Mechanics of Amorphous Polymers and Polymer Nanocomposites during High Rate Deformation

by

Adam Dustin Mulliken

Master of Science in Mechanical Engineering
Massachusetts Institute of Technology, 2004
Bachelor of Engineering
Thayer School of Engineering at Dartmouth College, 2002
Bachelor of Arts, Engineering Sciences
Dartmouth College, 2002

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Abstract

It has been suggested that a polymer’s macroscopic mechanical response to a general loading case is governed by its ability to access various primary and secondary molecular mobilities. Specifically, under conditions of high strain rate, restricted secondary molecular motions are thought to bring about enhanced stiffness and strength. In accordance with this theory, an experimental protocol and associated analytical techniques were established to better understand the rate- and temperature-dependent mechanical behavior of two exemplary amorphous polymers, PC and PMMA. The experiments included dynamic mechanical thermal analysis (DMTA), as well as uniaxial compression tests over a wide range of strain rates. In both cases, the polymer exhibited a distinct transition in the rate-dependent yield behavior, under the same temperature/strain rate conditions as the observed viscoelastic \( \beta \)-transition. Drawing off of previous research in the field of polymer mechanics, a new continuum-level constitutive model framework is proposed to account for the contributions of different molecular motions which become operational in different frequency/rate regimes. This model is shown to capture well the unique rate-dependent yield behavior of PC and PMMA, as well as the compressive stress-strain response under isothermal conditions.

Through the rest of the thesis, additional features are integrated into the model to allow for more accurate predictions of mechanical response under high-rate, impact loading. Adiabatic conditions are captured by considering the heat evolved during dissipative plastic deformation. The corresponding temperature rise predicted by the model is corroborated by experimental measurements obtained via infra-red techniques during the split-Hopkinson bar test. In conjunction with the implementation of adiabatic heating, the model’s kinematic framework is altered in order to also capture the effects of thermal expansion. Finally, drawing off of existing experimental data in the literature, the implementation of pressure-dependence in the model is revised.

In the final portion of this thesis, the generality of the experimental and theoretical methods is explored. The techniques are applied in the study of the rate-dependent mechanical behavior of a variety of polymer-based material systems, including a PC-POSS nanocomposite, homopolymer PVC, a plasticized PVC, and a PC-triptycene co-polymer. In every case, the methods garnered important insight into both macroscopic phenomena and the molecular mechanisms of deformation resistance.

Thesis Supervisor: Mary C. Boyce
Title: Kendall Family Professor of Mechanical Engineering
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Personally, I must first and foremost thank my advisor Professor Mary Boyce. It is her passion for polymer mechanics which provided the driving force behind my research. I originally sought to work with Professor Boyce because of the opportunities I expected would come to me as her student, as well as her reputation as a teacher and mentor. On both fronts my expectations were far exceeded. Through my relationship with Professor Boyce, I travelled to numerous scholarly conferences, throughout the United States and abroad, and presented my work to some of the top scientists in the field; I published this work in a number of esteemed journals, both as a co-author and as a first author; I had my name on a patent; I investigated novel material systems with potentially far-reaching applications. Most notably, I performed all of my research under the careful guidance and tutelage of the leading lady of modern day mechanics - Professor Mary Boyce. I am forever grateful to her for taking such a keen interest in my personal education.

As Professor Boyce and I together delved for the first time into topics of high-rate mechanics, I received considerable training and assistance on the experimental side. Over my four years, I was fortunate to almost always have either Omprakash Samudrala or Sai Sarva working at my side. Both men came to MIT as postdoctoral associates versed in the intricacies of high-rate experimental mechanics, and both were crucial in setting up and overseeing the experimental facilities which I so often utilized. I received more formal training in split-Hopkinson bar testing in particular during a summer spent at Sandia National Laboratories/California, through the Engineering Sciences Summer Institute. The high-rate temperature measurement capability reported in this thesis was established only through the joint efforts of a number of researchers. Jin Yi, a postdoctoral associate with the Boyce group, designed the initial set-up under the guidance of Todd Bjerke of the
Army Research Laboratories; the final set-up was designed, constructed, and validated with considerable assistance from George Perry (Perry Amplifier Co., Brookline, MA), Ray Gurgenian (Fermionics Corp., Simi Valley, CA), and especially fellow graduate student Mohit Garg.

During my four years at MIT, I also had the opportunity to collaborate with a number of graduate students outside of the Department of Mechanical Engineering, especially as I sought to extend the experimental and theoretical techniques to novel material systems. The research presented in Chapter 7 of this thesis represents the fruits of these collaborations. On the PC-POSS material system, Ed Kopesky (Department of Chemical Engineering) assisted in the material design and synthesis; on the PC-Triptycene co-polymer work, Nick Tsui (Department of Materials Science and Engineering) created the polymer blends, made the specimens, and helped to conduct the mechanical tests; for the PVC and plasticized PVC, Sharon Soong (Department of Chemical Engineering) made the materials, conducted the majority of the experiments, and assisted with the modelling.

I would also like to acknowledge those people within my department at MIT who I worked with, in particular the students, faculty, and staff in the Mechanics and Materials Division of the Department of Mechanical Engineering. Among this group, I would especially like to thank H. "Jerry" Qi, my mentor and role model, as well as Una Sheehan, Nici Ames, Professor David Parks, Rajdeep Sharma, and Nuo Sheng.

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Preface

Amorphous polymers in their glassy state are used extensively in engineering applications where they are expected to resist moderate- and high-rate impact. These applications span both commercial and military interests, ranging from machine guards, eyeglasses and bus windows to jet canopies and protective visors. The choice of amorphous, 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. Many amorphous polymers have also shown an intrinsic ability to resist deformation and failure upon impact, though the mechanisms behind this resistance have not been well understood. Optimization in the design of polymeric components can only be done empirically, unless there exists an accurate theoretical model which is predictive of the rate- and temperature-sensitive mechanical behavior over a relevant range of processing and operating conditions. The ultimate goal of this thesis research was to develop such a constitutive model for amorphous polymers, targeting the large strain behavior under moderate- and high-rate deformation, but with general capability to predict behaviors for a wide range of engineering applications.

This thesis research draws heavily upon previous work in the field of polymer mechanics - experimentation, analysis, and constitutive modelling. Most notably, the dissertation builds upon a Master's thesis presented by the author to the Department of Mechanical Engineering two years prior (2004). In that thesis, a new constitutive model for amorphous, glassy polymers was outlined, based on experimental observations over a wide range of strain rates ($10^{-4}$ s$^{-1}$ to 5000 s$^{-1}$). This model was shown to capture a distinct transition in the rate-dependent yield behavior of both polycarbonate (PC) and poly(methyl methacrylate) (PMMA) by accounting for restricted secondary molecular mobilities ("$\beta$-motions") under conditions of low temperature and/or high strain rate. In Chapter 2 of the dissertation, the work of this Master's thesis is described in-depth, including slight adjustments and
additions based on two years of hindsight. All necessary background information is given in Chapter 1, which provides a thorough review of nearly 70 years of research into the rate-dependent behavior of amorphous polymers. This introductory chapter touches upon experimental techniques, macroscopic phenomena, molecular theory, as well as modelling efforts, and shall help to put the work of this entire dissertation into context.

The ensuing chapters of the dissertation each address a different aspect of the mechanical behavior of amorphous polymers which is not thoroughly considered - if considered at all - by the constitutive model presented in Chapter 2. Chapter 3 is concerned with thermal expansion, which can occur in the absence of mechanical loading or in conjunction with adiabatic deformation. An experimental investigation into the temperature- and stretch-dependent thermal expansion coefficient of PC and PMMA is presented, as well as a new thermo-elasto-plastic framework for the constitutive model which has capability to capture thermal expansion. In Chapter 4, the concepts of energy storage and dissipation during polymer deformation are addressed, from both an experimental and a theoretical modelling point of view. These effects have important ramifications especially at moderate and high rates, where dissipated energy results in a temperature rise in the polymer. This temperature rise - as much as 100°C under ballistic impact - can significantly reduce the flow stress of the polymer and also drive thermal expansion. Finally, Chapter 5 deals with pressure effects, which play an important role in the response of a polymeric structure under impact. Pertinent data from the literature is presented as motivation for a revised treatment of the effect of pressure on the initial elastic, yield and post-yield stress-strain behavior. These additional complexities - thermal expansion, energy storage and dissipation, and pressure effects - may not be significant in every engineering application. However, their treatment described herein completes the constitutive model in satisfaction of the ultimate goal of the thesis. The final proposed model, in its most complete and general form, is summarized in Chapter 6.

In Chapters 2 through 6, the experimental data and model predictions presented are limited to the behaviors of two exemplary amorphous polymers, PC and PMMA. In Chapter 7, the generality of the experimental and theoretical methods is explored. The experimental protocol and theoretical framework, including the constitutive model, are extended to a variety of polymer-based material systems, including a PC-POSS nanocomposite, homopolymer PVC, a plasticized PVC, and a PC-triptycene co-polymer. In each case, the methods of
this thesis garnered new insight in regards to the rate-dependent behavior of the material. Together, these shorter studies demonstrate that the model framework and the methods on which it is built are in fact transferable to the study of other polymeric materials, and that in the future they shall provide an efficient means to evaluate new material systems for impact applications.
Chapter 1

Introduction: Rate Dependence of Amorphous Polymers

This dissertation is concerned mainly with the rate-dependent mechanical behavior of amorphous polymers, with a focus on predicting large strain behavior at very high rates of strain. These amorphous materials are classified as such due to the lack of long-range order in their microstructure; in the unstressed state, the polymer macromolecules are randomly oriented. The chains interact with one another through weak van der Waals forces, and form a network due to 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 stress-strain behavior of amorphous polymers has been well-documented. A representative curve is given in figure 1-1; pictured is the true stress-true strain\(^1\) behavior of a polycarbonate (PC) in uniaxial compression at a constant true strain rate of \(10^{-3} \text{ s}^{-1}\). During the initial loading phase, the material exhibits nonlinear viscoelastic behavior; at very small strains (\(\leq 0.03\)), the elastic behavior is linear. The elastic region is the result of

\[^1\text{The quantities of true stress and true strain provide an accurate measure of stress and strain in a deformed material. While engineering stress is defined as the force divided by the initial area, true stress is defined as the force divided by the current area; likewise, true strain is the integral of the change in material length divided by the current material length. True stress (\(\sigma_{\text{true}}\)) and true strain (\(\epsilon\)) can be approximated from engineering stress (\(\sigma_{\text{eng}}\)) and engineering strain (\(\epsilon_{\text{eng}}\)):}

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

Thus, the greater the strain level, the larger the deviation between engineering measures of stress and strain and true measures of stress and strain.
intermolecular interactions between chains (van der Waal forces), where the chain segments partially and reversibly rotate and/or translate 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", whereby 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(s) of maximum stretch. In a compression test, this corresponds to equi-biaxial alignment of

Figure 1-1: True stress-true strain behavior of polycarbonate (PC) in uniaxial compression at a strain rate of $10^{-3}$ s$^{-1}$. 
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 molecular chains are stretched and aligned and begin to approach their extension limit in the maximum stretch direction - that causes strain hardening in amorphous polymers. In figure 1-1, the entropic hardening effect is seen to dominate the stress-strain response at strains beyond ~25-30%.

The stress-strain behavior described above is strongly dependent upon strain rate. As the strain rate is increased, both the initial elastic modulus and the stress level required for plastic flow increase. As an example of this, the rate-dependent stress-strain behavior of poly(methyl methacrylate) (PMMA) is given in figure 1-2. The yield strength of PMMA is observed to increase by almost 100% over this range of strain rates, from very low (3x10^{-4} s^{-1}) to moderate (0.1, 0.3 s^{-1}). Furthermore, the strain hardening effect appears to be negligible at the higher rates. However, at these moderate strain rates the material is thermally softening, as the thermodynamic condition of the test is no longer isothermal. There is not sufficient time for all of the heat generated by plastic deformation to escape to the environment, and consequently the temperature-sensitive polymer softens. This observed transition - from an isothermal to an adiabatic test condition - is dictated by the specific specimen geometry, the rate of deformation, the thermal properties of the
polymer, and the heat transfer properties of the surroundings. For the curves of figure 1-2, the characteristic specimen length was \( \sim 6.35 \text{ mm} \). As is evidenced here, the temperature dependence of the mechanical behavior of amorphous polymers is very closely linked to the strain rate dependence. This important feature of amorphous polymer behavior must be carefully accounted for in any predictive model.

### 1.1 Early Theoretical Models

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 provides a model for the shear strain rate as a function of shear stress, as given below:

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

where \( \dot{\gamma}_0 \) is a frequency parameter, \( \Delta H \) is the activation energy required for one transition, \( \Omega \) is the activation volume\(^2\), 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 \( T \). Equation 1.1 may be rearranged, and simplified in this case\(^3\), to give an equation for shear stress as

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

\(^2\)More precisely, \( \Omega \) is the product of a local activation volume and a local shear strain, though the entire term is often referred to as the activation volume [m\(^3\)].

\(^3\)The simplification comes from a physical understanding of the plastic flow event. Using the definition of the hyperbolic sine, we re-write equation 1.1 as:
a function of strain rate:

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

(1.2)

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 PC and poly(vinyl chloride) (PVC) 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 re-wrote equation 1.2 in order to express the tensile yield stress \( \sigma_y \) in terms of the axial strain rate \( \dot{\varepsilon} \):

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

(1.3)

where \( \bar{A} \) and \( \bar{C} \) are lumped parameters, differing in value from the \( A \) and \( C \) of equation 1.2; \( Q \) 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 1-3). It is concluded, then, that PC yield is controlled by just a single activated process, with constant activation energy \( Q \) and activation volume \( \Omega \), over the range of temperatures and strain rates tested. For the PVC data, Bauwens et al. (1969) found similar agreement between the Eyring model and their experimental results, but only within a region of 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. Robertson simplified the structure of a polymer chain down to a planar "zig-zag"
Eyring model parameters for the PC data of figure 1-3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\dot{A}$</td>
<td>[Pa/°K]</td>
<td>4077</td>
</tr>
<tr>
<td>$Q$</td>
<td>[kcal/mol]</td>
<td>75.5</td>
</tr>
<tr>
<td>$\dot{C}$</td>
<td>[s]</td>
<td>$1.0 \times 10^{-31}$</td>
</tr>
</tbody>
</table>

Figure 1-3: Eyring yield stress model fit to the PC data of Bauwens-Crowet et al. (1969)
with bond angles that transition between a low-energy, preferred state (called \textit{trans}), and a higher energy, flexed state (called \textit{cis}). As the shear stress is increased in the polymer, the fraction of bonds in the cis position increases, as compared to the unstressed, glassy state, and overall material stiffness decreases. Eventually, at some transient state, the polymer at temperature $T$ will behave like a fluid at temperature $T_1 > T_g$. Robertson developed an analytical expression for this temperature $T_1$ by assuming that the transition from trans to cis states is a thermally-activated, distributed process, with activation energy given by the empirical Williams-Landel-Ferry (WLF) equation (Ferry, 1961). Finally, Robertson gives an analytical expression describing the flow of this "fluid" at temperature $T_1$:

$$\dot{\gamma} = \frac{\tau}{\eta_g} \exp \left[ -2.303 \left( \frac{c_1^\theta c_2^\theta}{T - T_g} + c_2^\theta \left( \frac{T_1}{T} - c_1^\theta \right) \right) \right]$$  \hspace{100pt} (1.4)

where $\eta_g$ is the viscosity at the glass-transition temperature under shear stress $\tau$ and $c_1^\theta$ and $c_2^\theta$ are parameters from the WLF equation.

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 for PMMA are given in figure 1-4. The model performs 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. In Argon’s theory, the main barrier resisting the thermally-activated molecular movements that govern plasticity is \textit{inter}molecular forces. Argon’s vision of molecular-level plastic deformation in glassy polymers is described as stress-induced alignment of previously-kinked chains (figure 1-5). The theory is built upon analysis of the reverse problem: a molecular chain which transitions from aligned to kinked. By approximating the molecular chain as an elastic cylinder, the free energy change associated with a singular kinking event is calculated. In order to develop an expression for the macroscopic shear strain rate, Argon considers not only this intramolecular activation barrier, but also the stability of the new (kinked) configuration. 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
Figure 1-4: Comparison of Robertson model prediction and experimental data for the yield stress of PMMA at strain rates of $1.04 \times 10^{-4}$ s$^{-1}$, $5.21 \times 10^{-4}$ s$^{-1}$, and $2.51 \times 10^{-3}$ s$^{-1}$ (Robertson, 1966)

weighs heavily upon the influence of intermolecular forces.

The final expression of Argon’s model is given as the equation for shear strain rate, $\dot{\gamma}$. Mathematically, it is almost identical to the rate equation for the Eyring model, assuming only forward progress:

$$\dot{\gamma} = \gamma_0 \nu_a N_a \exp \left[ \frac{-\Delta G}{2kT} \right]$$  \hspace{1cm} (1.5)

where $\gamma_0$ is the unit increment of shear strain that results from the production of a pair of kinks, $\nu_a$ is a frequency term capturing the rate at which the kinking process occurs, and $N_a$ is the volume density of activated states.$^4$ The activation free energy $\Delta G$ is given as a function of the shear stress $\tau$, the shear modulus $\mu$, and hydrostatic pressure $p$:

$$\Delta G = \frac{3\pi \mu \omega^2 a^3}{16(1 - \nu)} \left[ 1 - 8.5(1 - \nu) \left( \frac{\tau}{\mu} \right)^{\frac{3}{2}} \right] + 0.15\mu a^3(\omega - \omega_c)^2 \left( \frac{p}{\mu} \right)$$ \hspace{1cm} (1.6)

where $\nu$ is the Poisson ratio, and $\omega$ and $a$ are geometrical parameters of the kinked elastic cylinder. Argon’s model captured contemporary experimental findings, that the pressure

$^4$Oftentimes, equation 1.5 is seen with $\gamma_0$, $\nu_a$, and $N_a$ lumped into one, pre-exponential frequency parameter, $\gamma_0$ (of units s$^{-1}$).
Figure 1-5: 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)
Figure 1-6: 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)
dependence of the yield stress is paralleled by the pressure dependence of the shear modulus (Brown, 1971), and that the temperature dependence of the yield stress is related to the temperature dependence of the shear modulus (Argon, Andrews, Godrick, & Whitney, 1968). Even without complete data on the pressure, temperature, and strain rate (frequency) dependence of the shear modulus, Argon was able to fit his model quite well to existing data on the rate- and temperature-dependent yield behavior of polyethylene terephthalate (PET; figure 1-6) and polystyrene (PS; not pictured). This data covered both low and high temperatures (-123°C to 77°C), and strain rates ranging from very low (10^{-4} s^{-1}) to medium (10^2 s^{-1}).

All three theoretical models - the Eyring, the Robertson, and the Argon - proved capable in their ability to predict contemporary data for the rate- and temperature-dependent yield stress of various amorphous polymers. However, at the same time, yield data was beginning to emerge in the literature which could not be captured any of these models. In most cases, this data corresponded to studies including tests at low temperature and moderate to high rates of deformation. Thus, starting in the 1960s, a more general modelling approach was suggested, paving the way for new theory in regards to the intermolecular forces resisting plastic deformation.

1.2 Influence of Secondary Transitions

1.2.1 Early Discovery

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 1-7). 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. In either region, the data could be fit with the original Eyring theory of viscosity - see the table adjoining figure 1-7. However,
material behavior over the entire set of data could not be captured with the single-process explanation that the Eyring model provided.

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. Using an Instron-type universal testing machine, Roetling investigated the yield behavior of PMMA at temperatures ranging from 30°C to 90°C, and strain rates ranging from $10^{-5} \text{ s}^{-1}$ to almost 10 s$^{-1}$. His results are summarized in figure 1-8. Like Bauwens, Roetling found that the single-process Eyring theory was unable to fit his entire data set, as the PMMA yield strength transitioned between two distinct regimes of rate sensitivity over the range of temperatures/strain rates accessed in tension tests.

In later studies, Roetling and the Bauwens group documented the same type of yield transition in the rate- and temperature-dependent data of a variety of amorphous polymers: poly(ethyl methacrylate) (PEMA) (Roetling, 1965a), PVC (Bauwens et al., 1969), and PC (Bauwens-Crowet, Bauwens, & Homès, 1972; Bauwens, 1972). In each case, the temperature/strain rate location and distributed nature of the yield transition was found to be unique. For PEMA, a sharp yield transition was identified at $10^{-4} \text{ s}^{-1}$ (30°C), beyond which the material is twice as sensitive to changes in strain rate (figure 1-9). In PVC, the transition is more gradual, and at room temperature is centered around $10^{-1} \text{ s}^{-1}$ (Bauwens et al., 1969). For the case of PC, it was not possible to increase the strain rate enough to observe a transition at room temperature (Bauwens-Crowet et al., 1969). However, a distinct transition was observed in the temperature-dependent yield data, located at -80°C ($\dot{\varepsilon} \sim 10^{-3} \text{ s}^{-1}$) and shown in figure 1-10 (Bauwens-Crowet et al., 1972).

Ultimately, both Roetling and the Bauwens group would explain their experimental findings in terms of the Ree-Eyring theory (Ree & Eyring, 1955, 1958). The Ree-Eyring theory is essentially a modification, to a more general form, of the original Eyring theory (1936).\(^5\) The Ree-Eyring theory simply allows for multiple rate-activated processes to be acting in tandem, rather than just a single activated process as in the Eyring theory. When the associated model is expressed in terms of the polymer yield stress, as in equation 1.7,\(^5\)

\(^5\)The modifications were conceived of and presented in the 1950s, but were not applied in the study of polymer plasticity until the 1960s and 1970s.
Eyring model parameters for the PMMA data of figure 1-7

<table>
<thead>
<tr>
<th>Process 1 (α)</th>
<th>Process 2 (β)</th>
</tr>
</thead>
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<tr>
<td>Q [kcal/mol]</td>
<td>Q [kcal/mol]</td>
</tr>
<tr>
<td>98</td>
<td>26</td>
</tr>
</tbody>
</table>

Figure 1-7: 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: \( v_1 = 0.0625 \text{ mm/min}, v_2 = 0.25 \text{ mm/min}, v_3 = 1.25 \text{ mm/min}, v_4 = 6.25 \text{ mm/min}, \) and \( v_5 = 31.4 \text{ mm/min}. \) Specimen gage length for all tests was 40 mm.
Ree-Eyring model parameters
the PMMA data of figure 1-8

<table>
<thead>
<tr>
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<th>$\beta$</th>
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<tbody>
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<td>7060</td>
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<tr>
<td>$Q$ [kcal/mol]</td>
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<td>24</td>
</tr>
<tr>
<td>$C$ [s]</td>
<td>$8.19 \times 10^{-40}$</td>
<td>$1.39 \times 10^{-11}$</td>
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</tbody>
</table>

Figure 1-8: PMMA yield data by Roetling fit with the Ree-Eyring model (Roetling, 1965b)
Ree-Eyring model parameters for the PEMA data of figure 1-9

<table>
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</thead>
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<td>22500</td>
</tr>
<tr>
<td>$Q [\text{kcal/mol}]$</td>
<td>98</td>
</tr>
<tr>
<td>$C [\text{s}]$</td>
<td>$6.99 \times 10^{-56}$</td>
</tr>
</tbody>
</table>

Figure 1-9: Poly(ethyl methacrylate) yield data by Roetling fit with the Ree-Eyring model (Roetling, 1965a)
Ree-Eyring model parameters for the PC data of figure 1-10

<table>
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<tr>
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<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{tension}$ [Pa/$^\circ$K]</td>
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<td>13000</td>
</tr>
<tr>
<td>$A_{compress}$ [Pa/$^\circ$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>$2.4 \times 10^{-31}$</td>
<td>$2.76 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

Figure 1-10: Temperature dependence of PC yield strength 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).
it is clear how each "process" adds another component to the value of the yield stress:

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

(1.7)

For practical use, Bauwens et al. (1969) developed a simplified two-process version of this equation:

\[
\frac{\sigma_y}{T} = \frac{\sigma_\alpha}{T} + \frac{\sigma_\beta}{T} = A_\alpha \left[\ln(2C_\alpha \dot{\varepsilon}) + \frac{Q_\alpha}{RT}\right] + A_\beta \sinh^{-1}\left[\frac{C_\beta \dot{\varepsilon}}{T} \exp\left(\frac{Q_\beta}{RT}\right)\right]
\]  

(1.8)

In this case the approximation \(\sinh^{-1}(x) \approx \ln(2x)\) (see footnote 2) is made on the first term, because only the \(\alpha\)-process is considered to be in a "high stress" state over the entire range of interest. Under the framework of the Ree-Eyring theory, the "processes" of plastic flow in amorphous polymers (labelled \(\alpha, \beta, \gamma\) etc.) are often associated with particular degrees of freedom of the polymer chains. Nonetheless, the Ree-Eyring theory, like its predecessor, makes no assumption in regards to the specific molecular mechanism(s) behind the rate dependence of plasticity in polymers.

Roetling and Bauwens' group attempted to fill this gap in the theory with molecular-level explanations of the observed macroscopic phenomena. Both essentially came to the same conclusion (Bauwens-Crowet & Homès, 1964; Roetling, 1965b): the transition in the yield behavior is due to restrictions on certain small-scale chain motions which are otherwise operative. Under conditions of low temperature and/or moderate to high strain rate, these motions require stress-assisted activation. Roetling (1965b) fit a two-process Ree-Eyring yield model to his PMMA data (figure 1-8) by assuming that the stress contribution of the lower energy activation process, the "\(\beta\)-process," was negligible at the lowest strain rates and highest temperatures, whereas at the higher strain rates and lowest temperatures, both the \(\alpha\) and \(\beta\) processes required stress-assisted activation. Afterwards, he compared his calculated activation energy for the \(\beta\)-process - \(\Delta H_2\) in equation 1.7 - 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 viscoelastic transition of PMMA that the other experimentalists had found. Similarly, Bauwens-Crowet et al. (1972) found strong correlation between their calculated PC \(\beta\)-process activation energy (9.6 kcal/mol) and the activation
energy of the PC viscoelastic $\beta$-transition measured via dielectric techniques (8 kcal/mol; Locati and Tobolsky, 1970). In both cases, the authors drew the conclusion that restrictions on the same molecular movements govern both phenomena: increased strengthening at high rates/low temperatures, as observed through increased rate-sensitivity of yield, and the secondary ($\beta$) transition in the viscoelastic behavior.

