is found by the fact that $N/3$ chains contribute in each of the principle directions. Therefore,

$$\sigma_i = \frac{NkT\sqrt{n}}{3} \lambda_i \mathcal{L}^{-1} \left(\frac{\lambda_i}{\sqrt{n}} \right) - p. \quad (4.16)$$

Figure 4.2(a) illustrates the geometry of the 3-chain model. The cube is oriented along the principle axes of stretch.

4.2.2 8-Chain Model

The model geometry for the 8-chain model proposed by [3] is as follows:

1. 8 chains, all of equal length $r_0 = \sqrt{n}l$, are connected at the center of a cube. A single chain extends from the center to an independent corner of the cube.
2. Because each chain has length r_0 , the sides of the undeformed cube have length a_0 and are equal to

$$a_0 = \frac{2}{\sqrt{3}} r_0.$$

3. If the cube is stretched in the principle directions by λ_1, λ_2 and λ_3 , the new box has sides $\lambda_1 a_0, \lambda_2 a_0$, and $\lambda_3 a_0$.

The components of all eight vectors that describe the deformed chains are given by simply the length of each corresponding box edge divided by 2 (since all of the chains are connected at the middle of the box). Therefore,

$$\vec{r} = \left\langle \pm \frac{a_0 \lambda_1}{2}, \pm \frac{a_0 \lambda_2}{2}, \pm \frac{a_0 \lambda_3}{2} \right\rangle$$

with respect to the chosen base $\{e_i\}$. Each chain has equal length of

$$r = \frac{a_0}{2} \sqrt{\lambda_1^2 + \lambda_2^2 + \lambda_3^2}$$

which gives the total stretch as

$$\lambda = \frac{r}{r_0} = \sqrt{\frac{\lambda_1^2 + \lambda_2^2 + \lambda_3^2}{3}}.$$

Therefore, the principle components of the Cauchy stress can be found by

$$\sigma_i = \lambda_i \frac{\partial \psi}{\partial \lambda} \frac{d\lambda}{d\lambda_i} = \frac{NkT\sqrt{n}}{3} \frac{\lambda_i^2}{\lambda} \mathcal{L}^{-1} \left(\frac{\lambda}{\sqrt{n}} \right) - p \quad (4.17)$$

where λ is the total stretch and λ_i is the stretch along the principle axes.

Figure 4.2(b) illustrates the geometry of the 8-chain model. Similar to the 3-chain model, the cube in which the polymer chains are contained is oriented along the principle axes of stretch.

4.2.3 Model Validation using Tension Tests

Both the 3-chain and 8-chain models are compared with classical elastic tension data from [43]. The data was collected from vulcanized rubber at room temperature at a stretch rate of $\dot{\lambda} = 0.01$.

Figure 4.2: Chain orientation for the (a) 3-chain and (b) 8-chain models.

Figure 4.3 presents the data as the engineering stress (true stress per unit stretch) f versus the stretch λ . The data takes on an expected ‘S’ shape and, as the vulcanized rubber reaches its maximum stretch before structural failure, the force begins to increase unbounded.

Model Calibration

The material constants $C = NkT$ (considered to be the bulk modulus) and n were calibrated by fitting data to a single uniaxial test and then used for each of the remaining tests. To evaluate n , one must consider the maximum length that a specimen can stretch. Consider the maximum extension of a single chain. A chain with n links, each with length l , will have a maximum stretch of $r_{\max} = nl$ and if the chain’s undeformed length is $r_0 = \sqrt{nl}$, then the maximum stretch is

$$\lambda_{\max} = \frac{r_{\max}}{r_0} = \frac{nl}{\sqrt{nl}} = \sqrt{n}.$$

Therefore, the maximum stretch of a sample before it locks (prior to structural failure) is equal to the square root of the number of links in the chain. Since the test is considered to be essentially isothermal, the bulk modulus C is calculated during this test.

Figure 4.3: Uniaxial and Biaxial data collected by Treloar

Model Implementation

To implement uniaxial stretch in the model, one must consider how the stretch is applied. Uniaxial stretch is applied strictly in one principal direction, $\lambda_1 = \lambda$. The remaining two principal components of stretch are found by using the incompressibility relationship $\lambda_1 \lambda_2 \lambda_3 = 1$ along with the assumption that $\lambda_2 = \lambda_3$. The final two principle components of stretch are determined to be $\lambda_2 = \lambda_3 = 1/\sqrt{\lambda}$.

