Low to High Strain Rate Deformation of Amorphous Polymers: Experiments and Modeling

by

Adam Dustin Mulliken

Bachelor of Engineering
Thayer School of Engineering at Dartmouth College, 2002
Bachelor of Arts, Engineering Sciences
Dartmouth College, 2002

Submitted to the Department of Mechanical Engineering in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE IN MECHANICAL ENGINEERING

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June 2004

© Massachusetts Institute of Technology 2004. All rights reserved.
Low to High Strain Rate Deformation of Amorphous Polymers: Experiments and Modeling
by
Adam Dustin Mulliken

Submitted to the Department of Mechanical Engineering
on May 7, 2004, in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE IN MECHANICAL ENGINEERING

Abstract

A combined experimental and analytical investigation has been performed to understand the mechanical behavior of two amorphous polymers - polycarbonate and poly(methyl methacrylate) - at strain rates ranging from $10^{-4}$ to $10^4$ s$^{-1}$. This spectrum of strain rates was achieved in tension/compression tests using a dynamic mechanical analyzer (DMA), a servo-hydraulic testing machine and a split-Hopkinson pressure bar. Tension tests on the DMA were used to characterize the time-temperature dependence of the elastic storage moduli and the loss factors of the two polymers. The DMA data provided a quantification of the rate-dependent shift of material transitions, and led to an analytical description of the elastic moduli at all rates and temperatures. Uniaxial compression tests were performed at strain rates of $10^{-4}$ s$^{-1}$ to 1 s$^{-1}$ using a servo-hydraulic testing machine. Stress-strain behavior of the materials was found to be rate-dependent in this regime, with yield strength increasing in a linear and non-linear fashion for PC and PMMA, respectively, with the logarithm of strain rate. High strain rate tests were performed using an aluminum split-Hopkinson pressure bar system. Material strengthening as a function of strain rate was observed to be dramatically greater in this high-rate regime for both materials. A physically-based constitutive model for large strain deformation of thermoplastics, which has been shown to be accurate at quasi-static rates of deformation, was then extended to encompass very high rate conditions. The revised model uses the viscoelastic material transitions quantified in DMA testing, as well an understanding of the molecular mechanisms of resistance to deformation at high rates, to capture the overall transition of the stress-strain behavior to a regime of increased rate-dependence of yield. The model is shown to be predictive of the behavior of these materials over a wide spectrum of strain rates.

Thesis Supervisor: Mary C. Boyce
Title: Professor of Mechanical Engineering
Acknowledgments

First and foremost, I would like to acknowledge my advisor, Professor Mary Boyce. It is her vision that has guided my work, and it is her constant pursuit of excellence that has inspired and driven me to new levels of achievement. To think upon where I started from two years ago, and how far I have come since then, I am awestruck. This immense personal growth that I feel is a testament to the time and energy that Professor Boyce has invested in my development. For this I am extremely grateful, and I look forward to even bigger challenges and continued growth.

I would also like to thank Dr. Omprakash Samudrala, for his invaluable contributions on the experimental side of this study. During his tenure as a post-doctoral associate at MIT, Omprakash oversaw the design and installation of the high rate testing facilities at the Institute for Soldier Nanotechnologies. Though Omprakash did not stay long enough to benefit from his own hard work, his legacy remains in the basement of NE-47, and in the high-rate experimental work of current and future ISN students. I am especially grateful to Omprakash for his guidance during the early stages of my split-Hopkinson bar experimentation, as I worked alongside of him and absorbed his passion for high-rate experimental mechanics.

In addition, I would like to thank the people of the Mechanics and Materials group at MIT, of which I am proud to now be a bona fide contributing member. This includes the senior graduate students, especially Nici Ames and Hang Qi, who have endured my endless barrage of questions. Someday, I hope to pay them back for all the answers that they provided. This group also includes the dynamic duo of Una and Ray, who, among many other things, diffuse the drama that pervades day-to-day life in the M&M group.

Finally, I would like to acknowledge the network of family and friends that has supported me through all the ups and downs of graduate student life at MIT. Without people to lean on, the failures become overwhelming; without people to celebrate with, the successes become meaningless. Thanks especially to the family in Kingston and Boston, Niaz, Katrina, Hang, and the boys from Silver Lake. I'm keepin' it real, guys.
Contents

1 Introduction .................................................................................................................. 15

2 Background ................................................................................................................. 17
   2.1 Rate Dependence of Amorphous Polymer Behavior .................................................. 17
   2.2 Theoretical Models of Amorphous Polymer Plasticity ................................................ 20
   2.3 Low-Temperature/High-Rate Strengthening of Polymers ........................................... 35
   2.4 Split-Hopkinson Bar Testing of Polymers ................................................................. 60

3 Dynamic Mechanical Analysis ......................................................................................... 85
   3.1 DMA Theory ............................................................................................................. 87
   3.2 Experimental Approach ........................................................................................... 89
   3.3 Results and Discussion ............................................................................................ 90
   3.4 Data Analysis .......................................................................................................... 101

4 Compression Testing ...................................................................................................... 109
   4.1 Experimental Procedure .......................................................................................... 109
      4.1.1 Low to Moderate Rate Testing ......................................................................... 110
      4.1.2 High Rate Testing ............................................................................................ 111
   4.2 Results and Discussion ............................................................................................ 116
      4.2.1 Low to Moderate Rate Testing ......................................................................... 116
      4.2.2 High Rate Testing ............................................................................................ 119

5 Constitutive Model ........................................................................................................ 129
   5.1 Existing Model .......................................................................................................... 129
      5.1.1 Kinematics ........................................................................................................ 131
      5.1.2 Material Description and Constitutive Relations ................................................. 133
      5.1.3 Summary .......................................................................................................... 136
   5.2 Proposed Model ........................................................................................................ 137
      5.2.1 Kinematics ........................................................................................................ 138
      5.2.2 Material Description and Constitutive Relations ................................................. 141
      5.2.3 Summary .......................................................................................................... 144
      5.2.4 Numerical Implementation ................................................................................. 145
   5.3 Material Constants and Model Parameters .............................................................. 146
      5.3.1 Linear Elastic Springs ......................................................................................... 147
      5.3.2 Viscoplastic Dashpots ....................................................................................... 149

7
5.3.3 Langevin Spring ........................................... 158
5.4 Model Prediction ............................................. 159
  5.4.1 Model Behavior ......................................... 160
  5.4.2 Model v. Experiment ................................... 165

6 Conclusions and Future Work .............................. 173
A Relevant Chemical Structures ............................. 187
B Additional DMA Data ........................................ 189
C MATLAB Code for PC Modulus ............................ 195
D MATLAB Code for PMMA Modulus ......................... 197
E Additional Compression Data ............................... 201
References ....................................................... 209
## List of Figures

2-1 Stress-strain behavior of PC at $10^{-3}$ s$^{-1}$ ........................................... 18
2-2 Stress-strain behavior of PMMA at 5 rates: $10^{-4}$ to 0.3 s$^{-1}$ ..................... 20
2-3 Eyring model fit to PC data ............................................................................. 23
2-4 Robertson’s interpretation of a polymer chain in shear ..................................... 23
2-5 Robertson model fit to polystyrene experimental data ....................................... 25
2-6 Robertson model fit to PMMA experimental data ............................................. 26
2-7 Argon’s interpretation of molecular deformation .............................................. 27
2-8 Argon’s wedge disclination loop model for molecular kinking ......................... 28
2-9 Argon model fit to polystyrene experimental data ........................................... 30
2-10 Argon model fit to PET experimental data ..................................................... 31
2-11 Comparison of Ree-Eyring, Robertson, and Argon theory prediction ................. 33
2-12 Ree-Eyring and Argon models fit to PC experimental data .............................. 34
2-13 Eyring model fit to Bauwens’ PMMA yield data ............................................ 36
2-14 Ree-Eyring model fit to Roetling’s PMMA yield data ....................................... 37
2-15 Ree-Eyring model fit to Roetling’s PEMA yield data ....................................... 39
2-16 Ree-Eyring model fit to Bauwens’ PVC yield data .......................................... 41
2-17 PVC yield behavior master curve (Bauwens-Crowet et al) ............................. 42
2-18 Ree-Eyring model fit to Bauwens’ PC yield data (tension and compression) ......... 43
2-19 Ree-Eyring model fit to Bauwens’ PC yield data (tension) .............................. 44
2-20 Loss tangent of PC in the $\beta$-transition range (Bauwens) ............................ 46
2-21 Predicted loss tangent of PC at 9.5 Hz (Bauwens) ......................................... 46
2-22 Bauwens’ yield model fit to PC compression data ........................................... 47
2-23 PMMA compressive yield data (Bauwens-Crowet) ......................................... 48
2-24 Ree-Eyring model fit to PMMA master yield curve (Bauwens-Crowet) .......... 49
2-25 Loss tangent of PMMA in the $\beta$-transition range (Bauwens-Crowet) .............. 50
2-26 Bauwens’ yield model fit to PMMA compression data ................................... 51
2-27 Shear yield of PC as a function of temperature and strain rate (Wu and Turner) 51
2-28 Compressive stress-strain curves for PMMA, 77 - 336 K (Haussy et al) .......... 52
2-29 PMMA compressive yield data (Lefebvre and Escaig) .................................. 53
2-30 PMMA shear modulus data (Lefebvre and Escaig) ....................................... 54
2-31 Ree-Eyring model fit to PE yield data of Truss et al ....................................... 56
2-32 Schematic of a novel moderate-rate tensile apparatus (Foot et al) .................. 58
2-33 Ree-Eyring model fit to PET yield data of Foot et al ...................................... 59
2-34 Schematic of a split-Hopkinson pressure bar system ...................................... 60
2-35 Example strain gage signals from a SHPB test ............................................. 62
3-18 Shift of PMMA β-transition with strain rate .................................. 100
3-19 PC elastic modulus curve split into α and β components .......................... 102
3-20 Model prediction of the PC elastic modulus curve at $10^{-3}$ and $10^3$ s$^{-1}$ .......... 104
3-21 Predicted β-component of the PC elastic modulus at 5 strain rates .................. 104
3-22 Model prediction of the PC elastic modulus as a function of strain rate .......... 105
3-23 PMMA storage modulus curve at two rates (data) .................................. 106
3-24 PMMA elastic modulus curve split into α and β components ........................ 107
3-25 Model prediction of the PMMA elastic modulus curve at $10^{-3}$ and $10^3$ s$^{-1}$ .... 108
3-26 Predicted β-component of the PMMA elastic modulus at 5 strain rates ............. 108

4-1 PC Instron compression specimen, before and after deformation .................. 110
4-2 PC SHPB compression specimen, before and after deformation ................. 112
4-3 Typical strain gage signals from a SHPB test of PC .................................. 112
4-4 Force equilibrium plot from a typical SHPB test .................................. 114
4-5 Example of smoothed vs. unsmoothed SHPB data .................................. 115
4-6 PC true stress-true strain behavior at quasi-static rates .......................... 116
4-7 PC yield data at low to moderate strain rates .................................. 117
4-8 PMMA true stress-true strain behavior at quasi-static rates ..................... 118
4-9 PMMA yield data at low to moderate strain rates .................................. 119
4-10 PC true stress-true strain behavior at $\sim 2000$ s$^{-1}$ .......................... 120
4-11 PC true stress-true strain behavior at $\sim 3900$ s$^{-1}$ .......................... 121
4-12 PC true stress-true strain behavior at $\sim 5050$ s$^{-1}$ .......................... 121
4-13 PC true stress-true strain behavior at three high strain rates ............... 122
4-14 PC stress-strain behavior at low, moderate and high rates .................... 122
4-15 PC yield data at high strain rates .................................. 123
4-16 PC yield data at all strain rates .................................. 123
4-17 Trendlines over PC yield data indicating transition location .......... 124
4-18 PMMA true stress-true strain behavior at $\sim 800$ s$^{-1}$ .................................. 125
4-19 PMMA true stress-true strain behavior at $\sim 1400$ s$^{-1}$ .......................... 126
4-20 PMMA true stress-true strain behavior at low, moderate and high rates ........ 126
4-21 PMMA yield data at all strain rates .................................. 127

5-1 1D rheological interpretation of existing model .................................. 130
5-2 1D rheological interpretation of proposed model .................................. 137
5-3 Component-wise split of PC yield data .................................. 151
5-4 Component-wise split of PMMA yield data .................................. 152
5-5 Bauwens’ PC yield data, tension and compression .................................. 155
5-6 Model prediction of PC stress-strain behavior (uniaxial compression) ........ 162
5-7 Model prediction of PC yield behavior .................................. 163
5-8 Model prediction of PC stress-strain behavior near the glass transition ........ 163
5-9 Model-predicted PC yield strength as a function of temperature ............... 164
5-10 Model prediction of PMMA stress-strain behavior (uniaxial compression) .... 165
5-11 Model prediction of PMMA yield behavior .................................. 166
5-12 Model-predicted PMMA yield strength as a function of temperature ........ 166
5-13 PC stress-strain behavior, model v. experiment .................................. 169
5-14 PC yield behavior, model v. experiment ............................................. 169
5-15 Component-wise split of PC shear yield data: model and experiment .... 170
5-16 PMMA stress-strain behavior, model v. experiment ............................. 171
5-17 PMMA yield behavior, model v. experiment ........................................ 171
5-18 Component-wise split of PMMA shear yield data: model and experiment .. 172
6-1 PC stress-strain and temperature evolution, 1800 s\(^{-1}\) ................. 182
6-2 PC - fraction of plastic work converted to heat ..................................... 183
A-1 General chemical structure of polycarbonate ...................................... 188
A-2 General chemical structure of poly(methyl methacrylate) ..................... 188
B-1 PC storage modulus reference curve - all data ..................................... 190
B-2 PMMA storage modulus reference curve - all data ............................... 190
B-3 PC loss modulus as a function of temperature and strain rate in the region of the \(\alpha\)-transition - all data .......................... 191
B-4 PC \(\tan \delta\) as a function of temperature and strain rate in the region of the \(\alpha\)-transition - all data .......................... 191
B-5 PC loss modulus as a function of temperature and strain rate in the region of the \(\beta\)-transition - all data ........................................ 192
B-6 PC \(\tan \delta\) as a function of temperature and strain rate in the region of the \(\beta\)-transition - all data ........................................ 192
B-7 PMMA loss modulus as a function of temperature and strain rate in the region of the \(\alpha\)-transition - all data .......................... 193
B-8 PMMA \(\tan \delta\) as a function of temperature and strain rate in the region of the \(\alpha\)-transition - all data .......................... 193
B-9 PMMA loss modulus as a function of temperature and strain rate in the region of the \(\beta\)-transition - all data ........................................ 194
B-10 PMMA \(\tan \delta\) as a function of temperature and strain rate in the region of the \(\beta\)-transition - all data ........................................ 194
E-1 PC true stress-true strain behavior at 10\(^{-3}\) and 10\(^{-1}\) s\(^{-1}\) (all data) .... 202
E-2 PC true stress-true strain behavior at 10\(^{-1}\) and 1 s\(^{-1}\) (all data) ............ 202
E-3 PMMA true stress-true strain behavior at 10\(^{-4}\), 10\(^{-3}\), 10\(^{-1}\) and 8\(\times\)10\(^{-1}\) s\(^{-1}\) (all data) ......................................................... 203
E-4 PMMA true stress-true strain behavior at 3\(\times\)10\(^{-4}\), 10\(^{-2}\), and 3\(\times\)10\(^{-1}\) s\(^{-1}\) (all data) ......................................................... 203
E-5 PC stress-strain behavior at \(\sim\)1300 s\(^{-1}\) (all data) .............................. 204
E-6 PC stress-strain behavior at \(\sim\)2000 s\(^{-1}\) (all data) .............................. 204
E-7 PC stress-strain behavior at \(\sim\)2650 s\(^{-1}\) (all data) .............................. 205
E-8 PC stress-strain behavior at \(\sim\)3900 s\(^{-1}\) (all data) .............................. 205
E-9 PC stress-strain behavior at \(\sim\)5050 s\(^{-1}\) (all data) .............................. 206
E-10 PMMA stress-strain behavior at \(\sim\)800 s\(^{-1}\) (all data) .......................... 206
E-11 PMMA stress-strain behavior at \(\sim\)1400 s\(^{-1}\) (all data) .......................... 207
# List of Tables

2.1 Shift of PMMA $T_c$ with strain rate (Lefebvre and Escaig) ........................................... 55
2.2 Shift of PMMA $T_c$ with strain rate (Lefebvre and Escaig, data of Bauwens-Crowet) ................................................................. 55

3.1 Shift of PC and PMMA viscoelastic transitions with strain rate ................................. 92

5.1 Experimental yield test data for calculating PC model parameters. ...................... 151
5.2 PC model viscoplastic parameters $\dot{\gamma}_0$ and $\Delta G$ ...................................................... 151
5.3 Experimental yield test data for calculating PMMA model parameters. ........... 153
5.4 PMMA model viscoplastic parameters $\dot{\gamma}_0$ and $\Delta G$ ................................. 153
5.5 PC and PMMA strain softening model parameters. .................................................. 155
5.6 PC and PMMA Langevin spring model parameters. .................................................. 159
Chapter 1

Introduction

The mechanical behavior of polymeric materials has long been a topic of keen interest for scientists across many disciplines. The unique properties found within this class of materials has led to many industrial and commercial applications of polymers as engineering materials. Furthermore, slight variations during the synthesis, processing, and fabrication steps of manufacture have been found to create a very broad spectrum of both chemical and physical properties in polymers. By understanding the mechanical properties of these materials and the microscopic mechanisms controlling their mechanical behavior, we will be able to better design polymers and polymer-based systems for specialized tasks.

This particular study represents the basic science needed to help better design polymer-based systems to resist deformation and/or mechanical failure at high rates of strain. The application of most notable interest is the problem of impact, where strain rates can range anywhere from $10^1 \text{ s}^{-1}$ to $10^5$ or $10^6 \text{ s}^{-1}$. Polymers have long been an engineering solution to problems of impact in society: as eyeglasses, as visors, as components of athletic equipment, as shields, as car windows, as bumpers, and even as body armor. The choice of polymeric materials for these applications has been made appealing by their relative low density, as well as the transparency that is characteristic of amorphous homopolymers. Despite the long history between polymers and problems of impact, however, the behavior under high rates of deformation is not well understood. It was the goal of this study to develop such an understanding for amorphous polymers, from molecular mechanisms of resistance up to
stress-strain response, and to use this understanding in the development of a constitutive model that is accurate at all deformation rates.

In Chapter 2 of this thesis, all relevant work on the rate-dependence of polymeric materials will be thoroughly reviewed, from early theoretical models of polymer plasticity up to present split-Hopkinson pressure bar testing. Previous research will be combed for insights into the phenomena and corresponding molecular mechanisms of increased resistance to high-rate deformation, with a look towards developing a physically-based constitutive model that captures behavior at all rates of deformation. In Chapter 3, efforts to characterize the viscoelastic behavior of PC and PMMA, through dynamic mechanical experiments and a novel analytical method, will be described in detail. In Chapter 4, experimental details and results will be given for the low, moderate, and high strain rate testing of these amorphous polymers in uniaxial compression. In Chapter 5, a new constitutive model, developed from an existing three-dimensional large-strain model of thermoplastic behavior, will be presented. Model behavior will be compared with the experimental stress-strain data of the compression testing, for all strain rates tested. Chapter 6 will discuss future work needed to refine the proposed model, and will provide a specific example of how this model will aid in the design of a component intended to resist forces of impact.
Chapter 2

Background

2.1 Rate-Dependence of Amorphous Polymer Behavior

In this study, we have limited ourselves to an investigation of the rate-dependent behavior of amorphous polymers in their glassy state, with a focus on predicting behavior at very high rates of strain. These amorphous materials are classified as such due to their lack of higher-order structure; in the unstressed state, the polymer main chains are randomly oriented. In general, a microscopic view of these materials may be visualized as a bowl of spaghetti, where chains interact with one another through weak van der Waals forces, and form a network due to either occasional covalent cross-links or physical entanglements between chains. This disordered microscopic structure dictates a mechanical response that is very much dependent on the rate at which the polymer is deformed.

The unique stress-strain response of amorphous polymers has been well-documented. A representative curve is given in figure 2-1; pictured is the true stress-true strain\(^1\) behavior

\[ e = \ln(1 + e) \]
\[ \sigma_{true} = \sigma_{eng}(1 + e) \]

Thus, the greater the strain level, the larger the deviation between engineering measures of stress and strain and true measures of stress and strain.

\(^1\)The quantities of true stress and true strain provide an accurate measure of instantaneous stresses and strains in a deformed material. While engineering stress is defined as the instantaneous force divided by the initial area, true stress is defined as the instantaneous force divided by the instantaneous area; likewise, true strain is the integral of the instantaneous change in material length divided by the instantaneous material length. True stress ($\sigma_{true}$) and true strain ($e$) can be derived from engineering stress ($\sigma_{eng}$) and engineering strain ($e$) by assuming deformation to be a volume-conserving process:
CHAPTER 2. BACKGROUND

During the initial loading phase, the material exhibits nonlinear viscoelastic behavior; at very small strains ($< 0.03$), the elastic behavior is linear. The elastic region is the result of intermolecular interactions between chains (van der Waal forces), where the chain segments partially rotate and/or slide with respect to one another. As the stress level increases, more localized regions develop within the bulk material where the stress is large enough to overcome the secondary intermolecular forces and the chains rotate and/or slide to a new position. At this point, the response becomes markedly non-linear as the slope of the stress-strain curve decreases. Eventually, enough localized events have occurred and percolated through the material such that the entire material yields in plastic (permanent) deformation and "flows" without a further increase in stress. This relative maximum in the stress-strain curve is recognized as the polymer's yield point.

Following yield, the material exhibits a phenomenon known as "strain softening"; the stress needed to further deform the polymer decreases. The strain softening indicates that the intermolecular barriers to chain segment rotation have decreased with plastic strain,
which implies that the plastic straining process produces local structural changes in the material. These structural changes make local chain-segment rotation easier (i.e. chain rotation can be produced with lower stress). As plastic deformation increases, the chain segment rotations gradually evolve the network structure from an initial isotropic random configuration to a molecularly-oriented network with chains preferentially aligned in the direction of maximum stretch. This is easier to visualize in the case of a tensile test, as the chains become aligned and parallel to the pulling axis. In a compression test, it corresponds to equi-biaxial alignment of chains in the plane perpendicular to the compression axis. As the structure deviates from its natural disordered state with increased plastic straining, the entropy of the polymer decreases. It is this entropic change - most significant once the chain segments are aligned and begin to approach their extension limit in the maximum stretch direction - that causes strain hardening in amorphous polymers. Again, this effect is easier to visualize and is more pronounced in the case of a tensile test. However, one can see in the curve of figure 2-1 where the strain hardening takes over and eventually brings the stress well above the level of initial yield.

This stress-strain behavior is strongly dependent upon strain rate. As the strain rate is increased, the stress level required for plastic flow increases. This feature of amorphous polymer response will be particularly important as we attempt to predict behavior at increasingly higher strain rates. The rate-dependent stress-strain behavior of poly(methyl methacrylate) (PMMA) is depicted in figure 2-2. The yield strength of PMMA is observed to increase by almost 100% over this range of strain rates, from very low \((10^{-4} \text{ s}^{-1})\) to moderate \((0.1, 0.3 \text{ s}^{-1})\). Furthermore, the strain hardening effect seems to be negligible at the higher rates. However, at these moderate strain rates, the material is thermally softening: adiabatic test conditions cause the material’s temperature to increase. For all amorphous polymers, the temperature dependence of their mechanical behavior is very closely linked to their strain rate dependence. This is an additional factor that must be understood and captured when modeling and predicting high rate behavior.
Figure 2-2: True stress-true strain behavior of poly(methyl methacrylate) in uniaxial compression at five true strain rates.

2.2 Theoretical Models of Amorphous Polymer Plasticity

Perhaps the first model used to describe rate-dependent plastic flow in glassy, amorphous polymers was developed from Eyring’s general theory on activated rate processes (Eyring, 1936). Eyring’s theory is considered a "transition state" theory; the idea is that one molecule is transitioned from a particular state or potential energy well to another by overcoming an energy barrier. Eyring’s theory describes the rate at which this occurs, assuming that the medium undergoing transition is heterogeneous and that there is some form of distribution to this event throughout the material. When Eyring first presented his theory, he gave examples of how it could be applied to the study of viscosity in liquids and gases, diffusion, as well as plastic flow in glassy polymers. The theory makes no assumption about the specific molecular mechanism behind the rate dependence of plasticity in polymers. It is recognized, however, that shear stress is a driving force behind the unspecified activation process which allows polymer chains to transition to a new, plastically deformed configuration. The theory
yields a model for the shear strain rate as a function of shear stress, as given below:

\[ \dot{\gamma} = \dot{\gamma}_0 \exp \left( -\frac{\Delta H}{R\theta} \right) \sinh \left( \frac{\Omega \tau}{R\theta} \right) \]  

(2.1)

Where \( \dot{\gamma}_0 \) is a lumped material parameter (to be determined), \( \Delta H \) is the activation energy required for one transition, \( \Omega \) is the activation volume, and \( R \) is the universal gas constant. The variables in the model are the shear strain rate \( \dot{\gamma} \), the shear stress \( \tau \), and the absolute temperature \( \theta \). Equation 2.1 may be rearranged, and simplified in this case\(^2\), to give an equation for shear stress as a function of strain rate:

\[ \frac{\tau}{\theta} = A \left[ \ln(2C\dot{\gamma}) + \frac{\Delta H}{R\theta} \right] \]  

(2.2)

Note that the model predicts a linear relationship between shear yield stress and the logarithm of shear strain rate.

Bauwens, Bauwens-Crowet, and Homès in Belgium were one of the first groups to thoroughly test the validity of the Eyring theory and its application to the rate dependence of yield in amorphous polymer plasticity (Bauwens-Crowet, Bauwens, & Homès, 1969), (Bauwens, Bauwens-Crowet, & Homès, 1969). The large body of experimental data that they obtained in tensile yield strength tests of polyvinyl chloride (PVC) and polycarbonate (PC) allowed them to evaluate the Eyring model over one hundred twenty degrees in temperature (20°C to 140°C) and five decades of strain rate (10\(^{-5}\) s\(^{-1}\) to 1 s\(^{-1}\)). The group agreed with the Eyring assumption that at yield, an amorphous polymer exhibits pure viscous flow. At this relative maximum in the stress-strain curve, stress has a zero-valued rate of change, while strain is still increasing - the material is "flowing" without any further

\(^2\)The simplification comes from a physical understanding of the plastic flow event. Using the definition of the hyperbolic sine, we re-write equation 2.1 as:

\[ \dot{\gamma} = \frac{\dot{\gamma}_0}{2} \exp \left( -\frac{\Delta H + \Omega \tau}{R\theta} \right) - \frac{\dot{\gamma}_0}{2} \exp \left( -\frac{\Delta H - \Omega \tau}{R\theta} \right) \]

The first term may be considered the forward progress of the transition being modeled, since stress acts against (opposite sign) the activation energy. The second term, which captures the reverse or backward progress of the plastic transition, has been shown to be non-negligible in magnitude only in the cases of unloading or low stresses. In the work of the different researchers presented here, the unloading phase is almost never of interest, and stresses in loading are often assumed to be sufficiently high so that the second term may be disregarded. Simple manipulation of the remaining term leads to equation 2.2.
increase in stress. The group re-wrote equation 2.2 in order to express the tensile yield stress \( \sigma_y \) in terms of the axial strain rate \( \dot{\varepsilon} \):

\[
\frac{\sigma_y}{\theta} = \tilde{A} \left[ \ln(2\tilde{C}\dot{\varepsilon}) + \frac{Q}{R\theta} \right]
\] (2.3)

Where \( \tilde{A} \) and \( \tilde{C} \) are still lumped parameters, but are differing in value from the \( A \) and \( C \) of equation 2.2; \( Q \), however, is identical to \( \Delta H \). It is this equation that they fit to their experimental data on PC, with nearly perfect agreement between model and experiment (figure 2-3). To them, this agreement between theory and data was experimental proof that both the activation energy \( Q \) and activation volume \( \Omega \) are constant over at least these tested ranges of temperature and strain rate - there is just a single activated process controlling yield. For the PVC data, Bauwens et al found similar agreement between the Eyring model and their experimental results, but only within a region of very low strain rates (\( 10^{-5} \) to \( 10^{-2} \) s\(^{-1} \)).

Another widely-accepted model describing the rate-dependent plastic flow of glassy polymers was developed by Robertson (1966). The Robertson model proposed a specific mechanism for polymer yield; shear stresses induce structural changes within the polymer, and it is these structural changes that allow the polymer to deform into a new molecular arrangement. In developing his theory, Robertson simplified the structure of a polymer chain down to a planar "zig-zag" - see figure 2-4. He assumes that each covalent bond along this backbone chain acts independently of the ones neighboring it, and that each bond only has two possible structural states: a low-energy, preferred state (called \textit{trans}), and a higher energy, flexed state (called \textit{cis}). As the shear stress-field is increased in the polymer, the fraction of bonds in the cis position increases (as compared to the unstressed, glassy state). This increase in the number of cis states along the polymer chains causes the stiffness of the material as a whole to decrease. Eventually, at some transient state, the polymer at temperature \( \theta \) will behave like a fluid at temperature \( \theta_1 > T_g \). Robertson is able to develop an analytical expression for this temperature \( \theta_1 \), by assuming that the transition from trans to cis states is a thermally-activated process, and that there is a Boltzmann distribution governing the fraction of bonds that are in either state for a given shear stress. As a fi-
CHAPTER 2. BACKGROUND

Eyring model parameters for the PC data of figure 2-3

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\dot{\gamma}$ [Pa/s]</td>
<td>4077</td>
</tr>
<tr>
<td>Q [kcal/mol]</td>
<td>75.5</td>
</tr>
<tr>
<td>$\dot{C}$ [s]</td>
<td>$1.0 \times 10^{-31}$</td>
</tr>
</tbody>
</table>

Figure 2-3: Eyring yield stress model fit to the PC data of Bauwens-Crowet et al. (1969)

Figure 2-4: Robertson model of a molecular chain under stress (Robertson, 1966). The dashed line indicates the new location of the bond between molecule a and molecule b after a shear force f has induced a flexing of the bond from the trans to the cis state.
nal step in his theory, Robertson develops an analytical expression describing the flow of this "fluid" at temperature $\theta_1$. He assumes a linear relationship between the viscosity and shear strain rate, and employs the empirical Williams-Landel-Ferry (WLF) equation (Ferry, 1961) to define the activation energy. The final expression of Robertson's model is given as equation 2.4:

$$\dot{\gamma} = \frac{\tau}{\eta_g} \exp \left[ -2.303 \left( \frac{c_1^2 c_2^2}{\theta - T_g} + c_2^2 \left( \frac{\theta_1}{\theta} \right) - c_1^2 \right) \right]$$

(2.4)

Where $\eta_g$ is the viscosity at the glass-transition temperature under shear stress and $c_1^2$ and $c_2^2$ are parameters from the WLF equation. In the equations of Robertson's theory, there are only two unknown parameters, both of which appear in the expression for $\theta_1$: the volume $\nu$ associated with one bond along the backbone chain, and the energy $\Delta E$ associated with converting one such bond from the trans to the cis state. The three variables in his theory are the shear strain rate $\dot{\gamma}$, the shear stress $\tau$, and the absolute temperature $\theta$. 

To confirm the validity of his theory, Robertson compared his model with contemporary data on the tensile yield behavior of polystyrene and PMMA at various quasi-static rates of strain. The results are seen in figures 2-5 and 2-6. The model seems to perform fairly well against this limited, high-temperature and low strain rate data. Robertson attributes the slight discrepancies to the fact that available data was not in the form of true yield stress, but only engineering yield stress.

Argon (1973) presented an alternate theory for the rate-dependent plastic flow of glassy polymers. This theory postulated a molecular mechanism for plastic flow. In Argon's theory, the main barrier resisting the thermally-activated molecular movements that govern plasticity is intermolecular forces. Argon’s vision of molecular-level plastic deformation in glassy polymers is described as the alignment of previously-kinked chains in the direction of straining with the introduction of stress (figure 2-7).