Many of these same ideas were corroborated in a noteworthy lecture by R.F. Boyer of the Dow Chemical Company, on the topic of secondary transitions in polymers.\(^6\) The paper associated with this lecture (Boyer, 1968) draws off of a wide body of experimental data in the literature - ranging from nuclear magnetic resonance (NMR) spectroscopy to impact strength measurements - and provides a similar molecular explanation for the type of trends observed by Roetling and the Bauwens group. In the paper, Boyer surveys available data for eight different engineering plastics, and proceeds to explain how the mechanical behavior of each is affected by the existence, location, rate-dependent shifting, and molecular origins of secondary transitions.

In continuing work, Bauwens and his co-workers furthered their analytical techniques associated with the secondary transitions of amorphous polymers. Assuming that there was a time-temperature equivalence to the yield transition location (i.e. the transition could be induced by either lowering the test temperature or increasing the test strain rate), they developed a method for generating a "master" yield curve capable of predicting the polymer yield strength well beyond rates and/or temperatures accessed during laboratory testing (Bauwens et al., 1969; Bauwens-Crowet, 1973). Furthermore, Bauwens (1972) found that the distributed nature of the yield transition often correlated well with the distributed nature of the $\beta$ viscoelastic transition. Based on this finding, Bauwens proposed a modification to the Ree-Eyring yield equation (equation 1.8), taking into account the shape of the viscoelastic $\tan\delta$ $\beta$-peak. The Bauwens-modified Ree-Eyring yield model was shown to more accurately capture the yield transition of both PC (Bauwens, 1972) and PMMA (Bauwens-Crowet, 1973).


\(^6\)"Dependence of Mechanical Properties on Molecular Motion in Polymers," 1968 International Award in Plastics and Science Engineering lecture, New York City, May 8, 1968.
polymers. Like Bauwens, Fotheringham and Cherry found the original single-process Eyring model (1936) inadequate in capturing new experimental phenomena in the yield behavior of PMMA. However, they did not agree that adding multiple processes to the Eyring theory was necessary to explain the molecular mechanisms of yield or even to predict the experimental data across a wide range of temperatures and/or strain rates. Instead, Fotheringham and Cherry described a single, more complex "cooperative" activation process governing yield. The cooperative model for polymer yield, as first presented by Fotheringham and Cherry (1976), was justified by two points of contemporary molecular theory (Haward & Thackray, 1968): 1) yield is a cooperative process, involving the movement of multiple chain segments but not necessarily multiple types of chain motions of differing length scales 2) amorphous polymers exhibit the ability to recover upon unloading, suggesting that there is a component of the applied stress - the "recovery stress" - which does not contribute to driving plastic flow. Fortheringham and Cherry argue that the two-process model formulation of Bauwens and Bauwens-Crowet not only contradicts these two points, but also does not even capture yield behavior from a phenomenological standpoint. It is on these grounds that they present an alternate theory.

Fotheringham and Cherry’s cooperative model, like the models of Eyring and Bauwens and Bauwens-Crowet, is built upon a thermally-activated description of the yield process. As a necessary pre-condition to viscous flow, a polymer segment transitions from one energy state to another, higher-energy state by overcoming an energy barrier $Q$ through stress-assisted thermal activation. The probability (per unit time) of an individual polymer segment moving from the lower energy state to the higher state is given as:

$$p_1 = p_0 \exp \left( -\frac{Q}{kT} \right) \sinh \left( \frac{\tau^* v^*}{2kT} \right)$$

where $p_0$ is a constant, $Q$ is the activation barrier, $k$ is Boltzmann’s constant, $T$ is the absolute temperature, $v^*$ is the effective activation volume, and $\tau^*$ is the effective shear stress driving plastic flow. The effective shear stress is taken as the difference between the applied shear stress $\tau_a$ and the "recovery stress" $\tau_r$:

$$\tau^* = \tau_a - \tau_r$$

In the "cooperative" yield theory, $n$ polymer segments must simultaneously be in the higher
energy state for flow to occur. Thus, the relevant probability is not \( p_1 \), but \( p_n \):

\[
p_n = (p_1)^n = p_n^0 \exp \left( -\frac{nQ}{kT} \sinh^n \left( \frac{\tau^* v^*}{kT} \right) \right)
\]  \hspace{1cm} (1.11)

Then assuming that the cooperative transition of \( n \) segments leads to a macroscopic strain \( \varepsilon_0 \), the shear strain rate \( \dot{\gamma} \) may be written as:

\[
\dot{\gamma} = K \exp \left( -\frac{nQ}{kT} \sinh^n \left( \frac{\tau^* v^*}{kT} \right) \right)
\]  \hspace{1cm} (1.12)

where \( K \) is a lumped constant including \( \varepsilon_0 \), a transmission factor, and a frequency factor. Note that equation 1.12 is mathematically identical to the original Eyring equation (equation 1.1) in the case \( n=1 \). In practical applications of yield stress prediction, the variables are converted to an axial frame (\( \tau^* \rightarrow \sigma^* \), \( \dot{\gamma} \rightarrow \dot{\varepsilon} \), \( \sigma^* \) is replaced with the quantity \( \sigma_a - \sigma_r \)), and \( \sigma_a \) is set to \( \sigma_y \) (yield strength). In applying the cooperative model to the yield behavior of PMMA (1976) and high density polyethylene (HDPE) (1978), Fotheringham and Cherry calculated the majority of their parameters via numerical curve-fitting methods. The only parameter not calculated in this manner was the recovery stress, \( \sigma_r \); rate- and temperature-dependent values for \( \sigma_r \) were extrapolated from "stress-transient dip stress" experiments (Fotheringham & Cherry, 1978).

The work of Fotheringham and Cherry went relatively unnoticed until the cooperative yield model was revived some time later by Povolo and co-workers (Povolo & Hermida, 1995; Povolo, Schwartz, & Hermida, 1996). Povolo described the rate- and temperature-dependence of yield in both PMMA (1995) and PVC (1996) with equation 1.13 below (derived from equation 1.12, as described above):

\[
\frac{\sigma_y}{T} = \frac{\sigma_i}{T} + \frac{2k}{v} \sinh^{-1} \left[ \left( \frac{\dot{\varepsilon}^*}{\dot{\varepsilon}^*} \right)^{\frac{1}{n}} \right]
\]  \hspace{1cm} (1.13)

with \( \dot{\varepsilon}^* \) described by an Arrhenius relation:

\[
\dot{\varepsilon}^* = \dot{\varepsilon}_0 \exp \left( -\frac{\Delta H}{kT} \right)
\]  \hspace{1cm} (1.14)

The Povolo parameters \( \Delta H \), \( v \), \( \sigma_i \), and \( \dot{\varepsilon}_0 \) correspond directly with the Fotheringham and Cherry parameters \( nQ \), \( v^* \), \( \sigma_r \), and \( K \), respectively. In this more phenomenological version
of the cooperative model, Povolo and Hermida (1995) replaced the recovery stress, calculated experimentally by Fotheringham and Cherry (1978), with an "internal stress" determined through curve fitting. While all other parameters of the model are constants, Povolo found this internal stress to exhibit a temperature dependence of the form:

$$\sigma_i = \sigma_{i0} (T_c - T)$$  \hspace{1cm} (1.15)

where $\sigma_{i0}$ and $T_c$ are additional fitting parameters (constants). In figure 1-11, the Povolo cooperative model described by equations 1.13-1.15 is fit to the PVC yield data of Bauwens et al. (1969) with excellent agreement over a wide range of temperatures and strain rates. Nonetheless, the application of the cooperative yield model by Povolo and co-workers, and Fotheringham and Cherry (1976, 1978) before them, provided little physical insight into rate- and temperature-dependent behavior of amorphous polymers. For instance, there was no physical explanation for the linear temperature dependence of the internal stress (equation 1.15). Furthermore, the theory offered no insight into what these identical, cooperative segmental motions actually were, and it essentially disregarded contemporary experimental evidence of distinctly different molecular motions governing deformation resistance in different temperature/strain rate regimes.

Though contention did exist, most researchers through the 1970s and 1980s followed more closely the paths of Roetling and Bauwens in an attempt 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; they observed the same increased strengthening at low temperatures that both Roetling and the Bauwens group had seen (figure 1-12). The group of Haussy, Cavrot, Escaig, and Lefebvre (1980) studied the temperature-dependent compressive yield strength of PMMA, after Bauwens-Crowet (1973), and first attempted to fit a single-process Eyring model to all their data ($\dot{\epsilon} = 3.5 \times 10^{-5} \text{ s}^{-1}$). At temperatures below -73°C, the data conformed to the model well, using constant values for all three parameters; at temperatures above -73°C (which they refer to as "$T_c$"), a power-law stress dependence in the pre-exponential factor was necessary to fit the data. In continuing work, Lefebvre and Escaig (1985) found that the temperature location of $T_c$ shifts with strain rate, approximately 19°C per decade increase in strain rate. The combined data from the
Parameters for the Povolo cooperative yield model (equations 1.13-1.15) fit to the PVC yield data of figure 1-11

<table>
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<tr>
<td>$\dot{\epsilon}_0$ [s$^{-1}$]</td>
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<td>$\Delta H$ [kJ/mol]</td>
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<tr>
<td>$\sigma_0$ [MPa]</td>
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<tr>
<td>$T_c$ [K]</td>
<td>353</td>
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</table>

Figure 1-11: PVC tensile yield data of Bauwens et al. (1969) fit with a cooperative yield model (Povolo et al., 1996).
Figure 1-12: PC flow stress in shear as a function of temperature and strain rate. Data obtained from torsional tests on tubular specimens (Wu & Turner, 1975).

At the University of Leeds (U.K.), Truss, Clarke, Duckett, and Ward (1984) made a significant contribution to the understanding of yield phenomena in amorphous polymers, even though their testing was conducted on a crystalline thermoplastic. Their comprehensive study 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 different attached environmental chambers. They examined strain rates from $10^{-6}$ s$^{-1}$ to $10^{-1}$ s$^{-1}$ and temperatures from $-153^\circ C$ to $85^\circ C$; example test results are shown in figure 1-14. 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 1.16, of familiar form, was fit to all of their tension data. Equation 1.17, a 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.

\[
\frac{\sigma_y}{T} = \frac{k}{v_1} \left( \ln \dot{\varepsilon} - \ln \frac{\dot{\varepsilon}_{0,1}}{2} + \frac{\Delta H_1}{kT} \right) + \frac{k}{v_2} \sinh^{-1} \left[ \frac{\dot{\varepsilon}}{\dot{\varepsilon}_{0,2}} \exp \left( \frac{\Delta H_2}{kT} \right) \right]
\] (1.16)

\[
\frac{\tau_y}{T} = \frac{k}{v_1} \left( \ln \dot{\gamma} - \ln \dot{\gamma}_{0,1} + \frac{\Delta H_1 + p\Omega_1}{kT} \right) + \frac{k}{v_2} \sinh^{-1} \left[ \frac{\dot{\gamma}}{2\dot{\gamma}_{0,2}} \exp \left( \frac{\Delta H_2 + p\Omega_2}{kT} \right) \right]
\] (1.17)

In these equations, \( v_i, \dot{\varepsilon}_{0,i}, \) and \( \Delta H_i \) 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 – polyethylene's \( T_g \) – 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 transi-
Ree-Eyring model parameters for the polyethylene data of figure 1-14, following equation 1.16

<table>
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<td>$v$ [m$^3$]</td>
<td>$6.28 \times 10^{-27}$</td>
<td>$2.32 \times 10^{-27}$</td>
</tr>
</tbody>
</table>

Figure 1-14: 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: (o) $8.33 \times 10^{-2}$ s$^{-1}$, (□) $4.17 \times 10^{-3}$ s$^{-1}$, (×) $8.33 \times 10^{-4}$ s$^{-1}$, and (▽) $8.33 \times 10^{-5}$ s$^{-1}$ (Truss et al., 1984).
tion in the pressure-dependent yield data. Finally, they observed 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, which had already been shown to have a significant transition in its temperature-dependent yield behavior. As in other studies, they used a universal servo-hydraulic machine with attached environmental chamber to obtain yield data over quasi-static rates and a wide range of temperatures. Here, however, the authors also employed a novel moderate-rate tensile testing machine, driven by a flywheel, to extend their testing capabilities to rates on the order of $100 \text{ s}^{-1}$. The experimental data revealed a significant transition in both the temperature-dependent yield behavior (at $-23^\circ\text{C}$ for $\dot{\varepsilon} = 4.68 \times 10^{-2} \text{ s}^{-1}$) and the rate-dependent yield behavior (at $1 \text{ s}^{-1}$ for $0^\circ\text{C}$). Both phenomena were captured with a single fit of the two-process Ree-Eyring yield model (equation 1.16). The activation energy value for the $\beta$-process that they obtained 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.

1.2.2 Extension to High-Rate Behavior

To further the understanding of the secondary 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.

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 III (2000). A detailed schematic of a typical SHPB apparatus is given as figure 1-15. The test is initiated when high-pressure gas is released from the pressure chamber, causing the striker bar to eject from the barrel. When the striker bar impacts the first pressure bar, the "incident bar", a compressive stress wave is generated. This elastic 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 (approximately $10^3$ to $10^4$ s$^{-1}$). 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
Figure 1-16: Strain gage signals from a characteristic split-Hopkinson pressure bar test on PC.

the corresponding compressive, tensile, and compressive strains $\epsilon_i$, $\epsilon_r$, and $\epsilon_t$. Figure 1-16 provides an example of what these pulses might look like, during a test of 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 as:

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 u}{\partial t^2} \tag{1.18}$$

where $u$ is the displacement along the x-direction (in this case, the axis of the pressure bar), $t$ is time, and $c = \sqrt{E/\rho}$ is the acoustic wave speed in an elastic medium. A general solution to this equation is made particular by the application of appropriate boundary conditions. The difference between two solutions - one for the rate of displacement in the incident bar, one for the rate of displacement in the transmitted bar - leads to an expression for strain rate in the specimen. The measured elastic bar strains also yield expressions for the forces on the front and back surfaces of the specimen, as force equilibrium requires that the same forces be felt on the specimen faces and the ends of the pressure bars. Assuming these two forces - front and back - to be equal, that is, assuming the specimen has achieved "dynamic
equilibrium” and is undergoing homogeneous deformation, leads to a simplification of the final stress and strain rate equations:

\[ \dot{\varepsilon} = \frac{2c\varepsilon_r}{l_s} \quad (1.19) \]

\[ \sigma = \frac{A_b E_t \varepsilon_t}{A_s} \quad (1.20) \]

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 found via numerical integration of equation 1.19. Note 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.

Because there is still no standard method for the SHPB test, nor a standard design for the SHPB apparatus, an experimentalist faces many issues during application of the SHPB test method. These issues include: proper choice of bar material, axial alignment of the striker bars and pressure bars, optimization of the excitation, gain, and filtering settings for the amplifier/data acquisition system, accounting for the effects of wave dispersion, mitigation of frictional effects, and the selection of appropriate specimen geometry. Specimen geometry is perhaps the most critical issue. The specimen length determines the time to dynamic equilibrium, and hence the validity of the low-strain data, as well as the maximum theoretical strain and strain rate which can be achieved during a test (both are inversely proportional to the specimen length). Furthermore, the specimen geometry must be chosen in consideration of longitudinal and radial inertia effects, frictional forces, and buckling concerns. Recent review articles (Chen, Zhang, & Forrestal, 1999; Gray III & Blumenthal, 2000) have addressed the unique difficulties associated with testing polymeric materials in the SHPB system; the reader is directed to these references for further details on the test methods.

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. These authors studied the rate-dependent yield and compressive stress-strain behavior of two amorphous polymers - PMMA and cellulose acetate butyrate (CAB) - at strain rates ranging from \( 10^{-4} \text{ s}^{-1} \) to \( 10^3 \text{ s}^{-1} \). The tests at the highest rates were
conducted on a split-Hopkinson pressure bar system. For both polymers, they observed an increased rate sensitivity of yield at moderate and high rates. Also, by embedding a thermocouple in all of their compression specimens, Chou et al. observed a significant rise in the specimen temperature at these rates. They attributed this heat evolved to an adiabatic thermodynamic condition, and related it to an increase in the amount of strain softening at high rates.

Later, Walley and Field at the University of Cambridge (UK) published several related studies focused on the rate-dependent behavior of polymeric materials: Walley, Field, Pope, and Safford (1989), Walley, Field, Pope, and Safford (1991), Walley and Field (1994). During these studies, Walley, Field, and co-workers evaluated the rate-dependent compressive behavior of seventeen different polymers on four different apparatus, including a direct-impact Hopkinson bar\(^7\) for strain rates above \(10^3\, \text{s}^{-1}\). Some example stress-strain curves, from the study of PVC at strain rates of \(10^{-2}\, \text{s}^{-1}\) to \(10^4\, \text{s}^{-1}\), are given as figure 1-17.

In addition to studying the effects of friction in compression tests, Walley and Field had

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\(^7\)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.
hoped to combine the data from tests across the different strain rate regimes and discover which polymers exhibited increased strengthening at high rates (> $10^3$ s$^{-1}$). Of the seventeen different polymers that they tested, Walley and Field found that acrylonitrile-butadiene styrene (ABS), poly(ethylene terephthalate) (PET), polypropylene (PP), PVC, and poly(vinylidene fluoride) PVDF all exhibited an increased rate sensitivity of yield within the high rate regime. They supposed that the yield behavior of these materials would need to be interpreted in terms of the two-process Ree-Eyring modification to Eyring's viscosity theory.

Rietsch and Bouette (1990) were the first researchers to use SHPB testing in deliberate continuation of the work conducted by Bauwens (1972). That is, they attempted to use high-rate compression testing to further the evidence of a secondary transition in the yield behavior 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, Rietsch and Bouette were able to test PC in uniaxial compression at strain rates between 150 s$^{-1}$ and 3000 s$^{-1}$ and temperatures from -40°C to 60°C. Figure 1-18 is a 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 servo-hydraulic machine.

As expected, the data revealed a distinct transition in the rate-dependent yield behavior of PC, for all temperatures investigated. At room temperature, this transition appears at a strain rate of approximately 100 s$^{-1}$. Rietsch and Bouette successfully fit all of the yield data with a two-process Ree-Eyring model, following equation 1.8 proposed by Bauwens et al. (1969). By comparing the tables adjoining figures 1-10 and 1-18, we can see that there is relatively good agreement between the Ree-Eyring parameters calculated by Bauwens - fitting only temperature-dependent data - and the same parameters calculated by Rietsch and Bouette. The slight discrepancies may be attributed to the different brands, and hence different exact chemical compositions, of PC used in the two studies. In interpreting the data, Rietsch and Bouette agree with Bauwens, that the yield behavior transition is linked to the well-documented $\beta$-relaxation process of PC.

In studies that followed, a number of researchers corroborated the experimental findings of Rietsch and Bouette (1990). Moy, Weerasooriya, Hsieh, and Chen (2003) conducted uniaxial compression tests on PC at room temperature over the strain rate range $10^{-4}$
Ree-Eyring model parameters for the PC data of figure 1-18

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<td>Q [kcal/mol]</td>
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<td>C [s]</td>
<td>$4.10 \times 10^{-30}$</td>
<td>$2.9 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

Figure 1-18: PC yield data as a function of temperature and strain rate, fit with the Ree-Eyring model. Temperatures are as follows: (○) -40°C, (◇) -20°C, (△) 0°C, (■) 10°C, (◇) 20°C, (▼) 40°C, (▲) 60°C (Rietsch & Bouette, 1990).
s\(^{-1}\) to \(10^3\) s\(^{-1}\). They too found that PC transitions to a regime of increased strain rate sensitivity of yield, at a strain rate of approximately 300 s\(^{-1}\). Furthermore, Moy and co-workers found that the initial elastic modulus increases proportional to the yield strength with increases in strain rate. Recently, Siviour, Walley, Proud, and Field (2005) revisited the PC experiments of Walley and Field (1994), improving upon the test techniques and expanding the study to include temperature-dependent behavior (-50°C to 150°C) as well as rate-dependent behavior (\(10^{-4}\) s\(^{-1}\) to \(10^4\) s\(^{-1}\)). This time, the room temperature data revealed that PC exhibits an increased rate sensitivity of yield in the high-rate regime, as compared to the low-rate regime. In tests at constant rate (\(\sim 5500\) s\(^{-1}\)), a similar transition was observed in the temperature-dependent yield behavior, located at approximately 40°C. Through the extrapolation of DMA data, both of these yield transitions were found to occur under the same strain rate/temperature conditions as the viscoelastic β-transition.

Along these same lines, Cady and co-workers at Los Alamos National Laboratory presented a comprehensive study on the rate (\(10^{-3}\) s\(^{-1}\) to 2500 s\(^{-1}\)) and temperature (-55°C to 300°C) dependent behavior of two important engineering plastics, amorphous polyamideimide (PAI) and semi-crystalline PEEK (Cady, Blumenthal, Gray III, & Idar, 2003). With advanced SHPB techniques, including pulse shaping, this group was able to obtain accurate low-strain data in even the high-rate tests, and thus examine the relationship between temperature, strain rate, and the initial slope of the stress-strain curve ("loading modulus"). Cady et al. used this information to locate the glass-transition temperature of the two polymers at different strain rates, as the 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 1-19. It is reported 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 the loading modulus, yield stress, and flow stress all 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 rate- and temperature-dependent trends, is needed for accurately describing the mechanical behavior of thermoplastics at high rates of strain.

In recognition of the need for an appropriate constitutive model, and in consideration of more recent data detailing the behavior of amorphous polymers at high strain
Figure 1-19: Initial loading modulus as a function of temperature and strain rate for a) PEEK and b) PAI. These plots are intended to show the shift in $T_g$ with strain rate (Cady et al., 2003).

rates, Richeton, Ahzi, and co-workers (Richeton, Ahzi, Daridon, & Rémon, 2005a, 2005b; Richeton, Ahzi, Vecchio, Jiang, & Adharapurapu, 2006) have revived interest in the cooperative model. The mathematical form of the model that they present is nearly identical to that originally posed by Fotheringham and Cherry (1976, 1978), and later applied by Povolo and co-workers (Povolo & Hermida, 1995; Povolo et al., 1996), with two noteworthy exceptions: the form is altered for temperatures near $T_g$, and pressure dependence of yield is considered. However, the theoretical basis is changed considerably, in comparison with the ideas of Fotheringham and Cherry, and, to a lesser extent, the ideas of Povolo and co-workers. In decreasing the applied stress by an amount $\tau_r$ (equation 1.10), Fotheringham and Cherry (1976) were accounting for the fact that "... some of the applied stress is borne by an elastic recovery element and that this reduces the effective stress on the time dependent flow process." In the Richeton and Ahzi formulation (Richeton et al., 2005b), the recovery stress has become the internal stress, "... a structural parameter, which depicts the arrangement of defects inherited from past thermal history." As with Povolo and co-workers (Povolo et al., 1996), appropriate values for the internal stress are found from curve fitting.

Furthermore, the physical interpretation of the activation barrier in the model has been changed. In the original formulation (Fotheringham & Cherry, 1976), the activation energy of the cooperative process is given as the quantity $nQ$, where $n$ is the number of segments
Cooperative model parameters
for the PC data of figure 1-20

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<td>m [MPa/K]</td>
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<td>ΔHₛ [kJ/mol]</td>
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Ree-Eyring model parameters
for the PC data of figure 1-20

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<td>Q [kJ/mol]</td>
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<td>C [s]</td>
<td>4.10 x 10⁻³⁰</td>
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</table>

Figure 1-20: PC yield data as a function of strain rate (logarithmic scale), fit with both the cooperative and Ree-Eyring yield models (Richeton et al., 2005b). Experimental data and Ree-Eyring parameters have been taken from Rietsch and Bouette (1990).
acting cooperatively, and $Q$ is the activation energy for a single segment in viscous flow. In the Richeton-Ahzi model, the activation energy is taken to be the $\beta$-process activation energy, $\Delta H_\beta$, identical in meaning to $Q_\beta$ in the Ree-Eying yield model (equation 1.8). Richeton et al. (2005a) note that it is the first time the cooperative model has been linked to the $\beta$-process, which has been acknowledged by previous researchers as a plasticity precursor (e.g. Xiao, Jho, and Yee, 1994) and the source of enhanced strength at high rates/low temperatures in many amorphous polymers (e.g. Bauwens, 1972). In fitting the yield data of PMMA and PVC, Richeton et al. (2005b) find excellent agreement between their calculated $\Delta H_\beta$ and the $Q_\beta$ values calculated by Bauwens-Crowet and co-workers (Bauwens-Crowet et al., 1969; Bauwens-Crowet, 1973).

In order to capture yield behavior at and above $T_g$, Richeton et al. (2005b) proposed an altered form for the characteristic strain rate (the original expression is given by equation 1.14):

$$\dot{\epsilon}^*(T \geq T_g) = \dot{\epsilon}_0 \exp\left(-\frac{\Delta H_\beta}{kT_g}\right) \exp\left(\frac{\ln 10 \times c_1^0}{c_2^0 + T - T_g}\right)$$

(1.21)

where $c_1^0$ and $c_2^0$ are the parameters of the Williams-Landel-Ferry (WLF) equation, describing polymer time/temperature superposition above the glass transition. Richeton et al. also found it necessary to prescribe $\sigma_i = 0$ for temperatures above $T_g$, making $\sigma_i(T)$ a discontinuous function over any span including $T_g$. Furthermore, this treatment of the yield behavior at and above $T_g$ is based on an approximation that the temperature location of the glass transition does not change with strain rate; the experimental data of Cady et al. (2003) and Siviour et al. (2005), among others, contradicts this assertion.