For the biaxial model, equal stretch is applied in two of the principle directions, $\lambda_1 = \lambda_2 = \lambda$. The remaining principal component is again found using the incompressibility relationship $\lambda_1 \lambda_2 \lambda_3 = 1$. Therefore, $\lambda_3 = 1/\lambda^2$.

For both tests, the determination of the pressure p found in (4.16) and (4.17) are left uncalculated. The first term in (4.16) and (4.17) is the only part that can be directly evaluated for each principal direction. Since uniaxial stretch is all applied in one principal direction, it is known that the principal stress will be in the same direction, $\sigma = \sigma_1$. It is also known that the stress in the other two principal directions will equal zero. Likewise for biaxial stretch, the stress in the third principal direction is zero, $\sigma_3 = 0$. This condition is used to determine the pressure p .

Results

As can plainly be seen in Figures (4.4) and (4.5), the uniaxial data is predicted well by the 3-chain model (which should be apparent since calibration of material parameters was based on this test). However, the 3-chain model does not quantify the biaxial deformation well as it fails to take into account the cooperative nature of the chain network. Since each chain of the 3-chain model lays in a principal direction, a stress in each principle direction would allow each chain in that direction to be stretched to its maximum length $r_{\max}$ when it is clear that the limiting stretch for biaxial tension is less because of chain interaction.

Figures (4.6) and (4.7) show the 8-chain model prediction for uniaxial and biaxial tests. Again, the uniaxial data fits very well as expected; however, the 8-chain model seems to be more predictive of the biaxial test than the 3-chain model. This is due to the inherent interaction of the 8 chains in the model, none of which are aligned with a principal stretch. This results in the limiting stretch of the principal directions of the 8-chain network to be less than the limiting stretch of each individual chain. While the simplification the 3- and 8- chain models provide is desired for efficiency, higher accuracy is found when the chains

Figure 4.4: Data comparison with the 3-Chain model

Figure 4.5: Uniaxial and Biaxial model comparison for 3-Chain model

Figure 4.6: Data comparison with the 8-Chain model

are not lumped together into a finite number of orientations.

4.2.4 Full Network Model

The full network model takes into account all possible orientations, not lumping the N chains in a unit volume into a finite number of orientations, but considers a distribution of orientations. Beginning with a random distribution of N vectors describing the N chains in their reference state $\vec{r}_0$, Wu and van der Giessen [48] define a Chain Orientation Distribution Function (CODF), $C(\phi, \theta)$ to describe the relative density of chains whose orientations fall between (ϕ, θ) and $(\phi + d\phi, \theta + d\theta)$ at any instant given as $C(\phi, \theta) \sin \phi d\phi d\theta$. It can be inferred that C is implicitly a function dependent on a strictly increasing variable (like time) because it evolves during a deformation process. Therefore, the total number of chains found between (ϕ, θ) and $(\phi + d\phi, \theta + d\theta)$ is

$$dN = NC(\phi, \theta; t) \sin \phi d\phi d\theta$$

Following conservation laws, it is necessary that

$$\int_0^{2\pi} \int_0^\pi C(\phi, \theta; t) \sin \phi d\phi d\theta = 1 \quad (4.18)$$

for all values of ϕ, θ , and t . It is reasonable that, for an undeformed volume, the chains are oriented completely at random and C_0 should be a constant. The conservation from (4.18) implies $C_0 = 1/(4\pi)$.

Figure 4.7: Uniaxial and Biaxial model comparison for 8-Chain model

Two forms are considered when tracking a deformation. The Eulerian form describes the network's interaction at a given point (ϕ, θ) in orientation space. The Lagrangian form follows the motion of one point (ϕ_0, θ_0) in the network as it moves through orientation space. The standard transformation can be made so that, in terms of the initial orientation (ϕ_0, θ_0) ,

$$\int_0^{2\pi} \int_0^\pi C(\phi, \theta; t) \sin \phi d\phi d\theta = \int_0^{2\pi} \int_0^\pi C(\hat{\phi}, \hat{\theta}; t) \sin \hat{\phi} J d\phi_0 d\theta_0 \quad (4.19)$$

where

$$\begin{aligned} \hat{\phi} &= \hat{\phi}(\phi_0, \theta_0; t), \\ \hat{\theta} &= \hat{\theta}(\phi_0, \theta_0; t), \\ J &= \left| \frac{\partial(\hat{\phi}, \hat{\theta})}{\partial(\phi_0, \theta_0)} \right| = \frac{\partial \hat{\phi}}{\partial \phi_0} \frac{\partial \hat{\theta}}{\partial \theta_0} - \frac{\partial \hat{\phi}}{\partial \theta_0} \frac{\partial \hat{\theta}}{\partial \phi_0}. \end{aligned}$$