Argon's theory begins by modeling the reverse problem, with an elastic cylinder that becomes doubly-kinked via the introduction of a pair of wedge disclination loops (figure 2-8). Argon borrows from the previous work of Li and Gilman (1970) to develop an expression for the free energy associated with the formation of one of these wedge disclination loops, as a function of the cylinder/wedge geometry and the elastic constants of the medium. The kinking process leads to a strain increment in the elastic cylinder, which Argon uses to
Robertson model parameters for the polystyrene data of figure 2-5

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$</td>
<td>$\text{m}^2$</td>
<td>$1.68 \times 10^{-28}$</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>kcal/mol</td>
<td>1.43</td>
</tr>
<tr>
<td>$c_1^*$</td>
<td>$^\circ\text{C}$</td>
<td>17.44</td>
</tr>
<tr>
<td>$c_2^*$</td>
<td>$^\circ\text{C}$</td>
<td>51.60</td>
</tr>
<tr>
<td>$\eta_0$</td>
<td>$\text{Pa}\cdot\text{s}$</td>
<td>$10^{15.6}$</td>
</tr>
</tbody>
</table>

Figure 2-5: Comparison of Robertson model prediction and experimental data for the yield stress of polystyrene at a strain rate of 0.0033 s$^{-1}$ (Robertson, 1966)
Robertson model parameters for the PMMA data of figure 2-6

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu ) ( [m^3] )</td>
<td>( 1.4 \times 10^{-28} )</td>
</tr>
<tr>
<td>( \Delta E ) ( [\text{kcal/mol}] )</td>
<td>1.44</td>
</tr>
<tr>
<td>( c_1 ) ( [\text{C}] )</td>
<td>17.44</td>
</tr>
<tr>
<td>( c_2 ) ( [\text{C}] )</td>
<td>51.60</td>
</tr>
<tr>
<td>( \eta_0 ) ( [\text{Pa-s}] )</td>
<td>( 10^{13.6} )</td>
</tr>
</tbody>
</table>

Figure 2-6: Comparison of Robertson model prediction and experimental data for the yield stress of PMMA at strain rates of 0.000104 s\(^{-1}\), 0.000521 s\(^{-1}\), and 0.00251 s\(^{-1}\) (Robertson, 1966)
Figure 2-7: Argon interpretation of molecular deformation as a result of stress: previously kinked chains become aligned in the direction of straining. The reverse, and completely analogous, description is also pictured - previously straight chains become kinked (Argon, 1973)
CHAPTER 2. BACKGROUND

calculate the work done by a stress as it forms a pair of kinks. This calculation, combined with the previous expression for the free energy of a wedge disclination loop and an analysis of the dilatation caused by forming a kink, ultimately leads to a shear stress-dependent activation free enthalpy equation:

\[
\Delta G = \frac{3\pi \mu \omega^2 a^3}{16(1 - \nu)} \left[ 1 - 8.5(1 - \nu)^{\frac{5}{6}} \left( \frac{\tau}{\mu} \right)^{\frac{5}{6}} \right] + 0.15 \mu a^3 (\omega - \omega_c)^2 \left( \frac{p}{\mu} \right)
\] (2.5)

Where \(\omega\) and \(a\) are defined in figure 2-8, \(\mu\) is the shear modulus, \(\tau\) is the shear stress, \(\nu\) is Poisson’s ratio, and \(p\) is the pressure. In next developing an expression for the shear strain rate, Argon considered the stability of the new (kinked) configuration, and how likely the chain is to return to its original ground state after kinking. The theory assumes that each chain only interacts with its two closest neighbors, in the plane of kinking. To return to the ground state, the kinked chain would need to either kink in the opposite direction, or cause one of its neighboring chains to kink, thus relieving its stored elastic energy. It is here that the theory weighs heavily upon the influence of intermolecular forces.

Figure 2-8: Argon model for the formation of a double kink. Two wedge disclination loops are formed in a cylinder of radius \(a\) embedded in an elastic medium (Argon, 1973)
CHAPTER 2. BACKGROUND

The final expression of Argon’s model is given as the equation for shear strain rate:

$$\dot{\gamma} = \gamma_0 \nu_a N_a \exp \left[ -\frac{\Delta G}{2k\theta} \right]$$

(2.6)

Where $\gamma_0$ is the unit increment of shear strain that results from the production of a pair of kinks, $N_a$ is the volume density of activated states, $\nu_a$ is a frequency term capturing the rate at which the kinking process occurs, and $\omega_c$ is the critical angle size such that the kinking process produces cavitation (increases the free volume). Oftentimes, equation 2.6 is seen with $\gamma_0$, $\nu_a$, and $N_a$ lumped into one, pre-exponential parameter, $\dot{\gamma}_0$ (of units s$^{-1}$). In Argon’s model, there are four variables: the shear strain rate $\dot{\gamma}$, the shear stress $\tau$, the absolute temperature $\theta$, and the pressure $p$. Argon’s model captured contemporary experimental findings, that the pressure dependence of the yield point is paralleled by the pressure dependence of the shear modulus (Brown, 1971), and that the temperature dependence of the yield point is related to the temperature dependence of the shear modulus (Argon, Andrews, Godrick, & Whitney, 1968). At the time the model was presented, there was no complete data on the pressure, temperature, and strain rate (frequency) dependence of the shear modulus of any polymer. Despite the lack of this necessary information, Argon was able to fit his model quite well to existing data on the yield behavior of polystyrene and polyethylene terephthalate (PET) - see figures 2-9 and 2-10. This data covered both low and high temperatures (150 - 350 K), and strain rates ranging from very low ($10^{-4}$ s$^{-1}$) to medium ($10^2$ s$^{-1}$).

Both Argon and Robertson found success in developing a physically-based constitutive model for rate-dependent plasticity in amorphous polymers. They were successful in that each found contemporary data, either their own or that of another researcher, that they could fit their model to with at least moderate success. However, neither model was applied as often as the Ree-Eyring model (Ree & Eyring, 1955), (Ree & Eyring, 1958) in fitting rate-dependent yield data of amorphous polymers. The Ree-Eyring model is essentially a modification, to a more general form, of the original Eyring model (1936). It should be noted that the modifications were conceived of and presented in the 1950s, but it was not until the late 1960s and 1970s that new phenomena in the data - phenomena that will be
CHAPTER 2. BACKGROUND

Argon model parameters for the polystyrene data of figure 2-9

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega^2 a^3$</td>
<td>$m^3$</td>
<td>$2.15 \times 10^{-28}$</td>
</tr>
<tr>
<td>$\gamma_0$</td>
<td>$s^{-1}$</td>
<td>$1.6 \times 10^{13}$</td>
</tr>
<tr>
<td>$\mu(T)$</td>
<td>MPa</td>
<td>From data of Rudd and Gurnee (1957)</td>
</tr>
</tbody>
</table>

Figure 2-9: Comparison of Argon model prediction and experimental data for the temperature-dependent shear yield stress of polystyrene (Argon, 1973)
CHAPTER 2. BACKGROUND

Argon model parameters for the PET data of figure 2-9

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega^2 a^3$ [m$^3$]</td>
<td>$7.17 \times 10^{-28}$</td>
</tr>
<tr>
<td>$\gamma_0$ [s$^{-1}$]</td>
<td>$8.0 \times 10^{13}$</td>
</tr>
<tr>
<td>$\mu(T)$ [MPa]</td>
<td>From data of Illers and Breuer (1963)</td>
</tr>
</tbody>
</table>

Figure 2-10: Comparison of Argon model prediction and experimental data for the temperature-dependent shear yield stress of polyethylene terephthalate at seven different strain rates (Argon, 1973)
CHAPTER 2. BACKGROUND

discussed in detail in the ensuing pages of this background chapter - began to emerge that could not be captured by the Eyring, Robertson, or Argon models. It was only then that the Ree-Eyring model found its popularity.

The Ree-Eyring model simply allows for multiple rate-activated processes to be acting in tandem, rather than just a single activated process as in the Eyring model. When the model is expressed in terms of the polymer yield stress, as in equation 2.7, it is clear how each "process" adds another component to the value of the yield stress:

\[
\frac{\sigma_y}{\theta} = \sum_i \frac{1}{A_i} \sinh^{-1} \left[ \frac{C_i \dot{\varepsilon}}{\theta} \exp \left( \frac{\Delta H_i}{R \theta} \right) \right]
\]

(2.7)

Under the framework of the Ree-Eyring theory, the "processes" of plastic flow in amorphous polymers are often interpreted as the relaxation or activation of particular degrees of freedom of the polymer chains, which are otherwise hindered, upon the application of stress.

These three models - the Ree-Eyring model, the Robertson model, and the Argon model - were recently reviewed and scrutinized by Richeton, Ahzi, Daridon, and Rémond (2003). Each was compared against current quasi-static (10^{-3} \text{ s}^{-1} to 10^{1} \text{ s}^{-1}) and high rate (10^{3} \text{ s}^{-1} to 10^{4} \text{ s}^{-1}) experimental data on the yield strength of amorphous PC and PMMA. Figure 2-11, reproduced from their study, demonstrates how these models behave most differently in their prediction of yield strength at high strain rates. From figure 2-12, we see that the Ree-Eyring model is the only one capable of capturing the actual high rate behavior observed in the yield strength of PC. However, in the range of strain rates below 10^{2} \text{ s}^{-1}, all models perform equally well. In fact, these researchers point out how the Argon model and the Ree-Eyring model are mathematically very similar. If only one activated process is considered in the Ree-Eyring model, then both would predict a linear (or near linear, depending on how the shear modulus was represented in the Argon model) relationship between yield stress and the logarithm of strain rate.

As the study of the rate-dependent plastic deformation of amorphous polymers moved to include testing at low temperatures and medium to high rates of deformation, new phenomena began to emerge in the data, as was alluded to earlier. Certain materials are observed
Figure 2-11: Theoretical compressive yield stress vs. logarithm of strain rate (at 60°C) for three models of the rate-dependent yield of amorphous polymers: Ree-Eyring, Robertson, and Argon (Richeton et al., 2003)

to exhibit a sharp increase in their yield strength either below a certain temperature or beyond a certain rate of straining - this, along with its simplicity, is why the Ree-Eyring model became such a popular choice as a model to fit the yield data. The rest of this background chapter will focus on chronicling the history of our understanding, both experimental and theoretical, of this rate-dependent phenomena. It will cover the actual discovery and confirmation alongside a description of the new experimental techniques that were developed specifically for studying the high rate behavior of polymers. On the theoretical side, it will examine the application of the aforementioned theoretical models in fitting low temperature and medium to high rate data, as well as the development of explanations for the unexpected behaviors.
CHAPTER 2. BACKGROUND

Ree-Eyring and Argon model parameters for the PC data of figure 2-12

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_o$ [Pa/°K]</td>
<td>6000</td>
<td>$\omega^3 a^3$ [m$^3$]</td>
<td>$2.15 \times 10^{-28}$</td>
</tr>
<tr>
<td>$Q_o$ [kcal/mol]</td>
<td>67.8</td>
<td>$\gamma_0$ [s$^{-1}$]</td>
<td>$1.0 \times 10^{13}$</td>
</tr>
<tr>
<td>$C_o$ [s]</td>
<td>$4.1 \times 10^{-30}$</td>
<td>$\mu(T)$ [MPa]</td>
<td>663.9 at 20°C</td>
</tr>
<tr>
<td>$A_o$ [Pa/°K]</td>
<td>54000</td>
<td>$Q_o$ [kcal/mol]</td>
<td>5.0</td>
</tr>
<tr>
<td>$C_o$ [s]</td>
<td>$2.9 \times 10^{-7}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2-12: Comparison of Argon and Ree-Eyring models fit to PC compressive yield data at all rates (Richeton et al., 2003)
2.3 Low-Temperature/High-Rate Strengthening of Polymers: Evidence and Explanations

In the 1960s, two groups independently identified a transition in the nature of the rate-dependent yield in amorphous polymers. This transition seemed to occur after exceeding some material-dependent threshold in strain rate and/or temperature. Working in Belgium, Bauwens, Bauwens-Crowet, and Homés (1964) showed for the first time what they considered evidence of a "secondary transition" in the yield behavior of PMMA (figure 2-13). Testing the yield strength of this amorphous polymer over a large range of displacement rates (0.0625 mm/min to 31.4 mm/min, with a nominal gage length of 40 mm) and temperatures (22°C to 100°C), they found two distinct regions of behavior; these regions could be separated by either temperature or strain rate. The yield behavior of PMMA in each region was fit to the original Eyring theory of viscosity, and a corresponding activation energy was calculated for each region - see the table adjoining figure 2-13. However, material behavior over the entire set of data could not be captured with the single-process explanation that the Eyring model provided; they suggested that two processes were acting in parallel. It is for this reason that they assumed the existence of some sort of transition in the material behavior that was secondary to the well-known glass transition of the material. The changes in behavior through this transition were not as dramatic as those observed through the glass transition, but like the glass transition, the temperature at which this secondary transition took place seemed to be rate-dependent. Finally, they speculated that this transition was related to the relaxation/freezing in of a degree of freedom associated with side-chain rotation about the polymer main chains as the temperature went above/below this transition temperature and/or below/above the transition strain rate. See Appendix A for the chemical structure of PMMA.

At the Research Laboratories of the Rohm and Haas Company, Roetling (1965b) made an identical discovery during his own investigations into the tensile yield behavior of PMMA. Though neither Roetling nor the Bauwens group was aware of the work that the other was carrying out in the mid-1960s, their experimental results and theoretical explanations were strikingly similar. Using an Instron-type universal testing machine, Roetling investigated
Eyring model parameters for the PMMA data of figure 2-13

<table>
<thead>
<tr>
<th>Process 1 ($\alpha$)</th>
<th>Process 2 ($\beta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q$ [kcal/mol]</td>
<td>$Q$ [kcal/mol]</td>
</tr>
<tr>
<td>98</td>
<td>26</td>
</tr>
</tbody>
</table>

Figure 2-13: Tensile yield strength of PMMA as a function of displacement rate and temperature (Bauwens-Crowet & Homès, 1964). The slanted line d indicates the location of the supposed secondary transition - data on each side has been fit with the single-process Eyring model. Displacement rates are as follows: $v_1 = 0.0625$ mm/min, $v_2 = 0.25$ mm/min, $v_3 = 1.25$ mm/min, $v_4 = 6.25$ mm/min, and $v_5 = 31.4$ mm/min. Specimen gage length for all tests was 40 mm.
CHAPTER 2. BACKGROUND

Ree-Eyring model parameters
the PMMA data of figure 2-14

<table>
<thead>
<tr>
<th>Process</th>
<th>α</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>A [Pa/°K]</td>
<td>14700</td>
<td>7060</td>
</tr>
<tr>
<td>Q [kcal/mol]</td>
<td>81</td>
<td>24</td>
</tr>
<tr>
<td>C [s]</td>
<td>8.19×10^{-40}</td>
<td>1.39×10^{-11}</td>
</tr>
</tbody>
</table>

Figure 2-14: PMMA yield data by Roetling fit with the Ree-Eyring model (Roetling, 1965b)

the yield behavior of PMMA at temperatures ranging from 30°C to 90°C, and strain rates ranging from 10^{-5} s^{-1} to almost 10 s^{-1}. His results are summarized in figure 2-14. Like Bauwens, Roetling applied the Eyring viscosity theory at the yield point, where the material flows (strains) without an increase in the stress level. However, he too realized that the data could only be fit with a two-process modification of the Eyring model. Rather than just fitting two pieces of each curve with a separate Eyring model, he fit the Ree-Eyring model to the entire data set. Roetling found his constants for the model by assuming that the contribution of the lower energy activation process, which he called the "β-process," was negligible at the lowest strain rates and highest temperatures, whereas at the higher strain rates and lowest temperatures, both the α and β processes were important.
CHAPTER 2. BACKGROUND

To explain this yield phenomenon, Roetling compared his calculated activation energy for the \( \beta \)-process - \( \Delta H_2 \) in equation 2.7 - with contemporary calculated activation energies originating from creep measurements, dielectric measurements, and dynamical mechanical measurements. His \( \beta \)-process activation energy corresponded well with the activation energy of the secondary transition of PMMA that the other experimentalists had found. Thus, Roetling assumed that this unique yield behavior could be attributed to the secondary transition of PMMA. He went on to argue that this \( \beta \)-process, like the \( \alpha \)-process, corresponded to a particular degree of freedom of the polymer chains. Roetling concluded his theory by suggesting that the \( \beta \)-process corresponds to rotation of the main chains about their longitudinal axis, whereas the \( \alpha \)-process corresponds to rotation about an axis perpendicular to the longitudinal axis. He discounted the idea that this \( \beta \)-process is related to side chain motion.

Roetling (1965a) continued his examination of this yield phenomenon by testing the rate- and temperature-dependent tensile yield strength of a second amorphous polymer: poly(ethyl methacrylate) (PEMA). Again, he used an Instron-type universal testing machine to record the yield strength at temperatures ranging from 30°C to 80°C, and strain rates ranging from \( 10^{-5} \text{ s}^{-1} \) to almost \( 10 \text{ s}^{-1} \). The results can be seen in figure 2-15. As with PMMA, the PEMA yield curves had a nearly bilinear characteristic shape. Roetling again attributed this increased strengthening at medium strain rates and low temperatures to a secondary transition in the material. He fit the data with the Ree-Eyring model (the source of the curves in figure 2-15), and again argued the connection between the observed secondary transition and a particular degree of freedom of the polymer main chains.

Now following the work of Roetling, the Bauwens group continued their investigation into this secondary transition of amorphous polymers with tensile testing of PC and PVC over a wide range of temperatures and strain rates (Bauwens-Crowet et al., 1969), (Bauwens et al., 1969). Using an Instron universal testing machine with attached environmental chamber, they were able to test at temperatures ranging from 20°C to 140°C, and strain rates ranging from \( 10^{-5} \text{ s}^{-1} \) to nearly 1 \text{ s}^{-1}. As presented earlier (see figure 2-3), they found the generalized Eyring theory, with just one activated process, to fit perfectly to all of their PC yield strength data. However, they argue that they did not observe a sharp
Ree-Eyring model parameters for the PEMA data of figure 2-15

<table>
<thead>
<tr>
<th>Process</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A [Pa/°K]</td>
<td>22500</td>
<td>9000</td>
</tr>
<tr>
<td>Q [kcal/mol]</td>
<td>98</td>
<td>32</td>
</tr>
<tr>
<td>C [s]</td>
<td>$6.99 \times 10^{-56}$</td>
<td>$3.14 \times 10^{-17}$</td>
</tr>
</tbody>
</table>

Figure 2-15: Poly(ethyl methacrylate) yield data by Roetling fit with the Ree-Eyring model (Roetling, 1965a)
increase in strength at lower temperatures or higher rates of deformation, evidence of some sort of secondary transition, only because they were limited by the ranges of temperatures and strain rates that they could test at.

The tests on PVC, on the other hand, showed definite evidence of a secondary transition (figure 2-16). In fact, the group had chosen this particular material because of available data that showed it to have a local relaxation mode that was secondary to the $\alpha$-relaxation. The evidence in the literature, in the form of measurements of electrical and mechanical losses, indicated that this transition was far enough away from the glass-transition to be distinguishable, yet close enough that it might be witnessed in the yield behavior at attainable strain rates. Bauwens’ group found that the single-process Eyring model could be fit to either the high temperature/low strain rate region (to the left of line d in figure 2-16) or the low temperature/medium strain rate region (to the right of line d). However, only a Ree-Eyring modification to the model could be used to fit the entire data set, which in this case ranged from $-50^\circ$C to $70^\circ$C and $10^{-5}\text{ s}^{-1}$ to $1\text{ s}^{-1}$. The set of parallel lines over their data was generated from a two-process version of the Ree-Eyring equation for yield stress - equation 2.8. Here, the approximation $\sinh^{-1}(x) \cong \ln(2x)$ (see footnote 2) is made only on the first term, because only the $\alpha$-process is considered to be in a “high stress” state over the entire range of interest.

$$\frac{\sigma_y}{\theta} = \frac{\sigma_\alpha}{\theta} + \frac{\sigma_\beta}{\theta} = A_\alpha \left[ \ln(2C\alpha\dot{\epsilon}) + \frac{Q_\alpha}{R\theta} \right] + A_\beta \sinh^{-1} \left[ C_{\beta}\dot{\epsilon}\exp \left( \frac{Q_\beta}{R\theta} \right) \right] \quad (2.8)$$

Since the lines pertaining to each testing temperature were parallel, Bauwens’ group realized that a composite, master curve could be generated by shifting all curves to one reference temperature. They fit both the horizontal ($s_x$) and vertical ($s_y$) components of the shifting function to Arrhenius-type equations:

$$s_x = \frac{Q_\beta}{2.303R} \left[ \frac{1}{\theta} - \frac{1}{273} \right] \quad (2.9)$$

$$s_y = -A_\alpha \frac{Q_\alpha - Q_\beta}{R} \left[ \frac{1}{\theta} - \frac{1}{273} \right] \quad (2.10)$$
CHAPTER 2. BACKGROUND

Ree-Eyring model parameters for the PVC data of figure 2-16:

<table>
<thead>
<tr>
<th>Process</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A [Pa/K]</td>
<td>6860</td>
<td>9898</td>
</tr>
<tr>
<td>Q [kcal/mol]</td>
<td>70.5</td>
<td>14.0</td>
</tr>
<tr>
<td>C [s]</td>
<td>$1.0 \times 10^{-38}$</td>
<td>$4.26 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

Figure 2-16: Polyvinyl chloride yield data by Bauwens-Crowet et al. (1969) fit by the Ree-Eyring model. Slanted line d indicates location of supposed $\beta$-transition.
The master curve, along with these analytical expressions of the shifting function, could then be used to predict yield strengths at temperatures and strain rates that were not attainable in the laboratory. Figure 2-17 is the result of their shifting each curve to 0°C (273 K) along the slanted line d, with slope $s_y/s_x$.

A few years later, Bauwens-Crowet, Bauwens, and Homès (1972) revisited their study of the rate-dependent yield of PC (1969), this time extending their investigation to very low temperatures. They examined the tensile yield strength of PC from $-140^\circ C$ to $20^\circ C$ and $10^{-5}$ s$^{-1}$ to 1 s$^{-1}$, and also the uniaxial *compressive* yield strength from $-120^\circ C$ to $120^\circ C$ at a strain rate of $4.16 \times 10^{-3}$ s$^{-1}$. It was their intent to prove the existence of a secondary transition in the yield behavior of PC. Figure 2-18 is a plot of all of their compression data, as well as the tension data from tests at the same, quasi-static strain rate. Figure 2-19 presents all of their tension data. With the dashed lines in figures 2-18 and 2-19, the Bauwens group has divided their data into two regions: range I and range I'. The yield behavior of PC in range I had already been characterized by this group in a
Ree-Eyring model parameters for the PC data of figure 2-18

<table>
<thead>
<tr>
<th>Process</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{\text{tension}}$ [Pa/°K]</td>
<td>4260</td>
<td>13000</td>
</tr>
<tr>
<td>$A_{\text{compress}}$ [Pa/°K]</td>
<td>5600</td>
<td>54800</td>
</tr>
<tr>
<td>Q [kcal/mol]</td>
<td>75.5</td>
<td>9.6</td>
</tr>
<tr>
<td>C [s]</td>
<td>$2.4 \times 10^{-21}$</td>
<td>$2.76 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

Figure 2-18: Temperature dependence of PC yield point in both tension and compression. All tests were performed at the same strain rate: $4.16 \times 10^{-3}$ s$^{-1}$. Data has been fit with the Ree-Eyring model (Bauwens-Crowet et al., 1972).
Figure 2-19: Temperature and strain rate dependence of PC tensile yield point. Curves have been fit by the Ree-Eyring model, using the same model parameters listed with figure 2-18 (Bauwens-Crowet et al., 1972).

previous study (Bauwens-Crowet et al., 1969), and had been found to conform well to the original single-process Eyring model (see figure 2-3). However, just as they discovered in their study of PVC over a wide range of temperatures, the entire data set could only be fit with a two-process Ree-Eyring modification of the Eyring model. Again using equation 2.8, they generated the curves seen in figures 2-18 and 2-19. The Bauwens group found that the same values of activation energy $Q_\alpha$ and $Q_\beta$ could be used to fit the tension and compression data, but differing values of $A_\alpha$ and $A_\beta$ were needed to capture what they considered the pressure dependence of the yield point. To Bauwens' group, the Ree-Eyring model had proved to be a very appropriate choice for modeling the rate-dependent yield of this amorphous polymer. The group noted the existence of another model that was physically-based and had been shown to capture well the rate-dependent yield in PMMA: the Robertson model modified by Duckett, Rabinowitz, and Ward (1970) to incorporate pressure dependence. However, Bauwens-Crowet et al argued that the Ree-Eyring model
could perform just as well, if not better, in fitting the experimental results with much less complexity.

Bauwens (1972) continued the work by attempting to theoretically and experimentally explain the cause of this increased strengthening at low temperatures and high rates of strain in amorphous polymers. Already, his group had linked the $\beta$-process in their application of the Ree-Eyring theory with a secondary transition in the time and temperature dependent viscoelastic behavior of PC. They made this link by means of an activation energy comparison: their Ree-Eyring fit yielded a $\beta$-process activation energy of 9.6 kcal/mol, and the dielectric measurement of the secondary transition in PC, performed by Locati and Tobolsky (1970), gave a value of approximately 8 kcal/mol. Because these two values matched up so closely, they supposed that it was the same molecular movements governing both phenomena: increased strengthening at high rates/low temperatures, and the secondary ($\beta$) transition in the viscoelastic behavior. In the current study, Bauwens sought to connect the shape of the viscoelastic $\beta$ loss tangent (tan $\delta$) peak, measured via mechanical damping tests, with the shape of the transition in the yield curve. He theorized that the distributed nature of the event should manifest itself in the same manner in both curves.

In order to characterize the shape of the loss tangent peak associated with the $\beta$-transition, Bauwens employed a free-oscillation torsional pendulum in damping tests. Using an environmental chamber, he was able to characterize the loss tangent of PC at two frequencies around 1 Hz (cps) from -160°C to -20°C - the results are seen in figure 2-20. Though Bauwens' compression experiments on PC (Bauwens-Crowet et al., 1972) showed a transition in yield behavior at about -80°C, this damping data indicated a transition closer to -100°C. The difference could be accounted for in the rate-dependence of this transition's location; the compression experiments were carried out at $4.16 \times 10^{-3}$ s$^{-1}$, which would correspond to a frequency of approximately 9.5 Hz in his damping experiments. Using the results of figure 2-20, Bauwens was able to analytically generate the loss tangent curve at 9.5 Hz, based on the amount of shifting observed in his two tests around 1 Hz. This predicted curve, with a peak very close to -80°C, is seen in figure 2-21.

In order to relate the shape of this loss tangent curve in the $\beta$-transition regime to the shape of the transition in the yield plot, Bauwens proposed a new equation for predicting
Figure 2-20: Loss tangent of PC in the $\beta$-transition range at two frequencies around 1 Hz: 0.555 Hz (curve a) and 2.525 Hz (curve b) (Bauwens, 1972).

Figure 2-21: Predicted loss tangent of PC at 9.5 Hz in the $\beta$-transition regime, normalized by temperature. Also, the value of the double integral in equation 2.11, representative of a distribution of activation energies (Bauwens, 1972).
yield strength as a function of temperature:

$$\sigma = \sigma_a(T) + B \int_T^\infty \int_T^\infty \frac{\tan \delta(T)}{T} dT^2$$  \hspace{1cm} (2.11)

Where $\sigma_a$ has the same definition as in equation 2.8, B is a parameter to be determined, and $\tan \delta$ is the loss tangent. The double integral of the second term, used to capture the shape of the loss tangent peak, has been plotted in figure 2-21 alongside the loss tangent curve itself. Bauwens argued that this new equation, which allowed for a distributed definition of the activation energy, was more accurate than the equations of the Ree-Eyring model from which it was derived. In figure 2-22, the model has been fit quite successfully to the compressive yield data of their previous study (Bauwens-Crowet et al., 1972).

In an ensuing study, Bauwens-Crowet (1973) followed the now-established "Bauwens procedure" in characterizing the compressive yield behavior of PMMA. She began by generating compressive yield data over a large range of strain rates and temperatures (figure
Figure 2-23: PMMA compressive yield data. The set of curves is generated by shifting one line of best fit to the other temperatures along slanted line $d_c$ using the Arrhenius-type functions of equations 2.9 and 2.10 (Bauwens-Crowet, 1973).

Next, she formed a master yield curve by shifting the data of each temperature along the slanted line $d_c$ (figure 2-24). Again, the shifting functions were made to fit an Arrhenius form, similar to 2.9 and 2.10. Using the two-process Ree-Eyring model (equation 2.8), she attempted to fit the data of the master curve - this is the source of the dashed line in figure 2-24. Finding the Ree-Eyring fit unsatisfactory in capturing the distributed nature of the yield behavior transition, she turned to Bauwens’ yield model, incorporating the shape of the $\beta$ loss tangent peak to give a distribution of activation energies. She started with mechanical damping tests, examining the shape of the loss tangent in the region of the $\beta$-transition at two frequencies around 1 Hz. The curves she obtained are presented in figure 2-25. Next, she developed the analytical curve of the double integral in equation 2.11, which Bauwens had supposed would provide a more realistic representation of the activation energy for the $\beta$-process. In figure 2-26, she compares an appropriate scalar multiple of this curve with a plot of just the $\beta$-component of the compressive yield stress against
CHAPTER 2. BACKGROUND

Ree-Eyring model parameters for the PMMA data of figure 2-24

<table>
<thead>
<tr>
<th>Process</th>
<th>( \alpha )</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A [Pa/°K]</td>
<td>6960</td>
<td>36700</td>
</tr>
<tr>
<td>Q [kcal/mol]</td>
<td>98.5</td>
<td>25.6</td>
</tr>
<tr>
<td>C [s]</td>
<td>( 5.0 \times 10^{-52} )</td>
<td>( 4.67 \times 10^{-17} )</td>
</tr>
</tbody>
</table>

Figure 2-24: Master curve for the rate- and temperature-dependent yield of PMMA at 0°C. Curve is fit by Ree-Eyring model (dashed line); line \( d_e \) indicates shifting axis (Bauwens-Crowet, 1973).
Figure 2-25: Loss tangent of PMMA in the $\beta$-transition range at two frequencies around 1 Hz: 0.46 Hz (curve a) and 1.82 Hz (curve b) (Bauwens-Crowct, 1973).

temperature. Finding a satisfactory fit, she concludes that the Bauwens method is valid for modelling and predicting the rate-dependent yield of this amorphous polymer.

Through the 1970s and 1980s, other researchers tried to better understand and explain the rate-dependence of plasticity in amorphous polymers. Wu and Turner (1975) used torsional tests on tubular specimens of PC and polyethylene to examine the rate, temperature, and pressure dependence of flow stress, as well as various thermal activation parameters. They observed the same increased strengthening at low temperatures that both Roetling and the Bauwens group had seen, as depicted in the data of figure 2-27. However, Wu and Turner discounted the notion that yield behavior, such as that observed in their torsional tests, should be explained in terms of small strain viscoelastic behavior, as Bauwens had done with his damping tests. They chose to focus instead on the derivation of the rate, temperature, and pressure dependence of different thermal activation parameters, such as shear activation volume. In the end, they failed to provide any sort of theoretical interpretation of the microscopic mechanisms behind plastic flow in amorphous polymers.
CHAPTER 2. BACKGROUND

Figure 2-26: $\beta$-component of the compressive yield strength of PMMA fit with a scalar multiple of the double integral term in equation 2.11 (Bauwens’ yield model); the double integral was developed from the data of figure 2-25 (Bauwens-Crowet, 1973).

Figure 2-27: PC flow stress in shear, as a function of temperature and strain rate. Data was obtained from torsional tests on tubular specimens. (Wu & Turner, 1975).
Figure 2-28: PMMA compressive stress-strain behavior as a function of temperature. All tests were performed at the same strain rate: $3.5 \times 10^{-5} \text{ s}^{-1}$ (J. Haussy & Lefebvre, 1980).