Richeton et al. (2006) also propose changes to the cooperative model in order to account for the effects of hydrostatic pressure, though the changes are not tested against any experimental data. The modifications are based on limited experimental evidence (e.g. Rabinowitz, Ward, and Parry, 1970) indicating that the yield strength of amorphous polymers is linearly related to the hydrostatic pressure. Richeton et al. propose the following:

$$\sigma_y(P) = \sigma_y(0) + \alpha_p P$$

(1.22)

where $\sigma_y(P)$ is the yield strength at pressure $P$, $\sigma_y(0)$ is the yield strength under zero

\footnote{At temperatures below $T_g$, the internal stress is given as: $\sigma_i(T) = \sigma_i(0) - mT$, where the Richeton et al. cooperative model parameters $\sigma_i(0)$ and $m$ correspond to the Povolo et al. parameters $(\sigma_{i0} T_c)$ and $\sigma_{i0}$, respectively (equation 1.15).}
Cooperative model parameters for the PC, PMMA, and PAI data of figures 1-21 and 1-22

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<td>315</td>
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Figure 1-21: PC, PMMA, and PAI yield data as a function of both strain rate (logarithmic scale) and temperature, fit with the cooperative yield model (Richeton et al., 2005b).
Figure 1-22: PC, PMMA, and PAI yield data as a function of temperature at 0.01 s\(^{-1}\), fit with the cooperative yield model (Richeton et al., 2005b).
pressure, and $\alpha_p$ is the pressure sensitivity coefficient. Such formalism simply adds an additional term, $\alpha_p P$, to the end of the yield stress equation (equation 1.13).

Figures 1-20 to 1-22 demonstrate the success of the Richeton-Ahzi cooperative model in capturing rate- and temperature-dependent yield data for a variety of amorphous polymers. In figure 1-20, the cooperative model predictions are compared directly with predictions given by the two-process Ree-Eyring model, for the case of PC. The predictions of the two models appear very similar for strain rates greater than $10^{-3}$ s$^{-1}$, and both capture the experimental data at these rates very well. Below $10^{-3}$ s$^{-1}$, however, the cooperative model predicts a nearly constant yield stress (independent of strain rate), while the Ree-Eyring model predicts that yield stress will continue to decrease with decreasing rate. Unfortunately, this key difference in the model predictions is not tested against any experimental data. In the graphs of figures 1-21 and 1-22, the model is tested against a wide body of experimental data on PC, PMMA, and PAI, developed by the authors themselves (Richeton et al., 2006). In these cases, the model performs very well, accurately capturing experimental data that spans $\sim 200^\circ$C and eight decades in strain rate. In figure 1-22, it is even shown that the model is able capture the dramatic drop in yield strength as the polymer passes through its glass transition.

1.2.3 Molecular Origins

Sophisticated experimental techniques, especially in the realm of high strain rate ($\dot{\varepsilon} > 100$ s$^{-1}$) testing, have confirmed the existence of secondary transitions in the rate- and temperature-dependent mechanical behavior of many amorphous polymers. These transitions were first identified in the yield data of Roetting (1965b) and Bauwens-Crowet and Homès (1964); more recent experimental data, covering rate- and temperature-dependent modulus, yield, and post-yield stress-strain behavior, have elucidated the macroscopic phenomena associated with these secondary transitions. This body of data has led to improved phenomenological models capable of capturing the observed behaviors. At the same time, significant effort has been put towards understanding the specific molecular dynamics which govern these secondary transitions. This molecular-level research - both theoretical and experimental - aids in development of physically-based models, and also helps chemists to design polymers for specific applications. In particular, it may be possible to develop new polymers for low temperature and/or high rate applications by understanding the molecular motions.
which are involved with secondary transitions.

The molecular dynamics of glassy polymers are most often investigated with macroscopic techniques that probe viscoelastic behavior. It is well known that the viscoelastic behavior of any glassy, amorphous polymer is governed by multiple activated processes (see, for instance, Ferry, 1961). These different activated processes generally correspond to different segmental motions of the polymer's macromolecules. When a particular segmental motion becomes restricted, the corresponding process will require stress-assisted activation, and thus the polymer's viscoelastic behavior passes through a transition. As is now understood, these restricted motions also cause transitions in the rate-dependent yield behavior of many amorphous polymers. However, in that case, it is not as easy to deconvolute the contributions from different processes, and the transitions are not always as clear. By probing the viscoelastic behavior of a series of polymer homologues, with gradual adjustments in the backbone and/or side chain chemistry, one may gain insight into the particular molecular mobilities associated with various transitions.

Dynamic mechanical thermal analysis (DMTA) and dielectric analysis (DEA) are two techniques for probing the viscoelastic behavior of a glassy polymer, and are the two experiments most often used in studies of molecular dynamics. In a typical DMTA experiment, the specimen is loaded with a sinusoidally-varying strain (stress) amplitude, and the stress (strain) response is sampled. This material response is measured in two components: one in phase with the load program, characterized by the storage modulus $E'$, and one out of phase from the load program, characterized by the loss modulus $E''$. In a completely analogous manner, the DEA experiment involves loading the specimen with an oscillatory electric field, and measuring both the in-phase (capacitive) and out-of-phase (conductive) components of material response. In both cases, the response is measured as a function of test temperature and the frequency of the oscillations in the load program. So long as the activated processes of a particular polymer involve the motion of permanent dipoles, the dielectric experiment and its changing electric field will sample the same molecular dynamics induced by oscillatory mechanical loading.

The DMTA and DEA macroscopic techniques may be used in conjunction with "microscopic" spectroscopy methods such as nuclear magnetic resonance (NMR; see, for instance, McGrath, Ngai, & Roland, 1995), positron annihilation (Davis & Pethrick, 1998), and neutron scattering (Floudas, Higgins, Meier, Kremer, & Fischer, 1993). While these methods
are generally geared towards investigations of molecular structure, they can provide important information in regards to the length scale(s) and/or conformation states associated with a particular molecular motion. Nonetheless, there does not exist any technique for direct visualization of the molecular motions; the experimentalist is left to interpret available experimental data and theorize. For this reason, the specific molecular motions associated with the secondary transitions of many amorphous polymers are still in doubt (Hutchinson, 1997).

Experimental investigation into the molecular origins of secondary transitions began nearly fifty years ago. At this time, there was already a great deal of interest in both PC and PMMA, two amorphous polymers which are prominent in many engineering applications. Both polymers were known to have a pronounced secondary ($\beta$) transition. According to the review article of Illers, Kilian, and Kosfeld (1961), the $\beta$-transition of PC (figure 1-23) may be attributed to the restricted rotation of the highly-polar carbonate group about the main chain. They based this conclusion on a series of spectroscopic measurements, indicating that the $\beta$-transition peak observed via the dielectric technique was identical in both temperature location and intensity to that seen in DMTA experiments. Later, both Nielsen (1962) and Bussink and Heijboer (1964) presented experimental results and corresponding theory in agreement with the conclusions of Illers and co-workers. However, NMR measurements (Matuoka and Ishida, as cited by Boyer, 1968) pointed towards a different explanation: the PC $\beta$-transition is given by restricted rotation of the phenyl rings. These differing opinions were reconciled by Boyer (1968), who suggested that the $\beta$-motion is a rotation of the carbonate group, which in turn induces motion in the adjacent phenyl rings.
In the case of PMMA (figure 1-24), Illers, Kilina, and Kosfeld (1961) did not have sufficient data to identify the molecular origins of the $\beta$ transition. However, they cite contemporary NMR data which indicates that the entire ester side group is unable to move at temperatures below -196°C (well below the $\beta$-transition temperature). Over the next five years, significant research into the molecular mobilities of PMMA was conducted at TNO-Delft (Holland), including dielectric and dynamic mechanical experiments on a variety of PMMA homologues. In reviewing this work, Heijboer (1964) concludes that the PMMA $\beta$-transition is associated with restricted rotations of the entire ester side group about the main-chain. He suggests that further work is needed to understand the cooperative, intermolecular nature of this motion; that is, do side group rotations on one chain affect/induce/require side group rotations on neighboring chains?

In the mid-1960s, the cooperative nature of the PC $\beta$-motions was also unclear. However, over the past 15 years, studies involving PC homologues have yielded a great deal of insight on the subject. Yee and co-workers (Jho & Yee, 1991; Xiao & Yee, 1992) synthesized a series of bisphenol-A polycarbonate (BPA-PC; traditional polycarbonate) and tetramethylbisphenol-A polycarbonate (TMBPA-PC) block copolymers. In dynamic mechanical testing, they found that only those block copolymers with at least 9 monomer units in each block would exhibit the same two secondary transitions given by the constituent
homopolymers individually. Thus, Yee and co-workers conclude that the PC $\beta$-motions are intramolecular cooperative motions, involving approximately 7 adjacent monomer units. In another study, Floudas et al. (1993) tested a PC variant ("biphenyl" PC - BPPC) where adjoining phenyl rings were bonded together, such that $\pi$-flips of the individual phenyl rings could not occur. They found that this variation did not change the character or location of the PC $\beta$-transition, as accessed through dynamic mechanical testing. Thus Floudas and co-workers conclude that the phenyl ring $\pi$-flips alone do not constitute the $\beta$-motions\(^9\), and that there must be some amount of intra- or intermolecular cooperativity involved.

In a recent review article on molecular mobilities in amorphous polymers, Monnerie, Laupretre, and Halary (2005) present an even more complex view of the PC $\beta$-motions. Monnerie and co-workers suggest that the associated motion changes at the transition peak. On the low-temperature side, they say, the motion is mainly phenyl ring oscillations of moderate amplitude, and smaller motions of the adjoining carbonate groups. Since these motions are very local, there is minimal intramolecular or intermolecular cooperativity. On the high-temperature side, however, the motion is phenyl ring $\pi$-flips which induce motion not only on the same chain (intramolecular cooperativity), but also on neighboring chains (intermolecular cooperativity). Monnerie and co-workers (2005) present similar theory for the $\beta$-motions of PMMA: on the low-temperature side (below 0°C), the associated motion is an isolated $\pi$-flip of the ester side group; on the high-temperature side, it is a $\pi$-flip of the ester group coupled with an internal rotation of the attached main-chain units - a cooperative, intramolecular motion. This theory is in accordance with that of Heijboer (1964); unlike the case of PC, there exists a general consensus in regards to the molecular origins of the PMMA $\beta$-transition.

While in some cases the length scale and cooperative nature of these secondary molecular motions may still be in contention, it is clear that the motions are distinct from and much smaller in scale than those motions associated with the $\alpha$ (glass) transition. For the glass transition, it is generally agreed that the corresponding molecular motion is a cooperative rotation and/or translation of neighboring main chain segments with respect to one another (Dionisio, Alves, & Mano, 2004). These segments may be as long as 50 monomer units, depending on the particular polymer. Thus it is perhaps natural to develop a macroscopic

\(^9\)Up until this point, the pervading theory was that the PC $\beta$-motions are in fact phenyl ring $\pi$-flips (Hutchinson, 1997).
mechanical model for the polymer which considers separately the effects of the $\alpha$ and $\beta$ molecular mobilities. So long as the model is general enough, the exact details of the secondary molecular motions shall be inconsequential.

1.3 Constitutive Modelling

Throughout sections 1.1 and 1.2, a variety of theories related to the initiation of plastic flow in amorphous polymers were delineated. Many of these theories drew connections between the secondary molecular mobilities discussed in section 1.2.3 (above) and macroscopic phenomena observed experimentally. The models associated with these theories were, in general, designed for predicting yield strength under various temperature and rate conditions; nearly all of them are capable of predicting yield strength across a rate- or temperature-induced transition. However, none of these models are capable of predicting post-yield stress-strain behavior. For such predictions, a constitutive model is required. Framed in three-dimensions through the mathematics of continuum mechanics, a constitutive model is the ultimate link between materials science and predictive engineering tools based on the finite element method. Coupled with an appropriate material model, finite element analysis allows for efficient, cost-effective design and testing of engineering components through numerical simulation.

Significant effort has been put towards developing an appropriate constitutive model for amorphous polymers, to be used in finite element analysis, which is general enough to capture material behavior over a wide range of loading conditions. Though many different groups have participated in these efforts, it is the purpose of this section to review one particular lineage of constitutive models based mainly upon the work of Mary Boyce and co-workers. The constitutive model described later in this thesis may be considered the most recent addition to the family of Boyce models – a direct descendent of the ones before it. Note that, prior to the introduction of the Mulliken and Boyce model (Mulliken, 2004), there did not exist in this lineage a constitutive model capable of capturing and predicting the experimental phenomena of the secondary transitions.

The thermoplastic constitutive models of Boyce and co-workers can trace their origins to the seminal work of Haward and Thackray (1968). At a time when the study of large deformations in polymers was at a "primitive stage", Haward and Thackray proposed a
mathematical model to predict the stress-strain behavior of glassy thermoplastics under isothermal uniaxial tension. As shown in figure 1-25, the model is composed of three separate constituent elements to account for distinct contributions to the total deformation resistance. The linear (Hookean) spring accounts for initial elasticity; in this one-dimensional model, it is described by a single elastic constant, $E (\sigma = E\varepsilon)$. The non-linear spring is used to define the entropic resistance to large deformations, based on contemporary theories of rubber elasticity. Finally, the rate- and temperature-dependent resistance to plastic flow is captured with an Eyring-type dashpot. This component of the model draws the closest analogy to the yield models described in sections 1.1 and 1.2. It is defined by a simplified version of Eyring’s rate equation (equation 1.1):\
\[
\text{rate of flow} = K \sinh \left( \frac{V\tau}{2kT} \right)
\]  
(1.23)
where $k$ is Boltzmann’s constant, $\tau$ is the equivalent shear stress, $T$ is the absolute temperature, and $K$ and $V$ are constants to be determined.

The model of Haward and Thackray (1968) was shown to adequately capture major features of the stress-strain behavior of cellulose nitrate, cellulose acetate, and PVC, over a range of temperatures ($23^\circ\text{C}, 49^\circ\text{C},$ and $54^\circ\text{C}$) and strain rates ($3 \times 10^{-5} \text{ s}^{-1}$ to $2 \times 10^{-2} \text{ s}^{-1}$). More importantly, Haward and Thackray’s mathematical model provided a conceptual

Figure 1-25: Rheological interpretation of Haward and Thackray’s 1-D mathematical model for the large deformation behavior of glassy thermoplastics (Haward & Thackray, 1968).
framework upon which future constitutive models would be built. In these future models, the specific mathematical functions of the constituent components would become more refined, and the equations would be generalized to three dimensions. However, all of the models would retain the basic structure outlined by Haward and Thackray, whereby the total deformation resistance is decomposed into the contributions from intermolecular forces (linear elasticity and viscoplastic flow) and entropic resistance (rubber elasticity).

Among others, Argon (1973) agreed with the overarching concept of Haward and Thackray’s thermoplastic model. As reviewed in section 1.1, Argon proposed new theory in regards to the initiation of plastic flow in glassy polymers. Argon’s ideas would ultimately serve to refine the understanding and treatment of the intermolecular deformation resistance. His work was motivated in particular by two significant experimental findings: 1) the pressure dependence of the yield stress in many polymers is paralleled by the pressure dependence of the shear modulus (Brown, 1971), and 2) the temperature dependence of the yield stress is related to the temperature dependence of the shear modulus (Argon et al., 1968). Argon developed an expression for the free energy barrier to molecular mobility (equation 1.6) by approximating the molecular chains as elastic cylinders embedded in an elastic medium. With appropriate simplifications, and ignoring the explicit pressure dependency, the expression for the free energy barrier may be written as:

\[
\Delta G = \frac{3\pi \mu \omega^2 a^2}{16(1-\nu)} \left[1 - \left(\frac{\tau}{\frac{0.077\mu}{1-\nu}}\right)^{\frac{5}{6}}\right]
\]

(1.24)

where \(\tau\) is the shear stress, \(\mu\) is the shear modulus, \(\nu\) is the Poisson ratio, and \(\omega\) and \(a\) are geometrical parameters of idealized polymer molecule. This free energy barrier is inserted into a rate equation describing the thermally-activated and distributed nature of macroscopic plastic flow:

\[
\dot{\gamma} = \dot{\gamma}_0 \exp \left[-\frac{\Delta G}{2kT}\right]
\]

(1.25)

Where \(\dot{\gamma}_0\) is a pre-exponential frequency parameter, \(k\) is Boltzmann’s constant, and \(T\) is the absolute temperature.

Though mathematically similar to the rate equation of the Eyring theory (1936), Argon’s equations (1973) had a stronger physical basis, making them specific to plastic flow in glassy polymers. Compared to the form used by Haward and Thackray (equation 1.23), the Argon
model described a much more complex intermolecular resistance to plastic deformation. Argon’s theory suggested the existence of a barrier to plastic flow—a "shear resistance"—which was implicitly dependent on both temperature and pressure through the temperature and pressure dependence of the shear modulus.

Argon’s description of intermolecular deformation resistance would later be coupled with Haward and Thackray’s model scheme to form the Boyce-Parks-Argon ("BPA") constitutive model for glassy polymers (Boyce, Parks, & Argon, 1988c). This constitutive model was fully three-dimensional, following a finite-strain kinematic framework originally outlined by Onat and co-workers (Fardshisheh & Onat, 1972; Onat, 1988). In all three components of the model, the material description was refined to better account for the rate-, temperature-, and pressure-dependence of material response to large deformations, as well as the "strain softening" phenomenon (figure 1-1; discussion page 18).

The stress of the elastic spring was again calculated through Hooke’s Law, this time in three dimensions:

$$
T = \frac{1}{J} \mathcal{L}^e [\ln \mathbf{F}^e]
$$

(1.26)

Where $\mathbf{T}$ is the Cauchy (true) stress tensor, $J = \det \mathbf{F}^e$ is the elastic volume change, $\mathcal{L}^e$ is the fourth-order modulus tensor, and $\ln \mathbf{F}^e$ is the Hencky strain, derived from the elastic component of the deformation gradient. The modulus tensor is characterized by two elastic constants, such as the shear modulus $\mu$ and the bulk modulus $\kappa$:

$$
\mathcal{L}^e = 2\mu \mathcal{I} + \left(\kappa - \frac{2}{3}\mu\right) \mathbf{I} \otimes \mathbf{I}
$$

(1.27)

where $\mathcal{I}$ and $\mathbf{I}$ are the fourth-order and second-order identity tensors, respectively. In this model, the two elastic constants are assumed to both be functions of temperature.

As in Haward and Thackray’s model, the description of the entropic resistance is taken from rubber elasticity theory. Specifically, Boyce et al. use the non-Gaussian statistical mechanics network model of Wang and Guth (1952) to define the principal components of entropic back stress, $B_i$:

$$
B_i = C_R \frac{\sqrt{N}}{3} \left[ V_i^p \mathcal{L}^{-1} \left( \frac{V_i^p}{\sqrt{N}} \right) - \frac{1}{3} \sum_{j=1}^{3} V_j^p \mathcal{L}^{-1} \left( \frac{V_j^p}{\sqrt{N}} \right) \right]
$$

(1.28)

where the $V_i^p$ are the principal components of the left plastic stretch tensor and $\mathcal{L}^{-1}$ is the
inverse Langevin function, defined by $\mathcal{L}(\beta) \equiv \coth \beta - \frac{1}{\beta}$. The constants to be determined are: $N$, the number of rigid links between chain entanglements, and $C_R$, the rubbery modulus (a function of temperature).

Finally, the rate of viscoplastic flow in the Boyce-Parks-Argon constitutive model (1988c) is described by Argon’s theory (1973):

$$\dot{\gamma}^p = \gamma_0 \exp \left[ -\frac{A_s}{T} \left( 1 - \left( \frac{T}{s} \right)^{\frac{s}{\delta}} \right) \right]$$

Where two lumped parameters, $A$ and $s$, have been introduced for simplicity. $A$, which includes the geometrical parameters of Argon’s idealized molecule, is taken to be a constant with regards to rate, temperature, pressure, and deformation state; its value is determined from experimental yield data. The parameter $s$, on the other hand, is implicitly dependent upon temperature, as its initial value is proportional to the shear modulus:

$$s_0 = \frac{0.077\mu}{1 - \nu}$$

Based on Argon’s analysis, the shear yield strength $\tau$ will approach $s_0$ as the absolute temperature tends towards zero. Thus, $s$ is deemed to be the "athermal shear strength"; it essentially represents the polymer’s intrinsic shear resistance. That is, the shear resistance in the absence of any thermal motion or thermal activation. As plastic deformation occurs, the macromolecular structure is thought to re-arrange in such a way that the intermolecular barrier to plastic flow decreases. This phenomenon, known as strain softening, is captured in the Boyce-Parks-Argon model through an evolution in the shear resistance $s$:

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

where $h$ is the softening slope (a fitting parameter), and $s_{ss}$ represents the "steady-state" or preferred value of the shear resistance. Finally, Boyce et al. suggest that the shear resistance also be modified to capture the effects of hydrostatic pressure:

$$\tilde{s} = s + \alpha p$$

where $p$ is the pressure and $\alpha$ is a pressure coefficient. Thus, in their implementation of
Boyce-Parks-Argon model parameters for the PMMA predictions of figure 1-26

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<td>$C_R$ [MPa]</td>
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</tr>
</tbody>
</table>

Figure 1-26: PMMA rate-dependent tensile stress-strain behavior: Boyce-Parks-Argon constitutive model predictions vs. experimental results (Boyce et al., 1988c).

plasticity in the constitutive model, Boyce, Parks, and Argon have taken Argon’s theory for viscoplastic flow (1973) and consolidated the intermolecular shear resistance into a single parameter, $\tilde{s}$. This parameter is explicitly dependent upon pressure and deformation state, and implicitly dependent on temperature. Though it is neither implicitly not explicitly dependent on strain rate, the authors hint to this possibility for future versions of the model.

As part of her doctoral thesis work, Boyce (1987) implemented the constitutive model numerically for use with a commercial finite element code. In figure 1-26, the numerical predictions of PMMA tensile behavior are compared against experimental results. The model is shown to capture very well the characteristic features of the stress-strain curves, including initial elasticity, global yield, strain softening, and strain hardening. Over the next
Figure 1-27: Three-chain model representation of a molecular network in (a) undeformed, (b) uniaxial extension and (c) biaxial extension configurations (Arruda & Boyce, 1993a).

few years, the model would prove successful in predicting the behavior of glassy polymers in varying loading conditions (Boyce, Parks, & Argon, 1988a, 1988b, 1989; Boyce & Arruda, 1990; Boyce, Montagut, & Argon, 1992a). Not only did this model successfully capture phenomenological features of the mechanical behavior, but it do so from a sound physical basis, considering both micromechanisms of plastic flow as well as the effects of an evolving molecular network. The significance of the Boyce-Parks-Argon model is underscored by the fact that it brought together current theories of macromolecular physics with recent work in the fields of statistical mechanics, continuum mechanics, and computational mechanics.

The next notable installment in the evolution of the Boyce et al. constitutive model came in 1993, when Arruda and Boyce (1993a, 1993b) proposed a revision to the definition of the network resistance. At the time, a number of physically-based rubber elasticity models existed. These statistical mechanical models are generally defined by two main elements: the mathematical description of single-chain behavior, and the multi-chain representation of a macromolecular network. While most models described single chain behavior with a non-Gaussian formulation, they varied in their representation of the network. In the Wang and Guth model (1952) employed by Boyce, Parks, and Argon (1988c), three non-Gaussian chains arranged perpendicular in a unit cube (figure 1-27) are used to predict the entropic forces associated with large deformation. Arruda and Boyce (1993b) found this particular model, among others, incapable of predicting a dependence of the stress-stretch behavior on the deformation state. However, the classical rubber elasticity data of Treloar (1944) clearly showed a different stress-stretch curve for uniaxial extension vs. pure shear. Furthermore, Arruda and Boyce (1993b) found existing models which sampled all possible molecular orientations to be mathematically very cumbersome (see, for instance, Treloar, 1975).
Ultimately, Arruda and Boyce suggested a rubber elasticity model of their own design (1993b), which they then inserted into the Boyce-Parks-Argon constitutive model in place of the Wang and Guth (1952) form of network resistance (Arruda & Boyce, 1993a). In the Arruda-Boyce rubber elasticity model, the network is represented with eight centrally-connected non-Gaussian chains in a unit cube (figure 1-28); it is alternately referred to as the "eight-chain model". With just two physically-based parameters, this model represents a mathematically efficient way to sample all possible molecular orientations. In the eight-chain model, the principal components $B_i$ of the entropic back stress are given as:

$$B_i = C_R \frac{\sqrt{N}}{3} \mathcal{L}^{-1} \left( \frac{\Lambda_{\text{chain}}^p}{\sqrt{N}} \right) \left( \frac{(\Lambda_{1}^p)^2 - \frac{1}{3} I_1}{\Lambda_{\text{chain}}^p} \right)$$

(1.33)

where the $\Lambda_i^p$ are the principal plastic stretches (from $\text{FP}$), the first invariant $I_1$ is defined as:

$$I_1 = (\Lambda_{1}^p)^2 + (\Lambda_{2}^p)^2 + (\Lambda_{3}^p)^2$$

(1.34)

and $\Lambda_{\text{chain}}^p \equiv \sqrt{\frac{I_3}{3}}$ is the average plastic chain stretch. With this description of rubber elasticity in place, the revised glassy polymer model was able to successfully predict the strong deformation state-dependence of the stress-strain behavior of both PC (figure 1-29) and PMMA (figure 1-30). Furthermore, the model was shown to capture the unique anisotropic character of the molecular chain network which evolved as a function of the deformation state (Arruda & Boyce, 1993a; Boyce, Arruda, & Jayachandran, 1994). The critical revision in the formulation of the Boyce et al. (1988c) constitutive model proposed by Arruda and Boyce (1993a) greatly enhanced its functionality. Previously, model parameters determined in tension tests only capably predicted material response in tension-dominated deformation.
Arruda-Boyce model parameters for the PC
predictions of figure 1-29, following equations 1.26 to 1.32

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<td>$\gamma_0$ [s$^{-1}$]</td>
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<td>$C_R$ [MPa]</td>
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</table>

Figure 1-29: PC stress-strain behavior in uniaxial compression and plane strain compression: Arruda-Boyce constitutive model predictions vs. experimental results (Arruda & Boyce, 1993a).