Under the assumption that the CODF is given, (4.19) can be rewritten as

$$\int_0^{2\pi} \int_0^\pi C \sin \phi d\phi d\theta = \int_0^{2\pi} \int_0^\pi C_0 \sin \phi_0 d\phi_0 d\theta_0$$

and we have the relationship

$$C(\phi, \theta; t) = C_0 \frac{\sin \phi_0}{\sin \phi} J^{-1}. \quad (4.20)$$

The energy of the entire network is given by the sum of the free energies of the

individual chains,

$$\begin{aligned}\Psi &= \int \psi dN \\ &= N \int_0^{2\pi} \int_0^\pi \psi(\lambda) C(\phi, \theta; t) \sin \phi d\phi d\theta\end{aligned}$$

where ψ is given in (4.7).

To calculate the principle directions of the Cauchy stress tensor, (4.9) is used and

$$\sigma_i = \lambda_i \frac{d\Psi}{d\lambda_i} - p$$

where p is an additional hydrostatic pressure term and

$$\frac{d\Psi}{d\lambda_i} = N \int_0^\pi \int_0^{2\pi} \frac{d\psi}{d\lambda_i} C \sin \phi d\phi d\theta.$$

Therefore, the Eulerian form of the principle values of stress is calculated to be

$$\sigma_i = NkT\sqrt{n} \int_0^\pi \int_0^{2\pi} C \mathcal{L}^{-1} \left(\frac{\lambda}{\sqrt{n}} \right) \lambda u_i^2 \sin \phi d\phi d\theta \quad (4.21)$$

where m_i is the component of the unit direction vector $\mathbf{u} = \mathbf{r}/r$ for any vector $\mathbf{r}$ defined by ϕ and θ so that

$$u_1 = \sin \phi \cos \theta, \quad u_2 = \sin \phi \sin \theta, \quad u_3 = \cos \phi.$$

The CODF can be explicitly expressed as

$$C(\phi, \theta; \lambda_i) = C_0 \lambda^3(\phi, \theta; \lambda_i)$$

and (4.21) can be rewritten as

$$\sigma_i = \frac{NkT}{4\pi} \sqrt{n} \int_0^\pi \int_0^{2\pi} \mathcal{L}^{-1} \left(\frac{\lambda}{\sqrt{n}} \right) \lambda^4 u_i^2 \sin \phi d\phi d\theta. \quad (4.22)$$

The Lagrangian form of the principle stresses can be found by directly transforming (4.21) so that

$$\sigma_i = NkT\sqrt{n} \int_0^\pi \int_0^{2\pi} C \mathcal{L}^{-1} \left(\frac{\lambda}{\sqrt{n}} \right) \lambda \frac{\lambda_i^2 (u_i^0)^2}{\lambda^2} \sin \phi J d\phi_0 d\theta_0. \quad (4.23)$$

Noting the transformation in (4.20), (4.23) can be rewritten as

$$\sigma_i = \frac{NkT}{4\pi} \sqrt{n} \int_0^\pi \int_0^{2\pi} \mathcal{L}^{-1} \left(\frac{\lambda}{\sqrt{n}} \right) \frac{\lambda_i^2 (u_i^0)^2}{\lambda} \sin \phi_0 d\phi_0 d\theta_0. \quad (4.24)$$

The principle components of stress defined in (4.16), (4.17), (4.22), and (4.24) predict uniaxial stress-strain curves very well; however, they are limited to active polymers due to the bulk modulus $Y = NkT$ and that they do not incorporate so called “strain softening” which occurs in frozen polymers after the initial yield.

4.3 Models for Large Strain in Frozen Polymers

Polymers that exhibit inelastic behavior are considered to be in a frozen state. They are susceptible to plastic deformations which occur after two physically distinct barriers are overcome:

1. The material must be stressed to exceed the intermolecular resistance to rotation, and
2. upon further deformation, molecular alignment (orientational hardening) creates internal entropic resistance to further deformation.