The group of Haussy, Cavrot, Escaig, and Lefebvre (1980) also performed a more thermodynamic analysis on the yield behavior of amorphous polymers. However, they chose to follow more closely the theories of Eyring and Bauwens. Like Bauwens-Crowet (1973), this group studied the temperature-dependent compressive yield strength of PMMA, but only at one quasi-static strain rate: $3.5 \times 10^{-5} \text{ s}^{-1}$. While Bauwens-Crowet only went as low as 250 K, this group tested temperatures down to 77 K. Some of the stress-strain curves they obtained can be seen in figure 2-28. Against this data, they tested the application of a simple Arrhenius law, equation 2.12. This can be seen as a more general form of the single-process Eyring model (equation 2.1), where the simplification described in footnote 2 has been made.

$$
\dot{\epsilon}(\sigma, \theta, \epsilon) = \dot{\epsilon}_0(\sigma, \theta, \epsilon) \exp \left[ \frac{-\Delta G_a(\sigma, \theta, \epsilon)}{kT} \right]
$$

(2.12)

In this expression, they have left open the possibility that both the activation free energy $\Delta G_a$ and the pre-exponential factor $\dot{\epsilon}_0$ could be stress-dependent. In Bauwens’ application of the Eyring and Ree-Eyring theories, the pre-exponential factors were always taken as
constants. Haussy et al found this assumption to be valid at temperatures below 200 K, as the relation between stress and temperature is purely exponential (yield stress is linearly related to the logarithm of temperature). However, an analysis of the dependence of the activation parameters on temperature led them to believe that the pre-exponential factor must be somehow stress-dependent above a critical temperature, $T_c \sim 200$ K; they propose a power law fit. In attempting to explain this phenomenon, Haussy et al liken the deformation mode below $T_c$ to crystal plasticity. They calculated an activation volume on the order of 1.5-2 monomer units, and thus suggest that plastic deformation is given by a broad distribution of very localized events that act in a cooperative manner to cause flow on the macroscopic scale. Beyond $T_c$, the best they can say is that they agree with Bauwens, that deformation is somehow related to the $\beta$-relaxation process.

Lefebvre and Escaig (1985) continued this work with more PMMA compression tests, this time at three different strain rates: $3.5 \times 10^{-5}$ s$^{-1}$, $2 \times 10^{-4}$ s$^{-1}$, and $7 \times 10^{-4}$ s$^{-1}$. Their data is presented in figure 2-29. In a theoretical analysis of this data, they began with the assumption that the temperature dependence of the Gibbs free energy ($\Delta G_a$ in equation
2.12) is related closely to the temperature dependence of the shear modulus, $\mu$. They proposed that the large drop-off in the value of the shear modulus through the secondary material transition is responsible for the change in the yield behavior. Lefebvre and Escaig criticized other theoreticians, such as Argon, who had developed expressions for the Gibbs free energy that incorporated the shear modulus, but then used the $\mu(\theta)$ data from tests around 1 Hz in the validation of their respective models. Though no other information was available to many of these researchers, Lefebvre and Escaig believed that it was not an accurate treatment because of the strong variation in the $\mu(\theta)$ curve with respect to test frequency. They do acknowledge the procedure introduced by Bauwens (1972), where the loss tangent data used in his model is derived from a shift, to the proper frequency, of the available data. However, Lefebvre and Escaig seem to think that his procedure does not have enough physical or theoretical basis.

In their own analysis, Lefebvre and Escaig measured the shear modulus of PMMA over three decades of frequency, from 1 Hz to 1000 Hz, using both a torsional pendulum and a Metravib viscoelasticimeter (figure 2-30). The next step was to use this data to examine

![Figure 2-30: PMMA shear modulus as a function of temperature and test frequency (Lefebvre & Escaig, 1985).](image)
**Table 2.1:** Shift of PMMA $T_c$ with strain rate (Lefebvre & Escaig, 1985)

<table>
<thead>
<tr>
<th>Strain Rate [$s^{-1}$]</th>
<th>$T_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3.5 \times 10^{-5}$</td>
<td>230±10 K</td>
</tr>
<tr>
<td>$2.0 \times 10^{-4}$</td>
<td>245±10 K</td>
</tr>
<tr>
<td>$7.0 \times 10^{-4}$</td>
<td>255±10 K</td>
</tr>
</tbody>
</table>

**Table 2.2:** Shift of PMMA $T_c$ with strain rate, using data of Bauwens-Crowet (1973) (Lefebvre & Escaig, 1985)

<table>
<thead>
<tr>
<th>Strain Rate [$s^{-1}$]</th>
<th>$T_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4.0 \times 10^{-5}$</td>
<td>240±10 K</td>
</tr>
<tr>
<td>$4.0 \times 10^{-3}$</td>
<td>270±10 K</td>
</tr>
<tr>
<td>$4.0 \times 10^{-1}$</td>
<td>300±10 K</td>
</tr>
</tbody>
</table>

the variation with stress of the Gibbs free energy, for which they had derived a stress- and shear modulus-dependent expression via thermodynamic analysis. With this examination, they were able to locate again the critical transition temperature $T_c$ above which $\Delta G_d$ is no longer temperature dependent. In the previous study, Haussy, Cavrot, Escaig and Lefebvre (1980) had shown that below $T_c$, PMMA behavior is accurately described by the Eyring theory. As might be expected, Lefebvre and Escaig found that the location of $T_c$ shifted with strain rate (table 2.1). Using their own shear modulus data, they performed the same analysis on the PMMA yield data of Bauwens-Crowet (1973) to determine the $T_c$ shift (table 2.2). The results of these two tables are fairly consistent: table 2.1 indicates that the transition in the PMMA yield behavior shifts at 19.25°K per decade in strain rate, whereas table 2.2, from the data of Bauwens-Crowet (1973), indicates that the transition shifts 15°K per decade in strain rate. Lefebvre and Escaig leave to another study any sort of discussion on the correlation between the shifting $T_c$ value and specific molecular motions.

Truss, Clarke, Duckett, and Ward (1984) also made significant contributions to the understanding of rate-dependent yield phenomena in amorphous polymers. Though their testing actually was conducted on polyethylene, a crystalline thermoplastic, much can still be garnered from their research. They examined the rate, temperature, and pressure dependence of yield in polyethylene with two different apparatus. For studying just the rate and temperature dependence of yield, they used an Instron tensile testing machine with
CHAPTER 2. BACKGROUND

Ree-Eyring model parameters for the polyethylene data of figure 2-31, following equation 2.13

<table>
<thead>
<tr>
<th>Process</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\ln \epsilon_0$ [s^{-1}]</td>
<td>63.5</td>
<td>42.7</td>
</tr>
<tr>
<td>$\Delta H$ [kcal/mol]</td>
<td>57</td>
<td>32</td>
</tr>
<tr>
<td>$\nu$ [m^3]</td>
<td>$6.28 \times 10^{-27}$</td>
<td>$2.32 \times 10^{-27}$</td>
</tr>
</tbody>
</table>

Figure 2-31: Temperature and strain rate dependence of the tensile yield strength of Rigidex R50 polyethylene. Curves have been fit with the Ree-Eyring model. Strain rates are as follows: (○) $8.33 \times 10^{-2}$ s^{-1}, (□) $4.17 \times 10^{-3}$ s^{-1}, (×) $8.33 \times 10^{-4}$ s^{-1}, and (▼) $8.33 \times 10^{-5}$ s^{-1} (R.W. Truss & Ward, 1984).

different attached environmental chambers. They examined strain rates from $10^{-6}$ s^{-1} to $10^{-1}$ s^{-1} and temperatures from 120 K to 300 K. Example test results are shown in figure 2-31. For studying the pressure dependence of yield, they used a unique high-pressure torsional apparatus that could provide hydrostatic pressures on the test specimen up to 600 MPa. Sets of data from both test procedures were explained in terms of the Ree-Eyring theory, with two activated processes acting in parallel. Equation 2.13, of familiar form, was fit to all of their tension data. Equation 2.14, a slight modification of the Ree-Eyring model to more directly capture the pressure dependence of the shear yield strength, was fit to all
of their torsional data.

\[
\frac{\sigma_y}{\theta} = \frac{k}{\nu_1} \left( \ln \dot{\varepsilon} - \ln \frac{\dot{e}_{0,1}}{2} + \frac{\Delta H_1}{k\theta} \right) + \frac{k}{\nu_2} \sinh^{-1} \left( \frac{\dot{\varepsilon}}{\dot{e}_{0,2}} \exp \left( \frac{\Delta H_2}{k\theta} \right) \right)
\]  

(2.13)

\[
\frac{\tau_y}{\theta} = \frac{k}{\nu_1} \left( \ln \dot{\gamma} - \ln \dot{\gamma}_{0,1} + \frac{\Delta H_1 + p\Omega_1}{k\theta} \right) + \frac{k}{\nu_2} \sinh^{-1} \left( \frac{\dot{\gamma}}{2\dot{\gamma}_{0,2}} \exp \left( \frac{\Delta H_2 + p\Omega_2}{k\theta} \right) \right)
\]  

(2.14)

In these equations, \( \nu_1, \dot{e}_{0,1}, \) and \( \Delta H_1 \) are the usual Ree-Eyring parameters (proportional or equivalent to the \( A_i, C_i, \) and \( Q_i \) parameters used by Bauwens, respectively), \( k \) is Boltzmann’s constant, and \( \Omega_i \) is a new parameter for directly capturing dependence on hydrostatic pressure, \( p \). In their tension data, Truss et al observed what many other researchers had seen before: at some low temperature, the material yield behavior undergoes a transition that causes the strength to greatly increase with decreasing temperature. This transition location shifted with strain rate, increasing in temperature with increasing strain rate. They noted that, at least qualitatively, temperature and strain have the same effect on the yield strength; testing at low temperatures would produce the same results as testing at high rates. They supposed, too, that pressure has a similar effect, though they could not get hydrostatic pressures high enough to be able to witness a transition in the pressure-dependent yield data. Finally, their most important observation was that each of the activated processes has its own temperature, rate, and pressure dependencies.

Foot, Truss, Ward, and Duckett (1987) continued this work with testing on amorphous PET, hoping to further the evidence that the strain rate dependence of yield is ultimately the same as the temperature dependence of yield. They used a standard Instron with attached environmental chambers to attain strain rates from \( 4.5 \times 10^{-6} \text{ s}^{-1} \) to \( 4.5 \times 10^{-2} \text{ s}^{-1} \) and temperatures of 77 K to 323 K. They also employed a novel moderate-rate tensile testing machine, driven by a flywheel, to obtain strain rates up to 51 \text{ s}^{-1}. A schematic of this device can be seen in figure 2-32. In all of their testing, this group was concerned with both the variation in yield stress and failure mode with strain rate. Figure 2-33 demonstrates some of their yield stress results, where again it is seen that the polymer behavior undergoes a significant transition at a certain threshold level determined by both strain rate and temperature. The location of the transition can be thought of as shifting with either temperature or strain rate. Foot et al were again able to fit all of their experimental
results, including now tests at moderate rates of strain, to the two-process Ree-Eyring model. Equation 2.13 is the source of the curves in figure 2-33. The activation energy value for the $\beta$-process that they obtain from curve fitting - 17.1 kcal/mol - agrees very well with the PET $\beta$-relaxation activation energy reported by Thompson and Woods (1956): 17 kcal/mol. It is assumed then that the same molecular motions governing the linear viscoelastic material response, at least in the "$\beta$-region", also govern the material’s yield behavior.

To further the understanding of these transitions in the rate-dependent behavior of amorphous polymers, the natural progression was to perform tests at higher strain rates, as Foot et al (1987) had attempted with their novel flywheel tensile apparatus. A variety of test methods have since been employed for studying the high strain rate ($>100 \text{s}^{-1}$) behavior of amorphous polymers, but none as frequently or with as much success as split-Hopkinson pressure bar testing.
Ree-Eyring model parameters for the PET data of figure 2-33, following equation 2.13

<table>
<thead>
<tr>
<th>Process</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\ln \dot{\varepsilon}_0$ [s$^{-1}$]</td>
<td>50.9</td>
<td>32.9</td>
</tr>
<tr>
<td>$\Delta H$ [kcal/mol]</td>
<td>45</td>
<td>17.1</td>
</tr>
<tr>
<td>$\nu$ [m$^2$]</td>
<td>$1.21 \times 10^{-27}$</td>
<td>$8.60 \times 10^{-28}$</td>
</tr>
</tbody>
</table>

Figure 2-33: Temperature and strain rate dependence of the tensile yield strength of amorphous PET. Curves have been fit with the Ree-Eyring model. Test temperatures are as follows: (▼) 213 K, (△) 223 K, (□) 273 K, (○) 295 K, and (■) 333 K (R.W. Truss & Ward, 1984).
CHAPTER 2. BACKGROUND

2.4 Split-Hopkinson Bar Testing of Polymers

The split-Hopkinson pressure bar (SHPB) is still the primary method for testing the mechanical properties of materials in homogeneous deformation at high rates of strain. The test set-up is drastically different from methods used to test materials at lower rates, as will be discussed. The importance of the SHPB as a tool in the study of mechanical behaviors of materials has been on the rise in recent decades; ever-improving finite element simulation capabilities in the realm of dynamic loading conditions have demanded accurate data and constitutive models for material response at high rates of deformation. However, there is still no standard design for the split-Hopkinson bar apparatus, and many issues related to the application of this unique test method, especially in the investigation of "low-impedance" materials such as amorphous polymers, are still in contention.

The general theory of classic split-Hopkinson pressure bar testing has been well documented. See for example Davies (1948), Kolsky (1949), or, more recently, Follansbee (1985), Meyers (1994), and Gray (2000). A detailed schematic of a typical SHPB apparatus is given as figure 2-34. The test is initiated when high-pressure gas is released from the pressure...
chamber, causing the striker bar to eject from the barrel at velocities ranging from 5 to 25 meters per second. When the striker bar impacts the first pressure bar, the "incident bar", a compressive stress wave is generated. The stress pulse, with duration directly proportional to the length of the striker bar, travels down the incident bar at the speed of sound in an elastic solid, $c$:

$$c = \sqrt{\frac{E}{\rho}}$$  

(2.15)

Where $E$ is the Young’s Modulus of the pressure bar (loaded in uniaxial compression), and $\rho$ is the density of the bar material. Of course, care is taken in the design of the pressure/bar system so that the amplitude of the stress pulse never exceeds the yield strength of the bar material. The wave travels the length of the incident bar until it reaches the specimen interface. Because of the material mismatch at this interface, a portion of the incident pulse is reflected back down the incident bar as a tensile wave, and the remaining portion transmits through the specimen and down the second pressure bar (the "transmission bar"). When the wave passes through the specimen, and portions of it reverberate from one end of the specimen to the other, the material being tested will deform at a high rate of strain. The three stress pulses of interest - the incident, the reflected, and the transmitted - are recorded with strain gages mounted on the pressure bars which capture the corresponding compressive, tensile, and compressive strains $\varepsilon_i$, $\varepsilon_r$, and $\varepsilon_t$. Figure 2-35 provides an example of what these pulses might look like, during a test of amorphous PC.

The theory behind SHPB testing, developed in some detail in the citations listed previously, is based on the assumption of one-dimensional wave propagation. Acoustic wave propagation in elastic mediums is a topic that has been well-understood since the 18th Century; in this case, the problem is further simplified by the one-dimensional assumption. A general equation of motion may be written for this one-dimensional propagation as:

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 u}{\partial t^2}$$  

(2.16)

Where $u$ is the displacement along the x-direction (in this case, the axis of the pressure bar), $t$ is time and $c$ is the wave speed as defined in equation 2.15. A general solution to this equation is made particular by the application of appropriate boundary conditions.
Relationships are then made between \( u(x,t) \) and strain and stress, recognizing that strain is a spatial derivative of displacement, and that force equilibrium requires that the same forces be felt on the specimen faces and the ends of the pressure bars. Assuming these forces to be equal on both the front and back faces of the specimen, that is, assuming the specimen has achieved "dynamic equilibrium" and is undergoing homogeneous deformation, leads to a simplification of our final equations. In the end, we find that the specimen strain rate is directly proportional to the strains of the reflected pulse, and that specimen stress is directly proportional to the strains of the transmitted pulse:

\[
\dot{\varepsilon} = \frac{2\alpha \varepsilon_r}{l_s} \tag{2.17}
\]

\[
\sigma = \frac{A_b E \varepsilon_t}{A_s} \tag{2.18}
\]

Where \( l_s \) is the length of the specimen, \( A_b \) is the cross-sectional area of the bar, and \( A_s \) is the cross-sectional area of the specimen. In practice, strain is most often found via numerical integration of equation 2.17.
Because there is still no standard procedure for SHPB testing, and because there is still no standard design for the SHPB apparatus, an experimentalist faces many issues during application of the SHPB test method. In the initial set-up of the system, near-perfect uniaxial alignment of the striker bar and pressure bars is crucial to the assumption of one-dimensionality. If the pressure bars suffer strong reaction forces from their bearings, compression/tension will meet extra resistance and the stress pulse will be altered in shape. Also, if the contact between the striker and incident bars is misaligned, the stress pulse will carry an unacceptable amount of high-frequency "noise" riding on the top of the main wave. In order to minimize the ratio of noise to amplitude in the gage signals, the excitation and gain settings of the amplifier/data acquisition system must be optimized, and the pressure bar material must be chosen appropriately. Furthermore, some researchers (see, for instance, Gong, Malvern, and Jenkins (1990)) insist that the pulses recorded at the strain gage locations are not the same as the pulses acting at the specimen interface, due to effects of dispersion. Extra steps in the data analysis are suggested to deal with this issue.

Perhaps the most critical issue faced in the application of SHPB test methods is the selection of specimen geometry. There are many considerations that must go into the selection of specimen geometry. The assumption of dynamic equilibrium is valid only after a certain number of reverberations of the stress wave through the specimen; the time duration of this "ringing-up" period is dependent upon the length of the specimen. If one is in need of very accurate low-strain data, perhaps in the case of a brittle material that only exhibits elastic behavior, a specimen of shorter length may be necessary given the dynamic equilibrium consideration. However, when the ratio of specimen length to the specimen diameter (L/D) becomes small, both frictional effects and radial inertia effects may distort the results of the data. In the same way, if the L/D ratio is large, longitudinal inertia effects may become non-negligible, and elastic or plastic buckling could be a concern. Davies and Hunter (1963) theorized that for materials with Poisson ratio close to 0.33, and specimens of right circular cylinder geometry, longitudinal and radial inertia effects would cancel each other out at an L/D ratio of 0.5. Furthermore, specimen geometry will dictate the limits of the test: both the maximum theoretical strain and maximum theoretical strain rate are
inversely proportional to the length of the specimen, and stress in the specimen is of course inversely proportional to the cross-sectional area.

In 1995, a new section was added to the High-Rate Testing chapter of the ASM Handbook: "Split-Hopkinson Pressure Bar Testing of Soft Materials" by Gray and Blumenthal of Los Alamos National Laboratory. This article provides a very thorough summary of the unique difficulties associated with testing polymeric materials in the SHPB system. It covers, among other things, methods of validating stress-state equilibrium, ways in which to study the temperature-dependence of polymer behavior in the SHPB, special specimen preparation methods, finite-element modeling of the SHPB test of soft materials, and the effects of specimen geometry on test results. It also covers the selection of proper pressure bar material, with an in-depth discussion of the complicated application of bar material such as PMMA that is low-impedance and viscoelastic in nature. The article draws upon the experimental findings and published test methods of almost every research group that had studied polymers in a SHPB apparatus to date. The reader is directed here for further details on the different aspects and complications of testing polymeric material with the SHPB.

Though the history of testing polymeric material with the split-Hopkinson bar system can be traced back to Kolsky (1949), Chou, Robertson, and Rainey (1973) produced the first set of SHPB data significant to the understanding of high-rate strengthening in amorphous polymers. In their 1973 publication, these researchers emphasized the scarcity of public-knowledge data on the compressive mechanical behavior of polymeric materials; they are able to list only a handful of studies involving high-rate compressive behavior. For their own work, Chou, Robertson, and Rainey tested the compressive stress-strain behavior of two amorphous polymers - PMMA and cellulose acetate butyrate (CAB) - and two semi-crystalline polymers - polypropylene and nylon 6-6 - at strain rates from $10^{-4}$ s$^{-1}$ to $10^3$ s$^{-1}$. For their low and medium rate tests, they used a specially-designed servo-hydraulic instrument that could be operated in "open-loop" mode to obtain strain rates of 1 s$^{-1}$ to 50 s$^{-1}$. For high-rate testing, they employed a split-Hopkinson pressure bar system. In all of their tests, they embedded a thermocouple in the specimen, so that they might examine the effects of adiabatic heating on stress-strain behavior. Figure 2-36 depicts the specimen
heating curves (temperature rise vs. strain) and stress-strain curves for PMMA tests at a variety of strain rates. Figure 2-37 is a plot of stress level as a function of strain and strain rate, derived from all of their PMMA stress-strain curves. To Chou, Robertson, and Rainey, it was evident that, by some unspecified mechanism, amorphous polymers such as PMMA and CAB exhibit significant increased strengthening when deformed at high rates of strain. Also, they hypothesized that the temperature rises observed could account for the apparent strain-softening at the highest rates of strain. Certainly, they concluded, this heating effect could not be neglected in analyzing the dynamic behavior of polymeric materials.

Another early study on the SHPB behavior of polymeric materials was performed by Briscoe and Nosker (1985). Briscoe and Nosker used a SHPB to study the compressive stress-strain behavior of high-density polyethylene (HDPE) at 293 K. They then compared their results with those of other researchers, who had used the impact test and corresponding
Figure 2-37: Stress level as a function of strain and strain rate for compression testing of PMMA. High rate data was obtained from a split-Hopkinson bar system (Chou et al., 1973).
Figure 2-38: High-density polyethylene stress at 10% strain, as reported by Briscoe and Nosker (present work) using a SHPB, as well as other researchers (Briscoe and Hutchings, B+H, K+H) using Taylor impact tests (Briscoe & Nosker, 1985).

theory developed by G.I. Taylor (1948) to examine high-rate strengthening in HDPE. Since HDPE does not exhibit a well-defined yield point, all of these researchers took the value of stress at 10% strain (calling it the 10% flow stress) as characteristic of the material strength for a particular rate/temperature combination. Figure 2-38 demonstrates how the 10% flow stress SHPB data of Briscoe and Nosker compared with previous data obtained from Taylor impact tests. While the other researchers were thought to have discovered high-rate strengthening in HDPE, Briscoe and Nosker used their own data to discount this notion and conclude that HDPE is well described by the single-process Eyring theory over the strain rate range $10^{-2}$ s$^{-1}$ to $10^4$ s$^{-1}$ at 293 K. These researchers also contributed to the advancement of SHPB test methods for polymers by specifying petroleum jelly as an ideal lubricant, and demonstrating that tests without lubrication might give flow stress values that were exaggerated by as much as 40%.

S.M. Walley, of the Cavendish Laboratory at the University of Cambridge (UK), has published several studies focused on the rate-dependent behavior of polymeric materials; see for instance Walley, Field, Pope, and Safford (1989), Walley, Field, Pope, and Safford (1991), Walley and Field (1994). During these studies, Walley and his colleagues evaluated
the rate-dependent compressive behavior of seventeen different polymers on four different apparatus, including a direct-impact Hopkinson bar\(^3\) for strain rates above \(10^3\) s\(^{-1}\). Some example stress-strain curves, from the study of PVC at strain rates of \(10^{-2}\) s\(^{-1}\) to \(10^4\) s\(^{-1}\), can be seen in figure 2-39. In the earliest studies, Walley was concerned primarily with the effects of friction in his compression tests. He used "Avitzur's analysis" (1964) to investigate the amount of friction generated during moderate- to high-rate deformation of polymer annuli in a glass anvil dropweight system. His analysis was aided by a high-speed camera that allowed him to visualize, through the transparent anvils, the strain in the annuli over the duration of the tests. His conclusion, summarized in figure 2-40, was that petroleum jelly is a far superior lubricant to either gun barrel lubricant or silicone gel. In this regard, he agreed with the findings of Briscoe and Nosker (1985).

Besides investigating frictional effects in his tests, Walley had hoped to combine the data from tests across the different strain rate regimes and discover which polymers exhibited

---

\(^3\)A direct-impact Hopkinson bar is very similar in design and theory to the split-Hopkinson pressure bar, with the key difference being that there is no incident bar in the direct-impact system; the striker bar hits the specimen directly.
Figure 2-40: An evaluation of the performance of three different lubricants in moderate-rate compression tests of polymer annuli. Lubricants have been evaluated via Avitzur's analysis (1964), essentially a comparison of the radial strain of the hole and radial strain of the polymer. $m = 0.0$ indicates perfect lubrication (no frictional effects) (Walley et al., 1989).
increased strengthening at high rates. In the seventeen different polymers that he tested, he found three distinct behaviors. Examples of each of these behavior can been seen in figures 2-41 to 2-43. First, there were those polymers that did in fact demonstrate increased strengthening at strain rates above $\sim 10^3$ s$^{-1}$ (figure 2-41): ABS, PET, PP, PVC, and PVDF. Walley supposed that the yield behavior of these materials would need to be interpreted in terms of the two-process Ree-Eyring modification to the Eyring viscosity theory. Secondly, there was a group of polymers which exhibited no increased strengthening at high rates of strain (figure 2-42): acetal, HDPE, moist nylon 66, dry nylon 6, moist nylon 6, and PBT. The material behavior of these polymers would be well-predicted by the general Eyring viscosity theory. Finally, there was a surprisingly large group of polymers that actually
exhibited decreased strengthening at strain rates above \(10^3\) s\(^{-1}\) (figure 2-43): noryl, dry nylon 66, PC, PEEK, and PES. Walley and his colleagues attributed this unusual behavior to a thermal effect; they thought that increased adiabatic deformation of these materials at high rates caused their strength to decrease. However, this finding has not been repeated since, and in fact, multiple consequent studies on PC in particular have demonstrated the exact opposite behavior - increased strengthening at high rates of strain. This discrepancy between the Walley data and that of others suggests that there may exist some issues regarding either his test technique or data reduction.

Rietsch and Bouette (1990) were the first researchers to use SHPB testing in deliberate continuation of the work done by Bauwens (1972) and Bauwens-Crowet (1973). That is, they attempted to use high-rate compression testing to further the evidence of a secondary transition in the material response of PC. This data, they supposed, would fit to the very same Bauwens-modified Ree-Eyring model that had been used to explain the increased strengthening of PC at low temperatures, in terms of the \(\beta\)-peak of the viscoelastic loss tangent. With their SHPB system, these researchers were able to test PC in uniaxial compression at strain rates between \(150\) s\(^{-1}\) and \(3000\) s\(^{-1}\), and temperatures from 233 K to 333 K. Figure 2-44 is summary of the yield strength values obtained from these tests, as well as the yield strength values obtained in quasi-static tests (\(10^{-4}\) s\(^{-1}\) to \(10^{-2}\) s\(^{-1}\)) on a low-speed Instron.
Ree-Eyring model parameters for the PC data of figure 2-44

<table>
<thead>
<tr>
<th>Process</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$ [Pa/sK]</td>
<td>6000</td>
<td>54000</td>
</tr>
<tr>
<td>$Q$ [kcal/mol]</td>
<td>68</td>
<td>5</td>
</tr>
<tr>
<td>$C$ [s]</td>
<td>$4.10 \times 10^{-7}$</td>
<td>$2.9 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

Figure 2-44: PC yield data as a function of temperature and strain rate, fit with the Ree-Eyring model. Temperatures are as follows: (o) -40°C, (♦) -20°C, (△) 0°C, (■) 10°C, (_TRIANGLE/) 20°C, (△) 40°C, (＞) 60°C (Rietsch & Bouette, 1990).
CHAPTER 2. BACKGROUND

As proposed, all of their data was successfully fit with a two-process Ree-Eyring model; equation 2.8, the first Ree-Eyring yield equation proposed by Bauwens, is the source of the curves in figure 2-44. By comparing the tables adjoining figures 2-18 and 2-44, we can see that there is relatively good agreement between the Ree-Eyring parameters calculated by Bauwens and the same parameters calculated by Rietsch and Bouette. The largest discrepancy is in the calculated values of activation energy: Bauwens and Rietsch & Bouette found values of 75.5 kcal/mol and 68 kcal/mol, respectively, for the α-process and 9.6 kcal/mol and 5 kcal/mol, respectively, for the β-process. This fact could be entirely attributable to the different brands (hence differences in exact chemical compositions) of PC used in the two studies. The Lexan PC (GE Plastics) tested by Rietsch and Bouette consistently demonstrated a yield strength 30% less than the yield strength of the Makrolon PC (Bayer) of Bauwens, even at quasi-static strain rates. Nonetheless, a definite material transition in PC yield behavior is predicted by both studies, and the temperature/strain rate location of this transition in the two studies is in very good agreement. Reitsch and Bouette agree with Bauwens, that the transition is linked to the well-documented β-relaxation process of PC. Again, this link is made via a correlation of activation energy values. However, they take the explanation a step further: they state that this material process is connected to the rotational freedom of phenyl groups in the main chains. Above a certain strain rate threshold (or equivalently, below a certain temperature threshold), this particular microscopic rotational freedom of the polymer chains can not be activated, and the material as whole becomes stiffer and more difficult to flow - hence the increase in stress levels.

The next significant study on the SHPB behavior of polymeric materials was a purely experimental one. Diouh, Leevers, and Williams (1993) focused on the effects of specimen geometry in split-Hopkinson bar testing of polymers. Using their data on PC, polyetheretherketone (PEEK), medium density polyethylene (MDPE), and high density polyethylene (HDPE), they called into question the findings of Rietsch and Bouette (1990) and Chou et al. (1973). They claimed that the only reason these researchers saw dramatic increased strengthening at high rates of strain was because of the specimen lengths that they chose to test. Diouh, Leevers, and Williams used three different test apparatus to cover the stress-strain behavior of their chosen materials: a servo-hydraulic Instron for low rates, a Mayes
Figure 2-45: PC yield strength as a function of strain rate at 296 K for two different specimen thicknesses: (□) 4.4 mm thick specimens; (●) 1.5 mm thick specimens. All specimens had a diameter of 12.7 mm (Dioh et al., 1993)

machine for medium rates, and a SHPB for high rates. They chose all specimens to have a diameter of 12.7 mm, with thicknesses of either 4.4 mm or 1.5 mm. In general, they found that tests on the thinner specimens would predict a lower yield or flow stress at high rates of strain than the tests on 4.4 mm specimens. In figures 2-45 and 2-46, their data on PC and MDPE is summarized. They admit that even if the 1.5 mm data is used, some rate-dependent polymer behavior (such as the behavior of PC) can not be fit to the single-process Eyring model. However, they conclude that other researchers have misinterpreted even the existence of high-rate strengthening mechanisms in certain polymers based on questionable data.

In this study, Dioh, Levers, and Williams present valid findings, albeit without even the suggestion of an explanation. Nonetheless, the body of work presented in this introduction, especially the low temperature data of other researchers and the qualitative relationship between low temperature and high rate behavior, indicates that this group was at least partially incorrect in their assumptions. The L/D ratio of their specimens, even those with
Figure 2-46: MDPE flow stress as a function of strain rate at 296 K for two different specimen thicknesses: (□) 4.4 mm thick specimens; (●) 1.5 mm thick specimens. All specimens had a diameter of 12.7 mm (Dioh et al., 1993)

a thickness of 4.4 mm, were very low - 0.35 and 0.12. It is very possible that these thin specimens incorrectly under-predicted strength values as a result of prevalent radial inertia effects in their SHPB tests, and in fact, the specimens with thickness of 4.4 mm provide results that are closer to true behavior. Now, most researchers use an L/D ratio of 0.5 in their SHPB tests of polymers (Chen, Zhang, & Forrestal, 1999). However, the mere existence of this study, as well as the number of times it has been cited since publication, emphasizes the fact that many SHPB test methods and theoretical considerations are still in contention.