Soon afterwards, the model was refined again in order to enhance its functionality as an engineering design and analysis tool. Specifically, Arruda, Boyce, and Jayachandran (1995) proposed revision to the treatment of both temperature and strain rate effects in the model. These revisions were motivated in part by the results of uniaxial compression testing on PC and PMMA at a variety of temperatures ($20^\circ$C, $50^\circ$C, $75^\circ$C) and strain rates ($0.001$ s$^{-1}$, $0.01$ s$^{-1}$, $0.1$ s$^{-1}$). The corresponding stress-strain calculations, in conjunction
Arruda-Boyce model parameters for the PMMA predictions of figure 1-30, following equations 1.26 to 1.32

<table>
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<tr>
<td>$E$ [MPa]</td>
<td>3205</td>
</tr>
<tr>
<td>$\nu$</td>
<td>0.33</td>
</tr>
<tr>
<td>$s_0$ [MPa]</td>
<td>138.5</td>
</tr>
<tr>
<td>$s_{aa}/s_0$</td>
<td>0.87</td>
</tr>
<tr>
<td>$\gamma_0$ [s$^{-1}$]</td>
<td>2.8x10$^7$</td>
</tr>
<tr>
<td>$h$ [MPa]</td>
<td>315</td>
</tr>
<tr>
<td>$A$ [K/MPa]</td>
<td>100.7</td>
</tr>
<tr>
<td>$C_R$ [MPa]</td>
<td>8.0</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>N/A</td>
</tr>
<tr>
<td>$\sqrt{N}$</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Figure 1-30: PMMA stress-strain behavior in uniaxial compression and plane strain compression: Arruda-Boyce constitutive model predictions vs. experimental results (Arruda & Boyce, 1993a).
with infrared specimen temperature measurements, provided key information in regards to the coupling of thermal and mechanical response in glassy polymer behavior. Arruda et al. (1995) proposed, for one, altering the kinematic framework in order to capture the effects of thermal expansion. Following the routine delineated by Weber and Boyce (1989), the total deformation gradient was multiplicatively decomposed into three components: \( F^e \) (elastic), \( F^p \) (plastic), and \( F^{th} \) (thermal expansion). Arruda et al. also suggested a more sophisticated treatment of the temperature dependence of the rubbery modulus, \( C_R = n k T \), where \( n \) is the chain density. In this version of the model, the chain density was given a temperature dependence in accordance with the theory and birefrigence measurements of Raha and Bowden (1972):

\[
n(T) = B - D \exp \left( -\frac{E_a}{RT} \right)
\]

(1.35)

where \( R \) is the universal gas constant, \( B \) and \( D \) are constants to be determined, and \( E_a \) is the thermal dissociation energy. Values for \( B \), \( D \) and \( E_a \) were given by Raha and Bowden (1972) and used directly in this model. Furthermore, Arruda et al. required that

\[
n(T)N(T) = \text{constant}
\]

(1.36)

in order to conserve mass in the system. Thus, the limiting chain extensibility \( (\sqrt{N}) \) also was indirectly given a temperature dependence, calculated from equation 1.36.

With all of these temperature-dependent effects built into the model, it was finally necessary for Arruda et al. (1995) to prescribe a method for calculating temperature rise in the polymer under adiabatic conditions. It was assumed that the work of the entropic back stress is stored energy, while the inelastic work associated with the viscoplastic dashpots is purely dissipative. Therefore, from the first law of thermodynamics, the temperature rise in the polymer is given as:

\[
\dot{T} = \frac{\text{trace}(T' \cdot D^p)}{\rho c}
\]

(1.37)

where \( T' \) is the deviatoric component of the driving stress (stress acting on the dashpot), \( D^p \) is the rate of plastic stretching, \( \rho \) is the material density, and \( c \) is the specific heat. These methods were thoroughly tested against experimental data using thermomechanically-coupled finite element simulations of the uniaxial compression tests. The finite element model successfully predicted the isothermal-to-adiabatic transition observed experimentally, as well as
the corresponding thermal expansion and thermal softening of the polymer under adiabatic conditions. In all cases, the material model capably predicted the measured stress-strain curve.

Over the last fifteen years, other application-specific modifications to the constitutive model have been proposed. Hasan, Boyce, Li, and Berko (1993) introduced a variant form of the model to capture the effects of physical ageing and thermal history. Later, Hasan and Boyce (1995) proposed changes to the model to enable it to predict non-linear viscoelasticity. In 1998, Bergstrom and Boyce extended the model framework to the behavior of elastomeric materials. For this particular application, the model structure was altered slightly from that introduced by Haward and Thackray (figure 1-25). In the Bergstrom-Boyce model, the elastic spring and dashpot are in series, both parallel to the non-linear entropic spring; the two sides of the model represent the equilibrium and time-dependent non-equilibrium components of elastomeric material response. The Bergstrom-Boyce model later proved successful in predicting the behavior of both filled elastomers (Bergstrom & Boyce, 2000) and soft, biological tissues (Bergstrom & Boyce, 2001).

More recently, a new constitutive model was proposed for the behavior of amorphous polymers (Mulliken, 2004), framed within the kinematics of Bergstrom and Boyce (1998, 2000). This model, developed especially for predicting behavior under high rates of deformation, is the subject of Chapter 2 of this thesis.
Chapter 2

Preliminary Experiments and Proposed Constitutive Model

An initial investigation into the high-rate mechanical behavior of amorphous polymers was presented by the author in a Master of Science thesis to the Department (Mulliken, 2004). For this thesis, a wide range of experimental results were analyzed, ultimately leading to a new constitutive model for the rate- and temperature-dependent finite strain behavior of amorphous polymers. In this chapter, both the experimental results and proposed constitutive model of Mulliken (2004) are revisited. Where appropriate, additional experimental data and analysis have been added, and slight adjustments in the constitutive model are suggested. In subsequent chapters of the dissertation, more comprehensive revisions and refinements of the model are proposed.

Portions of this chapter have been reprinted from International Journal of Solids and Structures, Vol. 43, A.D. Mulliken and M.C. Boyce, "Mechanics of the rate-dependent elastic-plastic deformation of glassy polymers from low to high strain rates", pages 1331-1356, copyright 2005, with permission from Elsevier.

2.1 Introduction

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 established in the literature. On the experimental side, investigation of viscoelastic behavior was chosen as one focal point, in order to gain more fundamental understanding of the material tran-
sitions, and to further the linkages between material viscoelastic, yield, and stress-strain behavior. The effects of these transitions ($\alpha$, $\beta$) on yield and post-yield behavior over a wide range in strain rates, extending up to 1000 s$^{-1}$, was then experimentally explored in large strain compression testing. On the analytical side, the concept of decomposing material resistance to elastic deformation and to initial yield into contributions from two different molecular processes (see, for instance, Bauwens et al., 1969) proved central to the analysis and modelling techniques introduced here.

2.2 Materials

Two amorphous polymers were chosen for investigation in this study: Lexan® 9034 polycarbonate manufactured by GE Plastics, and Plexiglas® G poly(methyl methacrylate), manufactured by Altuglas. All specimens were machined directly from sheet stock and stored in a dessicator cabinet for 3-5 days prior to testing to eliminate any variability in the data caused by changing humidity levels. The Plexiglas G PMMA sheet is produced through a traditional cell cast method, and thus little molecular chain orientation is expected in the as-cast sheet. The PC sheet, on the other hand, is produced through an extrusion process and is known to exhibit slight chain orientation in the extrusion direction. While this orientation may significantly affect the accessibility of various local failure modes in certain loading situations, it has little to no effect on the viscoelastic, yield and post-yield behavior during uniaxial compression.

2.3 Dynamic Mechanical and Thermal Analysis

2.3.1 Experimental Method

Dynamic mechanical and thermal analysis experiments were performed on a TA Instruments Q800 Dynamic Mechanical Analyzer (DMA). 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. 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 total 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 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 over the range $1.9 \times 10^{-3} \text{ s}^{-1}$ to $3.2 \times 10^{-1} \text{ s}^{-1}$, depending on the exact specimen gage length and displacement amplitude prescribed.\(^1\)

Again, storage modulus and loss modulus information was recorded, and corresponding loss tangent calculations were made.

### 2.3.2 Results and Analysis

Representative storage modulus and loss modulus curves taken at 1 Hz for PC and PMMA are plotted in figures 2-1 and 2-2, respectively. In both storage modulus curves, there is clear evidence of a glass (α) transition, through which the storage modulus drops off by three orders of magnitude. In the case of PC (figure 2-1), this transition is centered around 150°C; for PMMA (figure 2-2), it is centered around 115°C. As expected, the loss modulus curves exhibit a relative maximum in the region of these glass transitions. For both materials, the α-transition is associated with restricted rotations and translations of large segments of the polymer main chains.

The loss modulus curves of figures 2-1 and 2-2 may also act to identify the temperature location of the secondary (β) viscoelastic transitions of PC and PMMA. In the PC curve (figure 2-1), there is a β-peak located at approximately -95°C - far enough away from the α-peak that the corresponding effect on the storage modulus curve is clear. The storage modulus drops from ~3 GPa at -100°C to ~2 GPa at -25°C and then to ~1.7 GPa at 100°C. For PC, the β-transition is taken to be correlated with the molecular mobility of shorter segments (approximately seven monomer units) of the main chain.

\(^1\)The 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 an average strain rate can be calculated:

$$\dot{\epsilon} = \frac{\text{strain}}{\text{time}} = \frac{\Delta \epsilon}{\frac{1}{4} \omega} = \frac{4 \omega \Delta \epsilon}{l_g} \quad (2.1)$$

Where $\Delta \epsilon$ is the displacement amplitude and $l_g$ is the specimen gage length.
Figure 2-1: PC storage modulus (solid line) and loss modulus (dashed line) as a function of temperature at $3.2 \times 10^{-3}$ s$^{-1}$ (1 Hz). The loss modulus peaks centered at -95°C and 150°C correspond to the $\beta$ and $\alpha$ transitions, respectively.

Figure 2-2: PMMA storage modulus (solid line) and loss modulus (dashed line) as a function of temperature at $2.1 \times 10^{-3}$ s$^{-1}$ (1 Hz). The loss modulus peaks centered at 15°C and 115°C correspond to the $\beta$ and $\alpha$ transitions, respectively.
In the case of PMMA (figure 2-2), the large \( \beta \)-peak overlaps the \( \alpha \)-peak a considerable amount at this frequency, and thus only one combined effect is seen in the storage modulus reference curve. The storage modulus drops from \( \sim 5 \) GPa at \(-100^\circ\text{C}\) to \( \sim 4 \) GPa at \(-25^\circ\text{C}\) and then to \( \sim 1.5 \) GPa at \( 100^\circ\text{C}\). The PMMA \( \beta \)-transition, centered at \( 15^\circ\text{C} \), is correlated with the mobility of the ester side groups with respect to the main chain.

Further DMA testing was conducted in order to determine the rate-dependent shifts of the transition locations. Using the locations identified in figures 2-1 and 2-2, 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 2-3, representative PC loss tangent (\( \tan \delta \)) curves in the region of the \( \alpha \) and \( \beta \) transitions are plotted as a function of temperature and strain rate. The \( \beta \)-transition is observed to shift to higher temperatures with increasing strain rate, according to an Arrhenius-type relation. By tracing the precise temperature location of the \( \beta \)-peak with increasing strain rate, the shift factor was quantified: the PC \( \beta \)-transition was found to shift approximately \( 15.3^\circ\text{C} \) per decade increase in strain rate.

Table 2.1: Shift of PC and PMMA viscoelastic transitions (\( \tan \delta \)) with strain rate.

<table>
<thead>
<tr>
<th></th>
<th>Shift of ( \alpha )-transition</th>
<th>Shift of ( \beta )-transition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(^{\circ}\text{C}/\text{decade strain rate})</td>
<td>(^{\circ}\text{C}/\text{decade strain rate})</td>
</tr>
<tr>
<td>PC</td>
<td>4.7</td>
<td>15.3</td>
</tr>
<tr>
<td>PMMA</td>
<td>11.1</td>
<td>25.2</td>
</tr>
</tbody>
</table>
An identical procedure was used to quantify the rate-dependent shifts of the α and β transitions of both PC and PMMA—the results are summarized in Table 2.1. While in all cases the rate-dependent shift was found to be Arrhenius in nature, testing over a wider range of frequencies would likely indicate that the α-transition shifts are better described by either the Williams-Landel-Ferry (WLF) or Vogel-Fulcher-Tammann (VFT) model. In that case, the rate-dependent shift of the α transitions could not be characterized by a single parameter, as we have shown here.

In order to predict the elastic behavior at all strain rates and temperatures, the DMA data over the tested frequency and temperature conditions is utilized together with a novel time-temperature shift that takes into account the different rate dependencies of the α and β transitions. The specific techniques are borne from the same concept which underlies the Ree-Eyring yield models (see, for instance, Bauwens-Crowet et al., 1972): total deformation resistance may be decomposed into the contributions from different thermally-activated processes, each with their own unique rate and temperature dependencies. In this case, the analytical approach enables accurate characterization of the rate-dependent elastic behavior at the high strain rates (≥1000 s⁻¹) experienced during ballistic impact events.

As a first step, the storage modulus reference curves of PC (figure 2-1) and PMMA (figure 2-2) were each analytically decomposed into an α-component and a β-component, based on clues in the storage modulus and loss modulus curves. For the case of PC, the structure of the storage modulus reference curve lends itself well to decomposition: as the curve is traced with decreasing temperature, a significant upturn appears at approximately -25°C. Based on the loss modulus measurements, this upturn is observed to correlate with the onset of the restriction of the β-process. Following this analysis, the PC storage modulus reference curve was separated into an α- and a β-component, as shown in figure 2-4. These components were then taken to shift with strain rate by the amounts determined via experimental examination of the transition locations, summarized in Table 2.1. The entire modulus curve could then be reconstructed for any particular strain rate by first shifting the components of the reference curve by the appropriate amounts, and then summing the components at every temperature.

---

2Shift factors are determined from temperature locations of the α and β peaks in the tanδ curves. Alternatively, shift factors could be determined by tracking the α and β peaks in the loss modulus curves. For PC and PMMA in this study, shift factors differ by 1-2°C/decade strain rate when the loss modulus is used rather than tan δ.
Figure 2-4: 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.

Figure 2-5: Model prediction of the PC elastic modulus curve at five strain rates: $10^{-4} \text{s}^{-1}$ to $10^4 \text{s}^{-1}$. The vertical dashed line represents room temperature (298 K).
This decompose/shift/reconstruct (DSR) method enables the prediction of the elastic modulus of PC and PMMA at temperatures and strain rates well beyond the capabilities of the DMA instrument. Figure 2-5 shows the DSR model prediction of the PC elastic modulus curve at five different strain rates, ranging from $10^{-4} \text{ s}^{-1}$ to $10^{4} \text{ s}^{-1}$. The curve not only shifts to the right (increased temperatures) with increasing strain rate, but it also changes shape due to the different shift factors of the $\alpha$ and $\beta$ components of the curve.\(^3\)

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 $\beta$-transition in figure 2-5 to predict the transition strain rate. Again, this $\beta$-transition is identified by the upturn in the storage modulus curve. At strain rates of about $1 \text{ s}^{-1}$ and lower, the upturn has not yet shifted past room temperature (vertical dashed line) - the small-scale main-chain $\beta$-motions of PC are not yet restricted, and the $\beta$ contribution to the overall elastic modulus is negligible. However, as the strain rate is increased to $100 \text{ s}^{-1}$, the transition shifts past room temperature and the $\beta$ contribution rapidly becomes more significant with increasing strain rate. Since the same basic mechanisms which govern elasticity in amorphous polymers also govern yield and viscoplastic behavior, we would expect to observe a transition in the room temperature yield behavior of PC at a similar strain rate - about $100 \text{ s}^{-1}$.

Application of the DSR method to the PMMA data was not as straightforward as it was in the case of PC, mainly because of the interaction between the $\alpha$ and $\beta$ processes across almost every temperature at the reference strain rate. A suitable decomposition of the storage modulus data (figure 2-6) was developed not only from the PMMA storage and loss modulus curves, but also from the methods which best suited the PC decomposition. Combining this analytical decomposition with the experimentally-derived shift factors for the $\alpha$ and $\beta$ processes, again it was possible to predict at what strain rate we would expect to see a significant transition in the PMMA yield behavior at room temperature. Figure 2-7 shows the PMMA elastic modulus at six different strain rates, as predicted by the DSR model, along with a vertical dashed line representing room temperature. Based on the

\(^3\)Note that this behavior could be alternatively captured with an implementation of linear viscoelastic theory, by considering multiple relaxation processes such as in a Prony series representation. Further discussion on this topic is given in Chapter 6.
Figure 2-6: 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.

Figure 2-7: Model prediction of the PMMA elastic modulus curve at six strain rates: $10^{-6}$ s$^{-1}$ to $10^4$ s$^{-1}$. The vertical dashed line represents room temperature (298 K).
curves of this figure, the PMMA transition is expected to occur at a strain rate between $10^{-5}$ s$^{-1}$ and $10^{-4}$ s$^{-1}$.

In modelling both the PC and PMMA modulus with this DSR technique, it is probable that the predictions at and above the glass transition will be unsatisfactory, especially at very high rates. This is due to the treatment of the $\alpha$-transition as an Arrhenius phenomenon, when in fact its rate-dependent shifting would be better described with either a WLF or VFT equation. Nonetheless, the data measured from 1 Hz to 100 Hz indicated a linear relationship between $T_a$ and $\log(\omega)$; it is expected that this would still be a good approximation for at least 2-3 decades higher in frequency. Furthermore, we are primarily concerned with behavior well below the glass transition, even when considering the heat evolved under (high-rate) adiabatic deformation. For other material systems with a lower glass transition temperature, this will be a concern which requires closer attention.

2.4 Uniaxial Compression

2.4.1 Experimental Method

Uniaxial compression tests were carried out on PC and PMMA over seven decades of strain rate: $10^{-5}$ s$^{-1}$ to approximately 6000 s$^{-1}$. Uniaxial compression was selected as the deformation mode because it dictates a homogeneous stress and deformation state to large strains, making interpretation of the data straightforward. Low to moderate rate testing ($10^{-5}$ s$^{-1}$ to 1 s$^{-1}$) was conducted on an Instron servo-hydraulic testing machine. A specially-designed feedback loop between the extensometer (which locally measures the current height of the specimen) and the actuator 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 small misalignment. All specimens were of right circular cylinder geometry, with diameter of 12.7 millimeters and length of 6.35 millimeters. 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. This particular length-to-diameter ratio (1:2) was chosen in order to be consistent with the geometry of the high rate specimens.

High strain rate testing (700 s$^{-1}$ to 6000 s$^{-1}$) was performed on a compressive split-
Hopkinson bar test apparatus designed in cooperation with and built by Physics Applications, Inc. of Dayton, Ohio. This apparatus employs solid aluminum pressure bars, both with a length of approximately 2.3 meters and a diameter of 19.05 millimeters. The theory of split-Hopkinson bar testing has been well-documented; see for instance Davies (1948), Kolsky (1949), or Gray III (2000). Recently, issues unique to testing low-impedance, low yield strength materials such as glassy polymers have been a topic of research for several investigators; this line of work is summarized by Gray III and Blumenthal (2000).

Specimens for split-Hopkinson bar testing were also of right circular cylinder geometry. Previous work has suggested that length-to-diameter ratios of 1:2 or less are necessary in the testing of low-impedance materials, in order to minimize wave attenuation in the strain gage signals (Gray, Blumenthal, Trujillo, & Carpenter, 1997; Chen et al., 1999). Also, a length-to-diameter ratio of 1:2 has been shown to be optimal in negating the effects of radial and longitudinal inertia in the specimen (Davies & Hunter, 1963). Thus, for most tests, the split-Hopkinson bar specimens were machined to a diameter of 5 millimeters and length of 2.5 millimeters. Since PMMA deformed in a ductile manner over such a narrow range of striker bar velocities, additional tests were conducted on this material in a different geometry. Thinner specimens (diameter = 5 millimeters, length = 2 mm) were used to extend tests to larger strains. Results showed no dependence of specimen geometry on the measured stress-strain behavior. All specimens were lubricated with a thin layer of petroleum jelly on both faces, and little to no barrelling was ever observed. Dynamic equilibrium was achieved before yield in all tests, due to the short specimen lengths. Since DMA testing was used to characterize the rate-dependent elastic moduli, the pre-yield data at high rates was not of consequence and therefore pulse-shaping was unnecessary.

2.4.2 Results and Discussion

During low to moderate rate compression testing on the servo-hydraulic instrument, both PC and PMMA specimens deformed in a ductile manner up to the tested true strain of 0.80, corresponding to a deformed height ratio \( h/h_0 = 0.45 \). The homogeneous nature of the deformation was confirmed via post-mortem analysis of the test specimens; little to no barrelling was observed in either the PC or PMMA.

In the case of high rate testing, the PC specimens deformed in a ductile manner over the tested strain rates, ranging from 1200 s\(^{-1}\) to 4000 s\(^{-1}\) (true strain rate at yield).
the PMMA tests, brittle failure of the specimens occurred prior to yield at strain rates above 2000 s$^{-1}$. At rates lower than 2000 s$^{-1}$, yield and significant post-yield deformation were observed prior to a brittle failure. In both materials, true strain rates were found to vary over the duration of the tests. However, despite the absence of pulse-shaping techniques, the strain rate varied no more than 25% for both PC and PMMA. Figure 2-8 shows representative true strain rate histories, along with the corresponding true stress-true strain curves, for tests on PC and PMMA where the greatest variation in strain rate was observed.

The results of all uniaxial compression testing of PC are summarized in figures 2-9 and 2-10. Figure 2-9 provides a comparison of representative high-rate true stress-true strain curves (1350 s$^{-1}$, 3900 s$^{-1}$, and 5050 s$^{-1}$) with representative low to moderate rate curves (10$^{-3}$ s$^{-1}$, 10$^{-2}$ s$^{-1}$, 10$^{-1}$ s$^{-1}$, and 1 s$^{-1}$). All of the curves indicate the expected features of material response to large-strain uniaxial deformation: initial linear elasticity, non-linear transition to global yield, followed by strain softening and subsequent 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 2-10 shows the PC yield strength as a function of strain rate across all of the tested strain rates. Within the low to moderate rate regime, the yield stress is found to increase linearly with the logarithm of strain rate, indicating that yield behavior in this regime could be accurately explained and/or predicted in terms of a single 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. In the high-rate regime, again the yield strength is found to increase in an approximately linear fashion with the logarithm of strain rate. However, the slope of the data line is much greater in this high-rate regime. 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 yield data generated here indicates that the transition is centered around a strain rate of approximately 150 s\(^{-1}\); this transition strain rate is consistent with the DSR model prediction.

The results of all uniaxial compression testing of PMMA are summarized in figures 2-11 and 2-12. Figure 2-11 shows representative true stress-true strain curves for PMMA across
Figure 2-10: PC true yield stress as a function of strain rate (logarithmic scale) - low to high strain rates. Each data point represents an average of at least two tests on either the servo-hydraulic Instron (●) or the compressive split-Hopkinson bar (○).
Figure 2-11: Representative curves of PMMA true stress-true strain behavior in uniaxial compression at six low, moderate, and high rates. Reported high strain rates are averages over the duration of the tests.
Figure 2-12: PMMA true yield stress as a function of strain rate (logarithmic scale) - low to high strain rates. Each data point represents an average of at least two tests on either the servo-hydraulic Instron (●) or the compressive split-Hopkinson bar (○).
all of the tested strain rates. In this case, the characteristic shape of the stress-strain curve is not the same at all rates. At moderate strain rates, the PMMA exhibits significantly more post-yield softening than at low strain rates, as also seen in the work of Arruda et al. (1995). The increased softening effect has been shown to be due to non-isothermal test conditions as the strain rate is increased. A fraction of the plastic work is converted to heat, and thus the polymer experiences thermal softening with increased plastic straining when the strain rate is sufficiently high such that all of the heat is not transferred out of the specimen. The flow stress of PMMA is more temperature sensitive than that of PC, and therefore thermal softening is clearly apparent only in the PMMA data.

The yield stress of PMMA over all of the tested strain rates is documented in figure 2-12. In this case, the material transition seems to occur entirely within the strain rate regime accessed in quasi-static testing, where the yield stress is found to increase in a non-linear fashion with the logarithm of strain rate. This result is consistent with the work of Bauwens-Crowet and Homès (1964) and Roetling (1965b). Though the DSR model for PMMA predicted a material transition, related to the restriction of \( \beta \)-motions, at a strain rate between \( 10^{-5} \text{s}^{-1} \) and \( 10^{-4} \text{s}^{-1} \), figure 2-12 shows a kink in the yield data close to \( 10^{-2} \text{s}^{-1} \). However, yield data could not be obtained at strain rates lower than \( 10^{-5} \text{s}^{-1} \). It is possible that the yield curve begins to deviate slightly from linearity at \( 10^{-5} \text{s}^{-1} \) to \( 10^{-4} \text{s}^{-1} \), but changes only become pronounced at strain rates two to three 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 2-2; in this figure, the \( \beta \)-peak at a strain rate of \( 10^{-3} \text{s}^{-1} \) 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 the rate-dependent behavior. Also, the combined analytical and experimental results presented thus far serve to reinforce the postulated link between the transition in the yield behavior of amorphous polymers and the rate dependence of the \( \alpha \) and \( \beta \) transitions in the viscoelastic behavior. Finally, with new insight, this fundamental understanding of the material transitions will be used as the foundation for a proposed constitutive model for the three-dimensional rate-dependent finite strain deformation of amorphous polymers.
2.5 Constitutive Model

The constitutive model proposed builds upon prior modelling of the three-dimensional rate-, temperature-, and pressure-dependent finite-strain deformation of thermoplastic materials. The original model was introduced in its components by Boyce et al. (1988c) and Arruda and Boyce (1993b, 1993a). The model has been shown to be predictive of the stress-strain behavior of PC (Arruda & Boyce, 1993b; Boyce et al., 1994) and PMMA (Boyce et al., 1988c; Arruda et al., 1995) at low to moderate strain rates (10^{-3} \text{s}^{-1} to 1 \text{s}^{-1}), at temperatures from 20°C to 90°C, and in four states of deformation: plane strain compression, simple shear, uniaxial tension, and uniaxial compression. Previously, the model had not been tested against high rate or low temperature data. Here, we propose revisions to the model in order to provide predictive capabilities for high rate and low temperature loading.

Following the structure originally described by Haward and Thackray (1968), the three-dimensional model of Boyce and co-workers (1988, 1993) has three components: 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. 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 (elastic spring and viscoplastic dashpot), and entropic resistance to chain alignment (Langevin spring). In the proposed constitutive model, it is assumed that the intermolecular deformation resistance may be further decomposed into the contributions from multiple rate-activated processes, each associated with a distinct molecular-level motion.