Figure 4.8 illustrates the plastic deformation of a shape memory polymer due to these sources of resistance, first described by Haward and Thackray [22]. The distinct yield around $\varepsilon = 5\%$ is caused by the polymer's intermolecular resistance to rotation and once this resistance is overcome, the polymer chains are free to flow and molecular alignment begins. The increase in stress around $\varepsilon = 10\%$ is due to the polymer chains aligning due to the deformation. As the molecules align, the configurational entropy decreases, which causes the second source of resistance.

Argon [1] developed a rate dependent micro-mechanical model to describe the intermolecular resistance and Wang and Guth [46] modeled the entropic resistance by implementing a non-Gaussian statistical mechanics network model for rubber elasticity. Boyce et. al. [7] incorporated these two models to predict the plastic deformation of glassy polymers, and with recent additions, have predicted the polymer response with great success.

Figure 4.8: Nonlinear characteristics of the stress-strain relation in a shape memory polymer. Data was collected by C. Yakacki.

4.3.1 Intermolecular Resistance to Flow

Consider a single polymer chain as depicted in Figure 4.1. Each molecule has the ability to rotate at its bond with adjacent molecules in the chain; however, each chain is affected by surrounding chains. The neighboring chains impose an impedance which, when overcome, causes a double-kinking of the molecular chain. Based on this assumption, Argon [1] developed a constitutive equation for the plastic shear strain rate as

$$\dot{\gamma}^p = \dot{\gamma}_0 \exp \left(\frac{-As_0}{T} \left[1 - \left(\frac{\tau}{s_0} \right)^{5/6} \right] \right) \quad (4.25)$$

where $\dot{\gamma}_0$ is the pre-exponential factor proportional to the attempt frequency, A is a constant, $s_0 = 0.077\mu/(1 - \nu)$ is the athermal shear strength, μ is the elastic shear modulus, ν is Poisson's ratio, T is absolute temperature, and τ is the applied shear stress.

Boyce et. al. [7] extended the shear strain rate to include pressure and an evolving shear strength such that

$$\dot{s} = h \left[1 - \left(\frac{s}{s_{ss}} \right) \right] \dot{\gamma}^p \quad (4.26)$$

where h is the rate of resistance with respect to plastic strain, s is the shear strength, and s_{ss} is the steady state shear strength. The value s_0 in (4.25) is then replaced by $s + ap$ where p is pressure and a is a pressure dependent constant.

4.3.2 Molecular Alignment

Once the polymer is sufficiently stressed so that the intermolecular resistance is overcome, the molecules begin to align along the principle direction of plastic strain. The alignment of polymer chains reduces the configurational entropy, thus increasing stress. This stress is termed the backstress and can be defined using Langevin statistics and the network models outlined in Section 4.2. The principle values of backstress can therefore be defined as

$$B_i = \frac{NkT\sqrt{n}}{3} \left[V_i \mathcal{L}^{-1} \left(\frac{V_i}{\sqrt{n}} \right) - \frac{1}{3} \sum_{j=1}^3 V_j \mathcal{L}^{-1} \left(\frac{V_j}{\sqrt{n}} \right) \right] \quad (4.27)$$

using the 3-chain model and

$$B_i = \frac{NkT\sqrt{n}}{3} \mathcal{L}^{-1} \left(\frac{\lambda}{\sqrt{n}} \right) \frac{V_i^2 - \lambda^2}{\lambda} \quad (4.28)$$

using the 8-chain model. The values of N , k , T , $\mathcal{L}^{-1}$ are given as previously defined in Section 4.1.1. The values V_i are the plastic stretch in the principal directions defined by the kinematics of finite strain and λ is the total stretch of the chain.

4.3.3 Finite Strain Kinematics

Consider an isotropic body deformed from reference position $\mathbf{x}_0$ to its current state $\mathbf{x}$. The deformation gradient, which maps each point from the reference position to its deformed position is

$$\mathbf{F} = \nabla_{\mathbf{x}} \mathbf{x}_0.$$

The deformation gradient can be decomposed into its elastic and plastic parts [29] (denoted by superscripts e and p respectively),

$$\mathbf{F} = \mathbf{F}^e \mathbf{F}^p. \quad (4.29)$$

Typically one cannot deduce how much of the the applied deformation is characterized in each part of the decomposition. $\mathbf{F}^p$ can be determined through complete elastic unloading to a stress-free state and describes the amount of permanent molecular orientation the material has sustained. $\mathbf{F}^p$ can be decomposed further into its stretch and rotational components using polar decomposition;

$$\mathbf{F}^p = \mathbf{V}^p \mathbf{R}^p = \mathbf{R}^p \mathbf{U}^p$$

where $\mathbf{V}^p$ and $\mathbf{U}^p$ are the left and right stretch tensors respectively, the principal components of which define the plastic stretch in the definition of backstress. The elastic portion of $\mathbf{F}$ can be decomposed similarly, however it is assumed that $\mathbf{F}^e$ is strictly generated through stretch and therefore $\mathbf{R}^e = \mathbf{I}$.