These issues of contention, unique to the split-Hopkinson bar testing of soft, low-impedance materials, were once again reviewed by Chen et al. (1999). Chen and his colleagues, with many years of split-Hopkinson bar testing between them, describe a number of test methods that their groups had found especially successful in applying the SHPB to polymeric materials. For instance, Chen found a great deal of success in "pulse shaping." Pulse shaping is a way in which an experimentalist may achieve dynamic equilibrium at
CHAPTER 2. BACKGROUND

an earlier point (earlier in terms of total strain) in a test. The method is especially useful when information concerning a material's low strain elastic behavior is sought. Oftentimes, data preceding the achievement of dynamic equilibrium is otherwise disregarded. The pulse shaper itself is a thin disk of ductile material, usually of strength and diameter markedly less than the strength and diameter of the pressure bars. The disk is located between the incident bar and the striker bar, so that upon impact, it plastically deforms and consequently "shapes" the stress pulse that travels down the incident bar.

Without pulse shaping, the incident wave can usually be approximated as a square wave - see figure 2-35. With pulse shaping, the incident wave has a much more gradual leading edge, a longer rise time. Since it takes a set finite number of reverberations of the stress wave through the specimen to achieve dynamic equilibrium, and since the speed of the wave through the specimen is determined only by the elastic modulus and the density of the specimen material, the time to dynamic equilibrium is fixed. However, by changing the slope of the leading edge of the stress pulse via pulse shaping, the experimentalist can control the strain level at the time when dynamic equilibrium is achieved. Researchers have found this method of pulse shaping to provide a more constant strain rate over the duration of a test, and also to decrease much of the high-frequency noise that is ordinarily present. Chen et al. (1999) report success in using copper pulse shapers, and also polymer and tissue paper pulse shapers.

The main focus of their study, however, was the material make-up of the pressure bars. They point out that the customary steel pressure bars have such high impedance, oftentimes the portion of the stress wave that transmits through soft, low-impedance specimens is indiscernible in the transmission bar signal. They discuss in detail the use of viscoelastic bars as an alternative, citing a number of more recent researchers who have attempted to apply this method. However, they conclude that there is an unacceptable amount of uncertainty in the interpretation and analysis of signals from pressure bars whose behavior is strongly rate-, temperature-, and pressure-dependent. Chen, Zhang, and Forrestal (1999) propose a new pressure bar system design: both pressure bars are manufactured from aluminum, and the transmission bar is hollow. The reasoning behind this design is explained entirely by equation 2.18. In order to obtain a transmitted pulse with larger strains $\varepsilon_l$ for the same
stress level, either the Young's Modulus of the material (E) or the ratio of the bar cross-section \((A_b)\) to the specimen cross-section \((A_s)\) would need to be reduced. The proposed design reduces both. Chen, Zhang, and Forrestal implemented this design and obtained very smooth data for the high-rate behavior of a silicone rubber, where stress levels never exceeded 15 MPa for true strains up 80% (figure 2-47). Currently, no other research group has acted to replicate this design in their SHPB system. That is, no other group has published any data derived from such a system.

Also in 2003, the researchers at Los Alamos National Laboratory presented a study of their own on the high-rate behavior of polymeric materials in split-Hopkinson bar testing. Cady, Blumenthal, Gray, and Idar concentrated on interpreting all of their findings with a look towards the future - the development of a physically-based constitutive model for thermoplastic materials that can accurately capture all aspects of high-rate behavior. They used both a servo-hydraulic universal testing apparatus and a compressive split-Hopkinson bar system with aluminum pressure bars and a hollow transmission bar (Chen et al., 1999).
Figure 2-48: High-rate stress-strain behavior of PEEK as a function of temperature. All data was recorded at approximately the same strain rate on a compressive split-Hopkinson bar system (Cady et al., 2003).

bar to study the rate- and temperature-dependent behavior of amorphous polyamideimide (PAI) and semi-crystalline PEEK at strain rates from $10^{-3}$ s$^{-1}$ to 2500 s$^{-1}$ and temperatures from -55°C to 300°C. A number of significant trends manifested themselves in this large body of data. Because of their advanced SHPB techniques, including pulse shaping, this group was able to obtain accurate low-strain data and examine the relationships between temperature, strain rate, and the initial slope of the stress-strain curve for the two materials. They refer to this initial slope as the characteristic "loading modulus" of the material. For both materials, Cady et al found that loading modulus would increase with either decreasing temperature or increasing strain rate, for all temperatures below the glass-transition temperature. Above the glass-transition temperature, loading modulus appeared to increase with increasing temperature. Figure 2-48 depicts the high-rate stress-strain behavior of PEEK both above and below the glass-transition temperature (~150°C). With this information on the loading modulus across a broad range of temperatures, Cady et al could locate fairly well the glass-transition temperature for a particular strain rate; loading
modulus drops dramatically over a small range of temperatures centered around $T_g$. They observed this glass transition to shift with strain rate, as demonstrated in the data of figure 2-49. They report that the PEEK $T_g$ shifts from about 145°C at $10^{-3}$ s$^{-1}$ to about 160°C at 2200 s$^{-1}$, while the PAI $T_g$ shifts about 10°C over three decades of strain rate. Furthermore, these researchers report that both yield stress and flow stress increase with either increasing strain rate or decreasing temperature - the two seem qualitatively equivalent. They conclude by emphasizing the fact that a constitutive model, which can capture all of these temperature and rate dependent trends, is needed for accurately describing the mechanical behavior of thermoplastics at high rates of strain.

Most recently, Swallowe and Lee (2003) followed the experimental procedure of their predecessors to examine the high-rate strengthening phenomenon: they used two different apparatus, one for low rates and one for high rates, to study stress-strain behavior at strain rates of $10^{-4}$ s$^{-1}$ to $10^3$ s$^{-1}$ over the temperature range 293-363 K. However, Swallowe and Lee attempted to be more precise in their choice of material, and also incorporated two new experiments into the approach in hopes of understanding the mechanism that controls this phenomenon. They chose to test only amorphous polymers - PMMA and polystyrene - in order to eliminate any strengthening effects that may be attributed to crystalline phases.
They performed dynamic mechanical thermal analysis (DMTA), as well as high-precision density measurements before and after compression, to examine two possible mechanistic sources of the increased strengthening observed in yield behavior. Furthermore, the experimental apparatus of their high-rate testing was not a split-Hopkinson bar apparatus, but rather a specialized dropweight system. Figure 2-50 presents the yield data for all of their PMMA compression testing at two particular temperatures: 323 K and 363 K.

The curves of figure 2-50 are striking: PMMA exhibits a large decrease in strengthening at high rates. This finding is contrary to intuition, considering especially the evidence of increased strengthening at high rates observed by other researchers in the behavior of different amorphous polymers, as well as the increased strengthening at low temperatures observed by other researchers in the behavior of PMMA. However, this PMMA data is not contrary to any reported data presented in this introduction, since no other group investigated the high-rate behavior of PMMA. If the high-rate testing had been performed on a SHPB apparatus, it would be easy to evaluate the validity of their findings by looking at the gage signals, checking the accuracy of the dynamic equilibrium assumption, and/or
analyzing chosen specimen geometries; in this case of a specialized apparatus, the reader is provided no basis on which to formulate criticisms. Also, the authors do not provide a clear explanation as to why this decreased strengthening might occur; they attribute some of the effect to temperature increases in the specimen, but acknowledge that calculated temperature rises could not cause the material strength to decrease as much as was observed.

As a second, and perhaps more important, component of their study, Swallowe and Lee experimentally investigated two theories as to the mechanisms of increased strengthening observed in high-rate deformation of amorphous polymers. Ironically, they used as a test material the very same PMMA that had shown decreased strengthening in their own tests. First, they tested the hypothesis that at high-rates of deformation, amorphous polymers undergo increased strengthening as a result of density increases. With a precision density measurement instrument, they recorded PMMA specimen densities before and after compression. They found virtually no changes in the density, and thus eliminated density arguments as a possible theoretical explanation of the increased strengthening phenomenon. Secondly, following the theories of Bauwens et al, they attempted to link the rate-dependent shift of the viscoelastic \( \beta \)-relaxation of PMMA with increased strengthening. With the DMTA, they recorded characteristic viscoelastic properties - storage modulus, loss modulus, and loss tangent - around the \( \alpha \)- and \( \beta \)-transitions for frequencies of 0.1 Hz and 100 Hz (figure 2-51). Examining the peaks of the loss modulus and loss tangent curves at just these two frequencies, they observed the \( \alpha \)-transition to shift at \( \sim 7^\circ \)C per decade of strain rate, and the \( \beta \)-transition to shift at \( \sim 35^\circ \)C per decade of strain rate. Since these shifting factors would cause the \( \beta \)-transition to shift past the \( \alpha \)-transition at a strain rate near 1 s\(^{-1} \), they concluded that this \( \beta \)-relaxation could not be the cause of increased strengthening at high strain rates. More or less by process of elimination, Swallowe and Lee attribute the increased strengthening of amorphous polymers at high rates of strain to decreases in activation volume.

Most recently, Moy, Weerasooriya, Hsieh, and Chen (2003) corroborated the results of Rietsch and Bouette (1990) and Walley and Field (1994), among others, with a thorough study of the rate-dependent mechanical behavior of PC. They too followed the established experimental pattern for examining the high-rate strengthening phenomenon: they used two
Figure 2-51: Dynamic mechanical thermal analysis (DMTA) data for PMMA at two frequencies: 0.1 Hz (dashed lines) and 100 Hz (solid lines). Curves are for the storage modulus ($E'$), loss modulus ($E''$), and loss tangent (Tan $\delta$). The shifting $\beta$-transition is located by the relative peak in the loss modulus curve (Swallowe & Lee, 2003).
CHAPTER 2. BACKGROUND

Figure 2-52: Compressive stress-strain behavior of PC as a function of strain rate at room temperature (Moy et al., 2003).

different apparatus, one for low rates and one for high rates, to study stress-strain behavior at strain rates of $10^{-4} \text{s}^{-1}$ to $10^3 \text{s}^{-1}$ at room temperature. This group took great care in designing their high-rate split-Hopkinson bar experiments; in addition to their data (figures 2-52 and 2-53), they provide extensive post-test analysis that confirms its validity. While their testing techniques were perhaps more advanced than those of previous researchers, the results nonetheless are the same: PC yield strength is found to transition to a regime of greater strain rate sensitivity, at a strain rate of approximately $300 \text{s}^{-1}$. Also, these researchers compared the pre-yield data from all of their stress-strain curves and concluded that the initial elastic modulus is also very sensitive to changes in strain rate. The elastic modulus was found to increase proportional to the yield strength with increases in strain rate.
Figure 2-53: Compressive yield strength of PC as a function of strain rate at room temperature (Moy et al., 2003).
Chapter 3

Dynamic Mechanical Analysis

The experimental program of this study as a whole was devised in order to better understand and explain the linkages between the time and temperature dependence of the material behavior as probed through measurements of the viscoelastic behavior and as probed through the rate-dependent elastic-plastic stress-strain behavior of amorphous polymers. Special focus was placed upon material transitions at moderate and high rates of strain, and the ways in which the transition locations shift with both temperature and strain rate.

Dynamic mechanical analysis is one way to investigate material transitions in the viscoelastic behavior. The viscoelastic material transitions of polymers, the topic of interest in this portion of the study, are usually labelled as $\alpha$, $\beta$, $\gamma$, $\delta$, etc. in Greek alphabetical order with decreasing temperature at which they occur. The $\alpha$-transition is also commonly known as the glass transition; through this small range of temperature, the mechanical properties of the polymer dramatically change, as material behavior transitions from glassy to rubbery with increasing temperature. All other viscoelastic relaxation transitions are considered "secondary" transitions, for changes in material behavior are comparatively much less dramatic. Figure 3-1 provides a schematic of how these transitions might affect the elastic modulus of a typical polymer.

Considerable work has been carried out in order to better understand the molecular-level origins of these observed material transitions in the viscoelastic behavior of amorphous polymers. This work, incorporating dynamic mechanical analysis, as well as nuclear magnetic resonance (NMR) and dielectric measurements of various polymers, has been summarized
Secondary transitions

Temperature

Figure 3-1: Schematic of the temperature dependence of the modulus in a typical polymer (Ward & Hadley, 1993)

by Ward and Hadley (1993). It is now known that the glass transition is associated with the rotational freedom of polymer main chain segments between cross-links. At temperatures above the glass transition temperature \( T_g \), this degree of freedom is completely unrestricted. The molecular origins of secondary transitions, on the other hand, have been more difficult to characterize. In amorphous polymers in general, they may be attributed to side-group rotations, various degrees of freedom of the main chains, or motions of the end-groups. In PC, the \( \beta \)-transition has been attributed to the rotational freedom of the main-chain phenyl group (Rietsch & Bouette, 1990); in PMMA, it has been attributed to the rotational freedom of the ester side-group (Ward & Hadley, 1993), (Swallowe & Lee, 2003). The general chemical structure of these two amorphous polymers can be found in Appendix A. Owing to the different molecular origins of these various material transitions, each transition has been observed to have its own rate-dependence. That is, the temperature location at which they occur has been seen to shift different amounts with changing strain rate. The ultimate goal of the DMA testing of this study was to quantify the rate-
dependent shifts of these various transitions, in order to develop an analytical description of the elastic moduli of PC and PMMA at all rates and temperatures.

### 3.1 DMA Theory

Dynamic mechanical analysis (DMA) instruments in general are capable of applying oscillatory load programs in tension/compression, three-point bending, or shear through either displacement, strain, or force control. The response of the viscoelastic specimen to this oscillatory loading is supposed to have two components: one in phase with the load program, characteristic of the elastic, solid-like response, and one out of phase from the load program, characteristic of the viscous, fluid-like response. For instance, a particular sinusoidal load program may be prescribed under strain control:

\[
\epsilon(t) = \epsilon_0 \sin \omega t
\]  

(3.1)

Where \( \epsilon_0 \) is the strain amplitude and \( \omega \) is the frequency of oscillations. The stress response to this particular load program can be broken into two components:

\[
\sigma(t) = \sigma_0 \sin(\omega t + \delta) = \sigma_0 \cos \delta \sin \omega t + \sigma_0 \sin \delta \cos \omega t
\]  

(3.2)

Where \( \sigma_0 \) is the stress amplitude of the oscillatory response, and \( \delta \) is the phase lag of the viscous response. Equivalently, equation 3.2 may be written as:

\[
\sigma(t) = \epsilon_0 E' \sin \omega t + \epsilon_0 E'' \cos \omega t
\]  

(3.3)

Where

\[
E' = \frac{\sigma_0 \cos \delta}{\epsilon_0}
\]  

(3.4)

and

\[
E'' = \frac{\sigma_0 \sin \delta}{\epsilon_0}
\]  

(3.5)

By decomposing the material response in such a manner, two parameters have been developed: one that is characteristic of the elastic response \( (E') \), and one that is characteristic
CHAPTER 3. DYNAMIC MECHANICAL ANALYSIS

Figure 3-2: Schematic of the storage modulus ($G_1$), loss modulus ($G_2$), and tan $\delta$ curves of a typical polymer through its glass transition temperature, $T_g$ (Ward & Hadley, 1993)

of the viscous response ($E''$). $E'$, known as the "storage modulus", is a measure of the energy stored during viscoelastic deformation. In the case of uniaxial tension/compression DMA testing, the storage modulus is approximately equivalent to the Young's Modulus. $E''$, known as the "loss modulus", is a measure of the energy dissipated during viscoelastic deformation. A third important viscoelastic quantity is the loss tangent, or tan $\delta$:

$$\tan \delta = \frac{E''}{E'}$$  \hspace{1cm} (3.6)

It has been observed that both the loss modulus and the tan $\delta$ have a relative maximum at or near the temperature location of material transitions. This phenomenon is demonstrated in figure 3-2, which provides a schematic of the storage modulus, loss modulus, and tan $\delta$ curves of a typical polymer through its glass-transition temperature. The amplitude and distribution of these transition "peaks" are governed by the molecular-level origins of the transition, and also by the significance of the particular transition in the overall material response. In many amorphous polymers, the peak corresponding to the glass-transition will
have the greatest amplitude, and secondary transition peaks will have both lower amplitude and greater width. By tracing the temperature location of these different peaks at various test frequencies in a dynamic mechanical analysis instrument, it is possible to quantify the rate dependence of the material transitions.

3.2 Experimental Approach

In order to narrow the breadth of this study on amorphous polymers, two materials were chosen for investigation: Lexan® polycarbonate manufactured by GE Plastics, and Plexiglas® G poly(methyl methacrylate) manufactured by AtoHaas. All material was supplied in sheet form from Dr. Alex Hsieh of the Army Research Laboratories.

DMA testing was performed on a TA Instruments Q800 Dynamic Mechanical Analyzer. Rectangular PC and PMMA specimens were machined from sheet stock approximately 1.6 millimeters thick; final specimens had approximate dimensions of 20 mm x 3 mm x 1.6 mm. Prior to testing, specimens were stored in a dessicator cabinet for 3-5 days to eliminate any variability in the data caused by humidity levels. The specimens were loaded in the DMA with a tensile pre-load (0.01 N); displacement control mode was used to oscillate about the pre-strain level such that strain levels never exceeded 0.1% at temperatures below T_g. Materials were first tested over the entire temperature range of the DMA instrument - from -140°C to 180°C - at a frequency of 1 Hz. The storage modulus and loss modulus were measured as a function of temperature, and the corresponding loss tangent (tan δ) was calculated. In this manner, a storage modulus "reference curve" was established for each material, and approximate temperature locations of significant material transitions could be determined. The two materials were then tested at frequencies of 1 Hz, 10 Hz, and 100 Hz, over small ranges in temperature around the identified material transitions. The particular frequencies of these tests corresponded to strain rates in the range 1.9×10^{-3} s^{-1} to 3.2×10^{-1} s^{-1}, depending on the exact specimen gage length and displacement amplitude prescribed.1

Again, storage modulus and loss modulus information was recorded and corresponding tan δ

1The test frequency is converted to a strain rate by examining one-quarter of a cycle in the sinusoidal load program. The time duration of this quarter cycle is known from the test frequency, and the strain amplitude achieved during this time can be calculated from the prescribed displacement amplitude and the known specimen gage length. The increase in strain over this time is approximated to be linear, and thus a
calculations were made, with the expectation that rate-dependencies could be quantified by tracing the temperature location of the relative peaks in the loss modulus and loss tangent with increasing frequency.

3.3 Results and Discussion

Representative storage modulus reference curves for PC and PMMA are plotted in figures 3-3 and 3-4, respectively. All reference curves were generated from tests at 1 Hz, corresponding to strain rates on the order of $10^{-3}$ s$^{-1}$. To confirm the accuracy of these curves, each reference test was repeated until at least three identical curves were produced; all data can be found in figures B-1 and B-2 of Appendix B. In these storage modulus reference curves, both the primary and secondary transitions are identified by significant changes in slope. Through the secondary transitions, the modulus gradually changes by a factor of two or three; through the $\alpha$-transition ($T_g$), the modulus rapidly changes by almost three orders of magnitude.

The temperature locations of these transitions in the PC and PMMA viscoelastic behavior can be estimated from figures 3-5 and 3-6, respectively. These curves represent the loss modulus values measured during the same tests used to produce the representative storage modulus reference curves. In both cases, it is observed that only two significant transitions occur over the range of temperatures allowed by the DMA instrument: the $\alpha$-transition and the $\beta$-transition. It is possible that other transitions, of less importance to the overall material response, are also present, but are overshadowed in magnitude by these two most important ones. For these particular strain rates, the significant PC transitions occur at $\sim$150$^\circ$C and $\sim$95$^\circ$C; the significant PMMA transitions occur at $\sim$115$^\circ$C and $\sim$15$^\circ$C. It can be inferred from figure 3-6 that the PMMA $\beta$-transition plays a very significant role in the overall room-temperature response of the material, more so than the $\beta$-transition of PC.

"constant" strain rate can be calculated:

$$\dot{\varepsilon} = \frac{\text{strain}}{\text{time}} = \frac{d_0}{l_g} \frac{1}{4\omega}$$

Where $d_0$ is the displacement amplitude and $l_g$ is the specimen gage length.
CHAPTER 3. DYNAMIC MECHANICAL ANALYSIS

The rest of the DMA testing was conducted in order to determine the rate-dependent shifts of the transition locations. Using the locations identified in figures 3-5 and 3-6, small ranges of temperature in the region of the $\alpha$ and $\beta$ transitions were examined at 1 Hz ($\sim 10^{-3}$ s$^{-1}$), 10 Hz ($\sim 10^{-2}$ s$^{-1}$), and 100 Hz ($\sim 10^{-1}$ s$^{-1}$). In figure 3-7, representative curves of the PC loss modulus $\alpha$-peak at 1 Hz, 10 Hz, and 100 Hz are plotted as a function of temperature and strain rate. Figure 3-8 presents the same information as figure 3-7, except that the loss tangent ($\tan \delta$) is used as a characteristic measure rather than the loss modulus. Full data - three curves at each frequency - can be found in Appendix B, figures B-3 and B-4. Since both the loss modulus and the loss tangent curves have a relative maximum at or near the temperature location of the material transition, and since the peaks in both cases should theoretically shift the same amount with changes in strain rate, it was assumed that either measure could be used to quantify the rate-dependent transition shift. In this case, the loss tangent was chosen because it was marginally easier to precisely identify the temperature location of the peak in these curves. Figure 3-9 demonstrates how the rate-dependent shift of the PC $\alpha$-transition was quantified, using the loss tangent peak locations from three tests at each frequency. The PC $\alpha$-transition was found to shift $4.65^\circ$C per decade increase in strain rate.

An identical procedure was followed in order to quantify the shifts of all other transitions: PC $\beta$-transition (figures 3-10 to 3-12, B-5, B-6), PMMA $\alpha$-transition (figures 3-13 to 3-15, B-7, B-8), and PMMA $\beta$-transition (figures 3-16 to 3-18, B-9, B-10). For both the PC $\beta$-transition and the PMMA $\alpha$-transition, the loss tangent data was more smooth and consistent than the loss modulus data, and thus was chosen as the source data for quantifying the shifts. In the case of the PMMA $\beta$-transition, however, the loss tangent peak at 100 Hz had shifted so much that it greatly overlapped the $\alpha$-peak and a relative maximum could not be determined; here, the loss modulus data was used to quantify the shift. The results of this quantification procedure are summarized in table 3.1.
Table 3.1: Shift of PC and PMMA viscoelastic transitions with strain rate.

<table>
<thead>
<tr>
<th></th>
<th>Shift of $\alpha$-transition [°C/decade strain rate]</th>
<th>Shift of $\beta$-transition [°C/decade strain rate]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>4.65</td>
<td>15.32</td>
</tr>
<tr>
<td>PMMA</td>
<td>11.07</td>
<td>25.20</td>
</tr>
</tbody>
</table>

Figure 3-3: PC storage modulus as a function of temperature at $3.2\times10^{-3}$ s$^{-1}$ (1 Hz).
Figure 3-4: PMMA storage modulus as a function of temperature at $2.1 \times 10^{-3}$ s$^{-1}$ (1 Hz).

Figure 3-5: PC loss modulus as a function of temperature at $3.2 \times 10^{-3}$ s$^{-1}$ (1 Hz). The peaks centered around $\sim 95^\circ$C and $\sim 150^\circ$C correspond to the $\beta$ and $\alpha$ transitions, respectively.
CHAPTER 3. DYNAMIC MECHANICAL ANALYSIS

Figure 3-6: PMMA loss modulus as a function of temperature at $2.1 \times 10^{-3} \text{ s}^{-1}$ (1 Hz). The peaks centered around $\sim 15^\circ \text{C}$ and $\sim 115^\circ \text{C}$ correspond to the $\beta$ and $\alpha$ transitions, respectively.

Figure 3-7: PC loss modulus as a function of temperature and strain rate in the region of the $\alpha$-transition.
Figure 3-8: PC loss tangent (\(\tan \delta\)) as a function of temperature and strain rate in the region of the \(\alpha\)-transition.

Figure 3-9: Temperature location of PC loss tangent peak corresponding to the \(\alpha\)-transition, as a function of strain rate. Data points were derived from multiple tests at frequencies of 1 Hz, 10 Hz, and 100 Hz. By fitting the data, the transition location is found to shift 4.65°C per decade increase in strain rate.
Figure 3-10: PC loss modulus as a function of temperature and strain rate in the region of the $\beta$-transition.

Figure 3-11: PC loss tangent ($\tan \delta$) as a function of temperature and strain rate in the region of the $\beta$-transition.
Figure 3-12: Temperature location of PC loss tangent peak corresponding to the \(\beta\)-transition, as a function of strain rate. Data points were derived from multiple tests at frequencies of 1 Hz, 10 Hz, and 100 Hz. By fitting the data, the transition location is found to shift 15.32°C per decade increase in strain rate.

Figure 3-13: PMMA loss modulus as a function of temperature and strain rate in the region of the \(\alpha\)-transition.
CHAPTER 3. DYNAMIC MECHANICAL ANALYSIS

Figure 3-14: PMMA loss tangent ($\tan \delta$) as a function of temperature and strain rate in the region of the $\alpha$-transition.

Figure 3-15: Temperature location of PMMA loss tangent peak corresponding to the $\alpha$-transition, as a function of strain rate. Data points were derived from multiple tests at frequencies of 1 Hz, 10 Hz, and 100 Hz. By fitting the data, the transition location is found to shift $11.07^\circ C$ per decade increase in strain rate.
CHAPTER 3. DYNAMIC MECHANICAL ANALYSIS

Figure 3-16: PMMA loss modulus as a function of temperature and strain rate in the region of the $\beta$-transition.

Figure 3-17: PMMA loss tangent ($\tan \delta$) as a function of temperature and strain rate in the region of the $\beta$-transition.
Figure 3-18: Temperature location of PMMA loss tangent peak corresponding to the $\beta$-transition, as a function of strain rate. Data points were derived from multiple tests at frequencies of 1 Hz, 10 Hz, and 100 Hz. By fitting the data, the transition location is found to shift 25.20°C per decade increase in strain rate.
3.4 Data Analysis

The ultimate goal of this study was to develop a constitutive model for amorphous polymers that is accurate at all strain rates and temperatures. It was necessary, then, to use the DMA data to establish an analytical expression for both the PC and PMMA elastic (storage) modulus at any particular temperature/strain rate combination. The process of developing such an analytical expression would provide a better understanding of the transitions in material behavior for these amorphous polymers, as well as provide guidance in the formulation of a constitutive model. The end product would provide comprehensive information about the elastic constants of these materials, information which has been absent from even the most sophisticated existing constitutive models.

To develop these analytical expressions of the elastic modulus for PC and PMMA, the reference curves of figures 3-3 and 3-4 were each decomposed into an \( \alpha \)-component and a \( \beta \)-component. The components were supposed to shift with strain rate by the amounts determined via experimental examination of the transition locations, summarized in table 3.1. The entire modulus curve could be reconstructed for any particular strain rate by first shifting the components of the reference curve by the appropriate amounts, and then summing them at every temperature. This novel method of analyzing the DMA data would thus provide an analytical expression of the elastic modulus for any particular temperature/strain rate combination. The method is based on the assumption that two separate molecular processes, each with its own rate and temperature dependence, act in tandem to control the response of the material to elastic deformation.

For the case of PC, the structure of the storage modulus reference curve (figure 3-3) lends itself well to decomposition. As the curve is traced with decreasing temperature, a significant upturn appears at \(~-95^\circ \text{C}\). From the loss modulus measurements of figure 3-5, this upturn may be correlated with the onset of the restriction of the \( \beta \)-process. That is, at temperatures below \(-95^\circ \text{C}\), the rotational freedom of the phenyl group in the main chain becomes inhibited. In order to simplify the decomposition of the curve, it is assumed that the shape at temperatures above the upturn can be completely attributed to restrictions on the \( \alpha \)-process; were it not for the onset of an additional resistance to elastic deformation, the
CHAPTER 3. DYNAMIC MECHANICAL ANALYSIS

Figure 3-19: PC elastic modulus curve at $3.2 \times 10^{-3} \text{ s}^{-1}$ decomposed into $\alpha$ and $\beta$ components. Curves have been generated from polynomial fits of the split data.

curve would continue on at the same slope as before. Following this logic, the PC storage modulus reference curve was separated into an $\alpha$ and a $\beta$ component, as shown in figure 3-19.

In order to have useful and efficient analytical expressions of these components for numerical implementation, the two curves were further broken down into segments that could be fit with polynomials of degree four or lower. Figure 3-19 is in fact generated from these polynomial fits of the split data. In the analytical expressions, both components are given a nominal constant rubbery modulus of $\sim 5 \text{ MPa}$ for all temperatures above the transition region. The numerical implementation of the shifting algorithm, as well as the polynomial fits for each component, can be found in the MATLAB files of Appendix C.

With this numerical implementation of the decompose/shift/reconstruct (DSR) method, it is possible to predict the elastic modulus of PC at all temperatures and strain rates. Figure 3-20 shows the DSR model prediction of the elastic modulus curve at $10^{-3} \text{ s}^{-1}$ and $10^{3} \text{ s}^{-1}$. The whole curve not only shifts to the right (increased temperatures) with increasing strain rate, but it also changes shape. As demonstrated in this figure, we are able to use the
DSR model to predict the polymer's elastic modulus at temperatures and strain rates well beyond the ranges allowed by the dynamic mechanical analysis instrument - a strain rate of $10^3$ s$^{-1}$ is well beyond the frequencies capabilities of the Q800 DMA.

Perhaps more significantly, this DSR method can also be used to predict at what strain rate we would expect to observe a significant transition in material behavior. Assuming that this significant material transition - most often observed in the yield behavior of the polymer - is brought on by the restriction of the same molecular motion associated with the $\beta$-transition of the viscoelastic behavior, we may look to the shifting $\beta$-component to predict the transition strain rate. Figure 3-21 shows just the $\beta$-component of the PC elastic modulus at five different strain rates, as predicted by the DSR model. Also, a vertical line has been added at room temperature. At strain rates below about 1 s$^{-1}$, the $\beta$-component has not yet shifted past room temperature - the motion of the phenyl groups is not yet restricted, and the $\beta$ contribution to the overall elastic modulus is negligible. However, once the strain rate is increased to 10 s$^{-1}$ or 100 s$^{-1}$, the $\beta$ contribution observed at room temperature becomes significant, and it continues to increase rapidly with increasing strain rate. It is this effect of the shifting $\beta$-component which causes a sharp upturn in the overall predicted elastic modulus curve (figure 3-22 - elastic modulus as a function of the logarithm of strain rate, room temperature) at a strain rate of about 10 s$^{-1}$. Since the same mechanisms which govern elasticity in polymers also govern yield and plasticity, we would expect to observe a transition in the yield behavior at a similar strain rate.

For the case of PMMA, the application of the DSR method is not as straightforward; simple examination of the structure of the storage modulus reference curve (figure 3-4) provides little insight as to how the decomposition should be carried out. Thus other clues in the data must be sought in order to make this decision. The loss modulus curve of figure 3-6 indicates that the $\alpha$ and $\beta$ transitions are very close in temperature, and in fact likely overlap each other even at the strain rate of the reference test. Also, the relative sizes of these loss modulus peaks indicate that the $\beta$-transition, though more gradual than the $\alpha$ transition, has a large impact upon the overall material response. Our final clue comes from an additional plot of measured data, figure 3-23. This graph shows the PMMA storage modulus at $6.0 \times 10^{-3}$ s$^{-1}$ and $2.2 \times 10^{-1}$ s$^{-1}$, in the region of the $\alpha$-transition. This portion
CHAPTER 3. DYNAMIC MECHANICAL ANALYSIS

Figure 3-20: Model prediction of the PC elastic modulus curve at $10^{-3}$ s$^{-1}$ and $10^3$ s$^{-1}$.

Figure 3-21: Model prediction of the $\beta$-component of the PC elastic modulus curve at five strain rates, ranging from $10^{-4}$ s$^{-1}$ to $10^4$ s$^{-1}$. The vertical dotted line represents room temperature (298 K).
of the modulus curve is observed to change shape considerably, for an increase in strain rate of less than two orders of magnitude. Thus, it may be assumed that the $\alpha$ and $\beta$ components are interacting in this region; the large disparity between the shift factors (25.20°C/decade for $\beta$, 11.07°C/decade for $\alpha$) causes the overall shape to change for a relatively small change in strain rate.