As in most practical applications of the Ree-Eyring yield theory (see, for instance, Bauwens et al., 1969) the proposed model only considers the primary (\(\alpha\)) process and the most significant secondary process (\(\beta\)). PC and PMMA data indicates that the contributions from other secondary processes are either hidden within the contribution of the \(\beta\)-process, or are non-existent over the range of temperatures and strain rates capable in mechanical testing. The \(\alpha\)-process is associated with rotations of large segments of the polymer main-chain; 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, \(\beta\)-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 shorter main-chain
Figure 2-13: A one-dimensional rheological interpretation of the proposed constitutive model for rate-dependent thermoplastic behavior.

segments, including phenyl ring \( \pi \)-flips. The model assumes that the \( \alpha \) and \( \beta \) molecular processes are sufficiently de-coupled, so that overall material response may be approximated as the simple superposition of the two.

A one-dimensional rheological depiction of the proposed constitutive model is presented as figure 2-13. In this model, the \( \beta \)-process is given its own elastic-viscoplastic component, in parallel with the existing "\( \alpha \)" 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 \( \beta \)-component will be fairly compliant, and most, if not all, intermolecular resistance will be generated in the elastic spring and viscoplastic dashpot of the \( \alpha \)-component. At low temperatures and high strain rates, the \( \beta \)-process will require stress assistance, and the intermolecular resistance will be two-part. The entropic hardening definition remains unchanged from the original model. A fully three-dimensional constitutive model has been built up from this one-dimensional understanding, beginning with the kinematics of finite strain.

### 2.5.1 Kinematics

The finite strain kinematic framework of the model follows that presented in Bergstrom and Boyce (1998, 2000), Boyce, Socrate, and Llana (2000), and Boyce, Kear, Socrate,
and Shaw (2001), with the main difference being that every relationship pertaining to the intermolecular resistance is developed in duplicate here. Throughout the derivations of this section, 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 2-13). All quantities specific to the $\alpha$ and $\beta$ components will be given those subscripts as well. Boldface type indicates tensorial quantities in this three-dimensional formulation.

The total deformation gradient $\mathbf{F} \equiv \partial \mathbf{x}/\partial \mathbf{X}$, mapping a material point from the reference position $\mathbf{X}$ to its current location $\mathbf{x}$, acts in full on each of the three main components of the model:

$$\mathbf{F}_A = \mathbf{F}_A = \mathbf{F}_B = \mathbf{F}$$

(2.2)

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

$$\mathbf{F}_A = \mathbf{F}^p_A \mathbf{F}^A_A$$

(2.3)

$$\mathbf{F}_A = \mathbf{F}^p_A \mathbf{F}^A_A$$

(2.4)

The plastic deformation gradients $\mathbf{F}^p_A$ and $\mathbf{F}^p_B$ 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, it is assumed that all plastic deformation is volume preserving, i.e. $\det \mathbf{F}^p_A = \det \mathbf{F}^p_B = 1$. Following polar decomposition of the deformation gradients, the deformation of the relaxed configuration may be expressed as the product of a stretch and a rotation:

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

(2.5)

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

(2.6)

We may examine the rate at which deformation takes place in the body through the velocity gradient $\mathbf{L} = L_A = L_B = \dot{\mathbf{F}} A F^{-1}$. The velocity gradient is decomposed into elastic and
plastic components:

\[
L_{Aa} = L_{Aa}^e + F_{Aa} L_{Aa}^p F_{Aa}^{-1} = L_{Aa}^e + \tilde{L}_{Aa}^p \tag{2.7}
\]

\[
L_{Ab} = L_{Ab}^e + F_{Ab} L_{Ab}^p F_{Ab}^{-1} = L_{Ab}^e + \tilde{L}_{Ab}^p \tag{2.8}
\]

where

\[
\tilde{L}_{Aa}^p = \tilde{D}_{Aa}^p + \tilde{W}_{Aa}^p \tag{2.9}
\]

\[
\tilde{L}_{Ab}^p = \tilde{D}_{Ab}^p + \tilde{W}_{Ab}^p \tag{2.10}
\]

and \( \tilde{D}_{Aa}^p \) and \( \tilde{D}_{Ab}^p \) (symmetric tensors) represent the rates of plastic stretching in the loaded configuration; similarly, \( \tilde{W}_{Aa}^p \) and \( \tilde{W}_{Ab}^p \) (skew tensors) are the rates of plastic spin in the loaded configuration. In this analysis, plastic flow is assumed to be irrotational, i.e. \( \tilde{W}_{Aa}^p = \tilde{W}_{Ab}^p = 0 \). Note that this does not restrict either the elastic or the plastic rotation tensors to be the identity matrix. It follows, then, that

\[
\dot{F}_{Aa}^p = F_{Aa} e^{e-1} \tilde{D}_{Aa}^p F_{Aa}^e F_{Aa} = F_{Aa} e^{e-1} \tilde{D}_{Aa}^p F_{Aa} \tag{2.11}
\]

\[
\dot{F}_{Ab}^p = F_{Ab} e^{e-1} \tilde{D}_{Ab}^p F_{Ab}^e F_{Ab} = F_{Ab} e^{e-1} \tilde{D}_{Ab}^p F_{Ab} \tag{2.12}
\]

The final expressions in equations 2.11 and 2.12 are integrated to obtain \( F_{Aa}^p \) and \( F_{Ab}^p \); the elastic portion of the deformation gradients are then obtained via

\[
F_{Aa}^e = F_{Aa} F_{Aa}^{p-1} \tag{2.13}
\]

\[
F_{Ab}^e = F_{Ab} F_{Ab}^{p-1} \tag{2.14}
\]

The kinematics derived here are general; the material-specific model is defined by the constitutive laws which connect the rates of shape change (plastic stretching) with the stress in the deforming material. Each rate of shape change is given as the product of a magnitude – the plastic strain rate \( \gamma_A^p \) or \( \gamma_B^p \) – and a direction tensor, \( N_{Aa}^p \) or \( N_{Ab}^p \):

\[
\tilde{D}_{Aa}^p = \gamma_A^p N_{Aa}^p \tag{2.15}
\]

\[
\tilde{D}_{Ab}^p = \gamma_A^p N_{Ab}^p \tag{2.16}
\]
where \( N^p_{A\alpha} \) and \( N^p_{A\beta} \) are taken to be coaxial with the deviatoric stresses acting on the \( \alpha \) and \( \beta \) components of the intermolecular network (A), respectively:

\[
N^p_{A\alpha} = \frac{T'_{A\alpha}}{T'_{A\alpha}} \tag{2.17}
\]

\[
N^p_{A\beta} = \frac{T'_{A\beta}}{T'_{A\beta}} \tag{2.18}
\]

The material model described here provides constitutive laws for \( \dot{\gamma}^p_\alpha \) and \( \dot{\gamma}^p_\beta \), as well as the stress tensors \( T_{A\alpha} \), \( T_{A\beta} \) and \( T_B \).

### 2.5.2 Material Description

The intermolecular contribution (element A) to the material stress state is related to the deformation by the constitutive laws for the linear elastic springs:

\[
T_{A\alpha} = \frac{1}{J^{\alpha}} \mathcal{L}^e_{\alpha} \left[ \ln V^e_{A\alpha} \right] \tag{2.19}
\]

\[
T_{A\beta} = \frac{1}{J^{\beta}} \mathcal{L}^e_{\beta} \left[ \ln V^e_{A\beta} \right] \tag{2.20}
\]

Where \( T_{Ai} \) \((i = \alpha, \beta)\) is the Cauchy (true) stress; \( J_i = \det F^e_{Ai} \) is the elastic volume change; \( \mathcal{L}^e_i \) is the fourth-order modulus tensor; and \( \ln V^e_{Ai} \) 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 \( \kappa \):

\[
\mathcal{L}^e_{\alpha} = 2\mu_{\alpha}\mathcal{I} + \left( \kappa_{\alpha} - \frac{2}{3}\mu_{\alpha} \right) \mathbf{I} \otimes \mathbf{I} \tag{2.21}
\]

\[
\mathcal{L}^e_{\beta} = 2\mu_{\beta}\mathcal{I} + \left( \kappa_{\beta} - \frac{2}{3}\mu_{\beta} \right) \mathbf{I} \otimes \mathbf{I} \tag{2.22}
\]

where \( \mathcal{I} \) and \( \mathbf{I} \) are the fourth-order and second-order identity tensors, respectively. In general, the elastic constants are assumed to be \textit{functions of both temperature and strain rate}. Experimental data indicates that the pressure-dependence of the elastic constants should also be considered; this topic is addressed in Chapter 5.

It should be noted here that a more physically realistic description of rate-dependent elasticity could be given by an implementation of linear viscoelasticity theory into the model,
rather than a set of elastic springs which provide resistance according to the current strain rate and temperature. A linear viscoelastic formulation would allow the model to capture important small-strain phenomena, including creep and stress relaxation. Furthermore, a viscoelastic formulation would perhaps smooth out any numerical difficulties associated with fluctuating strain rates and strong gradients in either strain rate or temperature. These issues are addressed in Chapter 6, where an alternate model formulation is proposed including instead an linear viscoelastic description of the material elastic behavior. However, the current formulation is efficient in its implementation and is expected to capture all important features of material behavior in simulations of high-rate, impact events.

The stress in the non-linear hardening component, the network "back stress" due to entropic resistance to molecular alignment, is taken to be deviatoric and is defined as in the earlier models using the Arruda-Boyce 8-chain approximation:

\[
T_B = \frac{C_R \sqrt{N}}{3 \lambda_{\text{chain}}^p} \mathcal{L}^{-1} \left( \frac{\lambda_{\text{chain}}^p}{\sqrt{N}} \right) \tilde{\mathbf{B}}' \tag{2.23}
\]

where \( \lambda_{\text{chain}}^p = \sqrt{\text{trace}(\mathbf{B})/3} \) is the stretch on a chain in the eight-chain network; \( \mathcal{L} \) is the Langevin function defined by \( \mathcal{L}(\beta) \equiv \coth \beta - \frac{1}{\beta} \); \( \tilde{\mathbf{B}}' \) is the deviatoric part of the isochoric left Cauchy-Green tensor, \( \tilde{\mathbf{B}} = (\det \mathbf{F})^{-2/3} \mathbf{F} \mathbf{F}^T \); \( \sqrt{N} \) is the limiting chain extensibility; and \( C_R \equiv nk\theta \) is 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 magnitude of this 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 \( \alpha \) and \( \beta \) intermolecular stresses and the network (back) stress:

\[
\mathbf{T} = \mathbf{T}_{\alpha} + \mathbf{T}_{\beta} + \mathbf{T}_B \tag{2.24}
\]

The effective equivalent shear stresses \( \tau_\alpha \) and \( \tau_\beta \) are given by:

\[
\tau_\alpha = \sqrt{\frac{1}{2} \mathbf{T}_{\alpha}' \mathbf{T}_{\alpha}'} \tag{2.25}
\]

\[
\tau_\beta = \sqrt{\frac{1}{2} \mathbf{T}_{\beta}' \mathbf{T}_{\beta}'} \tag{2.26}
\]

Finally, two constitutive laws are prescribed for the \( \alpha \) and \( \beta \) viscoplastic behavior. In
the most general case, we must consider the forward and reverse progress of both activated processes:

\[ \dot{\gamma}_\alpha^P = 2\dot{\gamma}_{0,\alpha}^p \exp \left( -\frac{\Delta G_\alpha}{k\theta} \right) \sinh \left[ \frac{\tau_\alpha \left( \frac{\Delta G_\alpha}{s_\alpha + \alpha_{p,\alpha} p} \right)}{k\theta} \right] \]  

(2.27)

\[ \dot{\gamma}_\beta^P = 2\dot{\gamma}_{0,\beta}^p \exp \left( -\frac{\Delta G_\beta}{k\theta} \right) \sinh \left[ \frac{\tau_\beta \left( \frac{\Delta G_\beta}{s_\beta + \alpha_{p,\beta} p} \right)}{k\theta} \right] \]  

(2.28)

where \( \dot{\gamma}_{0,i} (i = \alpha, \beta) \) is the pre-exponential factor proportional to the attempt frequency; \( \Delta G_i \) is the activation energy; \( p \) is the pressure; \( \alpha_{p,i} \) is the pressure coefficient; and \( s_i \) is an internal variable. When this model is restricted to the glassy behavior of amorphous polymers, as is the case here, it may be assumed the stresses in the \( \alpha \) process are sufficiently high such that the reverse progress of plastic flow may be neglected (see footnote 2, Chapter 1, section 1). Therefore, for most practical applications of the model,

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

(2.29)

This approximation may not be made on the \( \beta \)-process, however; at low strain rates and moderate temperatures, the reverse progress of the \( \beta \)-process is non-negligible. Furthermore, its inclusion provides numerical stability during simulations where the deformation resistance of the \( \beta \)-process is minuscule.

In this definition of polymer viscoplasticity, the internal variable \( s_i \) represents a lumped "shear resistance". For both the \( \alpha \) and \( \beta \) processes, its initial value is related to the shear modulus and Poisson ratio, as first described by Argon (1973):

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

(2.30)

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

(2.31)

In the \( \alpha \)-process only, the shear strength \( s \) is taken to evolve to a preferred state with plastic straining:

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

(2.32)

where \( h_\alpha \) is the softening slope and \( s_{ss,\alpha} \) 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 in the \( \alpha \)-process captures the strain softening phenomenon. Overall, equations 2.28 and 2.29 capture the rate-, temperature-, and pressure-dependence of yield in the polymer, in addition to strain softening.

### 2.5.3 Model Implementation

The constitutive model outlined above has been implemented numerically into a commercial finite element code, ABAQUS/Explicit, through a user material subroutine (VUMAT). The application of this user material subroutine requires knowledge of the 14 material constants that define the components of the model:

**rate-dependent elastic springs**

\[
\mu_\alpha(\theta, \dot{\epsilon}) \quad \mu_\beta(\theta, \dot{\epsilon}) \quad \text{process-specific shear moduli as functions of temperature and strain rate}
\]

\[
\kappa_\alpha(\theta, \dot{\epsilon}) \quad \kappa_\beta(\theta, \dot{\epsilon}) \quad \text{process-specific bulk moduli as functions of temperature and strain rate}
\]

**viscoplastic dashpots**

\[
\dot{\gamma}^p_{0,\alpha} \quad \dot{\gamma}^p_{0,\beta} \quad \text{pre-exponential factors}
\]

\[
\Delta G_\alpha \quad \Delta G_\beta \quad \text{activation energies}
\]

\[
\alpha_{p,\alpha} \quad \alpha_{p,\beta} \quad \text{pressure coefficients}
\]

\[
h_\alpha \quad \text{softening slope}
\]

\[
s_{ss,\alpha} \quad \text{preferred state of athermal shear strength}
\]

**Langevin spring**

\[
C_R \quad \text{rubbery modulus}
\]

\[
\sqrt{N} \quad \text{limiting chain extensibility}
\]
Detailed explanation in regards to the determination of these material constants and model parameters is given in the section "Material Parameters" appended to this chapter. It is worth noting here, however, that the reduced DMA data is used directly in the definitions of the elastic springs, and that a piece-wise breakdown of the yield data is used in determining material constants necessary for defining the viscoplasticity.

2.6 Model v. Experiment

Figures 2-14 and 2-15 demonstrate the ability of the constitutive model to accurately predict the strain rate dependence of PC during uniaxial compression across a broad range of strain rates. Model results and experimental data for the stress-strain behavior at low \(10^{-3} \text{ s}^{-1}\), moderate \(1 \text{ s}^{-1}\), and high \(5050 \text{ s}^{-1}\) strain rates are depicted in figure 2-14. The constitutive model is able to capture the characteristic features of material response to large strain uniaxial deformation: initial linear elasticity, global yield, strain softening, and strain hardening.

The model is shown to capture the rate-dependence of the initial elastic modulus, by incorporating DMA viscoelastic analysis into the formulation. The model does not predict the non-linear transition to yield, as observed in the experimental curves; the model predicts yield as a sudden rather than distributed event. Hasan and Boyce (1995) and, more recently, Anand and Gurtin (2003) have detailed modifications to the model that would enable it to capture this feature of material response. However, for the intended high-rate, large deformation applications of the model, the slight discrepancy is not of concern.

Figure 2-15 is a plot of both model and experimental results for PC yield strength over seven decades of strain rate. The plot also shows the model breakdown of the PC yield strength, into \(\alpha\)-process and \(\beta\)-process contributions. Even across the transition strain rates, the model predicts the experimental yield strength with less than 5% error. The component-specific yield values indicate that the transition in the overall yield behavior begins when the \(\beta\)-contribution becomes non-negligible. It is clear that the success of the model lies in the decomposition of the intermolecular deformation resistance into the contributions from two distinct molecular processes. The original model, from which this model was derived, only accounted for one molecular process, and thus was only capable of predicting a linear relationship between yield strength and the logarithm of strain rate (or near linear,
Figures 2-16 and 2-17 provide the same comparison between model and experiment for PMMA as shown in figures 2-14 and 2-15 for PC. In figure 2-16, 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 emulates 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 moderate rate ($10^{-2}$ s$^{-1}$ to $10^{-1}$ s$^{-1}$) curves correspond to thermo-mechanically coupled response and the higher strain rate curves correspond to adiabatic deformation. Since the heat generated by plastic work does not have sufficient time to transfer to the surroundings, the temperature-sensitive polymer thermally softens during plastic straining. Recent experiments by Rittel (1999a) and Lerch, Gary, and Herve (2003) on PC have indicated that a polymer disk under high-rate ($10^3$ s$^{-1}$ to $10^4$ s$^{-1}$) compression may increase in temperature as much as 40°C with 80% plastic strain. Even at strain rates as low as $10^{-1}$ s$^{-1}$, Arruda et al. (1995) observed a 20°C temperature rise in PMMA disks under large strain compression. This is a critical issue in the high-rate deformation behavior of amorphous polymers, and will be addressed in Chapter 4 of this thesis.

Nonetheless, figure 2-17 demonstrates the ability of this constitutive model to accurately predict the yield strength of PMMA across a very broad range of strain rates. As before, the yield stress breakdown reinforces the fact that this model’s predictive capabilities are built upon a successful decomposition of intermolecular deformation resistance into two separate contributions - $\alpha$ and $\beta$.

## 2.7 Conclusions

The experimental techniques and corresponding analysis of this study have provided new insight into the rate-dependent behavior of amorphous polymers. Thorough viscoelastic characterization combined with compression testing over a wide range of strain rates has acted to experimentally characterize the influence of material transitions on the rate-dependent behavior of polycarbonate and poly(methyl methacrylate). Both of these polymers have
Figure 2-14: PC true stress-true strain behavior in uniaxial compression at low, moderate, and high strain rates: model prediction (dashed lines) and experiment (solid lines).

Figure 2-15: PC yield behavior in uniaxial compression as a function of strain rate, model prediction and experiment. 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 2-16: PMMA true stress-true strain behavior in uniaxial compression at low, moderate, and high strain rates: model prediction (dashed lines) and experiment (solid lines).

Figure 2-17: PMMA yield behavior in uniaxial compression as a function of strain rate, model prediction and experiment. In addition to the total yield strength, the numerically-predicted \( \alpha \) and \( \beta \) components of the yield strength are reported, for each strain rate.

been known to exhibit enhanced rate-sensitivity when deformed under high rates of loading, as compared to their behavior under quasi-static rates of loading. This enhanced rate-sensitivity is directly attributable to the restriction of secondary \( \beta \) molecular motions. The protocols described in this chapter may be applied to any polymer in order to
better understand and predict their mechanical behavior over a wide range of temperatures and strain rates.

In conjunction with the dynamic mechanical analysis (DMA) experiments of this study, 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 methods were validated through accurate predictions of the strain rate/temperature conditions of the PC and PMMA yield behavior transitions. By applying the techniques to other amorphous polymers and polymer-based material systems (e.g. polymer nanocomposites), it will be possible to identify, with viscoelastic data alone, those which may offer enhanced properties for impact applications and/or changes in the nature of their rate-sensitivity.

Following the experimental investigation and DMA analysis of PC and PMMA, a new constitutive model for the three-dimensional finite-strain deformation of amorphous polymers was proposed. This proposed model is built upon the transferable framework of an existing continuum-level constitutive model for the rate-, temperature-, and pressure-dependent finite strain deformation of thermoplastics. The model revisions are based on the same concepts which underly both the Ree-Eying yield theories and the viscoelastic analysis techniques introduced here: intermolecular resistance to deformation may be decomposed into the contributions of different molecular processes, each with their own unique rate and temperature dependence. Though the model introduced here only accounts for the primary ($\alpha$) and most significant secondary ($\beta$) processes, the contributions of other secondary processes (e.g. $\gamma$, $\delta$, etc.) could easily be incorporated if material response so dictated.

The proposed constitutive model is shown here to correctly predict yield stress values, as well as the strain rate regime of the transition in the yield behavior, for PC and PMMA. For the case of PC, the model correctly predicts the post-yield stress-strain behavior, up to 0.8 true strain, over the entire range of strain rates tested ($10^{-3}$ s$^{-1}$ to 4000 s$^{-1}$). However, the isothermal model does not capture the post-yield thermal softening seen in the PMMA stress-strain curves at moderate strain rates. This important aspect of material behavior at moderate and high rates is incorporated into a second revision of the model, following a comprehensive investigation of the influence of adiabatic heating and energy storage mechanisms on material deformation resistance (Chapter 4). For completeness, this
model will also incorporate the effects of thermal expansion (Chapter 3), which is a direct consequence of the adiabatic thermodynamic state, as well as a more appropriate treatment of pressure effects (Chapter 5). Combined with appropriate failure criteria, these features will enable the model to correctly simulate structural response to impact loading.

Material Parameters

Rate-dependent Elastic Springs

As described in section 2.5.3, the material description for the linear elastic springs requires knowledge of any two component-specific elastic constants; the values of these constants as a function of both temperature and strain rate must be determined.

The first set of elastic constants and their functional dependence on temperature and strain rate is derived directly from the DMA data. 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 2.3.2, 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 give the strain rate dependence of the moduli. Thus the DMA experimentation and analysis techniques provided here lead directly to half of the material constants needed to describe the linear elastic springs of the model: $E_{\alpha}(\theta, \dot{\epsilon})$ and $E_{\beta}(\theta, \dot{\epsilon})$.

Ideally, the values for the second elastic constants 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, the bulk modulus is the least likely to vary significantly with changing temperature or strain rate, even through the material glass transition. However, the question of how to split available bulk modulus values into $\alpha$ and $\beta$ contributions is not

---

4This suggestion has been generally accepted, despite a lack of accurate experimental data on the subject (Sane & Knauss, 2001). Recently, Qvale and Ravi-Chandar (2004) devised a new method of viscoelastic testing which allows for simultaneous characterization of the bulk and shear moduli as functions of time and temperature. Testing on PC and PMMA revealed that even through the glass transition, the bulk moduli will only change by a factor of 1/2, whereas the shear modulus will decrease by at least two orders of magnitude. The change in bulk modulus through $T_g$ is expected to be much less than the change observed through $T_f$, though data on this subject is virtually non-existent for any material.
a trivial one. We decided to scale the relative contributions of the $\alpha$ and $\beta$ processes in accordance with the analytical split of the DMA (Young’s Modulus) data, while maintaining a constant value for the overall bulk modulus of the polymer:

$$\frac{\kappa_\alpha(\theta, \dot{\varepsilon})}{\kappa_\beta(\theta, \dot{\varepsilon})} = \frac{E_\alpha(\theta, \dot{\varepsilon})}{E_\beta(\theta, \dot{\varepsilon})}$$

(2.33)

$$\kappa_\alpha(\theta, \dot{\varepsilon}) + \kappa_\beta(\theta, \dot{\varepsilon}) = \kappa^0$$

(2.34)

where $\kappa^0$ is the (constant) total bulk modulus, with value given by the material’s reported bulk modulus at standard rate ($\sim 10^{-3}$ s$^{-1}$), temperature ($25^\circ$C) and pressure (1 atm) conditions.

This treatment of the bulk behavior allows the process-specific bulk moduli, and hence all other elastic constants, to be defined by just a single addition material parameter ($\kappa^0$). Furthermore, a direct consequence of this method is that the Poisson ratio, while still a function of both temperature and strain rate, will always be the same in the two processes. As temperature approaches $T_g$, the value of this Poisson ratio will approach 0.5 (see figure 2-18). However, this treatment breaks down at temperatures above $T_g$, where it is expected that the bulk modulus will in fact change significantly. Furthermore, the overall bulk modulus may also change appreciably when $\beta$ motions become restricted; further research

Figure 2-18: Model-predicted PC elastic constants at $10^{-3}$ s$^{-1}$, according the functional dependence on rate and temperature of the process-specific Young’s moduli (section 2.3.2), as well as the treatment of bulk behavior described by equations 2.33 and 2.34.
Figure 2-19: Component-wise split of PC true shear yield stress data. Below the transition strain rate (~260 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 \( \gamma_0 \) and \( \Delta G \).

is needed on this point.

Again, the reader is directed to Chapter 6 for discussion on an alternate description of rate-dependent elastic behavior, including instead an implementation of linear viscoelasticity theory.

**Viscoplastic Dashpots**

Experimental yield data is used to solve for the pre-exponential factors \( \gamma_{0,\alpha}^p \) and \( \gamma_{0,\beta}^p \) and the activation energies \( \Delta G_\alpha \) and \( \Delta G_\beta \). First, the experimentally measured yield values must be decomposed into α and β contributions, a technique derived from the Ree-Eyring yield models. The component-wise split of the PC yield data is detailed in figure 2-19.