The velocity gradient describes the rate-kinematics and is given by

$$\mathbf{L} = \nabla_{\mathbf{x}} v = \dot{\mathbf{F}} \mathbf{F}^{-1} = \mathbf{D} + \mathbf{W} \quad (4.30)$$

where $\mathbf{D}$ is symmetric and describes the rate of deformation and $\mathbf{W}$ is skew-symmetric and describes the spin. Incorporating the decomposition from (4.29) into (4.30) yields

$$\mathbf{L} = \dot{\mathbf{F}}^e \mathbf{F}^{e-1} + \mathbf{F}^e \mathbf{L}^p \mathbf{F}^{e-1}$$

where $\mathbf{L}^p = \dot{\mathbf{F}}^p \mathbf{F}^{p-1} = \mathbf{D}^p + \mathbf{W}^p$ relate specifically to the relaxed configuration and $\mathbf{D}^p$ and $\mathbf{W}^p$ carry the same meaning as in (4.30).

The plastic straining rate is constitutively prescribed as

$$\mathbf{D}^p = \dot{\gamma}^p \tilde{\sigma}' / \sqrt{2} \tau \quad (4.31)$$

where $\tilde{\sigma}'$ is the normalized deviatoric portion of the Cauchy stress σ defined as

$$\tilde{\sigma}' = \sigma - \mathbf{F}^e \mathbf{B} \mathbf{F}^{e-1} / \det \mathbf{F}^e \quad (4.32)$$

such that $\mathbf{B}$ has principal values B_i , and the shear stress τ is approximated by

$$\tau = (\tilde{\sigma}' \tilde{\sigma}' / 2)^{1/2} \quad (4.33)$$

Equations (4.25), (4.26), (4.27) or (4.28), along with (4.31), (4.32), and (4.33) define the plastic deformation model. Figure 4.9 illustrates how this model for plastic deformation predicts the stress-strain relation. The experimental data was collected in [2] from compression tests run at room temperature on polycarbonate and the model implementations were done in [48]. The definition of the backstress was simplified using the 3-chain, 8-chain and full-network models for rubber elasticity. As is evident in each of the comparisons, the model is able to accurately predict the yield when the polymer chains begin to flow as well as the entropic hardening due to molecular alignment.

Again, like the models for large strain in active polymers, these models are unable to predict the stress-strain relation across the glass transition gap and further research is necessary in order to accurately quantify how a polymer reacts to deformation during and after going through its glass transition.

4.3.4 Phenomenological exponential model

The Duan-Saigal-Greif-Zimmerman (DSGZ) model is a phenomenological model designed to predict the nonlinear deformations for both glassy and active polymers. It implements ideas from four previously developed phenomenological models [16]: the Johnson-Cook model, the G'Sell-Jonas model, the Matsuoka model, and the Brooks model. The Johnson-Cook model was developed to describe the plastic behavior of ductile metals dependent on strain, strain rate and absolute temperature. The G'Sell-Jonas model describes the stress-strain relation of semicrystalline polymers in terms of strain, strain rate and absolute temperature; however, it does not predict the strain softening which occurs after yield in glassy polymers. The Matsuoka model predicts the yield and strain softening behavior

(a) 3-Chain model

(b) 8-Chain model

(c) Full Network model

Figure 4.9: Plastic deformation model's prediction of polycarbonate using (a) the 3-chain model, (b) the 8-chain model, and (c) the full-network model for the definition of the backstress.

of glassy polymers in terms of strain, strain rate, and relaxation time; however, it does not predict the stress increase which occurs after molecular alignment. The Brooks model predicts the yield and strain softening of a glassy polymer in terms of strain, strain rate and absolute temperature; however, like the Matsuoka model, it does not predict the stress increase after molecular alignment occurs. Key features from each of these models are used in defining the DSGZ model (details are found in [16]).