As with PC, certain assumptions were made concerning the make-up of the $\alpha$ and $\beta$ components in order to simplify the decomposition process. Based on the experimental observations discussed here, it was assumed that $\beta$-component of the storage modulus reference curve extends up to 400 K. However, it was assumed that the $\beta$-component curve rises gradually with decreasing temperature, as it does for the case of PC. Thus, the sharp rise in the overall modulus curve just below 400 K was attributed almost entirely to the $\alpha$-component. Again following the example of the PC decomposition, which had been facilitated by the large separation between the $\alpha$ and $\beta$ transitions, it was assumed that the $\alpha$-contribution to the overall elastic modulus increases in an approximately linear fashion with decreasing temperature. The rate of increase was determined from the
Figure 3-23: PMMA storage modulus curve, in the region of the $\alpha$-transition, at two strain rates.

The slope of the storage modulus curve at temperatures below about 240 K, assuming that the $\beta$-contribution "saturates" to a constant value at low temperatures and high strain rates. This assumed saturation then accounts for the decrease in slope of the overall modulus curve at 240 K. The shape of the $\beta$-component was determined from the difference between the experimental storage modulus curve and the assumed $\alpha$-contribution. The decomposition of the PMMA elastic modulus curve, based on all of the assumptions described here, is given as figure 3-24. Again, the components were further broken down into segments and fit with lower-order polynomial functions, for ease of numerical implementation. The polynomial functions and shifting algorithms for PMMA may be found in the MATLAB files of Appendix D. As can be seen in 3-25, the predicted elastic modulus curve not only shifts right (increasing temperatures) with increased strain rate, it also changes shape. Figure 3-26 shows the DSR model prediction of the $\beta$-contribution to the overall elastic modulus, at five different strain rates. It is clear from this figure that the $\beta$ contribution becomes significant at a very low strain rate - approximately $10^{-5}$ s$^{-1}$. Also, this figure shows the $\beta$ contribution to saturate at a strain rate just above 1 s$^{-1}$. We would expect the yield data
Figure 3-24: PMMA elastic modulus curve at $2.1 \times 10^{-3} \text{ s}^{-1}$ decomposed into $\alpha$ and $\beta$ components. Curves have been generated from polynomial fits of the split data.

for PMMA to show a significant transition at a strain rate close to $10^{-5} \text{ s}^{-1}$, coinciding with the onset of restricted side group motions.
CHAPTER 3. DYNAMIC MECHANICAL ANALYSIS

Figure 3-25: Model prediction of the PMMA elastic modulus curve at $10^{-3}$ s$^{-1}$ and $10^3$ s$^{-1}$.

Figure 3-26: Model prediction of the $\beta$-component of the PMMA elastic modulus curve at five strain rates, ranging from $10^{-8}$ s$^{-1}$ to 1 s$^{-1}$. The vertical dotted line represents room temperature (298 K).
Chapter 4

Compression Testing

Uniaxial compression tests were carried out on PC and PMMA with two different experimental apparatus: a servo-hydraulic testing machine and an aluminum split-Hopkinson pressure bar (SHPB) system. The servo-hydraulic machine was used to characterize material stress-strain behavior at low to moderate strain rates \((10^{-1} \text{ s}^{-1} \text{ to } 1 \text{ s}^{-1})\), while the SHPB system was used to characterize stress-strain behavior at high strain rates \((\sim 10^3 \text{ s}^{-1} \text{ to } 10^4 \text{ s}^{-1})\). Uniaxial compression was selected as the deformation mode because it dictates a homogeneous stress state; interpretation of the data is straightforward. The results of the compression testing described here would be used to better understand and explain the linkages between observed transitions in the viscoelastic behavior (Chapter 3) and transitions in the rate-dependent stress-strain behavior of amorphous polymers, as a crucial step towards developing a constitutive model that is accurate at all strain rates. Additionally, the compression data would be used to verify the predictive capability of the constitutive model.

4.1 Experimental Procedure

Compression testing was performed on the same materials as those used in dynamic mechanical analysis: Lexan® polycarbonate and Plexiglas® G poly(methyl methacrylate). All compression specimens were machined down from sheet stock supplied by Dr. Alex Hsieh of the Army Research Laboratories.
4.1.1 Low to Moderate Rate Testing

PC and PMMA were tested in uniaxial compression at strain rates of $10^{-4}$ s$^{-1}$ to 1 s$^{-1}$ on an Instron servo-hydraulic testing machine. A specially-designed feedback loop between the Instron and the data acquisition system was used to ensure a constant true strain rate over the duration of the tests. Thin Teflon sheets were placed between the Instron platens and specimen surfaces; WD-40 lubricant was used between the Teflon sheets and platens. The lower platen was fit with a spherical seat, to compensate for any misalignment in the load train. All specimens were of right circular cylinder geometry, with diameter of approximately 12.7 millimeters and length of approximately 6.35 millimeters. This particular length-to-diameter ratio (1:2), though not ideal for reducing friction, was chosen in order to be consistent with the geometry of the split-Hopkinson bar specimens. Specimens were machined down from sheet stock of thickness greater than 6.35 millimeters, with a parallel-face tolerance of less than three one-hundredths of a millimeter. In all of these tests, specimens were deformed to true strains of approximately 80%. Specimen geometry, before and after deformation, can be seen in figure 4-1.
4.1.2 High Rate Testing

All high strain rate compression testing was performed on a split-Hopkinson pressure bar (SHPB) test apparatus designed in cooperation with and built by Physics Applications, Inc. of Dayton, Ohio. The theory of split-Hopkinson bar testing, as well as the issues unique to testing low-impedance, low yield strength materials such as amorphous polymers, have been thoroughly reviewed in section 2.4 of this thesis.

The SHPB system used in this study employs solid Aluminum pressure bars, both with a length of approximately 2.3 meters and a diameter of 19.05 millimeters. The striker bar is of the same material and diameter, with a length of 0.61 meters. Strain gages are mounted equidistant from the specimen on the incident and transmission bars at a distance such that the incident and reflected waves will not interfere at the gage location. A Vishay system is used to continually provide an excitation voltage of 5.0 volts to the gage bridges, receive the low-level signals returned by the excited bridges, and condition and amplify the signals (1000 times) into high-level outputs for recording. The data acquisition system is completed by a LeCroy Waverunner DSO digital oscilloscope, which records these amplified signals at sampling rates as high as one point per one hundred nanoseconds.

In the tests of this study, specimens were of right circular cylinder geometry, with a diameter of 5.08 millimeters and a length of 2.54 millimeters. This 1:2 length-to-diameter ratio has been shown to be optimal in reducing the negative effects of radial and longitudinal inertia and friction (Davies & Hunter, 1963), (Chen et al., 1999), and the short specimen length allows for a small time to dynamic equilibrium. All specimens were lubricated with a thin layer of petroleum jelly on both faces, and little to no barrelling was ever observed. It was found in all tests that dynamic equilibrium was achieved before yield, and since the DMA testing was used to characterize the rate-dependent viscoelastic moduli, pre-yield data at high rates was not of consequence and therefore pulse-shaping was unnecessary. In these high-rate tests, specimens were deformed to true strains of 20% to 110%, depending on the particular material and striker bar velocity. Specimen geometry, before and after deformation, can be seen in figure 4-2.

Figure 4-3 provides an example of the incident and transmission bar raw signals for a typical test of PC on this system. The high-frequency noise in the signals, caused by
Figure 4-2: Typical PC uniaxial compression specimen, before (left) and after (right) deformation on SHPB apparatus. The deformed specimen has been strained to a true strain of 0.6, at a true strain rate of \( \sim 2600 \, \text{s}^{-1} \).

Figure 4-3: Typical strain gage signals from a SHPB test of PC. The true strain rate achieved in this test was approximately \( 4000 \, \text{s}^{-1} \).
imperfect alignment of the striker bar and the pressure bars, as well as dispersion effects, is

typical for a test where the material is low-impedance and large signal amplification factors

are necessary. This noise is often removed by smoothing methods or a Fourier transform;

smoothing was performed in this study as the final step in data analysis, as described later

in this section. Figure 4-3 indicates that even though the incident and reflected pulses

are very close, they do not interfere at the gage location. Also, this figure demonstrates

that the transmitted pulse has a satisfactory amplitude and amplitude-to-noise ratio for

data analysis - usually this is the most difficult criterion to achieve in SHPB testing of

low-impedance materials.

The analysis of this signal data is not straightforward. Equations 2.17 and 2.18, derived

in section 2.4 of this thesis, provide a theoretical relationship between the strain pulses

recorded in the gage signals and the stress and strain in the test specimen. However, the

selection of where exactly in the signals these pulses begin is ambiguous; the pulses must

be aligned properly in order to produce accurate data. A consistent and theoretically-based

method for determining the start point of these pulses was thus developed and implemented

into a MATLAB numerical routine. The key to this routine is the way in which the start

of the reflected and transmitted pulses are correlated. Since the strain gages are located on

the two pressure bars equidistant from the specimen interface, the reflected and transmitted

pulses should arrive at the incident bar gage location and transmission bar gage location,

respectively, at approximately the same time. The transmitted pulse actually arrives later

than the reflected pulse, later by the amount of time it takes the pulse to travel through

the specimen. This time may be calculated from the elastic wave speed of the specimen

(equation 2.15), and thus the start of the transmitted pulse may be aligned with the start of

the incident pulse precisely and consistently. All data reported here was analyzed following

this routine.

Figure 4-4 is a plot of force equilibrium in a SHPB test, developed from the strain gage

signals of figure 4-3. Force on the front face of the specimen is calculated from the incident

and reflected pulses; force on the back face of the specimen is calculated from the transmitted

pulse. The two force curves converge at ~25 microseconds, indicating that the specimen

has achieved a state of dynamic equilibrium after approximately three reverberations of the
stress wave. Large oscillations in the front force amplitude continue until ~80 microseconds, but in this test, global yield of the specimen did not occur until ~150 microseconds.

As a final step in the data analysis, stress and strain rate information was smoothed in order to remove the high-frequency oscillations. A simple moving-average scheme was used to perform this smoothing in MATLAB. Typically, spans between 50 and 100 were employed in the smoothing, over data sets of approximately 1000 points. The scheme automatically uses smaller spans at the ends of the data set, in order to preserve the number of data points. Figure 4-5 provides a comparison of smoothed and unsmoothed data, for a typical stress-strain curve derived from analysis of a SHPB test. Smoothing is shown to greatly improve the clarity of the curve, without compromising the integrity of the data. This smoothing method has the same effect as a Fourier transform to remove high-frequency noise, which has been justified in SHPB data analysis by many authors before.
Figure 4-5: Smoothed data over unsmoothed data. Stress-strain information was derived from the signals in figure 4-3; smooth data was developed with a moving-average scheme (span of 50 over 1000 total data points).
4.2 Results and Discussion

4.2.1 Low to Moderate Rate Testing

The results of low to moderate rate compression testing of PC and PMMA are summarized in figures 4-6 to 4-9. Figure 4-6 contains four representative curves of PC true stress-true strain behavior, one for each of the constant true strain rates this material was tested at: $10^{-3} \text{ s}^{-1}$, $10^{-2} \text{ s}^{-1}$, $10^{-1} \text{ s}^{-1}$, and $1 \text{ s}^{-1}$. Tests at each of these strain rates were repeated two to four times, in order to establish the repeatability of the results; complete data may be found in figures E-1 and E-2 of Appendix E. All of the curves in figure 4-6 indicate the expected features of material response to large-strain uniaxial deformation, discussed in detail in Chapter 2: initial linear elasticity, non-linear elasticity and global yield, strain softening, and strain hardening. It is observed that, in general, the relative significance of each of these features remains constant through this range of strain rates.

Figure 4-7 provides a plot of the PC yield behavior in this strain rate regime. The yield stress is found to increase linearly with the logarithm of strain rate. This result indicates
that the yield behavior could be accurately explained and/or predicted in the quasi-static regime by the general Eyring theory, with just one activated process. This finding is in agreement with the work of Bauwens et al. (1969), Walley and Field (1994), and Moy et al. (2003), among others.

Figure 4-8 contains representative curves of PMMA true stress-true strain behavior at four low to moderate strain rates: $3\times10^{-4}$ s$^{-1}$, $10^{-2}$ s$^{-1}$, $10^{-1}$ s$^{-1}$, and $3\times10^{-1}$ s$^{-1}$. Tests at each of these strain rates, as well as tests at three intermediate strain rates, were repeated two to four times, in order to establish the repeatability of the results; complete data may be found in figures E-3 and E-4 of Appendix E. PMMA was tested at more strain rates than PC in this rate regime, for material yield behavior was found to undergo a significant transition. PMMA behavior in this rate regime was also dissimilar from PC in that the stress-strain curves were observed to change shape considerably from low to moderate rates. The structure of the initial features - linear and non-linear elasticity, global yield - is relatively the same at all rates, but the amount of softening is found to increase dramatically, so much so that the apparent hardening in PMMA at 1 s$^{-1}$ is negligible.
CHAPTER 4. COMPRESSION TESTING

![Figure 4-8: Representative curves of PMMA true stress-true strain behavior in uniaxial compression at four low to moderate strain rates.](image)

This finding is consistent with the results of Arruda, Boyce, and Jayachandran (1995). The increased softening effect has been shown to be due to the adiabatic test conditions at moderate rates; some fraction of the plastic work is converted to heat, and thus the polymer experiences thermal softening with increased plastic straining. The flow stress of PMMA is more temperature sensitive than that of PC and thus thermal softening is clearly apparent only in the PMMA data.

The transition in PMMA yield behavior is documented in figure 4-9, a plot of the yield stress as a function of strain rate. The yield stress is found to increase in a non-linear fashion with the logarithm of strain rate, indicating that more than one activated process is controlling material response even at low rates. This result is consistent with the work of Bauwens-Crowet and Homès (1964), Roetling (1965b), and, more recently, Swallowe and Lee (2003). Also, figure 4-9 indicates that the yield strength of PMMA, like the elastic modulus, is much more sensitive to changes in strain rate than the yield strength of PC. Over the same rate regime, PMMA yield stress increases almost 80%, while PC yield stress increases less than 20%.
CHAPTER 4. COMPRESSION TESTING

4.2.2 High Rate Testing

The results of split-Hopkinson bar testing on PC are summarized in figures 4-10 to 4-16. All curves shown have been smoothed as described in the previous section. PC specimens deformed in a ductile manner over the tested high strain rates, ranging from $1200 \text{s}^{-1}$ to $4000 \text{s}^{-1}$ (true strain rate at yield). True strain rates were within 25% of a constant value over the duration of the tests. Figures 4-10 to 4-12 contain representative true stress-true strain curves, along with corresponding true strain rate histories, for tests at three of these strain rates; complete data can be found in figures E-5 to E-9 of Appendix E. In general, the curves demonstrate all of the same characteristic features as the low-rate curves: linear and non-linear elasticity, global yield, strain softening, and strain hardening. Figure 4-13 provides a comparison of four high-rate true stress-true strain curves. As before, the relative significance of the characteristic features remains nearly constant through the range of strain rates tested. Figure 4-14 provides a comparison of these high-rate curves with the low to moderate rate true stress-true strain curves. In general, the characteristic shape of the
true stress-true strain curve is the same at all rates. Unlike PMMA, the effects of thermal softening in PC appear to be minimal, even at high rates.

The rate-dependence of PC yield stress within the high-rate regime is pictured in figure 4-15. As with the low to moderate rate regime, the yield stress is found to increase in an approximately linear fashion with the logarithm of strain rate in the high rate regime. However, the slopes of the data point lines in the two rate regimes are markedly different, as can be seen in figure 4-16. This result agrees very well with the recent findings of Moy et al. (2003) - see figure 2-53. In the low to moderate rate regime, the yield stress increases approximately 4.1 MPa per decade increase in strain rate, whereas in the high rate regime, the yield stress increases approximately 23.0 MPa per decade increase in strain rate.

It is clear that PC undergoes a significant material transition as the strain rate is increased beyond a certain critical level, located between the test capabilities of the servo-hydraulic machine and the test capabilities of the split-Hopkinson bar apparatus. The trendlines over the yield data in figure 4-17 indicate that the transition is centered around a strain rate of approximately 152 s⁻¹. This transition strain rate is fairly consistent.
Figure 4-11: PC true stress-true strain behavior and corresponding strain rate history, for a test at a chamber pressure of 70 psi (~3900 s$^{-1}$).

Figure 4-12: PC true stress-true strain behavior and corresponding strain rate history, for a test at a chamber pressure of 90 psi (~5050 s$^{-1}$).
Figure 4-13: Representative curves of PC true stress-true strain behavior in uniaxial compression at three high-rate strain rates. Reported strain rates are averages over the duration of the tests.

Figure 4-14: Representative curves of PC true stress-true strain behavior in uniaxial compression at seven low, moderate, and high rates. Reported high strain rates are averages over the duration of the tests.
CHAPTER 4. COMPRESSION TESTING

Figure 4-15: PC true yield stress as a function of true strain rate (logarithmic scale) - high strain rates only. Each data points represents an average of at least five tests.

Figure 4-16: PC true yield stress as a function of true strain rate (logarithmic scale) - all strain rates. Each data points represents an average of 2-5 tests.
with that predicted by the DSR model (section 3.4), based on the assumption that the transition in the yield behavior is a direct result of the restriction of the same secondary molecular motion associated with the $\beta$-transition in the viscoelastic behavior. The DSR model actually predicted a transition strain rate closer to $10 \, s^{-1}$, but it must be understood that this transition is a distributed event. Without any yield data within the transition range, we have no information regarding the nature of the distribution; it is very possible that the transition in yield behavior actually begins close to $10 \, s^{-1}$.

The results of split-Hopkinson bar testing on PMMA are summarized in figures 4-18 to 4-21. All curves shown have been smoothed as described in the previous section. The high rate testing of PMMA was not as successful as the high rate testing of PC, in that the PMMA specimens failed in a brittle manner (before yield) at strain rates above $1400 \, s^{-1}$. Thus true stress-true strain curves were only obtained at two chamber pressures (striker velocities), corresponding to average true strain rates of approximately $800 \, s^{-1}$ and $1400 \, s^{-1}$. Representative curves, along with the corresponding true strain rate histories, are pictured.
CHAPTER 4. COMPRESSION TESTING

Figure 4-18: PMMA true stress-true strain behavior and corresponding strain rate history, for a test at a chamber pressure of 35 psi (~800 s⁻¹).

in figure 4-18 and figure 4-19, respectively; complete data demonstrating the repeatability of the curves may be found in figures E-10 and E-11 of Appendix E.

These true stress-true strain curves are plotted against characteristic curves at low and moderate strain rates in figure 4-20. The high rate curves do not extend beyond the region of strain softening, due to brittle failure at low strain levels. In fact, the apparent softening of the 1400 s⁻¹ curve is likely a combination of both strain softening and a drop-off in stress following fracture. In both high strain rate tests, however, global yield is achieved before fracture. Figure 4-21 is a plot of the average yield stress values recorded in these tests, along with the average yield stress values of all low to moderate strain rate tests. The high-rate yield stress values seem to fit the trendline indicated by the low and moderate rate yield stress values. This result is contrary to the findings of Swallowe and Lee (2003), but in line with the Bauwens yield model prediction, derived from low temperature testing and viscoelastic data (Bauwens-Crowet, 1973).

Though the DSR model for PMMA predicted a material transition, related to the restriction of β-motions, at a strain rate close to 10⁻⁵ s⁻¹, figure 4-21 shows a kink in the
CHAPTER 4. COMPRESSION TESTING

Figure 4-19: PMMA true stress-true strain behavior and corresponding strain rate history, for a test at a chamber pressure of 50 psi (~1400 s\(^{-1}\)).

Figure 4-20: Representative curves of PMMA true stress-true strain behavior in uniaxial compression at four low, moderate, and high rates. Reported high strain rates are averages over the duration of the tests.
yield data close to $10^{-2}$ s$^{-1}$. However, as with PC, yield data could not be obtained close to the predicted transition region. It is possible that the yield curve begins to deviate from linearity at $10^{-5}$ s$^{-1}$, but changes only become pronounced at strain rates three to four decades higher. Such a finding would be consistent with the distributed nature of the viscoelastic $\beta$-transition observed in the PMMA loss modulus data of figure 3-6; in this figure, the $\beta$ peak at a strain rate of $\sim 10^{-3}$ is observed to span two hundred and fifty degrees in temperature.

The experimental yield data presented here, especially in the case of PC, validates the DSR method as an analytical technique for predicting transitions in the rate-dependent behavior of amorphous polymers. With this tool, it will be possible to evaluate different polymers as potential materials for high-rate applications, based on a desire to exploit changes in material behavior. Also, the combined analytical and experimental results presented thus far serve to reinforce the long-assumed link between the transition in the yield behavior of amorphous polymers and the the $\beta$-transition in the viscoelastic behavior. Thirty years
ago, Bauwens (1972) built a successful yield model upon this supposition, after making a correlation between the two observed transitions via activation energy calculations. Finally, with new insight and new understanding, we shall use this fundamental understanding of the material transitions as the foundation for a proposed constitutive model for the three-dimensional rate-dependent finite strain deformation of amorphous polymers.
Chapter 5

Constitutive Model

The proposed constitutive model was derived from an existing model for the three-dimensional finite-strain deformation of thermoplastic materials. The revised model is built upon the same transferable framework, based at the continuum level, that has been used to accurately capture the stress-strain response of polymeric materials to various types of deformation. The new model, however, incorporates additional complexities in order to capture the understanding of molecular-level resistance to high rate deformation that has been developed in this study. This chapter will derive the structure of the proposed model, beginning with a thorough review of the existing model from which it was developed.

5.1 Existing Model

The existing constitutive model of the large strain elastic-viscoplastic behavior of thermoplastics, from which the proposed high-rate model of this study is developed, was introduced in its components by Boyce, Parks, and Argon (1988), Arruda, Boyce, and Quintus-Bosz (1993) and Arruda and Boyce (1993). The model has been shown to be predictive of the stress-strain behavior of PC (Arruda et al., 1993), (Boyce, Arruda, & Jayachandran, 1994) and PMMA (Boyce et al., 1988), (Arruda et al., 1995) at low to moderate strain rates ($10^{-3}$ s$^{-1}$ to 1 s$^{-1}$), at temperatures from 300 K to 363 K, and in four states of deformation: plane strain compression, simple shear, uniaxial tension, and uniaxial compression. Until recently, the model had not been tested against high-rate or low temperature data.
Figure 5-1: A one-dimensional rheological interpretation of the existing Boyce et al constitutive model for rate-dependent thermoplastic behavior.

A one-dimensional rheological interpretation of this original model is given as figure 5-1. There are three components to the model: a linear elastic spring, a viscoplastic dashpot, and a non-linear Langevin spring. The dashpot and elastic spring act in series, with the non-linear spring in parallel to both. The elastic spring and viscoplastic dashpot together capture an understanding of the intermolecular resistance to chain segment rotation. The elastic spring models the initial response of the material, and contains a portion of the stored energy attributed to reversible chain segment rotation. The viscoplastic element models the rate, temperature, and pressure dependence of yield, as well as the strain softening, and accounts for the energy that is dissipated during deformation. The Langevin spring captures the entropic strain hardening due to chain alignment. Inherent in this model structure is the assumption that the resistance to deformation may be decomposed into two parts: intermolecular resistance to chain-segment rotation, and entropic resistance to chain alignment. A fully three-dimensional constitutive model has been built up from this one-dimensional understanding, beginning with the kinematics of finite strain. The finite strain kinematic framework follows that presented in Bergstrom and Boyce (1998), Bergstrom and Boyce (2000), Boyce, Socrate, and Lana (2000), and Bergstrom and Boyce (2000).
Throughout the derivations of this chapter, terms relating to the combined elastic-viscoplastic element will be given a subscript of "A", and terms relating to the entropic-hardening element shall be given a subscript of "B" (as denoted in figure 5-1). Boldface type indicates tensorial quantities in this three-dimensional analysis.

5.1.1 Kinematics

Kinematic analysis begins with the deformation gradient, $F$. The deformation gradient maps a material point from its reference position $X$ to the current location $x$:

$$F = \frac{\partial x}{\partial X}$$

In this analysis of amorphous polymer deformation, the reference configuration may be interpreted as an undeformed, stress-free state, where molecular chains are randomly oriented. Upon loading, components A and B of the model (see figure 5-1) shall see the same deformation:

$$F_A = F_B = F \tag{5.1}$$

The deformation gradient in element A may be multiplicatively decomposed into elastic and plastic components via Kroner-Lee decomposition (Kroner, 1960), (Lee, 1969):

$$F_A = F_A^e F_A^p \tag{5.2}$$

$F_A^p$ may be interpreted as the mapping of a material point in the reference configuration to a material point in the "relaxed configuration", obtained by elastic unloading to a stress-free state. Also, the plastic deformation is assumed to be a volume-preserving process, such that $\det F_A^p = 1$. Thus all volume change is elastic:

$$J = \frac{\Delta V}{V_0} = \det F_A^e$$
We may also use polar decomposition to separate the deformation gradient into stretch and rotation components:

\[ \mathbf{F}_A = \mathbf{R}_A \mathbf{U}_A = \mathbf{V}_A \mathbf{R}_A \]  

(5.3)

Where \( \mathbf{R}_A \) is a rotation and \( \mathbf{U}_A \) and \( \mathbf{V}_A \) are the right and left stretch tensors, respectively.

Next, we examine the rate at which deformation takes place in the body through the velocity gradient, \( \mathbf{L} \):

\[ \mathbf{L} = \mathbf{L}_A = \frac{\partial \mathbf{v}}{\partial \mathbf{x}} \]

Where \( \mathbf{v} = \frac{\partial \mathbf{x}}{\partial \mathbf{t}} \) is the velocity of a material point in the current configuration. The deformation gradient and the velocity gradient are related:

\[ \mathbf{L}_A = \dot{\mathbf{F}}_A \mathbf{F}_A^{-1} \]

This velocity gradient may also be decomposed into elastic and plastic components:

\[ \mathbf{L}_A = \mathbf{L}_A^e + \dot{\mathbf{F}}_A^p \mathbf{F}_A^{p-1} \]  

(5.4)

Where

\[ \mathbf{L}_A^e = \dot{\mathbf{F}}_A^p \mathbf{F}_A^{p-1} = \mathbf{D}_A^p + \mathbf{W}_A^p \]  

(5.5)

\( \mathbf{D}_A^p \) (symmetric tensor) and \( \mathbf{W}_A^p \) (skew tensor) represent the rate of shape change of the relaxed configuration and the rate of spin of the relaxed configuration, respectively. In this analysis, plastic flow is assumed to be irrotational: \( \mathbf{W}_A^p = 0 \). Note that this does not restrict \( \mathbf{R}_A^p \) to be the identity tensor. This assumption brings about the evolution equation for the plastic deformation gradient, where we now have:

\[ \mathbf{D}_A^p = \dot{\mathbf{F}}_A^p \mathbf{F}_A^{p-1} \]

and therefore

\[ \dot{\mathbf{F}}_A^p = \mathbf{D}_A^p \mathbf{F}_A^p \]  

(5.6)
Equation 5.6 is integrated to obtain $F_A^p$; the elastic deformation gradient is then obtained via:

$$F_A^e = F_A F_A^{p-1}$$

Note that, in general, $F_A^e$ and $F_A^p$ will both contain rotations.

The kinematics derived here are general; the material-specific model is defined by the constitutive laws which connect the rate of shape change with the stress in the deforming material. This rate of shape change is given as the product of a magnitude - the plastic strain rate $\dot{\gamma}^P$ - and a direction tensor $N_A^p$:

$$D_A^p = \dot{\gamma}^P N_A^p \quad (5.7)$$

Where $D_A^p$ is taken to be coaxial with the deviatoric stress acting on component A:

$$N_A^p = \frac{T_A'}{|T_A'|} \quad (5.8)$$

The model developed by Boyce et al provides constitutive laws for $\dot{\gamma}^P$, $T_A$, and $T_B$.

5.1.2 Material Description and Constitutive Relations

The intermolecular contribution (A) to the material stress state is related to the deformation by a constitutive law for the linear elastic spring:

$$T_A = \frac{1}{J} L^e \ln U_A^e \quad (5.9)$$

Where $T_A$ is the intermolecular contribution to the Cauchy (true) stress, $J$ is the elastic volume change defined in equation 5.3, $L^e$ is the fourth-order modulus tensor, and $\ln U_A^e$ is the Hencky strain. In this model, the material is assumed to be initially isotropic, and thus the modulus tensor can be derived from any two elastic constants. In terms of the shear modulus $\mu$ and bulk modulus $\kappa$, the modulus tensor is given as:

$$L^e = 2\mu I + \left(\kappa - \frac{2}{3}\mu\right) I \otimes I$$
CHAPTER 5. CONSTITUTIVE MODEL

Where \( I \) and \( I \) are the fourth-order and second-order identity tensors, respectively. The elastic constants - in this case, \( \mu \) and \( \kappa \) - are assumed to be functions of temperature only.

The stress in the non-linear hardening component, due to the entropic resistance to alignment of the molecular network, is derived from the Arruda and Boyce eight-chain model of rubber elasticity (1993):

\[
T_B = \frac{C_R}{3} \frac{\sqrt{N}}{\lambda_{\text{chain}}^p} \mathcal{L}^{-1} \left( \frac{\lambda_{\text{chain}}^p}{\sqrt{N}} \right) B_B'
\]  

(5.10)

Where \( B_B' \) is the left Cauchy-Green tensor, \( B_B = F_B F_B^T \), and \( B_B' \) is its deviator:

\[
B_B' = B_B - \frac{1}{3} \text{trace}(B_B)
\]

\( \lambda_{\text{chain}}^p \) is the stretch on a chain in the eight-chain network, calculated from the first invariant of the stretch tensor:

\[
\lambda_{\text{chain}}^p = \sqrt{\frac{I_1}{3}} \quad (5.11)
\]

where

\[
I_1 = \text{trace}(B_B)
\]

\( \mathcal{L} \) is the Langevin function, defined as:

\[
\mathcal{L}(\beta) \equiv \coth \beta - \frac{1}{\beta}
\]

Finally, there are two material parameters in the constitutive law of equation 5.10: \( \sqrt{N} \), the limiting chain extensibility; and \( C_R \equiv n k \theta \), the rubbery modulus (where \( n \) is the number of chains per unit volume, \( k \) is Boltzmann's constant, and \( \theta \) is the absolute temperature). The stress captured by \( T_B \) is referred to as the "back stress", since it is an internal stress that acts against chain-stretching and chain-aligning deformation. The magnitude of the back stress increases asymptotically as the chain stretch approaches its limiting extensibility.