Following decomposition of the yield data, a pair of simultaneous equations is derived by applying the constitutive law for the rate of plastic straining (forward progress only; equation 2.29) to a particular process (α or β) at two different yield points corresponding to two different test strain rates. Appropriate values are substituted in for each of the variables in these equations: the component-specific shear yield values \( \tau \) are taken from the decomposed experimental yield data; the absolute temperatures \( \theta \) and the shear strain rates \( \dot{\gamma}^p \) are known from the corresponding test conditions, assuming that both processes
see the same loading conditions; and the pressures $p$ at yield are determined analytically from the total yield stress and the deformation mode (e.g. uniaxial compression). Also, at yield, the shear strength $s$ has not yet begun to decay - it evolves to a steady state only with plastic straining. Thus the $s$ values at yield may be calculated from equation 2.30 or 2.31 along with the component-specific elastic constants that correspond to the particular test temperature and strain rate. Finally, assuming that the component-specific pressure coefficients $\alpha_{p,\alpha}$ and $\alpha_{p,\beta}$ are known (discussed later), the only unknown quantities in the two equations are the pre-exponential factor $\gamma_0^p$ and the activation energy $\Delta G$; these are solved for simultaneously.

Because the $\beta$-process employs a more general description of plastic flow (forward and reverse progress), it may be necessary to adjust the parameter $\gamma_0^{\beta}$ after it has been calculated in this manner. For both PC and PMMA, the fit was optimized by dividing the calculated values of $\gamma_0^{\beta}$ by two. Alternatively, a pair of full rate laws (equation 2.28) could be solved simultaneously for $\gamma_0^{\beta}$ and $\Delta G$ via numerical methods.

In the constitutive equations of the viscoplastic dashpots, there are two other material constants to be specified: the pressure coefficients $\alpha_{p,\alpha}$ and $\alpha_{p,\beta}$. These parameters may be calculated from a quantitative comparison of tension and compression yield data derived from tests at the same temperature and strain rate. Bauwens-Crowet et al. (1972) provide yield data for PC, in both tension and compression, at $4.16 \times 10^{-3} \text{ s}^{-1}$ over the temperature range $-125^\circ\text{C}$ to $125^\circ\text{C}$. By isolating two regimes in this data - one dominated by the $\alpha$-process alone, one in which the both the $\alpha$ and $\beta$ processes are operative - again the yield data may be made component-specific. The component-specific empirical relationships between tensile and compressive yield lead to the PC pressure coefficients $\alpha_{p,\alpha}$ and $\alpha_{p,\beta}$.

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. In fitting the original (single process) constitutive model to experimental PMMA data, Arruda et al. (1995) used a pressure coefficient of 0.26. Based on the strain rates ($10^{-3} \text{ s}^{-1}$ to $10^{-1} \text{ s}^{-1}$) and temperatures ($23^\circ\text{C}$ to $75^\circ\text{C}$) of their tests, it may be assumed that this pressure coefficient is an average of the pressure coefficients of the $\alpha$ and $\beta$ processes. 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. A more sophisticated treatment of pressure effects, for both PMMA and PC, is described in Chapter 5.
For both PC and PMMA, the $\beta$-process pressure coefficient $\alpha_{p,\beta}$ is taken to be zero in the case of negative pressures. This modification of the original formulation is based upon an assertion that the secondary molecular motions associated the $\beta$-process are only affected by positive pressures, which reduce their mobility. By setting $\alpha_{p,\beta}$ equal to zero under conditions of negative pressure, we prevent the total $\beta$-process shear resistance $(s_\beta + \alpha_{p,\beta}p)$ from going to zero or even negative in the case of large negative pressures.

The remaining model parameters for the viscoplastic dashpots are related to the strain softening phenomenon. 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 parameters $h_\alpha$ and $s_{ss,\alpha}$ 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.

**Langevin Spring**

The Langevin spring behavior is described by two material parameters: the rubbery modulus $C_R$ and the limiting chain extensibility $\sqrt{\mathcal{N}}$. These parameters were determined by fitting model simulations to the stress-strain data, over the region dominated by strain hardening. Again, 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.
Table 2.2: PC and PMMA model parameters

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<tr>
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<tr>
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</tr>
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<td>$C_R$</td>
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Chapter 3

Thermal Expansion and Recovery

3.1 Background

Polymeric materials are known to exhibit significant volumetric expansion upon heating, up to an order of magnitude greater than that exhibited by metals. This characteristic thermal behavior has important consequences especially in applications where constrained polymeric components are exposed to heat, including microelectronic devices, medical devices, and aerospace systems. Furthermore, thermal expansion can be important under high-rate mechanical loading, when dissipated heat does not have sufficient time to escape to the environment and the component temperature may rise as much as 100°C. In such instances, the volume change associated with thermal expansion may be two to three orders of magnitude greater than the volumetric change induced by mechanical loading alone.

Previous research in this area has led to a number of constitutive models which take into account the effects of thermal expansion. Generally, these models consider thermal expansion as a separate and independent contribution to the total deformation. In the mathematics of continuum mechanics, this translates into a multiplicative decomposition of the total deformation gradient:

\[ F = F^e F^{th} \]  \hspace{1cm} (3.1)

where \( F^{th} \) is the volumetric deformation induced by heating/cooling and \( F^e \) is the elastic deformation induced by isothermal mechanical loading. Such a procedure has been followed in the finite strain thermoelasticity models of Blatz (1969), Crochet and Naghdi (1978), Morman, Jr. (1995), and, most recently, Humphrey and Rajagopal (1998). In most of these
models, the thermal component is taken to be isotropic as well as volumetric, such that:

\[ F^{th} = f(\theta)I \]  

However, Humphrey and Rajagopal (1998) suggest that a more general, anisotropic expression is needed in the case where thermal loading is applied after mechanical loading. During mechanical loading, the polymer's molecular network evolves from an initial state of random orientation into one in which the molecular chains are preferentially aligned along the direction(s) of principal stretch. Humphrey and Rajagopal assume that the evolving molecular network anisotropy will lead also to an anisotropic thermal response. This suggestion has important ramifications in modelling the thermomechanical response of ductile polymeric components under high-rate impact. Under impact, the ductile polymer will experience large tensile stretch – and hence significant molecular orientation – before failure, while also increasing in temperature as a result of the adiabatic thermodynamic condition. Nevertheless, there is little experimental data to corroborate Humphrey and Rajagopal's assertion, at least for the case of amorphous polymers.

Chou and co-workers have conducted extensive experiments on the temperature and orientation dependence of thermal expansion in semicrystalline polyethylene (PE) (Choy, Chen, & Ong, 1979; Choy, Chen, & Young, 1981; White & Choy, 1984) and semicrystalline poly(ether-ether-keytone) (PEEK) (Choy & Leung, 1990). For oriented PE (draw ratio = 11, crystallinity volume fraction = 0.8), Choy et al. (1979) report a transverse coefficient of thermal expansion (CTE) which is only 23% higher than the isotropic CTE, for tests near room temperature. At temperatures well below room temperature (5-10 K), however, the transverse CTE in the oriented PE was measured as nearly 100% greater than that in the isotropic PE (White & Choy, 1984). At both high and low temperatures, they found the longitudinal CTE to decrease with cold drawing. Similar behavior is noted in the review article of Porter and Wang (1995) for the case of semicrystalline polypropylene. However, as discussed at length by Choy et al., the level of crystallinity in the polymer is expected to have a large effect on even the orientation dependence of the CTE. Evidence on the orientation dependence of thermal expansion in amorphous polymers is much more limited. Elsner, Kempf, Bartha, and Wagner (1990) and Tong, Hsuen, Saenger, and Su (1991) separately conducted CTE experiments on thin films of amorphous polyimide and
found the thickness-direction CTE to be twice as large as the in-plane CTE; both groups attribute this phenomena to molecular alignment in the plane of the film, though the level of orientation is unclear. For the case of polystyrene, Porter and Wang (1995) report that the anisotropy in thermal expansion is small even at draw ratios as large as five, though a quantitative definition of "small" is not given.

3.2 Experiments

In anticipation of incorporating the effects of thermal expansion into the constitutive model described in Chapter 2, an experimental program was designed in order to test the assumption of the retention of isotropic thermal expansion for glassy, amorphous polymers. Specifically, experiments were aimed at investigating the functional dependence of the linear coefficient of thermal expansion (CTE) on the stretch state of the polymer, where stretch state is taken as a measure of molecular orientation.

3.2.1 Methods

Experiments were focused on the thermal expansion behavior of an exemplary amorphous polymer, poly(methyl methacrylate) (PMMA). The particular PMMA used in this study was of the same brand (G Plexiglas®, AtoHaas) tested in dynamic mechanical analysis and
uniaxial compression, as described in Chapter 2. The T_g for this polymer is approximately 115°C. Since the sheets of Plexiglas® PMMA are produced through a traditional cell cast method, no molecular chain orientation is expected in the as-cast sheet. Specimens were machined directly from these sheets as right circular cylinders, with both diameter and height of approximately 5 millimeters (figure 3-1(a)).

Prior to thermal testing, varying degrees of molecular orientation were induced in the virgin specimens via uniaxial compression (figure 3-1(b)). Uniaxial compression was conducted on a Zwick/Roell Z010 universal testing machine under strain control, at a constant engineering strain rate of 3×10^{-3} s^{-1}. To ensure homogeneous deformation, thin Teflon sheets were placed between the Zwick platens and the specimen surfaces, and WD-40 lubricant was used between the Teflon sheets and platens. Uniaxial compression is known to preferentially align the molecular chains of a polymer in a plane perpendicular to the loading axis. The degree of radial molecular alignment will depend upon the amount of inelastic axial strain. For this study, some cylindrical specimens were left undeformed (no molecular orientation), and the remaining cylinders were compressed to imposed true strain levels of either 54%, 80%, or 98%. Upon unloading, all elastic strain was recovered; additional inelastic strain was recovered at room temperature over the week between initial compression and CTE testing. The residual strains were measured just before CTE testing as 35%, 55%, and 68% (19%, 25%, and 30% strain recovered, respectively). These residual true strain levels correspond to axial stretch values of 0.70, 0.58, and 0.51, respectively.

After compression pre-treatment, the cylindrical PMMA specimens were used in thermal expansion experiments on a Perkin-Elmer Diamond Thermomechanical Analyzer (TMA). The specimens were loaded into an insulated temperature chamber and approached from the top by a quartz probe (figure 3-1(c)). After initial contact, the probe was held against the top surface of the specimen with a constant load of 0.03 N for the duration of the test. The chamber temperature was ramped from 25°C to approximately 140°C (T_g+25°C) at a constant rate of +5°C per minute. During thermal loading, the current height h of the specimen was measured by the quartz probe as a function of temperature, with a resolution

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1In the cell-cast method, sheets are molded individually by pouring the acrylic monomer and catalysts (the constituents of the polymer) into a glass frame. This frame is then moved to a temperature-controlled bath where it is slowly cured. Upon curing, the sheet will often shrink preferentially in the thickness direction as it is constrained in the length-width directions by adhesion to the glass frame. However, in a final step, the sheet is annealed outside of the frame in order to remove any residual stress and, correspondingly, any molecular orientation.
of 0.02 μm (compared to the undeformed height of ~5 mm). This data was recorded to a computer, and later used to calculate the axial thermal stretch $h/h_0$, where $h_0$ is the specimen height after compression. The height displacement data was also used to calculate the linear axial CTE, $\alpha$:

$$\alpha = \frac{1}{h_0} \frac{\partial h}{\partial T} \quad (3.3)$$

After reaching maximum temperature, the specimens were allowed to cool to room temperature in ambient air with data recording turned off. In some cases, the specimens were then re-tested under an identical thermal load program.

### 3.2.2 Results

The results of all PMMA CTE experiments are summarized in figures 3-2 to 3-4. Figure 3-2 shows typical curves of axial thermal stretch versus temperature for an undeformed ($h_0=5$ millimeters) cylinder. During both the first and second runs on the same specimen, it is observed that the specimen height increases in an approximately linear fashion with increases in temperature, up to $90^\circ$C. The corresponding CTE is calculated to be $9.74 \times 10^{-5}$ $^\circ$C$^{-1}$ on the first run and $9.00 \times 10^{-5}$ $^\circ$C$^{-1}$ on the second run, over the temperature range $40^\circ$C to $90^\circ$C. These values are consistent with that reported by the supplier, Altuglas International ($7.4 \times 10^{-5}$ $^\circ$C$^{-1}$).

At temperatures above $90^\circ$C, the first run curve of figure 3-2(a) shows an increasing rate of thermal expansion with increasing temperature; this rate reaches a maximum just beyond $T_g$. This phenomenon is attributed to inelastic recovery. Amorphous polymers are known to recover all inelastic strain over time as they tend towards a state of maximum entropy – thermodynamic equilibrium. For PMMA at room temperature, the recovery process can take months; for temperatures at and above $T_g$, when molecular chains are much more mobile, recovery is greatly accelerated such that it occurs on the order of seconds and minutes. In this case, even our "undeformed" specimens exhibited non-trivial (~4%) recovery as the chamber temperature approached and passed through the material glass transition. This result indicates that there is some degree of molecular orientation in the as-delivered sheet due to its processing history; this orientation is recovered upon heating through $T_g$. It is possible the cast sheet from which the specimens were cut was not sufficiently annealed, and the recovered strain is related to shrinkage incurred during curing.
Figure 3-2: PMMA axial thermal stretch as a function of temperature for an initially undeformed cylinder: (a) first and second runs, 25°C to 140°C (b) second run, 100°C to 140°C. The first and second runs were conducted on the same specimen, approximately two hours apart.

In the "undeformed" tests of this study, the first run essentially served to anneal the specimen, while the second run measured the intrinsic thermal expansion behavior of the polymer. By plotting the data of the second run on a different scale (figure 3-2(b)), it is observed that the PMMA rate of thermal expansion increases significantly through the glass transition, as might be expected. The calculated CTE in the rubbery region (135°C to 140°C) is $2.83 \times 10^{-4}$ °C$^{-1}$, or about three times greater than the CTE calculated over the range 40°C to 90°C.$^2$ The measured response in the first run is a combination of thermal expansion in the traditional sense and inelastic recovery. For this reason, an apparent thermal expansion is observed which is much greater than expected. However, the fact that the curves in figure 3-2(a) align very well for temperatures below 90°C indicates that the contribution of inelastic recovery is negligible up until this point.

The measured response of the deformed specimens, summarized in figure 3-3, is dominated by the inelastic recovery phenomenon. This is to be expected, as the uniaxial compression pre-treatment serves to orient the molecular chains in a plane perpendicular to the loading axis. Through thermal activation, the oriented chains will return to a random configuration where entropy is maximized. The apparent thermal expansion is observed to

---

$^2$This value is consistent with what is typically reported for rubbery materials. For instance, the CTE of silicon rubber is reported by Hatta, Takei, and Taya (2000) as $3 \times 10^{-4}$ °C$^{-1}$. 

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increase monotonically with increasing amount of pre-straining, as there is more inelastic deformation to recover. The recovery of stored inelastic energy is a separate mechanism from that which controls the intrinsic thermal expansion of the material, and will be addressed in Chapter 4. For the purposes of this study, we focus on the measured thermal expansion at temperatures where the inelastic recovery contribution is negligible. In the tests on undeformed specimens (figure 3-2), this range extended to 90°C; for the deformed specimens (curves of figure 3-3), appreciable recovery is observed at temperatures as low as 50°C.\(^3\)

Finally, the axial linear CTE for PMMA is given as function of imposed axial pre-stretch in figure 3-4. The CTE values were calculated from TMA data over the temperature range 30°C to 45°C, according to equation 3.3. Although this temperature range is narrow, data in this region is thought to be untainted by the effects of inelastic recovery. The CTE of PMMA is in fact found to vary with molecular orientation. As shown in figure 3-4, the axial CTE increases linearly with the level of off-axis chain alignment, over a wide range of stretch values. Data from previous studies on the orientation-dependence of thermal expansion (Choy et al., 1979; Porter & Wang, 1995) indicates that anisotropy in the thermal expansion

\(^3\)Note that these temperature cut-offs are specific to the particular heating rate used in the TMA (+5°C/min), as recovery is both time and temperature dependent. For a faster heating rate, the onset of recovery would shift to a higher temperature. During high-rate adiabatic deformation, there likely would not be sufficient time for any recovery to occur.
behavior evolves such that the volumetric expansion remains approximately constant. That is, 
\[
\alpha_1\alpha_2\alpha_3 = (\alpha_{iso})^3
\]  
(3.4)

where \(\alpha_i\) is the CTE along principal direction \(i\) and \(\alpha_{iso}\) is the isotropic CTE. Thus, to accommodate the increase in axial CTE with planar equibiaxial molecular orientation, the PMMA off-axis CTE must decrease. As the axial CTE increases from \(7.12 \times 10^{-5} \degree C^{-1}\) (no orientation) to \(1.09 \times 10^{-4} \degree C^{-1}\) (\(\lambda_{axial}=0.51\)), the off-axis CTE is expected to decrease to \(5.73 \times 10^{-5} \degree C^{-1}\).

As measured and predicted here, the CTE of PMMA will vary by as much as 50% with moderate molecular orientation. However, the amount of variation observed is less than the variation between thermal expansion coefficients of different thermoplastic materials, and is also less than the expected variation in CTE with temperature. As a first approximation, the thermal expansion behavior is here taken to be isotropic. This assumption is appropriate for applications in which either thermal expansion is not critical or molecular orientation is minimal.
Figure 3-5: Schematic representation of the Weber and Boyce (1989) thermo-elasto-plastic kinematic framework.
3.3 Modelling

Here a new constitutive model framework is proposed which allows the rate- and temperature-dependent model of Chapter 2 to also account for the effects of thermal expansion. The thermo-elasto-plastic kinematic framework proposed is based mainly upon the work of Weber and Boyce (1989), which has also been utilized in the models of Boyce, Montagut, and Argon (1992b) and Arruda et al. (1995). A schematic representation of this framework is given as figure 3-5.

In elasto-plastic deformation, the total deformation gradient is decomposed into elastic and plastic contributions (Kroner, 1960; Lee, 1969), and there is a single intermediate kinematic configuration – the "relaxed configuration" (see Chapter 2, section 2.5.1). In the thermo-elasto-plastic formulation introduced by Weber and Boyce, the total deformation gradient is multiplicatively decomposed into three contributions: elastic, thermal expansion, and plastic.

\[
F = F^e F^{th} F^p
\]  

(3.5)

As shown in figure 3-5, this breakdown leads to two intermediate configurations. One of these configurations is defined by the mapping \( F^{thp} \equiv F^{th} F^p \); in order to properly capture the temperature dependence of plastic flow, the calculation of the rate of plastic stretching takes place in this configuration (see Weber and Boyce, 1989). Alternatively, these calculations could be carried out in the loaded configuration. Here, the general thermo-elasto-plastic framework is extended to the two-process polymer constitutive model introduced in Chapter 2. For the component naming conventions (A, B, α, etc.), see figure 2-13.

3.3.1 Kinematics

As before, the total deformation gradient acts in full on each of the three main components of the model:

\[
F_{A_\alpha} = F_{A_\beta} = F_B = F
\]  

(3.6)
The deformation gradients in element $A$ are multiplicatively decomposed into elastic, thermal expansion, and plastic components following Weber and Boyce (1989):

\[
F_{A\alpha} = F_{A\alpha}^e F_{A\alpha}^{th} F_{A\alpha}^p
\]

\[
F_{A\beta} = F_{A\beta}^e F_{A\beta}^{th} F_{A\beta}^p
\]

It is assumed that all plastic deformation is volume preserving, i.e. $\det F_{A\alpha}^p = \det F_{A\beta}^p = 1$. Following polar decomposition of the deformation gradients, the deformation in all configurations may be expressed as the product of a stretch and a rotation:

\[
F_{A\alpha}^e = R_{A\alpha}^e U_{A\alpha} = V_{A\alpha}^e R_{A\alpha}^e
\]

\[
F_{A\beta}^e = R_{A\beta}^e U_{A\beta} = V_{A\beta}^e R_{A\beta}^e
\]

\[
F_{A\alpha}^{th} = R_{A\alpha}^{th} U_{A\alpha}^{th} = V_{A\alpha}^{th} R_{A\alpha}^{th}
\]

\[
F_{A\beta}^{th} = R_{A\beta}^{th} U_{A\beta}^{th} = V_{A\beta}^{th} R_{A\beta}^{th}
\]

\[
F_{A\alpha}^p = R_{A\alpha}^p U_{A\alpha}^p = V_{A\alpha}^p R_{A\alpha}^p
\]

\[
F_{A\beta}^p = R_{A\beta}^p U_{A\beta}^p = V_{A\beta}^p R_{A\beta}^p
\]

\[
F_{A\alpha}^{thp} = R_{A\alpha}^{thp} U_{A\alpha}^{thp} = V_{A\alpha}^{thp} R_{A\alpha}^{thp}
\]

\[
F_{A\beta}^{thp} = R_{A\beta}^{thp} U_{A\beta}^{thp} = V_{A\beta}^{thp} R_{A\beta}^{thp}
\]

We examine the rate at which deformation takes place in the body through the velocity gradient $L = L_{A\alpha} = L_{A\beta} = \dot{F}F^{-1}$. By substituting the expressions 3.7 and 3.8 into this definition, the velocity gradient too can be expressed in terms of elastic, thermal, and plastic components:

\[
L_{A\alpha} = L_{A\alpha}^e + F_{A\alpha}^e \left[ L_{A\alpha}^{th} + F_{A\alpha}^{th} L_{A\alpha}^p (F_{A\alpha}^{th})^{-1} \right] (F_{A\alpha}^e)^{-1}
\]

\[
L_{A\beta} = L_{A\beta}^e + F_{A\beta}^e \left[ L_{A\beta}^{th} + F_{A\beta}^{th} L_{A\beta}^p (F_{A\beta}^{th})^{-1} \right] (F_{A\beta}^e)^{-1}
\]
where $L_{A_i}^e \equiv \dot{F}_{A_i}^e (F_{A_i}^e)^{-1}$, $L_{A_i}^{th} \equiv \dot{F}_{A_i}^{th} (F_{A_i}^{th})^{-1}$, and $L_{A_i}^p \equiv \dot{F}_{A_i}^p (F_{A_i}^p)^{-1}$ $(i = \alpha, \beta)$. We also introduce the thermo-plastic velocity gradient, $L^{thp}$:

$$
L_{A_\alpha}^{thp} = F_{A_\alpha}^{thp} (F_{A_\alpha}^{thp})^{-1} = L_{A_\alpha}^{th} + F_{A_\alpha}^{th} L_{A_\alpha}^p (F_{A_\alpha}^p)^{-1} = D_{A_\alpha}^{thp} + W_{A_\alpha}^{thp} \quad (3.20)
$$

$$
L_{A_\beta}^{thp} = F_{A_\beta}^{thp} (F_{A_\beta}^{thp})^{-1} = L_{A_\beta}^{th} + F_{A_\beta}^{th} L_{A_\beta}^p (F_{A_\beta}^p)^{-1} = D_{A_\beta}^{thp} + W_{A_\beta}^{thp} \quad (3.21)
$$

where $D_{A_\alpha}^{thp}$ and $D_{A_\beta}^{thp}$ (symmetric tensors) represent the rates of thermo-plastic stretching; similarly, $W_{A_\alpha}^{thp}$ and $W_{A_\beta}^{thp}$ (skew tensors) are the rates of thermo-plastic spin. Here, the thermo-plastic flow is taken to be irrotational, i.e. $W_{A_\alpha}^{thp} = W_{A_\beta}^{thp} = 0$ (Weber & Boyce, 1989). It follows, then, that

$$
\dot{F}_{A_\alpha}^{thp} = D_{A_\alpha}^{thp} F_{A_\alpha}^{thp} \quad (3.22)
$$

$$
\dot{F}_{A_\beta}^{thp} = D_{A_\beta}^{thp} F_{A_\beta}^{thp} \quad (3.23)
$$

The expressions above may be integrated explicitly to obtain $F_{A_\alpha}^{thp}$ and $F_{A_\beta}^{thp}$, the elastic portion of the deformation gradients are then obtained via

$$
F_{A_\alpha}^e = F_{A_\alpha} (F_{A_\alpha}^{thp})^{-1} \quad (3.24)
$$

$$
F_{A_\beta}^e = F_{A_\beta} (F_{A_\beta}^{thp})^{-1} \quad (3.25)
$$

$F_{A_\alpha}^{th}$ and $F_{A_\beta}^{th}$ must be constitutively prescribed, allowing for the calculation of $F_{A_\alpha}^p$ and $F_{A_\beta}^p$:

$$
F_{A_\alpha}^p = (F_{A_\alpha}^{th})^{-1} F_{A_\alpha}^{thp} \quad (3.26)
$$

$$
F_{A_\beta}^p = (F_{A_\beta}^{th})^{-1} F_{A_\beta}^{thp} \quad (3.27)
$$

For any constitutive model which is defined within the thermo-elasto-plastic framework, it is most critical to develop an appropriate description of temperature-dependent plastic velocity gradient. Due to the assumption of irrotational plastic flow, the plastic velocity gradient will be identical to the rate of plastic stretching ($D_{A_\alpha}^{thp}$ and $D_{A_\beta}^{thp}$). In general, these
rates of stretching can be considered the sum of two contributions:

\[
\begin{align*}
D_{A\alpha}^{\text{thp}} &= \hat{D}_{A\alpha}^p (T_{A\alpha}, \theta, A_i) + \hat{M}_{A\alpha} (\theta, A_i) \dot{\theta} \\
D_{A\beta}^{\text{thp}} &= \hat{D}_{A\beta}^p (T_{A\beta}, \theta, A_k) + \hat{M}_{A\beta} (\theta, A_k) \dot{\theta}
\end{align*}
\] (3.28)

(3.29)

Where \( \hat{D}_{A\alpha}^p \) and \( \hat{M}_{A\alpha} \dot{\theta} \) \((i = \alpha, \beta)\) primarily capture the rate of plastic stretching and the rate of thermal stretching (thermal expansion) in the unloaded configuration, respectively.\(^4\) Both contributions depend upon the current temperature \( \theta \) and a list of tensorial internal variables, \( A_i \) or \( A_k \). The rate of plastic stretching also depends on the driving stress \( (T_{A\alpha} \text{ and } T_{A\beta}) \).