The model is constitutively defined as true stress σ in terms of true strain ε , true strain rate $\dot{\varepsilon}$, and absolute temperature T ,

$$\sigma(\varepsilon, \dot{\varepsilon}, T) = K (f(\varepsilon) + [s(\varepsilon, \dot{\varepsilon}, T) - f(\varepsilon)] \exp([\ln(g(\dot{\varepsilon}, T)) - C_4]\varepsilon)) h(\dot{\varepsilon}, T) \quad (4.34)$$

where

$$\begin{aligned} f(\varepsilon) &= (\exp(-C_1\varepsilon) + \varepsilon^{C_2}) (1 - \exp(-\alpha\varepsilon)), \\ s(\varepsilon, \dot{\varepsilon}, T) &= \frac{\varepsilon \exp\left(1 - \frac{\varepsilon}{C_3 h(\dot{\varepsilon}, T)}\right)}{C_3 h(\dot{\varepsilon}, T)}, \\ h(\dot{\varepsilon}, T) &= (\dot{\varepsilon})^m \exp\left(\frac{a}{T}\right), \end{aligned} \quad (4.35)$$

and $g(\dot{\varepsilon}, T)$ is the dimensionless form of $h(\dot{\varepsilon}, T)$. The values of K , C_1 , C_2 , C_3 , C_4 , a , m , and α are all material dependent constants used to calibrate the model. The function $s(\varepsilon, \dot{\varepsilon}, T)$ describes the shift behavior of the yield point with respect to strain rate and temperature. The steady state of the polymer is given by $f(\varepsilon)$ which incorporates the increase in stress after molecular alignment not captured by the Matsuoka and Brooks models. Multiplying the entire bracketed relation in (4.34) by the function $h(\dot{\varepsilon}, T)$ represents the stress dependence on strain rate and temperature. If the strain is applied at a constant rate, $h(\dot{\varepsilon}, T)$ is a constant value.

Chapter 5

Conclusion

A homogenized constitutive model for the thermomechanical properties of shape memory polymers under linear deformations is proposed in Chapter 2. Previous models relied on curve fitting of an unconstrained thermomechanical cycle to define the thermal strain. The desire to fully define the thermal strain led to explicit constitutive equations for the active and frozen states, as well as unique definitions for the cooling and heating processes. The physical process of strain storage is not fully understood so, to quantify the strain that is stored during glass transition (and when), the storage process was reviewed in detail. As a result, the temperature and strain dependent definition of stored strain is constructed uniquely. In concert with the strain storage process, the need to quantify the glass transition process by means of the state variable $\phi_f(T)$ led to the utilization of the $\tan \delta$ data as a physical identifier of the glass transition phenomenon. The $\tan \delta$ data peak identifies where the internal damping is greatest and is assumed to be the center of the glass transition process, thus allowing independent definitions of ϕ_f during heating and cooling. Previous models again relied on curve fitting to quantify ϕ_f , using data from a polymer that was previously cooled under tension during an unconstrained heating process; however, this leads to identical definitions of the frozen fraction during heating and cooling which, as is widely accepted, rarely happens. Use of homogenization principles led to the macroscopic definitions that are unique from the current literature. The proposed constitutive model in Section 2.6 in conjunction with the homogenized model accurately predicts the strain storage and release as well as the stress and strain evolution during the thermomechanical cycle.

Valuable insight can be gained through continued research of the underlying phys-

ical process that occurs during the glass transition so that calibration of the frozen fraction can be determined independently from the current $\tan \delta$ data fitting. Further investigation is necessary to incorporate thermal effects such as creep and strain relaxation, however the current model accurately predicts the thermomechanical response. Whereas the scope of the homogenized model was restricted to small deformations, implementation of the isothermal nonlinear deformation models presented in Chapter 4 is possible in future research. Experiments involving nonlinear deformations which bridge the glass transition are currently being investigated.

While industrial applications of shape memory polymer rods are still in preliminary research, the basic modeling principles are demonstrated in Chapter 3. Shape memory polymers are already being considered for beam (rolling longerons) and plate (self-repairing automobile panels) applications, for which the need for predictive models will arise. As the use of shape memory polymers continues to grow, the need to properly quantify and predict their thermomechanical characteristics grows in parallel.