The total stress in the polymer is given as the tensorial sum of the intermolecular stress and the network (back) stress:

\[
T = T_A + T_B
\]

(5.12)
The driving stress is used to specify the direction tensor \( \mathbf{N}_A^p \) in the plastic flow rule (equation 5.7):

\[
\mathbf{N} = \frac{1}{\sqrt{2\tau}} \mathbf{T}_A^p
\] (5.13)

The prime notation on the driving stress in this equation again indicates the deviatoric component. The effective equivalent shear stress \( \tau \) is given by:

\[
\tau = \sqrt{\frac{1}{2} \mathbf{T}_A^p \mathbf{T}_A^p}
\] (5.14)

Finally, a constitutive law for the viscoplastic behavior is prescribed, based on the Argon model for yield in glassy polymers (reviewed in Chapter 2):

\[
\dot{\gamma}^p = \dot{\gamma}_0^p \exp \left[ -\frac{\Delta G}{k\theta} \left( 1 - \frac{\tau}{s + \alpha_p p} \right) \right]
\] (5.15)

Where \( \dot{\gamma}_0^p \) is the pre-exponential factor proportional to the attempt frequency, \( \Delta G \) is the activation energy, \( p \) is the pressure, and \( \alpha_p \) is the pressure coefficient. The internal variable \( s \) is the athermal shear strength, related to the shear modulus and taken to evolve to a preferred state with plastic straining:

\[
s_0 = \frac{0.077\mu}{1 - \nu}
\] (5.16)

\[
\dot{s} = h \left( 1 - \frac{s}{s_{ss}} \right) \dot{\gamma}^p
\] (5.17)

Where \( h \) is the softening slope and \( s_{ss} \) is the "preferred state". This internal variable allows the temperature dependence of the yield stress to mimic the temperature dependence of the elastic shear modulus, and its evolution captures the strain softening phenomenon. Overall, equation 5.15 captures the rate-, temperature-, and pressure-dependence of yield in the polymer.
5.1.3 Summary

Kinematic Relations:

\[ F_A = F_B = F \]
\[ F_A = F_A^p F_A^p \]
\[ F_A^p = R_A U_A^p = V_A^p R_A \]
\[ L_A = L_A^e + F_A^p L_A^p F_A^e A^{-1} \]
\[ \dot{F}_A^p = D_A^p F_A^p \]
\[ D_A^p = \dot{p} N_A^p \]
\[ F_A^e = F_A F_A^{-1} \]

Kinematic Assumptions:

\[ \operatorname{det} F_A^p = 1 \]
\[ W_A^p = 0 \]

Constitutive Relations:

\[ T_A = \frac{1}{2} \mathcal{L}^e [\ln U_A^e] \]
\[ T_B = \frac{C_R}{\sqrt{N}} \mathcal{L}^e \left( \frac{\lambda_{\text{chain}}^p}{\sqrt{N}} \right) B_B' \]
\[ T = T_A + T_B \]
\[ \tau = \sqrt{\frac{1}{2} T_A' T_A} \]
\[ N = \frac{1}{2} \tau \]
\[ \dot{\gamma}^p = \gamma_0^p \exp \left[ -\frac{\Delta G}{k_B} \left( 1 - \frac{\tau}{s + \alpha p} \right) \right] \]
\[ S_0 = \frac{0.077 \mu}{1 - \nu}, \quad \dot{s} = \dot{h} \left( 1 - \frac{s}{s_{ss}} \right) \dot{\gamma}^p \]

Material Properties:

\[ \mu(\theta); \kappa(\theta) \]
\[ C_R; \sqrt{N} \]
\[ \Delta G; \gamma_0^p \]
\[ \alpha_p; \ h; \ s_{ss} \]
5.2 Proposed Model

The model proposed here is a modification of the three-component design of Boyce et al, such that there are two activated molecular processes, each with their own elastic and viscoplastic definitions, acting in parallel to each other and parallel to the non-linear entropic hardening component. A one-dimensional rheological depiction of the proposed constitutive model is presented in figure 5-2. This new model incorporates a sophisticated understanding and interpretation of the molecular mechanisms that act as barriers to high-rate deformation.

The basic principle behind the proposed model is the same principle that the Ree-Eyring yield theory is built upon: there are many activated processes which can potentially contribute to the overall behavior of the material. Physically, these activated processes may be interpreted as various molecular-level motions. Each particular process has a certain threshold, determined by both temperature and deformation rate, below which the associated molecular motion becomes restricted. Once a certain motion becomes restricted, the corresponding process is said to contribute to the overall deformation resistance of the material.
CHAPTER 5. CONSTITUTIVE MODEL

As in most practical applications of the Ree-Eyring theory, the proposed model only considers the primary (α) process and the most significant secondary process (β). Data indicates that the contributions from other secondary processes are either hidden within the contribution of the β-process, or are non-existent over the range of temperatures and strain rates capable in mechanical testing. The α-process is associated with rotations of the polymer main-chain segments; in the previous model of Boyce et al, the elastic-viscoplastic component was meant to simulate this process only. The proposed model considers a second, β-component to the intermolecular resistance: in the case of PMMA, it is associated with restricted rotations of the ester side-group; in the case of PC, it is restricted rotations of the main-chain phenyl group. The model assumes that the α and β molecular processes are sufficiently de-coupled, so that overall material response may be approximated as the simple superposition of the two.

In constructing the model, the β-process is given its own elastic-viscoplastic component, in parallel with the existing "α" elastic-viscoplastic component. The two components have unique material parameter definitions, such that their relative contributions vary with temperature and strain rate. At high temperatures and low strain rates, the β-component will be fairly compliant, and most, if not all, intermolecular resistance will be generated in the elastic spring and viscoplastic dashpot of the α-component. At low temperatures and high strain rates, the β-component shall become more stiff, and the intermolecular resistance will be two-part. The entropic hardening definition remains unchanged from the original model.

Details of the constitutive model formulation are developed in the following sections. All quantities specific to the α and β components will be given those subscripts.

5.2.1 Kinematics

The kinetic formulation follows the same form as before, except that now every relationship is developed in duplicate, for the unique quantities specific to the α and β components.

Upon loading, all components see the same deformation:

\[ \mathbf{F}_{A_{\alpha}} = \mathbf{F}_{A_{\beta}} = \mathbf{F}_{B} = \mathbf{F} \]  \hspace{1cm} (5.18)
We decompose the deformation gradients into elastic and plastic components, via Kroner-Lee decomposition:

\[
\begin{align*}
F_{A\alpha} &= F_{A\alpha}^c F_{A\alpha}^p \\
F_{A\beta} &= F_{A\beta}^c F_{A\beta}^p
\end{align*}
\]  \hspace{1cm} (5.19) \hspace{1cm} (5.20)

We assume the plastic deformation to be a volume-preserving process:

\[ \det F_{A\alpha}^p = \det F_{A\beta}^p = 1 \]  \hspace{1cm} (5.21)

All volume-changing deformation is elastic:

\[ \det F_{A\alpha}^e = \det F_{A\beta}^e = J \]  \hspace{1cm} (5.22)

Following polar decomposition of the deformation gradients, we may express the deformation of the relaxed configuration as:

\[
\begin{align*}
F_{A\alpha}^p &= R_{A\alpha}^p U_{A\alpha}^p = V_{A\alpha}^p R_{A\alpha}^p \\
F_{A\beta}^p &= R_{A\beta}^p U_{A\beta}^p = V_{A\beta}^p R_{A\beta}^p
\end{align*}
\]  \hspace{1cm} (5.23) \hspace{1cm} (5.24)

We express the velocity gradients in terms of their elastic and plastic components:

\[
\begin{align*}
L_{A\alpha} &= L_{A\alpha}^e + F_{A\alpha}^p L_{A\alpha}^e F_{A\alpha}^{e^{-1}} \\
L_{A\beta} &= L_{A\beta}^e + F_{A\beta}^p L_{A\beta}^e F_{A\beta}^{e^{-1}}
\end{align*}
\]  \hspace{1cm} (5.25) \hspace{1cm} (5.26)

where

\[
\begin{align*}
L_{A\alpha}^p &= \dot{F}_{A\alpha}^p F_{A\alpha}^{p^{-1}} = D_{A\alpha}^p + W_{A\alpha}^p \\
L_{A\beta}^p &= \dot{F}_{A\beta}^p F_{A\beta}^{p^{-1}} = D_{A\beta}^p + W_{A\beta}^p
\end{align*}
\]  \hspace{1cm} (5.27) \hspace{1cm} (5.28)
We require that plastic flow be irrotational in both the $\alpha$ and $\beta$ components,

$$W_{A\alpha}^p = W_{A\beta}^p = 0$$  \hspace{1cm} (5.29)

and therefore

$$F_{A\alpha}^p = D_{A\alpha}^p F_{A\alpha}^p$$  \hspace{1cm} (5.30)
$$F_{A\beta}^p = D_{A\beta}^p F_{A\beta}^p$$  \hspace{1cm} (5.31)

Equations 5.30 and 5.31 are integrated to obtain $F_{A\alpha}^p$ and $F_{A\beta}^p$; the elastic deformation gradients are then obtained via:

$$F_{A\alpha}^e = F_{A\alpha} F_{A\alpha}^{p-1}$$
$$F_{A\beta}^e = F_{A\beta} F_{A\beta}^{p-1}$$

Finally, the plastic flow rules are given by:

$$D_{A\alpha}^p = \dot{\gamma}_{A\alpha}^p N_{A\alpha}^p$$  \hspace{1cm} (5.32)
$$D_{A\beta}^p = \dot{\gamma}_{A\beta}^p N_{A\beta}^p$$  \hspace{1cm} (5.33)

Where

$$N_{A\alpha}^p = \frac{T'_{A\alpha}}{|T'_{A\alpha}|}$$  \hspace{1cm} (5.34)
$$N_{A\beta}^p = \frac{T'_{A\beta}}{|T'_{A\beta}|}$$  \hspace{1cm} (5.35)
5.2.2 Material Description and Constitutive Relations

As with the original structure of the model, the intermolecular contribution to the material stress state is related to the deformation by the constitutive laws for the linear elastic springs:

\[ T_{\alpha} = \frac{1}{J_{\alpha}} \mathcal{L}^e_{\alpha} \left[ \ln U^e_{\alpha} \right] \quad (5.36) \]
\[ T_{\beta} = \frac{1}{J_{\beta}} \mathcal{L}^e_{\beta} \left[ \ln U^e_{\beta} \right] \quad (5.37) \]

Where \( T_{\alpha}, (i = \alpha, \beta) \) is the Cauchy (true) stress, \( J_i \) is the elastic volume change defined in equation 5.22, \( \mathcal{L}^e_i \) is the fourth-order modulus tensor, and \( \ln U^e_{\alpha_i} \) is the Hencky strain.

It is assumed that the material is initially isotropic, and that the elastic behavior of the material may be decomposed into \( \alpha \) and \( \beta \) components. The modulus tensors may be derived from any two component-specific elastic constants, such as the shear modulus \( \mu \) and bulk modulus \( \kappa \):

\[ \mathcal{L}^e_{\alpha} = 2\mu_{\alpha}I + \left( \kappa_{\alpha} - \frac{2}{3}\mu_{\alpha} \right) I \otimes I \]
\[ \mathcal{L}^e_{\beta} = 2\mu_{\beta}I + \left( \kappa_{\beta} - \frac{2}{3}\mu_{\beta} \right) I \otimes I \]

Where \( I \) and \( I \) are the fourth-order and second-order identity tensors, respectively. The elastic constants - in this case, \( \mu_i \) and \( \kappa_i \) \( (i = \alpha, \beta) \) - are assumed to be \textit{functions of both temperature and strain rate}.

The stress in the non-linear hardening component, the network "back stress" due to the entropic resistance to molecular alignment, is defined exactly as before:

\[ T_B = \frac{C_R}{3} \sqrt{N} \mathcal{L}^{-1} \left( \frac{\lambda^p_{\text{chain}}}{\sqrt{N}} \right) B_B' \quad (5.38) \]

Where \( \lambda^p_{\text{chain}} \) is the stretch on a chain in the eight-chain network, \( \mathcal{L} \) is the Langevin function defined by \( \mathcal{L}(\beta) \equiv \coth \beta - \frac{1}{\beta} \), \( B_B' \) is the deviatoric part of the left Cauchy-Green tensor, \( F_B F_B^T \); \( \sqrt{N} \) is the limiting chain extensibility; and \( C_R \equiv nk\theta \) is the rubbery modulus.
The total stress in the polymer is given as the tensorial sum of the $\alpha$ and $\beta$ intermolecular stresses and the network (back) stress:

$$T = T_A + T_B$$

The driving stresses are used to specify the direction tensors $N_{A\alpha}$ and $N_{B\beta}$ in the plastic flow rules (equations 5.32 and 5.33):

$$N_{A\alpha} = \frac{1}{\sqrt{2\tau_A}} T_{A\alpha}'$$

$$N_{B\beta} = \frac{1}{\sqrt{2\tau_B}} T_{B\beta}'$$

The effective equivalent shear stresses $\tau_A$ and $\tau_B$ are given by:

$$\tau_A = \sqrt{\frac{1}{2} T_{A\alpha}' T_{A\alpha}'}$$

$$\tau_B = \sqrt{\frac{1}{2} T_{B\beta}' T_{B\beta}'}$$

Finally, two constitutive laws are prescribed for the $\alpha$ and $\beta$ viscoplastic behavior:

$$\dot{\gamma}_\alpha^P = \dot{\gamma}_{0,\alpha}^P \exp \left[ -\frac{\Delta G_\alpha}{k\theta} \left( 1 - \frac{\tau_A}{s_{\alpha} + \alpha_{p,\alpha} p} \right) \right]$$

$$\dot{\gamma}_\beta^P = \dot{\gamma}_{0,\beta}^P \exp \left[ -\frac{\Delta G_\beta}{k\theta} \left( 1 - \frac{\tau_B}{s_{\beta} + \alpha_{p,\beta} p} \right) \right]$$

Where $\dot{\gamma}_{0,i}^P (i = \alpha, \beta)$ is the pre-exponential factor proportional to the attempt frequency, $\Delta G_i$ is the activation energy, $p$ is the pressure, and $\alpha_{p,i}$ is the pressure coefficient. The internal variable $s_i$ is the athermal shear strength, related to the shear modulus and said
to evolve to a preferred state with plastic straining:

\[
\begin{align*}
  s_{0,\alpha} & = \frac{0.077\mu_\alpha}{1 - \nu_\alpha} \\
  \dot{s}_\alpha & = h_\alpha \left( 1 - \frac{s_\alpha}{s_{ss,\alpha}} \right) \dot{\gamma}_\alpha^p \\
  s_{0,\beta} & = \frac{0.077\mu_\beta}{1 - \nu_\beta} \\
  \dot{s}_\beta & = h_\beta \left( 1 - \frac{s_\beta}{s_{ss,\beta}} \right) \dot{\gamma}_\beta^p
\end{align*}
\]

Where \( h_i \) (\( i = \alpha, \beta \)) is the softening slope and \( s_{ss,i} \) is the "preferred state". This internal variable allows the temperature dependence of the yield stress to mimic the temperature dependence of the elastic shear moduli, and its evolution captures the strain softening phenomenon. In the most general form of this constitutive model, the strain softening phenomenon may be considered as the sum of the softening in the \( \alpha \) and \( \beta \) components. Overall, equations 5.44 and 5.45 capture the rate-, temperature-, and pressure-dependence of yield in the polymer, in addition to strain softening.
5.2.3 Summary

Kinematic Relations:

\[ F_{A_\alpha} = F_{A_\beta} = F_B = F \]
\[ F_{A_\alpha} = F^e_{A_\alpha} F^p_{A_\alpha} \]
\[ F_{A_\beta} = F^e_{A_\beta} F^p_{A_\beta} \]
\[ F^p_{A_\alpha} = R_{A_\alpha} U^p_{A_\alpha} = V^p_{A_\alpha} R_{A_\alpha} \]
\[ F^p_{A_\beta} = R_{A_\beta} U^p_{A_\beta} = V^p_{A_\beta} R_{A_\beta} \]
\[ L_{A_\alpha} = L^e_{A_\alpha} + F^e_{A_\alpha} L^p_{A_\alpha} F^{-1} \]
\[ L_{A_\beta} = L^e_{A_\beta} + F^e_{A_\beta} L^p_{A_\beta} F^{-1} \]
\[ \dot{F}^p_{A_\alpha} = D^p_{A_\alpha} F^p_{A_\alpha} \]
\[ \dot{F}^p_{A_\beta} = D^p_{A_\beta} F^p_{A_\beta} \]
\[ D^p_{A_\alpha} = \dot{\gamma}^p_{A_\alpha} N^p_{A_\alpha} \]
\[ D^p_{A_\beta} = \dot{\gamma}^p_{A_\beta} N^p_{A_\beta} \]
\[ F^e_{A_\alpha} = F_{A_\alpha} F^{e-1}_{A_\alpha} \]
\[ F^e_{A_\beta} = F_{A_\beta} F^{e-1}_{A_\beta} \]

Kinematic Assumptions:

\[ \det F^p_{A_\alpha} = \det F^p_{A_\beta} = 1 \]
\[ W^p_{A_\alpha} = W^p_{A_\beta} = 0 \]

Constitutive Relations:

\[ T_{A_\alpha} = \frac{1}{J_\alpha} \mathcal{L}^e_{A_\alpha} \left[ \ln U^e_{A_\alpha} \right] \]
\[ T_{A_\beta} = \frac{J_\beta}{J_\alpha} \mathcal{L}^e_{A_\beta} \left[ \ln U^e_{A_\beta} \right] \]
\[ T_B = \frac{C_B}{\chi_{\text{chain}}} \mathcal{L}^{-1} \left( \frac{\lambda_{\text{chain}}^p}{\sqrt{N}} \right) \mathbf{B}_B \]
\[ T = T_{A_\alpha} + T_{A_\beta} + T_B \]
Constitutive Relations (continued):

\[ \tau_\alpha = \sqrt{\frac{1}{2} T_{\alpha\alpha}' T_{\alpha\alpha}'}, \]
\[ \tau_\beta = \sqrt{\frac{1}{2} T_{\beta\beta}' T_{\beta\beta}'}, \]
\[ N_\alpha = \frac{1}{\sqrt{2\tau_\alpha}} T_{\alpha\alpha}' \]
\[ N_\beta = \frac{1}{\sqrt{2\tau_\beta}} T_{\beta\beta}' \]
\[ \dot{\gamma}_\alpha^P = \dot{\gamma}_{0,\alpha}^P \exp \left[ -\frac{\Delta G_\alpha}{k_\theta} \left( 1 - \frac{\tau_\alpha}{s_\alpha + \alpha_{p,\alpha}^P} \right) \right] \]
\[ \dot{\gamma}_\beta^P = \dot{\gamma}_{0,\beta}^P \exp \left[ -\frac{\Delta G_\beta}{k_\theta} \left( 1 - \frac{\tau_\beta}{s_\beta + \alpha_{p,\beta}^P} \right) \right] \]
\[ s_{0,\alpha} = \frac{0.077\mu_\alpha}{1 - \mu_\alpha}; \quad \dot{s}_\alpha = h \left( 1 - \frac{s_{0,\alpha}}{s_{ss,\alpha}} \right) \dot{\gamma}_\alpha^P \]
\[ s_{0,\beta} = \frac{0.077\mu_\beta}{1 - \mu_\beta}; \quad \dot{s}_\beta = h \left( 1 - \frac{s_{0,\beta}}{s_{ss,\beta}} \right) \dot{\gamma}_\beta^P \]

Material Properties:

\[ \mu_\alpha(\theta, \dot{\epsilon}); \quad \kappa_\alpha(\theta, \dot{\epsilon}) \]
\[ \mu_\beta(\theta, \dot{\epsilon}); \quad \kappa_\beta(\theta, \dot{\epsilon}) \]
\[ C_R; \sqrt{N} \]
\[ \Delta G_\alpha; \quad \dot{\gamma}_{0,\alpha}^P \]
\[ \Delta G_\beta; \quad \dot{\gamma}_{0,\beta}^P \]
\[ \alpha_{p,\alpha}; \quad h_\alpha; \quad s_{ss,\alpha} \]
\[ \alpha_{p,\beta}; \quad h_\beta; \quad s_{ss,\beta} \]

5.2.4 Numerical Implementation

In order to use this proposed constitutive model for predicting material response under various loading conditions, the kinematics and constitutive laws developed here were implemented numerically into a commercial finite element code, ABAQUS/Explicit. ABAQUS allows for user-defined material constitutive response through a VUMAT (explicit-code user material) subroutine that is linked to the Fortran source code. ABAQUS passes in a deformation gradient, along with a time step and material properties, and the VUMAT
CHAPTER 5. CONSTITUTIVE MODEL

subroutine returns the updated Cauchy stress tensor components. The VUMAT is called at each time increment, and loops through all material points (element integration points).

Like most user subroutines, the VUMAT for this particular constitutive model uses solution-dependent state variables to carry deformation information from one step to the next. For a 3D model, this VUMAT requires 41 state variables: absolute temperature $\theta$; plastic strain rates $\dot{\gamma}_\alpha^p$ and $\dot{\gamma}_\beta^p$; shear strength $s_\alpha$ and $s_\beta$; and the nine tensorial components of $F_{A\alpha}^p$, $F_{A\beta}^p$, $F_{A\lambda}^p$, and $F_{A\varphi}^p$. Symmetry in 2D models reduces the number of required state variables to 25. However, in both 2D and 3D, each state variable is actually an array of numbers, with an element (value) for that particular quantity at each integration point. At the beginning of each time step, the old (previous step) values of each of these quantities is recalled from the variable location; at the end of each time step, the new (current step) values are written to the variable locations. Under this framework, it is possible to create material constitutive response that is dependent upon deformation history, deformation state, and deformation rate.

The application of a user-defined material subroutine also requires passing necessary material constants and model parameters from the input deck - the text interface for model generation - into the material subroutine. The VUMAT associated with this model requires values for 15 material constants in the input deck: Poisson ratio $\nu$; plastic strain rate pre-exponential factors $\dot{\gamma}_{\alpha,0}^p$ and $\dot{\gamma}_{\beta,0}^p$; activation energies $\Delta G_\alpha$ and $\Delta G_\beta$; softening slopes $h_\alpha$ and $h_\beta$; pressure coefficients $\alpha_{p,\alpha}$ and $\alpha_{p,\beta}$; limiting chain extensibility $\sqrt{N}$; rubbery modulus $C_R$; bulk modulus $\kappa_B$ in component B; density $\rho$; specific heat $c_p$; and strain rate threshold $\dot{\epsilon}_{th}$. The determination of values for each of these material constants and model parameters shall be covered in-depth in the next section of this chapter.

5.3 Material Constants and Model Parameters

In order to implement the constitutive model developed here, a number of material constants and model parameters needed to be determined. This section shall cover the methodologies used to determine these necessary numerical values, for each of the model components: the linear elastic springs, the viscoplastic dashpots, and the Langevin spring.
5.3.1 Linear Elastic Springs

The constitutive laws for the linear elastic springs are given as:

\[
T_{A\alpha} = \frac{1}{J_{A\alpha}} L_{A\alpha}^e \left[ \ln U_{A\alpha}^e \right],
\]

\[
T_{A\beta} = \frac{1}{J_{A\beta}} L_{A\beta}^e \left[ \ln U_{A\beta}^e \right].
\]

The only material constants in these constitutive laws are contained within \( L_{A\alpha}^e \) and \( L_{A\beta}^e \), the fourth-order modulus tensors for the \( \alpha \) and \( \beta \) components, respectively. As discussed in section 5.1.2, the formulation of these modulus tensors requires knowledge of any two component-specific elastic constants. Since the DMA experimentation conducted in this study was performed in uniaxial tension, the elastic storage modulus measured is approximately equivalent to the material's Young's Modulus. By decomposing the measured storage modulus reference curves into \( \alpha \) and \( \beta \) components, as described in section 3.4, we analytically generated component-specific data for the Young's Modulus of the two materials. The component curves give the temperature dependence of these moduli, and the rate-dependent shifts of the corresponding viscoelastic transitions, also determined during DMA testing and analysis, give the strain rate dependence of these moduli. Thus the DMA experimentation and analysis techniques described in Chapter 3 of this thesis lead directly to half of the material constants needed to describe the linear elastic springs of the model: \( E_{A\alpha}(\theta, \dot{\varepsilon}) \) and \( E_{A\beta}(\theta, \dot{\varepsilon}) \).

Within the VUMAT subroutine, a framework was constructed for calculating these moduli values, depending on the current deformation state. Using the strain increment tensor \( \mathbf{E}^{\Delta t} \), a scalar equivalent strain increment was calculated for each integration point:

\[
\varepsilon_{eq} = \sqrt{\frac{2}{3} \mathbf{E}^{\Delta t} \mathbf{E}^{\Delta t}}
\]  

(5.50)

This equivalent strain increment was then simply divided by the time increment to give an estimate of the current strain rate. If the strain rate were too low (i.e. zero), then the threshold strain rate passed in from the input deck would instead be used as an estimate of the current strain rate. In the isothermal model, current temperature is the same as initial
CHAPTER 5. CONSTITUTIVE MODEL

...temperature, which is provided in the input deck. With the current strain rate and current temperature, \( E_\alpha \) and \( E_\beta \) are calculated at each time step following the numerical routines detailed in the MATLAB code of Appendices C and D. Thus, these two material properties are operationally assigned within the VUMAT.

Ideally, the values for the second elastic constants needed to form each of the modulus tensors would also be derived from rate- and temperature-dependent experimental data. For convenience, it was decided to instead take a second elastic constant as truly constant (in both temperature and strain rate). Of all the elastic constants - \( E, \mu, \kappa, \nu \), etc. - the bulk modulus \( \kappa \) is the least likely to vary significantly with changing temperature or strain rate. The bulk modulus may be written as:

\[
\kappa = \frac{E}{3(1-2\nu)}
\]

As the material passes through its glass transition, the Poisson ratio \( \nu \) increases from \( \sim 0.33 \) to \( \sim 0.49 \), but since the Young’s modulus \( E \) decreases by two orders of magnitude, the bulk modulus stays at least within the same order of magnitude. However, the question of how to split available bulk modulus values into \( \alpha \) and \( \beta \) contributions is not a trivial one. Also, we are predominately concerned with the glassy behavior of amorphous polymers in this study - changes in material behavior through the glass transition are not as important at this point. In the end, it was decided to take the Poisson ratio as a constant in both temperature and strain rate, and to give the \( \alpha \) and \( \beta \) components the same value of \( \nu \). A physical understanding of this material parameter suggests that both the \( \alpha \) and the \( \beta \) components should exhibit a Poisson ratio close to the Poisson ratio of the bulk material.

It should be noted, however, that once adiabatic heating and thermal softening phenomena are incorporated into the model, it will be very possible for the material to pass through its glass transition with increased plastic straining. At that point, the methods for calculating elastic constants will need revision. Constant values for the Poisson ratio were determined from extensive data in the literature. For PC, values were set as \( \nu_\alpha = \nu_\beta = 0.38 \); for PMMA, \( \nu_\alpha = \nu_\beta = 0.35 \).
5.3.2 Viscoplastic Dashpots

The viscoplastic dashpots of the proposed constitutive model are defined by the constitutive laws for the rate of plastic straining:

\[
\dot{\gamma}_\alpha^P = \dot{\gamma}_0^\alpha \exp \left[ \frac{-\Delta G_\alpha}{k\theta} \left( 1 - \frac{\tau_\alpha}{s_\alpha + \alpha_{p,\alpha}p} \right) \right]
\]

\[
\dot{\gamma}_\beta^P = \dot{\gamma}_0^\beta \exp \left[ \frac{-\Delta G_\beta}{k\theta} \left( 1 - \frac{\tau_\beta}{s_\beta + \alpha_{p,\beta}p} \right) \right]
\]

The model parameters in these equations are the pre-exponential factors \( \dot{\gamma}_0^\alpha \) and \( \dot{\gamma}_0^\beta \), the activation energies \( \Delta G_\alpha \) and \( \Delta G_\beta \), and the shear strength values \( s_\alpha \) and \( s_\beta \). In the development of the original constitutive model for thermoplastic behavior, from which this proposed model is derived, a method was devised for calculating the pre-exponential factor and the activation energy from experimental yield data. Two experimental shear yield values are used - either from tests at different temperatures or from tests at different shear strain rates. The constitutive law must hold true for both cases, so two simultaneous equations may be constructed by substituting the \((\tau_y, \theta)\) or \((\tau_y, \dot{\gamma})\) experimental data pairs into the constitutive equation. It is assumed that the temperatures or shear strain rates (whichever was not varied between experiments) are known, and that the material constant \( \alpha_p \) is known. The pressure at yield may be analytically determined from the shear yield stress and the deformation mode (e.g. uniaxial tension). Also, at yield, the shear strength \( s \) has not yet begun to decay - it evolves to a steady state only with plastic straining. Argon (1973) developed an analytical expression for the initial value of this internal variable:

\[
s_0 = \frac{0.077\mu}{1 - \nu}
\]

Thus the shear strength \( s \) at yield is also known, assuming that any two elastic constants are known. Since \( k \) is a constant (Boltzmann’s constant), everything in the two simultaneous equations are known, except for the model parameters \( \dot{\gamma}_0 \) and \( \Delta G \). The two equations in two unknowns are solved for these parameters of interest.

For the case of the revised model, where we now have two sets of pre-exponential factors and activation energies that need to be determined, we may apply the same methodology to
each component separately. Following previous discussion, two component-specific elastic constants may be analytically determined for any temperature/strain rate combination, and thus \( s_\alpha \) and \( s_\beta \) may be calculated from Argon's equation above. Both the \( \alpha \) and \( \beta \) components will see the same temperature and strain rate, and thus these variables are known from the test conditions. Assuming that the component-specific pressure coefficients \( \alpha_{p,\alpha} \) and \( \alpha_{p,\beta} \) are also known (discussed later), the only quantities that need to be resolved are the component-specific shear yield stress values.

The component-specific shear yield stress values are determined through a component-wise split of the experimental yield stress values. The technique is derived from the Ree-Eyring yield models, which assume that global yield strength may be decomposed into \( \alpha \) and \( \beta \) contributions. In order to determine the constants for their Ree-Eyring yield models, Roetling (1965) and Bauwens et al (1969), (1972) assumed that at the highest temperatures and lowest strain rates, only the \( \alpha \)-process contributes to the yield strength, since the \( \beta \)-process is fully relaxed. They then assume that at lower temperatures and higher strain rates, beyond the transition threshold, both the \( \alpha \) and \( \beta \) processes contribute to material yield strength. Following this procedure, the experimental yield data of this study was decomposed as described in figures 5-3 and 5-4.

In figure 5-3, the component-wise split of the PC shear yield data is shown. Below the transition strain rate, approximately 260 s\(^{-1}\), it is assumed that only the \( \alpha \)-process contributes to plastic deformation resistance; above the transition, \( \alpha \) and \( \beta \) both contribute. The \( \beta \) contribution in the \( \alpha+\beta \) strain rate regime was determined from the difference between the \( \alpha+\beta \) data trendline and the \( \alpha \) data trendline. The \( \alpha \) and \( \beta \) trendlines are then used to calculate component-specific shear yield stress values at two different strain rates. These values complete the set of information necessary for calculating the PC model parameters \( \gamma_{0,\alpha}^P \), \( \gamma_{0,\beta}^P \), \( \Delta G_\alpha \), and \( \Delta G_\beta \). Table 5.1 summarizes this information for the case of PC; table 5.2 provides the resulting values for the model parameters.

In figure 5-4, the component-wise split of PMMA shear yield data is shown. Since the Instron compression tests of this study did not provide yield data close to or below the predicted transition strain rate, additional yield data was needed. This necessary data was generated from the Ree-Eyring model and corresponding \( \alpha \)-process parameters.
Figure 5-3: Component-wise split of PC true shear yield stress data. Below the transition strain rate (~260 s\(^{-1}\)), it is assumed that only the \(\alpha\)-process contributes to plastic deformation resistance; above the transition, \(\alpha\) and \(\beta\) both contribute. Trendlines fit to the data are used to determine model parameters \(\gamma_0\) and \(\Delta G\).

Table 5.1: Experimental yield test data for calculating PC \(\alpha\)-process (left) and \(\beta\)-process (right) model parameters.