The rate of plastic stretching in this thermo-elasto-plastic framework can itself be considered the sum of two components:

\[
\begin{align*}
\hat{D}_{A\alpha}^p &= \text{sym} \left( \mathbf{F}_{A\alpha}^{\text{th}} L_{A\alpha}^p (\mathbf{F}_{A\alpha}^{\text{th}})^{-1} \right) + \text{sym} \left( \frac{\partial \mathbf{F}_{A\alpha}^{\text{th}} (T_{A\alpha}, \theta, A_i)}{\partial A_i} \mathbf{F}_{A\alpha}^{\text{th}} \right) \\
\hat{D}_{A\beta}^p &= \text{sym} \left( \mathbf{F}_{A\beta}^{\text{th}} L_{A\beta}^p (\mathbf{F}_{A\beta}^{\text{th}})^{-1} \right) + \text{sym} \left( \frac{\partial \mathbf{F}_{A\beta}^{\text{th}} (T_{A\beta}, \theta, A_k)}{\partial A_k} \mathbf{F}_{A\beta}^{\text{th}} \right)
\end{align*}
\] (3.30)

(3.31)

In these expressions, the first term is simply the symmetric part of the convected plastic velocity gradient. The second term represents that part of the thermal velocity gradient which evolves with a changing internal state; the second term vanishes if \( \mathbf{F}_{\text{th}} \) is not a function of the internal state (i.e. network orientation). Both terms are framed in the unloaded configuration.

The second contribution to the rate of plastic stretching is taken as the portion of the thermal velocity gradient which evolves with changing temperature:

\[
\begin{align*}
\hat{M}_{A\alpha} \dot{\theta} &= \text{sym} \left( \frac{\partial \mathbf{F}_{A\alpha}^{\text{th}} (T_{A\alpha} \theta, A_i)}{\partial \theta} (\mathbf{F}_{A\alpha}^{\text{th}})^{-1} \right) \dot{\theta} \\
\hat{M}_{A\beta} \dot{\theta} &= \text{sym} \left( \frac{\partial \mathbf{F}_{A\beta}^{\text{th}} (T_{A\beta} \theta, A_k)}{\partial \theta} (\mathbf{F}_{A\beta}^{\text{th}})^{-1} \right) \dot{\theta}
\end{align*}
\] (3.32)

(3.33)

Finally, combining equations 3.32 and 3.33 with equations 3.30 and 3.31, along with the

\[^4\text{Note, however, that in general } \hat{D}_{A\alpha}^p \neq \mathbf{F}_{A\alpha}^{\text{th}} L_{A\alpha}^p (\mathbf{F}_{A\alpha}^{\text{th}})^{-1} \text{ and } \hat{M}_{A\alpha} \neq L_{A\alpha}^{\text{th}} (\alpha, \beta).\]
irrotational constraint, the total thermo-plastic velocity gradients are given as:

\[
L^{thp}_{Aa} = D^{thp}_{Aa} = \text{sym} \left( F_{Aa}^{thP} L^{thP}_{Aa} (F_{Aa}^{thP})^{-1} + \frac{\partial F_{Aa}^{thP}}{\partial A_i} F_{Aa}^{thP} + \frac{\partial F_{Aa}^{thP}}{\partial \theta} (F_{Aa}^{thP})^{-1} \right) \quad (3.34)
\]

\[
L^{thp}_{A\beta} = D^{thp}_{A\beta} = \text{sym} \left( F_{A\beta}^{thP} L^{thP}_{A\beta} (F_{A\beta}^{thP})^{-1} + \frac{\partial F_{A\beta}^{thP}}{\partial A_k} F_{A\beta}^{thP} + \frac{\partial F_{A\beta}^{thP}}{\partial \theta} (F_{A\beta}^{thP})^{-1} \right) \quad (3.35)
\]

Thus a material model framed in the thermo-elasto-plastic kinematic framework requires explicit constitutive description of both the plastic velocity gradient \( L^{P}_{Aa} \) and \( L^{P}_{A\beta} \) and the thermal expansion component of the deformation gradient \( F_{Aa}^{th} \) and \( F_{A\beta}^{th} \).

### 3.3.2 Material Description

It has been suggested that macromolecular materials exhibit distinctly anisotropic thermal expansion behavior whenever the constituent chains are not completely random in their orientation. In accordance with this theory, Weber and Boyce (1989) offer a general expression for a thermal expansion tensor which depends not only upon temperature, but also the evolving internal state of molecular orientation:

\[
F^{th} = a_0 1 + a_1 V + a_2 (V)^2 \quad (3.36)
\]

where the coefficients \( a_0, a_1, \) and \( a_2 \) depend on temperature as well as the scalar invariants of the left stretch tensor, \( V \). In continuing work, Socrate and Boyce (1999) implemented techniques for considering evolving anisotropy in the thermal expansion behavior. However, in this study, we neglect the functional dependence of \( F^{th} \) on network orientation, as a first approximation. While the effect is measurable in PMMA, the thermal expansion behavior is not considered critical in the immediate applications of the model and thus the additional complexity is not warranted. Instead, the polymer thermal behavior is taken to be isotropic – a function only of temperature. This simplifying assumption has precedent in the work of Weber and Boyce (1989), as well as Crochet and Naghdî (1978) and Morman, Jr. (1995). It should be emphasized, however, that this is a first approximation. The experimental results of this study indicate that a more accurate treatment of the distinctly anisotropic thermal expansion behavior of amorphous polymers will be necessary in certain applications.

With the isotropic assumption, the thermal expansion tensor is taken to be purely
volumetric:

\[ \mathbf{F}_{A\alpha}^{th} = \mathbf{F}_{A\beta}^{th} = \hat{\beta}(\theta) \mathbf{1} \]  

(3.37)

where \( \beta \) is a scalar-valued function. Note that the description of thermal expansion in the \( \alpha \) and \( \beta \) processes is taken to be the same, so that the material will expand uniformly in both a macroscopic and a local sense. As there is now no component of the thermal velocity gradient which evolves with the internal state of the material, the second term in equations 3.34 and 3.34 (last term in equations 3.30 and 3.31) vanishes. The rate of thermo-plastic stretching simplifies then to

\[
\begin{align*}
\mathbf{D}^{th}_{A\alpha} &= \text{sym} \left( \mathbf{F}_{A\alpha}^{th} \mathbf{L}_{A\alpha}^{p} \left( \mathbf{F}_{A\alpha}^{th} \right)^{-1} \right) + \text{sym} \left( \frac{\partial \mathbf{F}_{A\alpha}^{th}}{\partial \theta} \left( \mathbf{F}_{A\alpha}^{th} \right)^{-1} \hat{\beta} \right) \\
\mathbf{D}^{th}_{A\beta} &= \text{sym} \left( \mathbf{F}_{A\beta}^{th} \mathbf{L}_{A\beta}^{p} \left( \mathbf{F}_{A\beta}^{th} \right)^{-1} \right) + \text{sym} \left( \frac{\partial \mathbf{F}_{A\beta}^{th}}{\partial \theta} \left( \mathbf{F}_{A\beta}^{th} \right)^{-1} \hat{\beta} \right)
\end{align*}
\]  

(3.38)  
(3.39)

The first term in equations 3.38 and 3.39 – the symmetric portion of the convected plastic velocity gradient – is described as the product of a magnitude (\( \dot{\gamma}_{A}^{p} \) or \( \dot{\gamma}_{A}^{p} \)) and a direction tensor (\( \mathbf{N}^{thp}_{A\alpha} \) or \( \mathbf{N}^{thp}_{A\beta} \)):

\[
\begin{align*}
\overline{\mathbf{D}}^{p}_{A\alpha} &= \text{sym} \left( \mathbf{F}_{A\alpha}^{th} \mathbf{L}_{A\alpha}^{p} \left( \mathbf{F}_{A\alpha}^{th} \right)^{-1} \right) = \dot{\gamma}_{A}^{p} \mathbf{N}^{thp}_{A\alpha} \\
\overline{\mathbf{D}}^{p}_{A\beta} &= \text{sym} \left( \mathbf{F}_{A\beta}^{th} \mathbf{L}_{A\beta}^{p} \left( \mathbf{F}_{A\beta}^{th} \right)^{-1} \right) = \dot{\gamma}_{A}^{p} \mathbf{N}^{thp}_{A\beta}
\end{align*}
\]  

(3.40)  
(3.41)

where \( \mathbf{N}^{thp}_{A\alpha} \) and \( \mathbf{N}^{thp}_{A\alpha} \) are taken to be coaxial with the deviatoric stresses (convected back to unloaded configuration) acting on the \( \alpha \) and \( \beta \) components of the intermolecular network (A), respectively:

\[
\begin{align*}
\mathbf{N}^{thp}_{A\alpha} &= \frac{\left( \mathbf{F}_{A\alpha}^{th} \right)^{-1} \mathbf{T}'_{A\alpha} \mathbf{F}_{A\alpha}^{th}}{|\mathbf{T}'_{A\alpha}|} \\
\mathbf{N}^{thp}_{A\beta} &= \frac{\left( \mathbf{F}_{A\beta}^{th} \right)^{-1} \mathbf{T}'_{A\beta} \mathbf{F}_{A\beta}^{th}}{|\mathbf{T}'_{A\beta}|}
\end{align*}
\]  

(3.42)  
(3.43)

The material model described in Chapter 2 provides constitutive laws for \( \dot{\gamma}_{A}^{p} \) and \( \dot{\gamma}_{A}^{p} \) (equations 2.29 and 2.28, as well as \( \mathbf{T}_{A\alpha} \) and \( \mathbf{T}_{A\beta} \) (equations 2.19 and 2.20), which are both used here without modification.

The second term in equations 3.38 and 3.39 – the portion the thermal velocity gradient which evolves with changing temperature – is calculated from the suggested form of \( \mathbf{F}^{th} \)
(equation 3.37):

\[
\text{sym} \left( \frac{\partial F_{th}^{th}}{\partial \theta} (F_{th}^{th})^{-1} \dot{\theta} \right) = \text{sym} \left( \frac{\partial F_{th}^{th}}{\partial \theta} (F_{th}^{th})^{-1} \dot{\theta} \right) = \dot{\alpha}(\theta) \dot{\theta} 1
\] (3.44)

where \( \alpha (= \text{dln} \beta / \text{d}\theta) \) is the temperature-dependent coefficient of thermal expansion. Thus, under the assumption of isotropic thermal behavior, the final expression for the thermoplastic velocity gradient is given as:

\[
L_{thp} = \gamma_{\alpha}^p N_{thp} + \alpha \dot{\theta} 1
\] (3.45)

\[
L_{thp} = \gamma_{\beta}^p N_{thp} + \alpha \dot{\theta} 1
\] (3.46)

The scalar function \( \beta(\theta) \) (equation 3.37) is determined through its relationship with the coefficient of thermal expansion. As a first approximation, the CTE \( \alpha \) is taken as a constant, independent of temperature. It follows, then, that

\[
F_{th}^{th} = F_{th}^{th} = \exp[\alpha(\theta - \theta_0)] 1
\] (3.47)

In this manner, the incorporation of thermal expansion effects in the glassy regime into the constitutive model of Chapter 2 requires just one additional parameter – the coefficient of thermal expansion, \( \alpha \). Appropriate values for \( \alpha \) may be determined experimentally, as described in section 3.2, and are also available in the literature for many common amorphous polymers. In order to capture behavior above \( T_g \), where the coefficient of thermal expansion has been measured as three times as large as that in the glassy regime, a modification of the theory is required. As a first approximation, this could be modelled with a step-wise function for \( \alpha \), where its constant value changes at \( T_g \). A more accurate procedure would require implementing a continuous function for the temperature-dependence of \( \alpha \).

3.4 Model Predictions

As originally implemented, the constitutive model described in Chapter 2 has the ability to predict the post-deformation recovery observed in TMA experiments. The model captures energy storage in both the entropic (Langevin) spring and the linear elastic \( \alpha \) and \( \beta \) springs, whereby the stress in the entropic spring is balanced by equal and opposite stress
in the $\alpha$ and $\beta$ springs. This stored energy drives recovery through the reverse progress of the viscoplastic flow rules. The ability of the model to predict strain recovery especially at high temperatures is enhanced by the fact that temperature dependence in the shear resistance $s$ is considered for temperatures up to and beyond $T_g$. When the model temperature approaches $T_g$, the shear resistance drops by at least an order of magnitude, accelerating (reverse) viscoplastic flow. Even by itself an increase in temperature towards $T_g$ will help enable recovery through the thermal activation model of yield. With the implementation also of thermal expansion effects, the constitutive model is now capable of predicting not only stress-free isotropic thermal expansion, but also the complex thermal response – including both thermal expansion and recovery – of a polymer which has previously been deformed. Here, this capability is demonstrated.

A simulation has been generated in a commercial finite element code (ABAQUS/Explicit) to mimic the thermal and mechanical loading of the experiments described in section 3.2. The finite element model is composed of a single, three-dimensional continuum element of original dimensions $1 \times 1 \times 1$, with boundary constraints and proper tie equations to ensure homogeneous deformation under compression (i.e. uniaxial compression). The simulation is divided into four sequential regimes, as described below:

**Displacement Control** Compress to $80\%$ true strain at $0.1 \text{ s}^{-1}$; unload at $0.1 \text{ s}^{-1}$ to zero stress

**Equilibration** Remove displacement boundary condition on element top surface and allow any additional recovery with time at zero total macroscopic stress and room temperature

**Temperature Control** Heat from $25^\circ\text{C}$ to $T_g + 5^\circ\text{C}$ at a rate of $1^\circ\text{C/s}$

**Controlled Recovery** Hold temperature constant at $T_g + 5^\circ\text{C}$ until all strain is recovered

Graphical representation of these four regimes is given in figure 3-6, along with the predicted material response as measured by the temporal history of top surface displacement (figure 3-6(a)), axial stretch (figure 3-6(c)), and compressive stress (figure 3-6(d)).

\footnote{In this case, "$T_g$" corresponds to the temperature at which the modulus in the $\alpha$ spring has decreased to a rubbery value ($\sim 5 \text{ MPa}$). According to formulation of rate-dependent elasticity in the model, this temperature depends on strain rate. When there is no appreciable mechanical deformation (zero strain rate), such as in this case, the elasticity is calculated from a nominal strain rate of $10^{-4} \text{ s}^{-1}$.}
Figure 3-6: PMMA recovery simulation loading history and results: (a) top surface axial displacement history (b) temperature history (c) axial stretch history and (d) true axial stress history. The dashed lines provide demarcation between the four simulation regimes: displacement control, equilibration, temperature control, and controlled recovery.
Within the displacement control regime (0s to 8.5s), the stress exhibits characteristic PMMA response to uniaxial compression: initial linear elasticity, global yield, strain softening, and strain hardening. At the peak stress, corresponding to 80% true strain, the axial stretch is 0.45; upon unloading, the stress drops to zero and elastic strains recover such that the axial stretch is 0.48 immediately after unloading. During the equilibration phase (8.5s to 58.5s), slight noise is observed in the stress response while the displacement is stable. Given a longer equilibration time, it is expected that the model would predict some strain recovery even at 25°C, especially if the material’s actual viscoelastic response were included in the model formulation (see Chapter 6). As the simulation enters the temperature control regime (58.5s to 172.5s), both stress and displacement appear to remain constant up to approximately 75s (~45°C). In actuality, the displacement is increasing linearly due to the model’s prediction of isotropic thermal expansion; the change is imperceptible on the scale of figure 3-6(a). The isotropic thermal expansion is shown on a more appropriate graph in figure 3-9, and will be discussed later.

At a temperature of approximately 45°C, recovery becomes significant and the displacement is observed to increase in an approximately linear manner with time (temperature). Once the simulated temperature reaches ~115°C (150s), the rate of recovery increases again. By the time the temperature has reached \( T_g + 5°C \), the majority of inelastic strain has been recovered such that the axial stretch is approximately 0.92. All remaining strain is recovered over a period of just 10-20 seconds, while holding the temperature constant at \( T_g + 5°C \). During the entire heating and controlled recovery processes, the magnitude of inelastic strain recovery overshadows the isotropic thermal expansion, which is described by a thermal expansion coefficient of \( 7.0 \times 10^{-5} °C^{-1} \).

Figures 3-7 to 3-9 provide alternate graphical representations of the recovery simulation results. Stage 1 (displacement control) is isolated in figure 3-7, which shows the predicted true stress-true strain response of PMMA under uniaxial compressive loading and unloading (0.1 s\(^{-1}\)). Stage 3 (temperature control) is isolated in figure 3-8, which is analogous to the experimental thermal stretch versus temperature plots given in figure 3-3. In order to provide a more complete comparison with the experimental result, in this case the temperature was continually increased beyond \( T_g \); stage 4 (recovery at constant temperature) was eliminated. For evaluation purposes, the curve in figure 3-8 may be compared with the experimental result for \( \lambda_{axial} = 0.51 \), as the axial stretch in this simulation was 0.48 before
Figure 3-7: Predicted material response during stage 1 of the recovery simulation: mechanical loading and unloading under uniaxial deformation.

Figure 3-8: Predicted material response during stage 3 of the recovery simulation: thermal expansion and strain recovery while heating at a constant rate of 1°C/s. Thermal recovery stretch is calculated by normalizing the current stretch by the stretch value after unloading, before heating (0.48).
Figure 3-9: Model predicted isotropic thermal expansion, 25°C to 35°C. The curve is the same as that plotted in figure 3-8, here on different x- and y-scales.

heating. The simulation curve mimics the experiment result in both character and magnitude, with the only difference being that recovery is activated at a slightly lower temperature in the simulation (45°C) than observed in the experiment (60°C). It is now readily apparent that the initial regime of linear recovery observed experimentally is not attributable to the secondary energy storage mechanism, for the model captures this component of the response by only considering the primary storage mechanism (entropic hardening). This regime may alternately be explained by a series expansion of the exponential rate equation describing (reverse) plastic flow, in which the first term would be linear in temperature with higher order terms becoming more significant at higher temperatures.6

By focusing on the narrow temperature range before recovery begins (figure 3-9), it may be observed that the normalized stretch is still increasing with increasing temperature. In fact, the increase is approximately linear in temperature, over the temperature range 25°C to 35°C. This predicted response may be attributed to the implementation of isotropic thermal expansion into the constitutive model. At higher temperatures, where recovery has been thermally activated, these effects of thermal expansion are greatly overshadowed by inelastic strain recovery.

6We also note that even though all major features and trends of the thermal recovery are captured, the model does not precisely match the experimental data. We attribute the discrepancy to our imprecision in fitting properties for the plastic flow rate (\(\dot{\gamma}_p^P, \dot{\gamma}_p^R, \Delta G_\alpha, \Delta G_\beta\)) such that temperature dependence of flow is optimally captured. This imprecision is addressed in Chapter 4 and Appendix B.
Figure 3-10: Model-predicted thermal stretch as a function of temperature and pre-strain. Thermal recovery stretch is calculated by normalizing the current stretch by the stretch value after unloading, before heating ($\lambda_{\text{axial}}$).

As a final evaluation of the model and its ability to predict post-deformation thermal response, a second simulation has been generated in which the mechanical loading is limited to 60% true strain ($\lambda_{\text{axial}}=0.58$ after unloading) during stage 1 (displacement control). All other features of this simulation are the same. In figure 3-10, the predicted thermal stretch as a function of temperature is compared against that in which the pre-loading extended to 80% strain ($\lambda_{\text{axial}}=0.48$ after unloading). The trend generally follows that observed experimentally and plotted in figure 3-3. With less pre-strain, less energy is stored in the material via molecular alignment, and thus there is less driving force behind thermally-activated recovery. Specimens with more pre-strain exhibit more recovery at lower temperatures. This effect is captured in the model by the Langevin spring, which, through its nonlinear formulation, predicts a very significant difference in total stored energy even between 60% and 80% true strain. As shown in figure 3-10, the model correspondingly predicts a very significant difference in the rate of recovery at lower temperatures, irrespective of the total strain which needs to be recovered. In the simulation with only 60% pre-strain, recovery does not begin to dominate the material response until almost 110°C; the region of linear recovery is very small in magnitude.
3.5 Conclusion

A series of experiments has been conducted in order to better understand the orientation-dependence of thermal expansion in an exemplary amorphous polymer, PMMA. PMMA cylinders were machined from isotropic sheet stock and then deformed to various levels of imposed true strain. This compression pre-treatment served to induce molecular orientation in the cylinders, in a plane perpendicular to the loading axis; the degree of orientation was increased by increasing the imposed true strain. After pre-treatment, the axial coefficient of thermal expansion was measured as a function of axial stretch, where the axial stretch is taken as a macroscopic measure of molecular orientation. The axial CTE was found to increase in an approximate linear manner with off-axis orientation. For an axial stretch of 0.51, the CTE increased by 50% relative to the isotropic, undeformed material.

Measurements of CTE were calculated from temperature-dependent expansion at temperatures close to room temperatures. At higher temperatures (>45°C), thermally-activated inelastic strain recovery dominated the material response such that the apparent thermal expansion was much greater than expected. As temperature is increased, energy stored in the molecular orientation drives the polymeric specimens back to their original undeformed geometry in which the molecular chains are randomly oriented. By testing specimens deformed to different levels of imposed strain (i.e. molecular orientation), it was discovered that both the magnitude and rate of recovery is related to the amount of energy stored in the system.

In the second portion of this study, a modelling approach is suggested, following the work of Weber and Boyce (1989). Thermal expansion is incorporated into the constitutive model through a multiplicative decomposition of the total deformation gradient into elastic, plastic, and thermal components. As a first approximation, the thermal component is taken to be volumetric and isotropic. Further research is suggested in order to develop a more accurate representation of thermal expansion, taking into consideration the experimental results presented here, i.e. dependence of the thermal expansion behavior on molecular orientation.

Finally, the constitutive model with thermal expansion effects incorporated is used in a finite element simulation of the recovery experiments. A one element model is loaded in homogeneous compression to 80% strain, unloaded to zero stress, and then heated at
a constant rate of temperature increase. At the lowest temperatures (25°C to 35°C), the observed response is that of isotropic thermal expansion. At higher temperatures, inelastic strain recovery is predicted through the thermally-activated reverse progress of plastic flow, driven mainly by the energy stored in the Langevin spring. The predicted thermal recovery stretch as a function of temperature mimics very closely that observed in a similar experiment. Furthermore, a second simulation in which the induced pre-strain was only 60% revealed a strong dependence of the rate of recovery on the total amount of energy stored, following the trend observed experimentally.
Chapter 4

Energy Storage and Dissipation During Adiabatic Deformation

4.1 Background

As evidenced by the stress-strain curves for PMMA shown in figure 4-1, the isothermal constitutive model presented in Chapter 2 is severely limited in its ability to accurately predict the post-yield stress-strain response of some amorphous polymers at moderate and high strain rates. For many amorphous polymers, including PMMA, the moderate- and high-rate finite-deformation behavior is significantly affected by thermal softening, and can not be accurately predicted with the isothermal assumption previously employed. A large fraction of the work associated with plastic straining is dissipative, and when the rate of deformation is sufficiently high such that all of the heat generated does not have time to transfer to the surroundings, the temperature-sensitive polymer thermally softens. In PMMA, the effect is so pronounced that orientation-induced strain hardening in the material is masked completely at high strain rates.

Similar observations have been made by Arruda et al. (1995) during uniaxial compression of PMMA over low ($10^{-3}$ s$^{-1}$) to moderate ($10^{-1}$ s$^{-1}$) strain rates, where, based on the specimen geometry and also the polymer’s thermal properties, the material response transitioned from nearly isothermal (complete heat transfer) to nearly adiabatic (no heat transfer). In this thermodynamic transition zone, the material response can only be understood through a fully-coupled thermo-mechanical analysis, considering heat transfer via
convection and conduction. At high strain rates, the material response is fully adiabatic and such considerations are unnecessary – all heat generated remains in the polymer. However, even under adiabatic conditions, the heating effect in polymers is complicated still by the fact that the fraction of inelastic work which is dissipated is well below unity, and has been found to be a function of post-yield strain. Thus it is actually a complicated interaction of energy storage and dissipation mechanisms on the molecular scale which dictates the amount of heat evolved during high-rate deformation.

A number of experimental studies have been conducted in order to compare, in a macroscopic sense, the relative contributions of these storage and dissipation mechanisms during inelastic deformation. Adams and Farris (1988) and, later, Oleynik and co-workers (Rudnev et al., 1991; Salamatine, Rudnev, Voenniy, & Oleynik, 1992) employed deformation calorimetry experiments on a variety of amorphous polymers. In deformation calorimetry, a mechanical test – typically uniaxial tension or compression – is conducted within a sealed chamber. The chamber is equipped with capability to accurately measure slight changes in air pressure brought on by the evolution of heat. The total work of deformation is calculated from the measured stress-strain response, the dissipated energy is calculated from the measured pressure change in the chamber, and the stored energy is calculated as the difference between the two, according to the first law of thermodynamics. Typical experimental
Figure 4-2: Polystyrene stress-strain behavior and energies of deformation as calculated by deformation calorimetry experiments (uniaxial compression, $\sim 10^{-2}$ s$^{-1}$, 298K). Reported are the total work ($A_e$), dissipated energy ($Q_e$), stored energy ($\Delta U_e$), and stored energy not recovered upon unloading ($\Delta U_{irr}$). Figure reprinted from Rudnev et al. (1991).

Figure 4-3: PC stress-strain behavior and energies of deformation as calculated by deformation calorimetry experiments (uniaxial compression, $\sim 10^{-2}$ s$^{-1}$, 298K). Reported are the total work ($A_e$), dissipated energy ($Q_e$), stored energy ($\Delta U_e$), and stored energy not recovered upon unloading ($\Delta U_{irr}$). Figure reprinted from Rudnev et al. (1991).
results from Rudnev et al. (1991) are given in figures 4-2 and 4-3. Through these fundamental experiments, both Oleynik's group and Adams and Farris discovered that only 45-85% of the work of inelastic deformation in amorphous polymers was dissipated, depending on both the strain and the particular polymer. Oleynik and co-workers (Rudnev et al., 1991; Salamatine et al., 1992) noted that at strains lower than 20-30%, typically more work was retained as stored energy in the polymer than was dissipated as heat.

Additional insight on the topic of energy storage in amorphous polymers has been gained through differential scanning calorimetry (DSC) experiments on pre-deformed specimens. During the DSC test, the temperature of a polymer sample is raised at a constant rate while the heat required is recorded. When stored energy is released, an exothermic peak appears; when additional heat is required to pass through a transition (e.g. T_g), an endothermic peak appears. Unlike the deformation calorimetry experiments, this DSC technique allows separate mechanisms of energy storage to be investigated independently. In early studies conducted by Berens and Hodge (1982) on polystyrene (PS) and Chang and Li (1988) on poly(vinyl chloride) (PVC), two exothermic peaks were identified: one pre-T_g, and one post-T_g. Chang and Li (1988) report that most of the plastic strain recovered through heating is associated with the second, post-T_g exotherm.