Bibliography

- [1] A. S. Argon. A theory for the low-temperature plastic deformation of glassy polymers. *Philosophical Magazine*, 28:39, 1973.
- [2] E. M. Arruda and M. C. Boyce. Evolution of plastic anisotropy in amorphous polymers during finite straining. *International Journal of Plasticity*, 9:697–720, 1993.
- [3] E. M. Arruda and M. C. Boyce. A three-dimensional constitutive model for the large stretch behavior of rubber elastic materials. *J. Mech. Phys. Solids*, 1993.
- [4] E. M. Arruda, M. C. Boyce, and R. Jayachandran. Effects of strain rate, temperature and thermomechanical coupling on the finite strain deformation of glassy polymers. *Mechanics of Materials*, 19:193–212, 1995.
- [5] I. Bellin. Polemeric triple-shape materials. In *Proc. Natl. Acad. Sci.*, number 48, pages 18043–18047, 2006.
- [6] J.S. Bergström and M.C. Boyce. Constitutive modeling of the large strain time-dependent behavior of elastomers. *J. Mech. Phys. Solids*, 46:931–954, 1998.
- [7] M. C. Boyce, D. M. Parks, and A. S. Argon. Large inelastic deformation of glassy polymers. part I: Rate dependent constitutive model. *Mechanics of Materials*, 7:15–33, 1988.
- [8] M. C. Boyce, G. G. Weber, and D. M. Parks. On the kinematics of finite strain plasticity. *J. Mech. Phys. Solids*, 37(5):647–665, 1989.
- [9] D. Campbell, R. Barret, M. S. Lake, L. Adams, and E. Abramson. Development of a novel, passively deployed roll-out solar array. IEEE Aerospace Conference, 2006.

- [10] Y. Chen and D. C. Lagoudas. A constitutive theory for shape memory polymers part I. large deformations. *Submitted*, 2008.
- [11] Y. Chen and D. C. Lagoudas. A constitutive theory for shape memory polymers part II. a linearized model for small deformations. *Submitted*, 2008.
- [12] N. Choi and A. Lendlein. Degradable shape-memory polymer networks from oligo[(l-lactide)-ran-clycolide]diethacrylates. *Soft Matter*, 3:901–909, 2007.
- [13] A. W. Cochardt. The origin of damping high strength ferromagnetic alloys. *Journal of Applied Mechanics*, 20:196–200, 1953.
- [14] D. K. Darooka, S. E. Scarborough, , and D. P. Cadogan. An evaluation of inflatable truss frame for space applications. In *Proceedings of the 42nd AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference and Exhibit*, number 1614, 2001.
- [15] J. Diani, Y. Liu, and K. Gall. Finite strain 3d thermoviscoelastic constitutive model for shape memory polymers. *Polymer Engineering and Science*, 46:486–492, 2006.
- [16] Y. Duan, A. Saigal, R. Greif, and M. A. Zimmerman. A uniform phenomenological constitutive model for glassy and semicrystalline polymers. *Polymer Engineering and Science*, 41(8):1322–1328, 2001.
- [17] P. J. Flory and J. Rehner Jr. Statistical mechanics of cross-linked polymer networks i. rubberlike elasticity. *J. Chem. Phys.*, 11:512–520, 1943.
- [18] K. Gall, C. M. Yakacki, Y. Liu, R. Shandas, N. Willett, and K. S. Anseth. Thermo-mechanics of the shape memory effect in polymers for biomedical applications. *Wiley InterScience Online*, 2005.
- [19] C. G'Sell. Dislocations in glassy polymers: Do they exist? are they useful? *Materials Science and Engineering*, A309-310:539–543, 2001.
- [20] C. G'Sell, H. El Bari, J. Peresz, J.Y. Cavaille, and G.P. Johari. Effect of plastic deformation on the microstructure and properties of amorphous polycarbonate. *Materials Science and Engineering*, 110:223–229, 1989.
- [21] P. Haupt. *Continuum Mechanics and Theory of Materials*. Springer, 2000.