<table>
<thead>
<tr>
<th></th>
<th>Test 1</th>
<th>Test 2</th>
<th></th>
<th>Test 1</th>
<th>Test 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\gamma) [s(^{-1})]</td>
<td>1.73x10(^{-3})</td>
<td>1.73x10(^{-1})</td>
<td>(\gamma) [s(^{-1})]</td>
<td>1.73x10(^3)</td>
<td>1.73x10(^4)</td>
</tr>
<tr>
<td>(\tau_{\gamma,\alpha}) [MPa]</td>
<td>39.34</td>
<td>43.99</td>
<td>(\tau_{\gamma,\beta}) [MPa]</td>
<td>8.90</td>
<td>19.67</td>
</tr>
<tr>
<td>(s_{\alpha}) [MPa]</td>
<td>72.72</td>
<td>73.62</td>
<td>(s_{\beta}) [MPa]</td>
<td>12.07</td>
<td>18.31</td>
</tr>
<tr>
<td>(\alpha_{p,\alpha}) [MPa]</td>
<td>0.168</td>
<td>0.168</td>
<td>(\alpha_{p,\beta}) [MPa]</td>
<td>0.245</td>
<td>0.245</td>
</tr>
<tr>
<td>(p_{\beta}) [MPa]</td>
<td>23.26</td>
<td>26.05</td>
<td>(p_{\gamma}) [MPa]</td>
<td>36.40</td>
<td>44.13</td>
</tr>
<tr>
<td>(\theta) [K]</td>
<td>298</td>
<td>298</td>
<td>(\theta) [K]</td>
<td>298</td>
<td>298</td>
</tr>
</tbody>
</table>

Table 5.2: PC model viscoplastic parameters calculated from the data of table 5.1

<table>
<thead>
<tr>
<th>Process</th>
<th>(\alpha)</th>
<th>(\beta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\dot{\gamma}_0) [s(^{-1})]</td>
<td>2.94x10(^{16})</td>
<td>3.39x10(^5)</td>
</tr>
<tr>
<td>(\Delta G) [J]</td>
<td>3.744x10(^{-19})</td>
<td>3.769x10(^{-20})</td>
</tr>
</tbody>
</table>
Figure 5-4: Component-wise split of PMMA true shear yield stress data: (●) data from current study and (▼) analytical data generated from α-process Ree-Eyring parameters of Bauwens-Crowet (1973). Below the transition strain rate (~10^{-3} s^{-1}), it is assumed that only the α-process contributes to plastic deformation resistance; above the transition, α and β both contribute. Trendlines fit to the data are used to determine model parameters γ₀ and ΔG.
Table 5.3: Experimental yield test data for calculating PMMA $\alpha$-process (left) and $\beta$-process (right) model parameters.

<table>
<thead>
<tr>
<th>Test</th>
<th>$\dot{\gamma}$ [$s^{-1}$]</th>
<th>$\tau_{\alpha}$ [MPa]</th>
<th>$s_{\alpha}$ [MPa]</th>
<th>$\alpha_{p,\alpha}$</th>
<th>$p_y$ [MPa]</th>
<th>$\theta$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.73 \times 10^{-6}$</td>
<td>51.83</td>
<td>76.59</td>
<td>0.26</td>
<td>30.42</td>
<td>298</td>
</tr>
<tr>
<td>2</td>
<td>$1.73 \times 10^{-4}$</td>
<td>57.52</td>
<td>84.49</td>
<td>0.26</td>
<td>33.71</td>
<td>298</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test</th>
<th>$\dot{\gamma}$ [$s^{-1}$]</th>
<th>$\tau_{\beta}$ [MPa]</th>
<th>$s_{\beta}$ [MPa]</th>
<th>$\alpha_{p,\beta}$</th>
<th>$p_y$ [MPa]</th>
<th>$\theta$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.73</td>
<td>48.06</td>
<td>73.74</td>
<td>0.26</td>
<td>68.19</td>
<td>298</td>
</tr>
<tr>
<td>2</td>
<td>$1.73 \times 10^2$</td>
<td>84.85</td>
<td>76.72</td>
<td>0.26</td>
<td>92.67</td>
<td>298</td>
</tr>
</tbody>
</table>

Table 5.4: PMMA model viscoplastic parameters calculated from the data of table 5.3

<table>
<thead>
<tr>
<th>Process</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\dot{\gamma}_0$ [$s^{-1}$]</td>
<td>$6.95 \times 10^{19}$</td>
<td>$1.77 \times 10^3$</td>
</tr>
<tr>
<td>$\Delta G$ [J]</td>
<td>$5.528 \times 10^{-18}$</td>
<td>$6.036 \times 10^{-29}$</td>
</tr>
</tbody>
</table>

given by Bauwens-Crowet (1973) in her study of the compressive yield behavior of PMMA. Analytically-generated data was shifted vertically (increased stress levels) until the analytical and experimental data points at $10^{-3}$ s$^{-1}$ coincided. During shifting, the slope of the analytical $\tau_\gamma$-$\log(\dot{\gamma})$ curve was held constant. This procedure for adding data assumes that although different brands of PMMA may have different strengths, they shall all have approximately the same sensitivity to changes in strain rate; in this case, the procedure is only applied within the $\alpha$-region, where strain rate sensitivity is minimal anyway (2-3 MPa increase in yield strength per decade increase in strain rate).

As with PC, it is assumed that below the transition strain rate, approximately $10^{-3}$ s$^{-1}$, only the $\alpha$-process contributes to plastic deformation resistance; above the transition, $\alpha$ and $\beta$ both contribute. The data trendlines in these two regimes are used to calculate component-specific shear yield stress values at two different strain rates. These values derived from figure 5-4 complete the set of information necessary for calculating the PMMA model parameters $\dot{\gamma}_{0,\alpha}$, $\dot{\gamma}_{0,\beta}$, $\Delta G_{\alpha}$, and $\Delta G_{\beta}$. Table 5.3 summarizes this information; table 5.4 provides the resulting values for the PMMA model parameters.

The remaining model parameters for the viscoplastic dashpots are the internal shear strengths $s_\alpha$ and $s_\beta$. As described earlier, the initial values of these parameters may be
prescribed through Argon’s relation, so long as two component-specific elastic constants are known:

\[ s_{0,\alpha} = \frac{0.077\mu_\alpha}{1 - \nu_\alpha} \]
\[ s_{0,\beta} = \frac{0.077\mu_\beta}{1 - \nu_\beta} \]

Section 5.3.1 details the procedure for determining two component-specific elastic constants. In the most general form of this constitutive model, both of these shear strength values evolve with plastic straining, in order to capture the strain softening phenomenon:

\[ \dot{s}_\alpha = h_\alpha \left( 1 - \frac{s_{ss,\alpha}}{s_{ss,\alpha}} \right) \dot{\gamma}_\alpha^p \]
\[ \dot{s}_\beta = h_\beta \left( 1 - \frac{s_{ss,\beta}}{s_{ss,\beta}} \right) \dot{\gamma}_\beta^p \]

For this study, strain softening in PC and PMMA was captured with evolution only in \( s_\alpha \); \( s_\beta \) was taken as a constant fraction of \( \mu_\beta \). The evolution of the shear strength is intended to model the structural changes associated with yield which help enable permanent chain segment motion; the decision to use only the \( \alpha \)-process to model this phenomenon is physically justified by the fact that the \( \alpha \)-motions are generally the dominant molecular motions of large strain deformation. Thus, for the purposes of this study, the only parameters to be determined were the softening slope \( h_\alpha \) and the preferred state \( s_{ss,\alpha} \). These parameters were determined by fitting the model to the data. Stress-strain curves generated in single-element simulations of uniaxial compression were compared to experimental stress-strain curves. Values for \( h_\alpha \) and \( s_{ss,\alpha} \) were iterated in parallel in order to achieve optimal agreement between the simulated and experimental stress-strain curves, over the region dominated by strain softening. The strain rates chosen for curve fitting were the lowest ones available, in order to avoid any thermal softening in the data associated with adiabatic heating. The PC and PMMA model parameters \( h_\alpha \) and \( s_{ss,\alpha} \), determined by curve fitting, are given in table 5.5.

In the constitutive equations of the viscoplastic dashpots, there are also two material constants to be specified: pressure coefficients \( \alpha_{p,\alpha} \) and \( \alpha_{p,\beta} \). In order to determine the pres-
Table 5.5: PC and PMMA strain softening model parameters determined by curve fitting.

<table>
<thead>
<tr>
<th>h₀ [MPa]</th>
<th>σₜₜ,₀ [MPa]</th>
<th>PC</th>
<th>PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>0.67ₜ₀,₀</td>
<td>200</td>
<td>0.73ₜ₀,₀</td>
</tr>
</tbody>
</table>

Figure 5-5: Temperature dependence of PC yield point in both tension and compression, at a strain rate of $4.16 \times 10^{-3} \text{s}^{-1}$ (Bauwens-Crowet et al., 1972). Data reveals the pressure dependence of yield, in the both the $\alpha$ and $\beta$ regions.

Sure coefficients of PC, we revisit the experimental data of Bauwens-Crowet et al. (1972). Figure 5-5 shows the temperature dependence of the PC yield strength in both tension and compression at a strain rate of $4.16 \times 10^{-3} \text{s}^{-1}$, as reported by Bauwens-Crowet et al.. The fact that the tension and compression data does not coincide at every temperature indicates that yield strength depends upon pressure. Furthermore, the fact that the slopes of the tension and compression data curves change by different amounts through the transition temperature ($-50^\circ \text{C}$) indicates that the $\alpha$ and $\beta$ processes have different pressure dependencies. Since the $\alpha$ and $\beta$ processes have been shown to have different temperature and strain rate dependencies, this finding is to be expected.
Within range I of figure 5-5, where the β-process contribution to yield strength is negligible, the relationship between the compressive yield strength and the tensile yield strength at any particular temperature is given as:

\[
\frac{\sigma_{yc}}{\sigma_{yt}} = 1.112
\]  

(5.51)

An α-process pressure coefficient may be derived from this empirical relationship by analyzing two hypothetical tests at the same temperature and strain rate: one performed in uniaxial tension, the other performed in uniaxial compression. For each of these tests, we apply the plastic strain rate flow rule at the point of yield:

\[
\dot{\gamma}^P = \dot{\gamma}_0^P \exp \left[ \frac{-\Delta G}{k\theta} \left( 1 - \frac{\tau_{yt}}{s + \alpha_p p_t} \right) \right]
\]  

(5.52)

\[
\dot{\gamma}^P = \dot{\gamma}_0^P \exp \left[ -\frac{\Delta G}{k\theta} \left( 1 - \frac{\tau_{yc}}{s + \alpha_p p_c} \right) \right]
\]  

(5.53)

Rearranging these equations:

\[
\tau_{yt} = (s + \alpha_p p_t) [C]
\]  

(5.54)

\[
\tau_{yc} = (s + \alpha_p p_c) [C]
\]  

(5.55)

Where \( C \) is a lumped constant with the same value in both cases. In the case of uniaxial tension and compression,

\[
p_t = -\frac{\sigma_{yt}}{3}
\]  

(5.56)

and

\[
p_c = \frac{\sigma_{yc}}{3}
\]  

(5.57)

Also, from our empirical relation,

\[
\sigma_{yt} = \frac{\sigma_{yc}}{1.112}
\]  

(5.58)

and

\[
\tau_{yc} = 1.112 \tau_{yt}
\]  

(5.59)
Substituting these relations into equations 5.54 and 5.55,

\[ \tau_{yt} = \left( s + \alpha_p \left( -\frac{\sigma_{yc}}{3.336} \right) \right) [C] \]  
(5.60)

\[ \tau_{yt} = \frac{1}{1.112} \left( s + \alpha_p \left( \frac{\sigma_{yc}}{3} \right) \right) [C] \]  
(5.61)

Finally, setting the right-hand sides of equations 5.60 and 5.61 equal and solving for the pressure coefficient, we obtain:

\[ \alpha_p = 0.168 \frac{s}{\sigma_{yc}} \]  
(5.62)

As a first approximation, we take the quotient \( \frac{s}{\sigma_{yc}} \) to be unity, and the \( \alpha \)-process pressure coefficient is given as 0.168.

In order to determine the \( \beta \)-process pressure coefficient, the range I data of figure 5-5 is examined. In this region, the data gives another empirical relationship between compressive yield strength and tensile yield strength:

\[ \frac{\sigma_{yc}}{\sigma_{yt}} = 2.275 \]  
(5.63)

Assuming this relationship to be the combined effect of the \( \alpha \) and \( \beta \) process pressure dependencies, we may determine the effect of the \( \beta \)-process alone by simple decomposition:

\[ \left( \frac{\sigma_{yc}}{\sigma_{yt}} \right)_\beta = \left( \frac{\sigma_{yc}}{\sigma_{yt}} \right)_{\alpha + \beta} - \left( \frac{\sigma_{yc}}{\sigma_{yt}} \right)_\alpha = 2.275 - 1.112 = 1.163 \]  
(5.64)

Starting with this new empirical relationship and following the same steps outlined for determining the \( \alpha \)-process pressure coefficient, the PC \( \beta \)-process pressure coefficient is found to be 0.245.

To determine the pressure coefficients for PMMA, sufficient yield data was not available from any single source in the literature, as had been the case for PC. Most studies lacked information concerning material yield behavior in the \( \alpha \)-dominated regime, since this occurs at such low strain rates and/or high temperatures. In fitting the original constitutive model to experimental PMMA data, Arruda et al. (1995) used a pressure coefficient of 0.26. Based on the strain rates \((10^{-3} \text{ s}^{-1} \text{ to } 10^{-1} \text{ s}^{-1})\) and temperatures (23°C to 75°C) of their tests,
it may be assumed that this pressure coefficient is an average of the pressure coefficients of the $\alpha$ and $\beta$ processes. Likely, the $\alpha$-process pressure coefficient is a bit lower than 0.26, and the $\beta$-process coefficient is a bit higher than 0.26. Without any knowledge of the actual breakdown, both the $\alpha$ and $\beta$ process pressure coefficients were set to 0.26, in order to maintain the average value used by Arruda et al.. In future applications of the model, it will be important to obtain more accurate values of these pressures coefficients. The pressure coefficients may be determined from tension and compression yield data at constant strain rate, over a temperature range that includes the material $\beta$-transition (as was done for PC). Likewise, the pressure coefficients may be determined from tension and compression yield data at constant temperature, over a sufficiently large range of strain rates. Also, the pressure dependencies of the two processes may be determined more directly, by experimentally quantifying the pressure-dependent shift of the $\alpha$ and $\beta$ transitions.

5.3.3 Langevin Spring

The Langevin spring, used in this constitutive model to capture the entropic resistance to chain alignment, is defined by the constitutive law for the "back stress" $T_B$:

$$ T_B = \frac{C_R}{3} \frac{\sqrt{N}}{\lambda_{\text{chain}}} \mathcal{L}^{-1} \left( \frac{\lambda_{\text{chain}}^p}{\sqrt{N}} \right) B'_B $$

This equation has two quantities that are not deformation-specific: the rubbery modulus $C_R$ and the limiting chain extensibility $\sqrt{N}$. Though these model parameters have physical meaning, values were obtained by fitting the model to the data. Stress-strain curves generated in single-element simulations of uniaxial compression were compared to experimental stress-strain curves. Values for $C_R$ and $\sqrt{N}$ were iterated in parallel in order to achieve optimal agreement between the simulated and experimental stress-strain curves, over the region dominated by strain hardening. Because of the interplay between strain softening and strain hardening at moderate strain values, the softening parameters $h_\alpha$ and $s_{ss,\alpha}$ often needed to also be adjusted in parallel, in order to obtain the most optimal fit. The strain rates chosen for curve fitting were the lowest ones available, in order to avoid any ther-
TABLE 5.6: PC and PMMA Langevin spring model parameters determined by curve fitting.

<table>
<thead>
<tr>
<th></th>
<th>PC</th>
<th>PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_R ) [MPa]</td>
<td>14.2</td>
<td>14.0</td>
</tr>
<tr>
<td>( \sqrt{\langle N \rangle} ) [( \sqrt{\nu} )]</td>
<td>2.3</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Normal softening in the data associated with adiabatic heating. The PC and PMMA model parameters \( C_R \) and \( \sqrt{\langle N \rangle} \), determined by curve fitting, are given in Table 5.6.

5.4 Model Prediction

Following numerical implementation of the constitutive model into ABAQUS/Explicit, and employing the material constants and model parameters described in the previous section, it is possible to explore material behavior in various loading situations through model-based predictions. These model-based predictions shall provide information regarding the role of the \( \alpha \) and \( \beta \) molecular processes in overall material response, for the various loading situations. This information in turn will help to develop a better theoretical understanding of the correlation between molecular structure and macroscopic mechanical response in amorphous polymers, for use in material design and selection.

Before this model may be used to predict and understand unknown material response, however, its accuracy must be verified in loading situations where material response has been well-documented. In this study, the constitutive model is validated by exploring predictions of material response to uniaxial compression, at a variety of strain rates. First, model behavior alone is examined, to ensure that the expected features of material response manifest themselves in the predicted behavior. Model behavior should reflect the theoretical understanding of deformation resistance that has been developed in Chapter 2 of this thesis. Secondly, model predictions are compared to the experimental data of this study. The simulated yield strengths and stress-strain curves should closely match the experimental yield strengths and stress-strain curves, from which the model parameters were derived.
5.4.1 Model Behavior

Constitutive model behavior for PC in uniaxial compression is given in figures 5-6 to 5-9. Figure 5-6 is a plot of true stress-true strain curves at four different strain rates, ranging from low \((10^{-3} \text{ s}^{-1})\) to high \((10^3 \text{ s}^{-1})\). These stress-strain curves were generated from single-element axisymmetric simulations in ABAQUS/Explicit. All simulations were isothermal, with heating effects neglected; the curves in figure 5-6 correspond to predicted material response at room temperature (298 K). The noise in the \(10^2 \text{ s}^{-1}\) curve is a consequence of numerical instability associated with "turning on and off"/activating the \(\beta\)-process, as this strain rate is almost identical to the transition strain rate at 298 K.

By carrying over the framework of the existing thermoplastics constitutive model, this new model is shown in figure 5-6 to capture the characteristic features of material response to large strain uniaxial deformation: initial linear elasticity, global yield, strain softening, and strain hardening. Also, the curves clearly demonstrate a rate-dependence, as expected. For instance, the model-predicted Young's Modulus is shown to increase with increasing strain rate, a result consistent with both the DMA and compression testing. This rate-dependence of the linear elastic region is a new feature of the model, the result of incorporating DMA viscoelastic analysis into the formulation.

The rate-dependence of the polymer yield point, as predicted by model simulations of uniaxial compression, is given as figure 5-7. While the original model was only capable of predicting a linear relationship between yield strength and the logarithm of strain rate (or near-linear, depending on how the shear modulus was defined), the new constitutive model clearly predicts a transition in material yield behavior. Again, this prediction is consistent with extensive data in the literature. Figure 5-7 also illustrates the relative contributions of the \(\alpha\) and \(\beta\) model components to the overall yield strength predicted. It is clear that the transition in the overall yield behavior begins when the \(\beta\)-contribution becomes non-negligible, as was intended. Although the plastic flow rule parameters \(\dot{\gamma_{0,\alpha}}, \dot{\gamma_{0,\beta}}, \Delta G_{\alpha}\), and \(\Delta G_{\beta}\) were determined from a piece-wise linear fit to the experimental data, the model-predicted yield curve is clearly non-linear in the transition regime. This feature of the model is a result of the unique viscoelastic property definitions which were developed from DMA analysis and factor into the predicted yield strength through the shear strength values \(s_o\).
and \( s_\beta \). The gradual transition that the model predicts is expected to be a realistic portrayal of the \( \beta \)-transition event, though no yield data was generated in this study for strain rates between 1 s\(^{-1}\) and 1200 s\(^{-1}\).

Figure 5-8 shows the model prediction of PC true stress-true strain behavior at 425 K, as a function of strain rate. This temperature is just below the glass-transition temperature of the PC used in this study, at a strain rate of 10\(^{-3}\) s\(^{-1}\). The model predicts a dramatic change in stress-strain behavior, as the strain rate is increased to moderate and high rates. This predicted phenomenon is conceptually identical to the \( \beta \)-transition in yield behavior: as strain rate is increased, the transition location shifts to a higher temperature. When the transition is located at or below the test temperature, that particular process contributes only a negligible amount to the overall deformation resistance. As strain rate is increased and the transition shifts to higher temperatures, beyond the test temperature, the associated process contributes significantly to the overall deformation resistance. In this case, the glass transition is very close to 425 K at the lowest strain rate (10\(^{-3}\) s\(^{-1}\)). However, the glass-transition location shifts 4.65°C per decade increase in strain rate, according to the DMA analysis that was incorporated into the model. Thus, as strain rate is increased, the predicted stress-strain response shows an increase in resistance to both elastic and plastic deformation. Though the phenomenon predicted in figure 5-8 is analogous to the predicted \( \beta \)-transition in the yield behavior, it is more dramatic in this case because there is no significant intermolecular resistance to deformation above the glass-transition.

In figure 5-9, the effect of the both the \( \alpha \) and \( \beta \) transitions on PC yield behavior can be seen. This plot shows the model-predicted PC yield strength as a function of both temperature and strain rate. The second curve from the top (25°C) is identical to the curve seen in figure 5-7; this room-temperature behavior may be used as a reference for comparing behaviors at other temperatures. The bottom curve shows yield behavior at 152°C, a temperature within the glass transition regime at a strain rate of 10\(^{-3}\) s\(^{-1}\). The effect of the proximity to the glass transition is clear: at the lowest strain rates, the slope of the yield curve drops off substantially. This effect, combined with figure 5-8, demonstrates that the model is able to predict a significant reduction in material deformation resistance associated with the relaxation of the \( \alpha \)-process. Also, the high temperature curve shows no
evidence of a $\beta$-transition - it has been shifted beyond the rate regime of interest. In the low temperature curve (-50°C), on the other hand, the $\beta$-transition has shifted in the opposite direction, towards a lower strain rate. At room temperature, the $\beta$-transition begins at a strain rate of approximately 100 s$^{-1}$; at -50°C, it occurs at 1 s$^{-1}$. In the second curve from the bottom (100°C), neither the $\alpha$ nor the $\beta$ transition is observed. For this particular temperature and range of strain rates, yield strength is linearly related to the logarithm of strain rate, and yield behavior could be modeled with the single-process Eyring theory.

Constitutive model behavior for PMMA in isothermal uniaxial compression is given in figures 5-10, 5-11, and 5-12. Figure 5-10 is a plot of true stress-true strain curves at four different strain rates, ranging from low (10$^{-3}$ s$^{-1}$) to high (10$^3$ s$^{-1}$). As with PC, these stress-strain curves were generated from single-element axisymmetric simulations in ABAQUS/Explicit, and correspond to isothermal material response at room temperature (298 K). In figure 5-10, the PMMA model is shown to capture the expected features of material response to large strain uniaxial deformation, as well as the experimentally-observed rate dependency. Figure 5-11 provides a more thorough examination of the rate-dependence...
Figure 5-7: Model prediction of PC yield behavior in uniaxial compression as a function of strain rate. In addition to the total yield strength, the numerically-predicted $\alpha$ and $\beta$ components of the yield strength are reported, for each strain rate.

Figure 5-8: Model prediction of PC true stress-true strain behavior at 425 K, as a function of strain rate. Curves were generated from single-element axisymmetric simulations of uniaxial compression.
Figure 5-9: Model prediction of PC yield behavior in uniaxial compression as a function of both temperature and strain rate. The highest temperature (152°C) is located within the glass-transition regime at a strain rate of $10^{-3}$ s$^{-1}$.

of this polymer’s yield point, as predicted by model simulations of uniaxial compression. In addition to the total yield strength, the numerically-predicted $\alpha$ and $\beta$ components of the yield strength are reported, for each strain rate. The $\beta$-component is shown to be non-negligible at strain rates as low as $10^{-4}$ s$^{-1}$, and just as large as the $\alpha$-component at $10^2$ s$^{-1}$. The PMMA model predicts a gradual transition in the yield behavior, owing to the introduction of $\beta$-process deformation resistance, extending from approximately $10^{-5}$ s$^{-1}$ to $10^{-2}$ s$^{-1}$. This unique yield behavior, and corresponding breakdown into $\alpha$ and $\beta$ process yield behavior, is consistent with the theoretical and experimental work on PMMA presented in Chapter 2.

Figure 5-12 shows the model-predicted yield strength of PMMA as a function of both temperature and strain rate. The second curve from the top (25°C) is identical to the curve seen in figure 5-11. The bottom curve shows yield behavior at 107°C, a temperature close to the glass-transition regime at a strain rate of $10^{-4}$ s$^{-1}$. The effect of the proximity to the glass transition is not apparent, since a yield strength could not be predicted for a strain rate of $10^{-4}$ s$^{-1}$. At this rate/temperature combination, neither the $\alpha$ nor the $\beta$ component of the
model contributes significantly to deformation resistance. Though evidence of a predicted \( \alpha \)-transition does not appear in the figure, all curves except for that corresponding to \(-50^\circ C\) show an increase in slope associated with the \( \beta \)-transition. The \( \beta \)-transition is shown to shift to increased strain rates with increased temperature, as is expected. At the lowest temperature (top curve), the \( \beta \) transition has shifted to a strain rate well below the range of interest, and the model predicts a near linear relationship between yield strength and the logarithm of strain rate. Over this entire range, material deformation resistance is governed by both the \( \alpha \) process and the \( \beta \) process - each process alone predicts a linear slope on this Eyring-type plot, and thus the combination is also a linear slope. These predictions agree very well with the experimental data of Bauwens-Crowet (1973).

5.4.2 Model v. Experiment

In the second phase of model validation, the numerical predictions of material response to large strain uniaxial deformation are compared to the experimental data of this study. The
Figure 5-11: Model prediction of PMMA yield behavior in uniaxial compression as a function of strain rate. In addition to the total yield strength, the numerically-predicted $\alpha$ and $\beta$ components of the yield strength are reported, for each strain rate.

Figure 5-12: Model prediction of PMMA yield behavior in uniaxial compression as a function of both temperature and strain rate. The highest temperature (107°C) is located close to the glass-transition regime at a strain rate of $10^{-4}$ s$^{-1}$.
success of the model was to be measured by the level of agreement between simulated yield strengths and stress-strain curves and experimental yield strengths and stress-strain curves.

Figures 5-13, 5-14, and 5-15 demonstrate the ability of the constitutive model to accurately predict PC material response in uniaxial compression, across a broad range of strain rates. Figure 5-13 is a plot of both model-predicted and experimental stress-strain behavior at low ($10^{-3}$ s$^{-1}$), moderate (1 s$^{-1}$), and high (5050 s$^{-1}$) strain rates. The largest deficiency observed in this plot is the inability of the model to capture the non-linearity of the elastic region of the curves. In the experimental data, yield is a distributed process, characterized by a gradual reduction in the slope of the stress-strain curve; in the model predictions, yield is a sudden event preceded by an elastic region of constant slope. As a result, the model-predicted yield point occurs at a lower strain value than in the experiments, and the curve that follows is offset from the experimental curve by 0.03-0.05 strain. If the curves are shifted such that the yield points are aligned, however, it becomes even more apparent that the model curves closely mimic the shape of the experimental curves at all strain rates, up to 80% strain.

Figure 5-14 is a plot of both the model-predicted and experimental yield strength of PC, across seven decades of strain rate. At all strain rates, the model predicts the experimental yield strength with less than 5% error. The larger discrepancies at the lowest and highest strain rates may be attributed to the interaction between the viscoplastic model parameters. While only two discrete values of the shear strength $s$ are used to calculate the pre-exponential factor and the activation energy for each process, the shear strength has a complicated dependence on both temperature and strain rate that can not be captured with just two points. Nonetheless, the amount of error introduced by this fact is certainly within acceptable limits, over the temperature/strain rate regime of interest. Figure 5-14 also emphasizes the most significant feature of the new constitutive model: the ability to accurately capture a transition in material behavior, associated with the restriction of secondary molecular motions. The model correctly predicts the strain rate regime of the transition, and gives us insight into its distributed nature, where experimental data is lacking.
Figure 5-15 emphasizes the fact that this ability of the model to correctly predict a transition in the yield behavior is directly attributable to a successful decomposition of intermolecular deformation resistance into the contributions from two distinct molecular processes. This plot is a comparison of the model-predicted and experimentally-derived breakdown of the PC shear yield strength, into $\alpha$ and $\beta$ contributions, across low, moderate, and high strain rates. The experimental curves are identical to those pictured in figure 5-3, derived from a piece-wise linear fit to the decomposed experimental data. The model-predicted data points are taken directly from numerical simulations of uniaxial compression, where it is possible to output the axial stress in the $\alpha$ and $\beta$ model components separately. These model-predicted data points are the shear stresses corresponding to the axial yield stress data points in figure 5-7. In all three regions - $\alpha$, $\beta$, and $\alpha+\beta$ - the model matches the experimental data very well. The model data, however, does not have the piece-wise linear character of the experimental curves; the transition regime is smoothed over by a gradual increase in the $\beta$-contribution. This natural smoothing is given by the influence of material elastic properties through the shear strength $s$, and is perhaps an even more realistic description of the transition process. By incorporating the viscoelastic behavior into the model yield process, the transition regime has the same character as the gradual transition in the storage modulus curve at the location of the $\alpha$-transition.

Figures 5-16, 5-17, and 5-18 provide the same comparison between model and experiment as 5-13, 5-14, and 5-15, respectively, for the case of PMMA. In figure 5-16, the model curves clearly capture the rate-dependence of the initial elastic portion and the yield point of the experimental curves at all strain rates. At the lowest strain rate, the model curve mimics very closely the entire experimental curve up to large strains. However, at moderate and high strain rates, there is a large discrepancy between model and experiment over the post-yield portion of the stress-strain curves. This is due to the significant thermal softening effects that are not accounted for in this isothermal constitutive model. In reality, the higher strain rates correspond to adiabatic deformation. Since the heat generated by plastic work does not have sufficient time to escape to the environment, the temperature-sensitive polymer thermally softens. Recent experiments by Rittel (1999) and Lerch, Gary, and Herve (2003) on PC have indicated that a polymer disk under high-rate compression may...
CHAPTER 5. CONSTITUTIVE MODEL

Figure 5-13: PC true stress-true strain behavior in uniaxial compression at low, moderate, and high strain rates: model prediction (dotted lines) and experiment (solid lines).

Figure 5-14: PC true yield strength in uniaxial compression as a function of strain rate: model prediction and experiment.
increase in temperature as much as 40°C with 80% plastic strain. This is a critical issue to be addressed in future iterations of the constitutive model. Nonetheless, figure 5-17 demonstrates the ability of this constitutive model to accurately predict the yield strength of PMMA across a very broad range of strain rates. Again, there is only slight discrepancy, on the order of 5%, owing to the difficulties in correctly calculating the viscoplastic model parameters. Finally, figure 5-18 reinforces the fact that this model's predictive capabilities are built upon a successful decomposition of intermolecular deformation resistance into two separate contributions.
Figure 5-16: PMMA true stress-true strain behavior in uniaxial compression at low, moderate, and high strain rates: model prediction (dotted lines) and experiment (solid lines).

Figure 5-17: PMMA true yield strength in uniaxial compression as a function of strain rate: model prediction and experiment.
Figure 5-18: Component-wise split of PMMA shear yield data. Dotted and solid lines are derived from experimental data, as described in figure 5-4; α-process (△), β-process (□), and α+β (●) markers are generated from model simulations, as in figure 5-11.
Chapter 6

Conclusions and Future Work

This study represents the basic science needed to help better design polymer-based systems to resist deformation and/or mechanical failure at high rates of strain. Though amorphous polymers have been used extensively as the structural material of engineering components that are designed to resist impact, mechanical behavior under high rates of deformation has not been well characterized. The first step in this study was to develop a thorough understanding of the high-rate behavior of amorphous polymers, from the molecular mechanisms of deformation resistance up to the macroscopic stress-strain response. Such an understanding was garnered through extensive literature searching, spanning all relevant work on the rate-dependence of polymeric materials. By drawing on the resources of previous published work, a comprehensive analytical and experimental research program was designed to characterize the mechanical behavior of amorphous polymers across a broad range of strain rates. The results of this research were then used to revise a physically-based constitutive model for large strain deformation of thermoplastics, which has been shown to be accurate at quasi-static rates of deformation. The revisions enable the predictive capabilities of the constitutive model to extend across moderate and high rates of strain, based on new understanding of the mechanisms of deformation resistance at these rates. This revised constitutive model, along with new analytical techniques associated with material viscoelastic behavior, shall allow for the scientific and systemic design of polymer-based material systems for high-rate applications.
The background research of this study, detailed in Chapter 2, was used to identify and understand the phenomena and mechanisms of rate-dependent polymer behavior. Early experimental data indicated the existence of an unknown strengthening mechanism in the moderate and high strain rate deformation of amorphous polymers. For a variety of these materials - PC, PMMA, PVC, PET - the yield behavior was observed to transition to a regime of increased strain rate sensitivity, beyond a threshold level particular to the polymer. Experiments indicated that this threshold level is determined by both temperature and strain rate; material transition could be induced by either decreasing the test temperature or increasing the test strain rate.

As the experimental evidence grew, theory emerged to address this unique transition phenomenon. The pre-existing Ree-Eyring theory (1955) was built into a yield model capable of capturing material yield behavior across a transition (see for instance Roetling (1965b), Bauwens-Crowet et al. (1969)). This Ree-Eyring theory was a modification of the general Eyring theory (1936) for rate-activated processes, to allow for the possibility of multiple rate-activated processes acting in tandem to control the flow of a material. When the Ree-Eyring theory is applied to polymer plasticity, it is assumed that these "processes" are related to specific degrees of freedom of the polymer chains. Thus the transition observed in the yield behavior is explained in terms of molecular-level motions: when a particular degree of freedom of the polymer chain suddenly becomes restricted at low temperatures and/or high strain rates, the overall material deformation resistance increases. At temperatures and strain rates below the transition threshold, only one restricted molecular motion (the "\(\alpha\)-process") contributes to material yield strength; above the transition threshold, the reported yield strength may be thought of as a measure of the combined deformation resistance originating from two restricted motions - \(\alpha\) and \(\beta\).

This theory, connecting molecular mechanisms of deformation resistance with macroscopic mechanical behavior, was furthered by the pioneering work of Bauwens (1972). Bauwens hypothesized a correlation between the observed transition in material yield behavior with the \(\beta\)-transition of the viscoelastic behavior. He argued that both transitions are governed by the same molecular motions, using measured activation energy values to corroborate his theory. He then built a modified version of the Ree-Eyring yield model,
based on viscoelastic loss tangent measurements, that was able to more accurately capture the distributed nature of the yield transition. Over the past three decades, the experimental and analytical work of other researchers has reinforced the ideas of Bauwens and his contemporaries. Split-Hopkinson bar testing has been employed repeatedly to confirm and examine the high-rate strengthening phenomenon in many amorphous polymers; the two-process Ree-Eyring yield model has been used extensively to capture material yield behavior over very large ranges in temperature and strain rate; measured activation energy values have been used to confirm Bauwens' hypothesis, concerning the connection between viscoelastic and yield behavior transitions; and specific molecular motions have been identified in association with the material \( \beta \)-transitions. In the case of PC, the \( \beta \)-transition has been attributed to the restriction of phenyl group rotations; in the case of PMMA, it is attributed to the restriction of ester side group rotations.

The combined experimental and analytical research program of this study was developed in consideration of the broad base of knowledge and theory that has been well-established in the literature. On the experimental side, investigation of viscoelastic behavior was chosen as a focal point, in order to gain more fundamental understanding of the material transitions, and to further the linkages between material viscoelastic, yield, and stress-strain behavior. On the analytical side, the concept of decomposing material deformation resistance into contributions from two different molecular processes proved central to the analysis and modeling techniques introduced here. This research is a natural continuation of previous efforts in other groups; both the approach to the problem and the solutions proposed here are backed by over three decades of experimental and theoretical conclusions.

Through dynamic mechanical analysis experiments, the viscoelastic behavior of PC and PMMA was investigated at low \( 10^{-3} \) to moderate \( 10^{-1} \) strain rates. Testing was conducted in uniaxial tension, using small rectangular specimens in a TA Instruments Q800 DMA. For each material, a storage modulus "reference curve" - elastic (Young's) modulus as a function of temperature - was established from viscoelastic measurements at a test frequency of 1 Hz. This test frequency corresponded to a strain rate of approximately \( 10^{-3} \) s\(^{-1} \). From the loss modulus and loss tangent measurements of the reference tests, the temperature location of significant viscoelastic transitions were determined. In both PC
and PMMA, only two significant transitions were identified for further investigation: the well-known \( \alpha \), or glass-transition, as well as a secondary, low-temperature \( \beta \)-transition. It is possible that other transitions, of less importance to the overall material response, are also present, but are overshadowed in magnitude by these two most important ones. Knowing that the temperature location of viscoelastic transitions are dependent upon strain rate, the nature of these two transitions were further investigated by increasing the test frequency. The rate-dependent shift of each significant transition was quantified by tracing the corresponding peaks in the loss modulus and loss tangent curves with increasing frequency. In both cases, the temperature location of the \( \beta \)-transition was found to be much more sensitive to changes in strain rate than the temperature location of the glass transition.

In conjunction with the DMA experiments, new analytical methods were developed in order to translate measured viscoelastic data into a predictive tool that could provide insight into the moderate and high-rate behavior of amorphous polymers. These analytical methods are derived from the same concept that is central to the Ree-Eyring yield model: material deformation resistance may be decomposed into the contributions from different molecular processes. In this case, the measured storage modulus reference curves are broken down into \( \alpha \) and \( \beta \) components, based on clues in the storage modulus and loss modulus curves. The components are then supposed to shift different amounts with changing strain rate, according to the rate-dependent shifts of the corresponding transitions. With this framework, it is possible to predict the elastic modulus of either PC or PMMA over a broad range of temperatures and strain rates, well beyond the test capabilities of the Q800 DMA. Also, by focusing on the \( \beta \)-contribution alone, it is possible to predict at what strain rate a significant material transition may occur. Furthermore, new insight into the distributed nature of the material transitions may be garnered from these analytical tools, when yield data is absent.

The new analytical methods introduced in this thesis may be applied to the measured viscoelastic behavior of any amorphous polymer or polymer-based material system (e.g. polymer-clay nanocomposite). Those glassy polymers or glassy polymer-based material systems which are found to have a significant low-temperature \( \beta \)-transition in the viscoelastic behavior, a \( \beta \)-transition that will shift past room temperature at moderate or high strain
rates, shall exhibit enhanced performance in resisting deformation and failure upon impact loading. Likewise, those elastomers or elastomer-based material systems which are found to have a glass-transition that will shift past room temperature at moderate or high strain rates shall exhibit enhanced strength under impact loading - perhaps an even more dramatic effect. Thus, by following the combined experimental/analytical techniques of this thesis, it is possible to identify, through viscoelastic analysis alone, those materials or material systems which are best suited for impact applications.

Though analysis of viscoelastic behavior is capable of providing a qualitative prediction of material response under high rates of deformation, the ultimate goal of this study was the development of a constitutive model. A constitutive model was desired so that fully three-dimensional finite-strain deformation behavior under high rates of loading could be accurately predicted. Through finite-element analysis, this constitutive model could be used to systematically design polymer-based components for high-rate applications, without introducing the costs and uncertainties of laboratory experiments. The background research on the rate-dependent behavior of amorphous polymers, as well as the viscoelastic analysis of PC and PMMA, were the first steps in the process of developing an appropriate constitutive model. The necessary next step in this process was an experimental investigation of the rate-dependent stress-strain behavior of PC and PMMA, across a broad range of strain rates. Material behavior under low and moderate strain rates would provide a reference to which high-rate behavior could be compared, and would also allow for the development of a more general constitutive model that is accurate at all strain rates.

All stress-strain tests were carried out in uniaxial compression, to allow for homogeneous deformation of the specimens and straightforward data analysis. Low \(10^{-4}\) s\(^{-1}\) to moderate \(1\) s\(^{-1}\) strain rate testing was conducted on a servo-hydraulic Instron. As expected, stress-strain behavior of the materials was found to be rate-dependent in this regime, with yield stress increasing in a linear and non-linear fashion for PC and PMMA, respectively, with the logarithm of strain rate. For the case of PC, the characteristic shape of the stress-strain curve was approximately constant over the range of tested strain rates. The PMMA curves, on the other hand, demonstrated an increased amount of thermal softening with
increased strain rate, owing to the combination of adiabatic deformation conditions and the extreme temperature sensitivity of the polymer.

High strain rate (700 to 6000 s\(^{-1}\)) testing was conducted on a split-Hopkinson pressure bar apparatus, using aluminum pressure bars and cylindrical specimens of length-to-diameter ratio 0.5. Material strengthening as a function of strain rate was found to be dramatically greater in the high rate regime for both materials. Combining the yield data from tests at all strain rates, it was clear that PC undergoes a significant material transition at a strain rate of approximately 10\(^2\) s\(^{-1}\). This transition strain rate is consistent with that predicted by DMA analysis, owing to the sudden restriction of secondary molecular motions. The material is more sensitive to changes in strain rate within the high-rate regime, beyond the transition, since two different molecular motions are being restricted. The PMMA data was evaluated in a similar fashion: yield strength values across all strain rates were combined, along with yield data generated from Ree-Eyring models in the literature. In this case, a more gradual transition was identified, beginning at a strain rate of approximately 10\(^{-4}\) s\(^{-1}\) - again, consistent with the DMA analysis prediction. It may be inferred, then, that restricted \(\beta\) motions contribute in a significant way to PMMA strength over both the Instron and split-Hopkinson bar rate regimes. Beyond the yield point, the PC specimens deformed in a ductile manner over all of the tested strain rates, exhibiting the same features of stress-strain behavior - strain softening, strain hardening - as observed at lower rates. The PMMA specimens, on the other hand, failed in a brittle manner during split-Hopkinson bar testing; beyond yield, very little stress-strain data could be obtained before global fracture ended the experiment.

Following the experimental investigation of the rate-dependent yield and stress-strain behavior of PC and PMMA, a new constitutive model for the three-dimensional finite strain deformation behavior of amorphous polymers was proposed. This proposed model is built upon the transferable framework of an existing constitutive model for the rate-, temperature-, and pressure-dependent finite strain deformation of thermoplastics. The existing model, first introduced in its components by Boyce et al. (1988), Arruda et al. (1993) and Arruda and Boyce (1993), has been shown to be predictive of the stress-strain behavior of PC and PMMA at low to moderate strain rates - see, for example, Arruda et al. (1993),
CHAPTER 6. CONCLUSIONS AND FUTURE WORK

Boyce et al. (1994), and Arruda et al. (1995). The structure of this physically-based model is based on the assumption that material deformation resistance may be decomposed into two parts: intermolecular resistance to chain segment rotation/sliding, and entropic resistance to chain alignment. The components of the model corresponding to intermolecular resistance - a linear elastic spring and a viscoplastic dashpot - are used to capture initial elasticity, the rate, temperature, and pressure dependence of yield, as well as the strain softening phenomenon. In the proposed model, it is suggested that intermolecular resistance to deformation may be further decomposed into the contributions of two different molecular processes, $\alpha$ and $\beta$. Thus, in the new model structure, there are two elastic-viscoplastic components in parallel where there originally had been one. The entropic hardening definition, based on the Arruda-Boyce 8-chain model of rubber elasticity (Arruda & Boyce, 1993), remains unchanged.

In order to fill the parameters and constants for this constitutive model, it was necessary to determine the process-specific elastic and plastic behavior of PC and PMMA. Since this feat is not possible through experimentation alone, analytical techniques are required. The process-specific elastic behavior of these materials was generated from the component-wise split of the storage modulus reference curves, into $\alpha$ and $\beta$ contributions. This viscoelastic analysis not only provided values for the process-specific elastic constants, but also provided an analytical description of their rate and temperature dependence. In the original constitutive model, the elastic constants were taken to be a function of temperature only. Also, the measured yield strengths were decomposed into $\alpha$ and $\beta$ contributions, as in the two-process Ree-Eyring yield model, following DMA predictions and clues in the yield plots. The component-specific yield values were then used to determine model parameters for the $\alpha$ and $\beta$ viscoplastic dashpots.

After numerically implementing this constitutive model into a commercial finite-element code, ABAQUS/Explicit, it was validated through simulations of uniaxial compression. Simulated stress-strain curves exhibited the characteristic features of material response to large strain uniaxial deformation: initial linear elasticity, global yield, strain softening, and strain hardening. The model clearly predicts a rate-dependence of the stress-strain behavior, as expected, as well as a transition in the material yield behavior. Examination of the $\alpha$ and
\( \beta \) contributions to predicted yield strength indicated that this transition occurs at the strain rate where the \( \beta \)-contribution becomes non-negligible, as was intended. Furthermore, the model naturally predicts a gradual change in the slope of the yield curve at the transition location, rather than a sharp upturn. This feature of the model, accomplished through the incorporation of DMA data in the formulation, is assumed to be a realistic representation of the transition event.

In a more quantitative evaluation of the constitutive model, simulated material response in uniaxial compression was compared to the experimental data of this study. For both PC and PMMA, the model accurately predicted material yield strength, with less than 5\% error, over seven decades of strain rate. Also, in both cases, the model predicted a transition in the yield behavior at a strain rate threshold consistent with that indicated by DMA analysis. In the case of PC, the model also accurately captured stress-strain response, up to large strains (\( \sim 0.8 \)), over low, moderate, and high strain rates. In the case of PMMA, brittle failure and thermal softening effects in the data, not accounted for in the model, prevented the simulations from accurately predicting stress-strain response (beyond yield) at moderate and high strain rates.

Using this model, it will soon be possible to predict unknown material response in complicated loading situations. The model will be especially useful in understanding mechanical behavior under high rates of deformation, when multiple processes contribute to deformation resistance and material response becomes especially complex. The model-based predictions will provide information regarding the role and relative contributions of the \( \alpha \) and \( \beta \) molecular processes in overall material response. This information in turn will help to develop a better theoretical understanding of the correlation between molecular structure and macroscopic mechanical response in amorphous polymers. Like the viscoelastic analysis, the model may be applied in material design and selection, in addition to component design and analysis through finite element techniques.

Before this constitutive model is capable of accurately predicting material response under impact loading, further refinements are required; the work to develop and implement
these model refinements shall be the focus of the study in the immediate future. As a first step, the effects of adiabatic heating conditions must be fully understood, and somehow incorporated into the model. Also, failure mechanisms are needed in the model before it can be used with finite element techniques in component design and optimization. Based on the experimental data presented here, these two features - adiabatic heating and failure mechanisms - will be especially important in capturing the true high-rate response of PMMA, which exhibited significant thermal softening at moderate strain rates and brittle failure at high strain rates.

Adiabatic deformation conditions is the first issue to be addressed in the future work of this study. A fundamental understanding of this issue begins with the First Law of Thermodynamics:

\[ \Delta U = Q - W \]  

(6.1)

Where \( \Delta U \) is the change in internal energy of a system, \( Q \) is the heat added to a system, and \( W \) is the work done by a system. From this energy balance, it follows that mechanical work done on a system will cause the internal energy of the system to increase, or it will cause the system to give off heat, or both. Since elastic deformation, by definition, is reversible, it is usually assumed that the associated mechanical work is entirely transformed into internal energy. Likewise, the mechanical work of plastic (permanent) deformation is usually considered to contribute only to heat generation. During adiabatic deformation, any heat generated from mechanical work does not have sufficient time to escape to the environment, and the material itself absorbs the excess heat.

The phenomena associated with adiabatic deformation are especially important in the characterization of temperature-sensitive polymeric materials, since the absorbed heat may affect material response dramatically. The effects of adiabatic deformation were observed in this study in the stress-strain curves of PMMA: at moderate strain rates, the material continued to soften with increased plastic straining. Assumably, some portion of the plastic work was being converted to heat, and the temperature of the polymer continued to increase with increased straining. Figure 6-1 shows the temperature rise in a PC specimen during split-Hopkinson bar deformation (uniaxial compression at 1800 s\(^{-1}\)), along with the corresponding true stress-true strain curve. Though the temperature rises almost 40\(^\circ\)C over the
duration of the test, the stress-strain curve does not exhibit the same thermal softening that is seen in PMMA curves at moderate rates, since the PC is much less temperature-sensitive.

In previous studies of adiabatic deformation, the portion of plastic work that contributes to heat generation has been given its own variable, $\beta$, ranging in value from 0 to 1. For metallic materials, the issue of adiabatic deformation conditions has been dealt with by taking $\beta$ to be a constant, equal to zero before yield and unity after yield. These assumptions have been backed by theory and infrared temperature measurements during split-Hopkinson bar testing (Kapoor & Nemat-Nasser, 1998). In the study of polymeric materials under high-rate deformation, however, adiabatic analysis is not as straightforward. Real-time temperature measurements, using both infrared technology and embedded thermocouples, have indicated that $\beta$ for these materials is a strong function of strain, and is always less than 1 (see, for example, Chou et al. (1973), Lerch et al. (2003), and Rittel (1999)). Figure 6-2 shows the calculated value of $\beta$ as a function of plastic strain for three high-rate compression tests of PC, as calculated from temperature measurements by Lerch et al. (2003). These curves show two distinct regions in the strain history where at least half of the plastic work
is not converted to heat. According to the First Law of Thermodynamics, a large portion of the plastic work in these regions is being converted to stored internal energy.

The immediate future of this study will involve developing a thorough understanding of the active energy storage mechanisms during plastic deformation of amorphous glassy polymers. Already, Hasan and Boyce (1993) have investigated these energy storage mechanisms through compression tests and differential scanning calorimetry (DSC). They ran numerous compression tests on polystyrene, PC, and PMMA to varying levels of plastic strain, and then subjected the deformed specimens to DSC analysis. Hasan and Boyce discovered a pre-$T_g$ exotherm that developed with increased plastic straining, up to 25% strain, and also a post-$T_g$ exotherm that increased with plastic straining beyond 25%. These two exotherms, corresponding to the release of stored energy, coincided with the strain-softening and strain-hardening phenomena, respectively. Future work in this study will involve correlating the mechanisms of energy storage with observed features of the high-rate heating and $\beta$-strain curves. Temperature measurements during moderate and high strain rate testing will also be used to determine the rate regime over which deformation transitions from isothermal to
adiabatic. By combining all of this information, it will be possible to incorporate thermal softening and high-rate heating effects into the constitutive model.

Another key feature that is absent from the current formulation of the constitutive model is local failure mechanisms. Without this feature, the model predicts material behavior which is infinitely ductile; catastrophic failure never occurs. Even limited testing under uniaxial compression has shown this to be a very inaccurate description of the true finite strain behavior of glassy amorphous polymers, especially when the strain rate reaches levels characteristic of impact loading. One common way to include failure mechanisms in a constitutive model-based finite element simulation is through an "element-kill" algorithm. During a simulation with element-kill included, elements are removed from the finite element component model if/when they reach a pre-defined failure criterion, such as a strain to failure. Since the strain to failure may be a function of temperature, pressure, and strain rate, extensive experimental data is needed to formulate an accurate element-kill criterion. Also, the mass that is lost in element removal must somehow be accounted for in post-processing energy calculations. It may be possible to link models of craze initiation and propagation, currently being developed at MIT, with an element-kill algorithm in order to create a realistic depiction of the local failure mechanisms which propagate into catastrophic component failure.

Beyond refinements to the constitutive model, the future work of this study will include high-rate characterization of other polymers and polymer-based material systems, as well as more rigorous testing of the model through simulations and experiments of ballistic-type impact loading. The combined experimental and analytical techniques of this study have demonstrated promise in their ability to understand the high-rate behavior of a particular polymer. Specifically, the DMA analytical techniques developed here have been used to accurately predict at what strain rate a significant material transition may occur, based on the location and rate-dependence of the viscoelastic $\beta$-transition. In the near future, polymer-based nanocomposites will be evaluated by these methods, in order to determine if the inclusion of inorganic or partially-inorganic nanoparticles enhance the ballistic properties of amorphous homopolymers. Qualitative predictions will be validated through both split-Hopkinson bar high-rate testing and experiments of projectile impact in a single-stage
gas gun system. These gas gun tests may also be used in further evaluation of the constitutive model proposed here. High-speed photographs of dynamic deformation contours and infrared temperature measurements on the target surface may be compared against model simulations of the same impact event. Such an analysis will allow for simultaneous validation of the modeling and simulation capabilities developed here and in future work.
Appendix A

Relevant Chemical Structures
Figure A-1: General chemical structure of polycarbonate (Harper & Petrie, 2003). Movements of the phenyl groups of the main chain are supposed to be responsible for the material $\beta$-process.

Figure A-2: General chemical structure of poly(methyl methacrylate) (Harper & Petrie, 2003). Movements of the ester side-groups are supposed to be responsible for the material $\beta$-process.
Appendix B

Additional DMA Data
Figure B-1: Three curves of the PC storage modulus as a function of temperature at an average strain rate of \(3.2 \times 10^{-3} \text{ s}^{-1}\) (1 Hz).

Figure B-2: Three curves of the PMMA storage modulus as a function of temperature at an average strain rate of \(1.9 \times 10^{-3} \text{ s}^{-1}\) (1 Hz).
Figure B-3: PC loss modulus as a function of temperature and strain rate in the region of the α-transition (all data). Approximate strain rates are as follows: solid lines, $3.2 \times 10^{-3}$ s$^{-1}$; dashed lines, $2.4 \times 10^{-2}$ s$^{-1}$; dotted lines, $2.4 \times 10^{-1}$ s$^{-1}$.

Figure B-4: PC loss tangent (tan δ) as a function of temperature and strain rate in the region of the α-transition (all data). Approximate strain rates are as follows: solid lines, $3.2 \times 10^{-3}$ s$^{-1}$; dashed lines, $2.4 \times 10^{-2}$ s$^{-1}$; dotted lines, $2.4 \times 10^{-1}$ s$^{-1}$.
Figure B-5: PC loss modulus as a function of temperature and strain rate in the region of the β-transition (all data). Approximate strain rates are as follows: solid lines, 4.2×10^{-3} s^{-1}; dashed lines, 3.4×10^{-2} s^{-1}; dotted lines, 3.3×10^{-1} s^{-1}.

Figure B-6: PC loss tangent (tan δ) as a function of temperature and strain rate in the region of the β-transition (all data). Approximate strain rates are as follows: solid lines, 4.2×10^{-3} s^{-1}; dashed lines, 3.4×10^{-2} s^{-1}; dotted lines, 3.3×10^{-1} s^{-1}. 
Figure B-7: PMMA loss modulus as a function of temperature and strain rate in the region of the $\alpha$-transition (all data). Approximate strain rates are as follows: solid lines, $6.0 \times 10^{-3}$ s$^{-1}$; dashed lines, $2.5 \times 10^{-2}$ s$^{-1}$; dotted lines, $2.2 \times 10^{-1}$ s$^{-1}$.

Figure B-8: PMMA loss tangent ($\tan \delta$) as a function of temperature and strain rate in the region of the $\alpha$-transition (all data). Approximate strain rates are as follows: solid lines, $6.0 \times 10^{-3}$ s$^{-1}$; dashed lines, $2.5 \times 10^{-2}$ s$^{-1}$; dotted lines, $2.2 \times 10^{-1}$ s$^{-1}$.
Figure B-9: PMMA loss modulus as a function of temperature and strain rate in the region of the β-transition (all data). Approximate strain rates are as follows: solid lines, $1.9 \times 10^{-3}$ s$^{-1}$; dashed lines, $1.8 \times 10^{-2}$ s$^{-1}$; dotted lines, $1.6 \times 10^{-1}$ s$^{-1}$.

Figure B-10: PMMA loss tangent (tan δ) as a function of temperature and strain rate in the region of the β-transition (all data). Approximate strain rates are as follows: solid lines, $1.9 \times 10^{-3}$ s$^{-1}$; dashed lines, $1.8 \times 10^{-2}$ s$^{-1}$; dotted lines, $1.6 \times 10^{-1}$ s$^{-1}$.
Appendix C

MATLAB Code for PC Modulus

function [E_alpha,E_beta,E_tot] = PC_TTS3(temp,rate)

% Calculate shift factors FOR EACH COMPONENT OF THE CURVE, based on rate,
% knowing that reference curves are at a strain rate of 0.0032/s
alpha_shift = 4.65*(log10(rate)-log10(0.0032));
beta_shift = 15.32*(log10(rate)-log10(0.0032));

E_beta = PC_Beta_Mod3(temp-beta_shift);
E_alpha = PC_Alpha_Mod3(temp-alpha_shift);

E_tot=E_beta+E_alpha;

*******************************************************************************
function [E] = PC_Alpha_Mod3(temp)

% Just the Alpha-Component of Storage Modulus

if (temp > 428.644)
    E = 4.86002441833989;
elseif (temp >= 288 & temp < 350)
    E = (-0.02306086434516)*temp^2 + (11.48073059696856)*temp + (2.480108386405953e+002);
elseif (temp >= 350 & temp < 400)
    E = (-8.357202410077351e-4)*temp^3 ...

195
APPENDIX C. MATLAB CODE FOR PC MODULUS

+  (0.94995691618253)*temp^2 ...
+  (-3.630554143313150e2)*temp ...
+  (4.797467535437449e4);

elseif (temp >= 400 & temp < 420)

E = (-0.00502285084013)*temp^4 ...
+  (8.17018189208807)*temp^3 ...
+  (-4.983713974434647e3)*temp^2 ...
+  (1.351133437322784e6)*temp ...
+  (-1.37365437985107e8);

elseif (temp >= 420 & temp <= 428.644)

E = (-0.01084301221167e4)*temp+4.64827812890091e4;

elseif (temp < 288)

E = (-0.00218084303030e3)*temp+2.26978369272727e3;

end

******************************************************************************
function [E] = PC_Beta_Mod3(temp)

% Just the Beta-Component of Storage Modulus

if (temp <=272.5 & temp >= 133)

E = (-1.306800962901414e-006)*temp^4 ...
+(0.00144379330492)*temp^3 ...
+(-0.51646708468688)*temp^2 ...
+(65.59530889260414)*temp ...
+(-1.527541558294103e+003);

elseif (temp < 133)

E=1033.67;

else

E = 5.492;

end
Appendix D

MATLAB Code for PMMA Modulus

function \([E\_\text{alpha}, E\_\text{beta}, E\_\text{tot}] = \text{PMMA\_TTS3}(\text{temp}, \text{rate})\)

% Calculate shift factors FOR EACH COMPONENT OF THE CURVE, based on rate, % knowing that reference curves are at a strain rate of 0.0021/s
alpha\_shift = 11.07*(\log10(\text{rate})-\log10(0.0021));
beta\_shift = 25.20*(\log10(\text{rate})-\log10(0.0021));

10

E\_beta = \text{PMMA\_Beta\_Mod3}(\text{temp} - \text{beta\_shift});
E\_alpha = \text{PMMA\_Alpha\_Mod3}(\text{temp} - \text{alpha\_shift});

E\_tot = E\_beta + E\_alpha;

******************************************************************************
function \([E] = \text{PMMA\_Alpha\_Mod3}(\text{temp})\)

% Just the Alpha-Component of Storage Modulus

if (temp < 363)
\[E = -8.15848542129034\times\text{temp} + 4.475923834772286\times10^3;\]
elseif (temp \geq 363 \& temp < 383)
\[E = (-0.00005114082546\times10^4)\times\text{temp}^2 + (0.03639460621328\times10^4)\times\text{temp} + (-6.32094773219500\times10^4);\]
elseif (temp \geq 383 \& temp \leq 393.5)
\[E = (-6.32094773219500\times10^4)\times\text{temp} + (0.03639460621328\times10^4)\times\text{temp} + (-6.32094773219500\times10^4);\]
else (temp \geq 383 \& temp \leq 393.5)
\[E = (-0.00005114082546\times10^4)\times\text{temp}^2 + (0.03639460621328\times10^4)\times\text{temp} + (-6.32094773219500\times10^4);\]
end
APPENDIX D. MATLAB CODE FOR PMMA MODULUS

E = (-0.09958764808220)*temp^3 ...
+ (1.12273126462127e+002)*temp^2 ...
+ (-4.22145672484135e+004)*temp ...
+ (5.295105130964123e+006);

elseif (temp > 393.5 & temp <= 407)

E = (-0.25880815529860)*temp^3 ...
+ (3.140811768159550e+002)*temp^2 ...
+ (-1.270565593538765e+005)*temp ...
+ (1.713342281946351e+007);

elseif (temp > 407)

E = 11.98917937651277;

end

*******************************************************************************
function [E] = PMMA_Beta_Mod3(temp)

% Just the Beta-Component of Storage Modulus

if (temp > 185 & temp <= 235)

E = (-0.00000092490694E3)*temp^3 ...
+ (0.00053537241545E3)*temp^2 ...
+ (-0.10390546427724E3)*temp ...
+ (8.50384180997852E3);

elseif (temp > 235 & temp <= 285)

E = (-0.00000084686447E4)*temp^3 ...
+ (0.00005817295889E4)*temp^2 ...
+ (-0.01401655194281E4)*temp ...
+ (1.34716632982836E4);

elseif (temp > 285 & temp <= 365)

E = (0.00003491886169E3)*temp^2 ...
+ (-0.03582235486598E3)*temp ...
+ (8.50078566759274E3);

elseif (temp > 365 & temp <= 383)

E = (-0.00000002661461E6)*temp^3 ...

end
APPENDIX D. MATLAB CODE FOR PMMA MODULUS

\[ + (0.00002988358375E6) \cdot \text{temp}^2 \ldots \\
+ (-0.01118638506001E6) \cdot \text{temp} \ldots \\
+ (1.39605788920328E6); \]

elseif (temp > 383)
    E = 6.4164;

elseif (temp <= 185)
    E = 1748.3;

end
Appendix E

Additional Compression Data
APPENDIX E. ADDITIONAL COMPRESSION DATA

Figure E-1: Complete data for the PC true stress-true strain behavior in uniaxial compression at two quasi-static strain rates: \(10^{-3} \text{ s}^{-1}\) (solid lines; two curves) and \(10^{-1} \text{ s}^{-1}\) (dotted lines; four curves).

Figure E-2: Complete data for the PC true stress-true strain behavior in uniaxial compression at two quasi-static strain rates: \(10^{-2} \text{ s}^{-1}\) (solid lines; three curves) and \(1 \text{ s}^{-1}\) (dotted lines; two curves).
Figure E-3: Complete data for the PMMA true stress-true strain behavior in uniaxial compression at four quasi-static strain rates: $10^{-4} \text{ s}^{-1}$ (solid lines; one curve), $10^{-3} \text{ s}^{-1}$ (dashed lines; two curves), $10^{-1} \text{ s}^{-1}$ (dash-dot lines; three curves), and $8 \times 10^{-1} \text{ s}^{-1}$ (dotted lines; two curves).

Figure E-4: Complete data for the PMMA true stress-true strain behavior in uniaxial compression at three quasi-static strain rates: $3 \times 10^{-4} \text{ s}^{-1}$ (solid lines; two curves), $10^{-2} \text{ s}^{-1}$ (dashed lines; three curves), and $3 \times 10^{-1} \text{ s}^{-1}$ (dotted lines; two curves).
APPENDIX E. ADDITIONAL COMPRESSION DATA

Figure E-5: PC true stress-true strain behavior derived from SHPB tests at a chamber pressure of 30 psi (all data; four curves). Average true strain rates across the duration of the tests is approximately 1300 s\(^{-1}\) (1250 s\(^{-1}\) at yield).

Figure E-6: PC true stress-true strain behavior derived from SHPB tests at a chamber pressure of 40 psi (all data; five curves). Average true strain rates across the duration of the tests is approximately 2000 s\(^{-1}\) (1800 s\(^{-1}\) at yield).
Figure E-7: PC true stress-true strain behavior derived from SHPB tests at a chamber pressure of 50 psi (all data; five curves). Average true strain rates across the duration of the tests is approximately 2650 s\(^{-1}\) (2300 s\(^{-1}\) at yield).

Figure E-8: PC true stress-true strain behavior derived from SHPB tests at a chamber pressure of 70 psi (all data; five curves). Average true strain rates across the duration of the tests is approximately 3900 s\(^{-1}\) (3150 s\(^{-1}\) at yield).
Figure E-9: PC true stress-true strain behavior derived from SHPB tests at a chamber pressure of 90 psi (all data; five curves). Average true strain rates across the duration of the tests is approximately 50 ± 50 s\(^{-1}\) (4000 s\(^{-1}\) at yield).

Figure E-10: PMMA true stress-true strain behavior derived from SHPB tests at a chamber pressure of 35 psi (all data; five curves). Average true strain rates across the duration of the tests is approximately 800 s\(^{-1}\) (600 s\(^{-1}\) at yield).
Figure E-11: PMMA true stress-true strain behavior derived from SHPB tests at a chamber pressure of 50 psi (all data; five curves). Average true strain rates across the duration of the tests is approximately 1400 s\(^{-1}\) (1300 s\(^{-1}\) at yield).
References


REFERENCES


REFERENCES


REFERENCES