- [22] R. N. Haward and G. Thackray. The use of a mathematical model to describe isothermal stress-strain curves in glassy thermoplastics. In *Proc. Roy. Soc. A.*, volume 302, pages 453–472, 1968.
- [23] D. Helm and P. Haupt. Shape memory behaviour: Modelling within continuum thermomechanics. *International Journal of Solids and Structures*, 40:827–849, 2003.
- [24] J. A. Hiltz. Shape memory polymers: Literature review. Technical report, Defence R&D Canada - Atlantic, 2002.
- [25] G. A. Holzapfel. *Nonlinear Solid Mechanics: A Continuum Approach for Engineering*. John Wiley and Sons, LTD, 2000.
- [26] M. Irie. *Shape Memory Materials*, chapter Shape Memory Polymers. Cambridge University Press, 1998.
- [27] H. M. James and E. Guth. Theory of the elastic properties of rubber. *Journal of Chemical Physics*, 11(10):455–481, 1943.
- [28] W. Kuhn and F. Grün. Relation between the elasticity constant and extension double diffraction of highly elastic substances. *Kolloid Z.*, 1942.
- [29] E. H. Lee. Elastic-plastic deformation at finite strain. *J. Appl. Mech.*, 36:1–6, 1969.
- [30] A. Lendlein and R. Langer. Biodegradable, elastic shape-memory polymers for potential biomedical applications. *Science*, 296(5573):1673–1676, May 2002.
- [31] Y. Liu, K. Gall, M. L. Dunn, and A. R. Greenberg. Thermomechanics of shape memory effect in polymers. In *Materials Research Society Symposium Proceedings*, volume 855E, 2005.
- [32] Y. Liu, K. Gall, M. L. Dunn, A. R. Greenberg, and J. Diani. Thermomechanics of shape memory polymers: Uniaxial experiments and constitutive modeling. *International Journal of Plasticity*, 22:279–313, 2006.
- [33] L. Mandelkern. *Crystallization of Polymers: Kinetics and mechanisms*, volume 2. Cambridge University Press, 2004.

- [34] G. B. McKenna and S. L. Simon. *Handbook of Thermal Analysis and Calorimetry*, volume 3, chapter The glass transition: its measurement and underlying physics, pages 49–109. Elsevier Science B.V., 2002.
- [35] T. Murayama. Determination of the glass transition of polymer by the autovibron. *Polymer Engineering and Science*, 22(12):788–792, 1982.
- [36] R. W. Ogden. Large deformation isotropic elasticity - on the correlation of theory and experiment for compressible rubberlike solids. In *Proceedings of the Royal Society of London*, volume A328, pages 567–583, 1972.
- [37] R. Pichè. An L-stable Rosenbrock method for step-by-step time integration in structural dynamics. *Computer Methods in Applied Mechanics and Engineering*, 126:343–354, 1995.
- [38] R. D. Siskind and R. C. Smith. A homogenized model for temperature-induced deformations in shape memory polymers. *In Preparation*, 2008.
- [39] R. C. Smith. *Smart Material Systems: Model Development*. SIAM Frontiers in Applied Mathematics, 2005.
- [40] S. Therkelson. Constitutive modeling of active polymers. Master’s thesis, Massachusetts Institute of Technology, 2005.
- [41] H. Tobushi, T. Hashimoto, S. Hayashi, and E. Yamada. Thermomechanical constitutive modeling in shape memory polymer of polyurethane series. *Journal of Intelligent Material Systems and Structures*, 8:711–718, 1997.
- [42] H. Tobushi, K. Okumura, S. Hayashi, and N. Ito. Thermomechanical constitutive model of shape memory polymer. *Mechanics of Materials*, 33:545–554, 2001.
- [43] L. R. G. Treloar. *Monographs on the Physics and Chemistry of Materials*. Oxford at the Clarendon Press, 1958.
- [44] L. R. G. Treloar. *The Physics of Rubber Elasticity*. Oxford, 1975.
- [45] A. M. Vinogradov and C. H. M. Jenkins. *Recent Advances in Gossamer Spacecraft*, chapter Functional Materials for Smart Gossamer Spacecraft, pages 165–190. American Institute of Aeronautics and Astronautics, 2005.

- [46] M. C. Wang and E. J. Guth. Statistical theory of networks of non-Gaussian flexible chains. *J. Chem. Phys.*, 20:1144, 1952.
- [47] I. M. Ward and D. W. Hadley. *An Introduction to the Mechanical Properties of Solid Polymers*. John Wiley and Sons, 1998.
- [48] P. D. Wu and E. van der Giessen. On improved network models for rubber elasticity and their applications to orientation hardening in glassy polymers. *J. Mech. Phys. Solids*, 41(3):427–456, 1993.
- [49] C. M. Yakacki, R. Shandas, C. Lannaing, B. Rech, A. Eckstein, and K. Gall. Unconstrained recovery characterization of shape-memory polymer networks for cardiovascular applications. *Biomaterials*, 28:2255–2263, 2007.