Following the work of Berens and Hodge (1982) and Chang and Li (1988), as well as the deformation calorimetry experiments of Oleynik and co-workers (Rudnev et al., 1991; Salamatine et al., 1992), Hasan and Boyce (1993) studied more carefully these two exothermic peaks. They deformed PS, PC, and PMMA to various levels of inelastic strain, then conducted DSC scans on the deformed specimens. For all three polymers, the first exotherm was found to increase in magnitude with increasing pre-strain, but only up to strain levels of 25-30%. This strain level corresponded well with the end of strain softening in the material. The post-T_g exotherm, on the other hand, only became significant at strains where hardening was readily apparent in the stress-strain behavior, but continued to increase in magnitude with increased amounts of pre-strain. Hasan and Boyce present corresponding theory in association with these experimental results. They suggest that these two exotherms are in fact the products of two separate energy storage mechanisms: the first, pre-T_g exotherm is associated with the microscopic structural changes that take place at small and moderate strains (<30%), while the post-T_g exotherm is associated with molecular orientation induced by large deformations. Both are mechanisms of inelastic
deformation which, as shown in these DSC experiments, are thermo-reversible.

Yet another experimental method employed in the study of material energy storage and dissipation is the direct measurement of specimen temperature rise during mechanical deformation. When obtained under adiabatic conditions, this temperature rise data allows for a direct calculation of the amount of energy dissipated. For the case of polymeric materials, the first study of this kind was conducted by Chou et al. (1973). Chou and co-workers embedded a thermocouple in compression specimens of various polymers, including PMMA, and monitored the temperature rise induced by both moderate and high-rate deformation. Though in every case the strains achieved were less than 20%, specimen temperatures were found to increase as much as 30°C at the highest rates. The thermocouple technique was later revived by Rittel (1998, 1999b), who reported a temperature rise in PC of 28°C at 45% true strain under split-Hopkinson bar compression (~6500 s⁻¹). However, it is generally accepted that the response time of even the smallest thermocouples is too slow to accurately measure temperature changes during a split-Hopkinson bar experiment.¹ This point is disputed by Rittel (1998).

Recently, infra-red (IR) detection techniques have been proposed as a means to more accurately measure specimen surface temperature during the split-Hopkinson bar experiment (Noble & Harding, 1994; Kapoor & Nemat-Nasser, 1998; Macdougall & Harding, 1998; Trojanowski, Macdougall, & Harding, 1998). In this technique, focusing optics are arranged around the specimen in order to direct surface radiation onto a small (100 μm × 100 μm) photovoltaic detector. By appropriately calibrating the system, the voltage output of the detector may be related to a temperature rise in the specimen. This technique has been applied in the study of adiabatic heating in polymeric materials by Trojanowski et al. (1998), Li and Lambros (2001), Buckley, Harding, Hou, Ruiz, and Trojanowski (2001), and Lerch et al. (2003). Li and Lambros (2001) and Lerch et al. (2003) both conducted the experiments on PC in split-Hopkinson bar compression; their results are plotted in figure 4-4 alongside the thermocouple measurements of Rittel (1999b). The spread of temperature measurements shown here, for a material which generally exhibits little variation in mechanical behavior from one brand to another, underscores that fact that available data in the literature is neither comprehensive nor consistent. Furthermore, it suggests that there

¹The typical split-Hopkinson bar experiment has a duration of 100-400 μs. An appropriate response time to measure associated temperature changes is 0.1-1 μs; the response time of a thermocouple is usually on the order of milliseconds.
are unresolved issues in one or both of these experimental techniques. One of these issues is the simple fact there is no uniformity in the proper set-up and technique for the IR experiment. For instance, Li and Lambros (2001) use a HgCdTe (mercury cadmium telluride) photovoltaic detector, focusing optics which include a large spherical mirror and a small flat mirror, and cylindrical specimens, whereas Lerch et al. (2003) use an InSb (indium antimonide) detector, a single biconvex lens for focusing, and large cubic specimens.

In light of the experimental results discussed here, revisions have been proposed in the constitutive model of Boyce and co-workers (Boyce et al., 1988b; Arruda & Boyce, 1993a). These revisions, first proposed by Boyce et al. (1992a), and later applied by Arruda et al. (1995), allow the model to capture the thermal softening phenomenon observed in PMMA through predictions of the heat evolved during adiabatic deformation. The method is to take the work of entropic hardening (the "backstress") as stored energy, with the work from the driving stress of viscoplastic deformation as dissipative. It is believed that the stored energy of molecular alignment is that which is recovered at temperatures at and above T_g, corresponding to the second exotherm measured by Hasan and Boyce (1993). Upon implementing these methods and applying them in thermo-mechanically coupled finite element simulations, Arruda et al. (1995) were able to capture well the dramatic change in PMMA stress-strain behavior from isothermal to adiabatic strain rates. Nonetheless, the
model predictions of specimen temperature rise, even at adiabatic rates, were much higher than those measured experimentally via a commercial IR detector.

In this study, the intent is to revisit both the experimental and theoretical methods already employed in previous research. The ultimate goal is to obtain a more accurate experimental measurement of the heat evolved during adiabatic deformation and, if necessary, appropriately modify the model's treatment of stored versus dissipated energy.

4.2 Experiments

An experimental program has been devised in order to better quantify that portion of the work of deformation which is dissipated as heat, for a sampling of amorphous polymers. Temperature measurements are conducted during low, moderate, and high-rate uniaxial compression tests through IR techniques. In accessing this broad spectrum of deformation rates, two separate experimental set-ups are employed. At low and moderate rates, a single-spot commercial IR detector is used in conjunction with an Instron servo-hydraulic mechanical testing instrument. For the high rate experiment, a custom high-speed IR detecting system with focusing optics has been built around a compressive split-Hopkinson bar.

In both experiments, temperature measurements are made based on the emission of surface radiation. Because the uniaxial compression test dictates a homogeneous deformation mode, non-uniformity in the specimen temperature shall only arise through heat transfer. Thus, at adiabatic rates, the specimen surface temperature at all locations is identical to the specimen internal temperature. Furthermore, the measured temperature rise under adiabatic deformation is irrespective of specimen geometry.

4.2.1 Methods

Low and Moderate Rates

Uniaxial compression tests at low to moderate strain rates (0.001 s\(^{-1}\) to 1 s\(^{-1}\)) were conducted on an Instron servo-hydraulic testing machine. PC and PMMA specimens were machined as right circular cylinders, with both diameter and height of 12.7 millimeters. During the test, stress and strain quantities are calculated from the load cell and extensometer output, respectively, while specimen surface temperature is calculated directly by
Figure 4-5: Schematic experimental set-up for temperature measurement under low and moderate strain rates.

A Mikron MI-N5+ Infraducer\textsuperscript{®}. This pre-calibrated infrared detector provides accurate temperature measurements based only upon an input surface emissivity. The minimum spot size for this detector, achieved by placing the detector exactly 100 millimeters from the specimen, is 2 millimeters. The response time is 0.08 seconds, and the accuracy is 1\% of measured value.\textsuperscript{2}

As shown schematically in figure 4-5, the IR detector is mounted on a two-axis adjustable stage approximately 100 millimeters from the specimen surface. Custom-built steel platens, trapezoidal in cross-section, are used to ensure that even at true strains of 100\%, no portion of the radiation cone is blocked by the presence of nearby loading rods. Furthermore, lubricating sheets of Teflon are cut and carefully arranged in such a manner that they too do not block any emitted radiation that otherwise would be collected at the detector location. An alignment laser mounted inside of the detector housing is used to focus the detector spot along the central axis of the specimen, approximately 3 millimeters from the top. This vertical location corresponds to the centerline of a specimen which has been deformed to a true strain of 80\% (only the lower rod of the Instron moves during a test). One hour before testing, specimen surfaces are painted with a black acrylic spray paint to increase their emissivity and thus increase the signal-to-noise ratio in radiation measurements. Without black paint, the emissivity of a transparent polymeric surface is between 0.85 and 0.90 (Lerch et al., 2003); with paint, the polymer acts as a black body with

\textsuperscript{2}Specifications provided by the manufacturer, Mikron Corp.
emissivity approaching unity. The emissivity value required for temperature calculations is entered as 0.95, for both PC and PMMA.

During the test, a specially-designed feedback loop between the extensometer and the actuator is used to ensure a constant true strain rate over the duration of the tests. For both PC and PMMA, multiple tests were conducted at constant true strain rates of 0.001 s\(^{-1}\), 0.01 s\(^{-1}\), 0.1 s\(^{-1}\), and 1.0 s\(^{-1}\). Following the thermodynamic analysis of Hall (1968), generalized by Chou et al. (1973) to the case of a polymer cylinder under compression, it is expected that both materials will transition between fully isothermal (0.001 s\(^{-1}\)) and fully adiabatic (1.0 s\(^{-1}\)) response over this range of strain rates.\(^3\) At the intermediate rates (0.01 s\(^{-1}\) and 0.1 s\(^{-1}\)), the thermodynamic condition is expected to be thermo-mechanically coupled, though very nearly adiabatic at 0.1 s\(^{-1}\). These results are consistent with the results of a slightly different analysis conducted by Arruda et al. (1995) for similar sized and shaped specimens.

**High Rates**

The experimental set-up used in the high-rate tests is shown in the photograph of figure 4-6 and is described schematically in figures 4-7 and 4-9. The optical/IR set-up generally follows that summarized by Li and Lambros (2001) and later described in more detail by Bjerke (2002), though here important changes are made in the alignment, calibration, and test techniques originally proposed. The components necessary for the measurement of surface temperature are built around the specimen location of the compressive split-Hopkinson bar described in Chapter 2 (section 2.4.1). These components include: a spherical and a flat mirror, a single-element IR detector, a pre-amplifier to the IR detector, a power supply for the pre-amplifier, and a digital oscilloscope for data acquisition.

The two mirrors that compose the optical set-up, both supplied by Edmund Optics, are gold-plated in order to minimize losses over the spectrum of infra-red wavelengths. The spherical mirror has a diameter and focal length of 152.4 millimeters (6 inches); the flat mirror has a diameter of 50.8 millimeters (2 inches). While this configuration allows for the optical magnification to be adjusted, here the two mirrors are located such that there is a

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\(^3\)This analysis takes into account not only the specimen geometry, but also the thermal properties of the two polymers and the possibility of heat conduction between the specimen and the Instron platens. As the thermal properties of PC and PMMA are quite similar, the analysis yields the same results for the two polymers, in general.
Figure 4-6: Experimental set-up for temperature measurement during split-Hopkinson bar compression.
1:1 correspondence between the sample spot size and the detector area (250μm x 250μm). The spherical mirror serves to focus the radiation emitted by the spot back onto the detector area, while the flat mirror simply re-directs, or "folds", the radiation signal.

The radiation is directed upon a single HgCdTe (mercury cadmium telluride) photovoltaic detector (Fermionics Corp., Simi Valley, CA) which is sensitive to radiation in the mid-infrared spectrum (6-12 μm). Prior to testing, this detector is cooled to 77K by filling the adjoining dewar with liquid nitrogen, which serves to increase the signal output by the detector. This signal is further amplified through a dedicated RF pre-amplifier (Perry Amplifier, Brookline, MA), optimized in both gain and frequency input/output for the characteristics of the Fermionics detector supplied. The pre-amplifier is powered by an Instek GPS-2303 multi-output regulated DC power supply, known to exhibit very little noise (~0.01%). The power supply is appropriately configured so as to give the necessary + and -12 V inputs to the pre-amplifier, while also preventing overload at excessive levels of current (>14 mA). Finally, the amplified signal is read into a Lecroy Waverunner® digital oscilloscope via high-impedance (1MΩ) coupling. This particular oscilloscope has a bandwidth of 500 MHz and capability to sample data at a rate of 4 gigasamples per second, though such rates are not necessary even in this experiment. During the test, split-Hopkinson bar strain gage signals and the IR detector signal are recorded simultaneously by the oscilloscope.

Due to the wide angle of radiation collected by the spherical mirror, there is potential for the moving split-Hopkinson bars to partially block the cone of radiation during the experiment. In the low and moderate rate tests, a similar concern was alleviated by inserting steel platens of trapezoidal cross-section between the specimen and the loading rods. In the high-rate experiment, such a technique is not possible. Therefore, specimens needed to be designed with sufficient length and diameter so as to avoid blockage of emitted radiation, while also maintaining an aspect ratio which is appropriate for the split-Hopkinson bar test (see, for instance, Gray III et al., 1997). The optimal geometry for the high-rate heating experiment was found to be right circular cylinder with length of 3.6 millimeters and diameter of 6.0 millimeters. This large specimen size, relative to the dimensions of the split-Hopkinson bar apparatus (section 2.4.1), limited the materials which could be tested. For instance, even at the highest striker bar velocities attainable, a PMMA specimen of 6.0

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4While the spherical mirror has a diameter of 6 inches, the spot size on the specimen has essentially negligible diameter and may be considered a point. The spherical mirror is located 12 inches from the specimen location, and thus the cone of radiation has a vertex angle of approximately 30°.
millimeter diameter would not yield in our apparatus. Here results are presented for two amorphous polymers—PC and PVC—with significantly lower high-rate yield stress than PMMA.

**Alignment and Focus** Before testing, the optical set-up must be properly aligned and focused. Due to the very small detector area and spot size, even slight misalignment or lack of focus can cause the detector signal to severely diminish in magnitude. Though the entire optical set-up is mounted on an optical table, both the fine alignment and focusing steps must be repeated with each new day of testing.

Both the spherical mirror and the IR detector are mounted on stages which are adjustable in three mutually-perpendicular directions, while the flat mirror is adjustable in two degrees of freedom. In the first step of coarse alignment, these three components' locations are adjusted so that their centerlines lie in the same vertical (z) plane as the specimen centerline. Next, the x and y locations of the components are adjusted such that the total optical path is roughly 24 inches (12 inches from the specimen to the spherical mirror; 12 inches from the spherical mirror to the detector). This ensures a 1:1 correspondence between the spot size on the specimen and the detector area.

Fine alignment is accomplished with a HeNe alignment laser (Edmund Optics), while there is no specimen in place. The laser is mounted behind the specimen location, located and aimed such that the beam passes through exactly the center of where the specimen will be located. By adjusting the horizontal tilt angles of the spherical and flat mirrors, the laser's beam is directed onto the center of the detector lens. This ensures that the system is properly aligned. In the final step of set-up, the optical system is focused. A mock specimen of black Teflon with a hole through the center is placed between the split-Hopkinson bars such that the through hole aligns perfectly with the path of the HeNe laser beam. The alignment laser is then removed and replaced with a fiber optic light. This light emits a conical rather than cylindrical beam, creating a shadowed image of the mock specimen on the outer face of the detector housing. The sharpness of the image is adjusted by moving the detector either forward or backward in the line of the projected image. Once the image is optimally focused on the face of detector housing, the housing is moved forward a known amount corresponding to the distance that the actual photovoltaic detector is set back inside of the housing.
**Calibration**  Calibration is necessary in order to correspond a change in the voltage signal which is output by the detector/amplifier assembly with a temperature change in the specimen. The experimental set-up configured for the calibration test is given in figure 4-7.

For calibration, another mock specimen is necessary, this time of identical material and geometry as the actual specimens to be tested. Unlike the actual specimens, however, a K-type bare-wire thermocouple is embedded in the mock specimen. A narrow hole is drilled approximately 0.5 millimeters from the surface, and the thermocouple bead is fixed in place with high-conductivity epoxy. The mock specimen with embedded thermocouple is placed on a hot plate and heated 80-100°C above room temperature. The exact temperature is monitored by an Omega RD8800 Recorder ("Data Acquisition #2" in figure 4-7), which has a built in cold-junction reference. Once at temperature, the heated specimen is removed from the hot plate and quickly sandwiched between the split-Hopkinson bars at the aligned/focused position. As the specimen cools, both the thermocouple temperature signal and the IR detector/amplifier signal (voltage) are recorded. Once the specimen reaches room temperature, the two data acquisition systems are stopped simultaneously. This calibration test is repeated 3-5 times. Variability is expected from one calibration test to another, as the technique allows very little time to ensure that the heated specimen is placed exactly at the correct aligned/focused position.\(^5\)

In the analysis of the calibration data, the IR signal and thermocouple temperature are aligned from their end points and plotted *backwards*, yielding a temperature rise versus voltage change curve such as that given in figure 4-8. As expected, as much as 25% variability is observed from one calibration curve to another. *The calibration curve which exhibits the greatest voltage change for a given rise in temperature is taken to be the most valid.* If the specimen were placed either out of alignment or out of focus, the amount of radiation received by the IR detector would only be decreased, leading to a lower voltage output for a given specimen temperature.

In previous studies (Trojanowski et al., 1998; Bjerke, 2002; Lerch et al., 2003), a chopper wheel was used in front of the IR detector during calibration in order to create a "pseudo-a.c." radiation/voltage signal. These authors imply that there is a component of the set-up which does not respond to constant or slowly-varying signals, and thus the chopper is

\(^{5}\)Once removed from the hot plate, the specimen originally at 100-120°C will cool to below 80°C in a matter of seconds. The high rate of cooling is exacerbated as soon as the specimen comes in contact with the highly-conductive aluminum pressure bars.
Figure 4-7: Schematic experimental set-up for temperature measurement during split-Hopkinson bar compression – calibration configuration.

Figure 4-8: Typical calibration curve for the custom IR detection experimental set-up diagrammed in figure 4-7, data and polynomial fit.
required to modulate the signal at a frequency of 10-100 Hz. However, the authors are in disagreement as to which particular component actually requires the modulated signal – Trojanowski et al. (1998) say that it is the detector, Bjerke (2002) says that it is the detector pre-amplifier, and Lerch et al. (2003) say that it is the electronics in general. In this study, calibration was conducted both with and without a chopper wheel. There was found to be no appreciable difference in the calibration curve, even for a range of chopper frequencies (30-100 Hz). Thus, in the final calibration tests, no chopper wheel was used.

The calibration procedure must be repeated with each day of testing, as the aligned/focused characteristics of the system are expected to change. Furthermore, the calibration must be repeated for each new material tested to account for variability in emissivity.

**Test** The test configuration is given in figure 4-9. The test is set up by first carefully locating the specimen at the correct aligned/focused position and sandwiching it between the split-Hopkinson pressure bars. As in an ordinary split-Hopkinson bar test, the specimen is both lubricated and held in place with a small amount of petroleum jelly. After initially locating the specimen at the aligned position, the entire bar and specimen assembly is then translated towards the striker bar approximately 1-2 millimeters. This is done to compensate for the translation of the incident bar during compression, assuring that the detector spot is focused on the center of the deformed specimen, not the undeformed. The exact amount of translation is calculated from an initial test without temperature measurement.

During the test, the IR signal and the split-Hopkinson bar strain gage signals (incident and transmitted) are recorded by the digital oscilloscope at a sampling rate of one point per 0.4 μs. Typical raw data, shifted so that the reflected, transmitted, and IR pulses start at the same point, is given as figure 4-10.

In previous studies, the specimens for IR tests at high rates were always painted black (see, for instance, Kapoor and Nemat-Nasser, 1998, Li and Lambros, 2001, Lerch et al., 2003). This was intended to increase the IR signal-to-noise ratio by increasing the emissivity of the specimen. In this study, tests at high rates revealed that the black paint detrimentally affects results. At large strains, the temperature of painted specimens was found in fact to be inferior to the temperature measured on unpainted specimens, despite the supposed increase in emissivity. It is likely that an evolution in the texture of the painted surface
Figure 4-9: Schematic experimental set-up for temperature measurement during split-Hopkinson bar compression – test configuration.

Figure 4-10: Typical raw data from a high-rate heating experiment: incident strain gage signal, transmitted strain gage signal, and IR detector signal.
during the test significantly altered its ability to radiate heat. This factor of uncertainty was eliminated from our experiments by conducting both the calibration and tests on unpainted specimens. If the test optics are properly focused and aligned, any corresponding decrease in signal amplitude will be inconsequential to the success of the experiment.

Additionally, extensive testing revealed that at larger strains the moving incident bar did in fact partially block the cone of radiation, despite efforts to mitigate this effect. Thus, at large strains, a portion of the spherical mirror is "darkened" and the measured specimen temperature rise is less than actual. The result is a temperature rise curve which resembles that of Lerch et al. (2003), reprinted in figure 4-4: at larger strains, the temperature appears to hold constant or even decrease despite increased deformation. To solve this problem, the spherical mirror was partially (~50%) covered with non-reflective tape on the incident bar side for both the calibration and test. This ensured that the effective area of the mirror collecting radiation would be the same in both the calibration and test, even if partial blockage of the radiation cone occurred. For further details on this experimental modification, see Garg, Mulliken, and Boyce (2006).

4.2.2 Results and Discussion

Low and Moderate Rates

Experimental results from testing at low and moderate strain rates is summarized in figures 4-11 to 4-14. For the case of PC, the characteristic stress-strain behavior (figure 4-11) remains relatively constant over this range of strain rates, despite the isothermal to adiabatic transition. Only at 1 s\(^{-1}\) is the thermal softening affect readily apparent, and even then the effect is slight. Nonetheless, as shown in figure 4-12, the specimen temperature rise is non-negligible at all rates except 0.001 s\(^{-1}\) (not shown). Even at 0.01 s\(^{-1}\), the temperature increases to approximately 15°C at a true strain of 0.78. However, the rate of temperature increase at 0.01 s\(^{-1}\) begins to decrease for strains greater than 0.5, owing to heat transfer. This effect is not seen in either the 0.1 or 1 s\(^{-1}\) curves, as the thermodynamic condition is nearly adiabatic.

It is unusual to note that the measured temperature rise at 1 s\(^{-1}\) is equal to or lower than the measured temperature rise at 0.1 s\(^{-1}\), for all levels of strain. This unexpected response is due to experimental error and not material behavior. Additional tests were conducted
Figure 4-11: PC true stress-true strain behavior in uniaxial compression at low and moderate strain rates.

Figure 4-12: Measured PC specimen surface temperature rise under uniaxial compression at low to moderate strain rates. The corresponding stress-strain curves are given in figure 4-11.
Figure 4-13: PMMA true stress-true strain behavior in uniaxial compression at low and moderate strain rates.

Figure 4-14: Measured PMMA specimen surface temperature rise under uniaxial compression at low to moderate strain rates. The corresponding stress-strain curves are given in figure 4-13.
on PMMA at 0.1 s\(^{-1}\) and 1 s\(^{-1}\) in which the specimen temperature was continuously recorded even after loading. For the tests originally at 0.1 s\(^{-1}\), the specimen temperature remained constant immediately after loading, and then eventually began to decrease, as might be expected. However, in the tests at 1 s\(^{-1}\), the measured temperature continued to increase after loading, approximately 5-7°C, indicating that perhaps the response time of the IR detector is not fast enough to capture the actual temperature rise real-time. Another possible source of experimental error at 1 s\(^{-1}\) is the black paint; during high-rate testing, the black paint was found to be detrimental to the experimental technique, in such a way that the measured temperature rise was lower than actual. As PC and PMMA have very similar thermal properties, and also the specimen geometry and test technique were identical, these effects are expected to be the same in the testing of PC, though similar diagnostic tests were not conducted with PC. Further tests at low and moderate strain rates are needed to verify these theories.

The measured temperature rise in PC at these low and moderate strain rates indicates that the PC does in fact heat significantly under thermo-mechanically coupled and adiabatic conditions. For this particular polymer, however, the associated changes in stress-strain behavior are minimal because of the relative lack of temperature sensitivity in the \(\alpha\)-regime, as measured by the DMA and indicated by yield and stress-strain data in the literature. From 0°C to 25°C, the storage modulus of PC only decreases by 3%; on the other hand, the storage modulus of PMMA decreases by 17% over the same temperature range. The mechanical behavior of PMMA is much more temperature-sensitive close to room temperature, and for this reason the effect of heating under moderate strain rates is observed to be much greater (figure 4-13). Even at 0.01 s\(^{-1}\), where conductive heat transfer still occurs, the thermal softening effect in PMMA is such that the apparent hardening has vanished.

The measured temperature rise of PMMA specimens under compression is given in figure 4-14. As was the case for PC, the curve at 0.01 s\(^{-1}\) exhibits the effects of heat transfer, as the rate of temperature increase begins to decrease significantly at a true strain of approximately 0.5. Owing to the greater mechanical work needed to deform PMMA to large strains, as compared to PC, the measured temperatures are slightly higher at all rates. In the test at 1 s\(^{-1}\), a temperature rise is measured which is higher than that measured at 0.1 s\(^{-1}\). Nonetheless, the difference between the two is still less than expected, based on the difference in mechanical work needed to deform PMMA at 1 s\(^{-1}\) versus 0.1 s\(^{-1}\). Again,
possible sources of experimental error include inadequate response time of the IR detector and an evolving texture of the black paint. In the tests at high rates, both of these possible sources of error are eliminated, as is the possibility of any heat transfer.

**High Rates**

High strain rate testing was conducted on both PC and PVC. Due to the large specimen geometry, it was not possible to access a range of strain rates within the split-Hopkinson bar regime, which is typically 500 s\(^{-1}\) to 5000 s\(^{-1}\). Numerous tests were conducted on each material at one strain rate: 2550 s\(^{-1}\) for PC and 3100 s\(^{-1}\) for PVC. In both cases, the observed deformation was homogenous.

The PC tests are summarized in figure 4-15. One typical true stress-true strain curve is pictured, along with three measurements of temperature rise under the same strain rate. Together, the three temperature rise curves demonstrate the repeatability of the newly-implemented test method. This repeatability is a direct consequence of precise positioning of the specimen prior to testing; in the calibration test, when such precise positioning was not possible, measured temperature-IR voltage curves varied by as much as 25%.

In the case of PC, again the observed true stress-true strain curve has the same character as curves observed at low and moderate strain rates. In fact, despite the adiabatic thermo-dynamic condition and expected thermal softening, the PC exhibits less thermal softening in the high rate curve of figure 4-15 than it does at low and moderate rates (figure 4-11). As is discussed later, this decrease in softening in the case of PC is thought to be linked to the restriction of \(\beta\)-motions. The measured temperature rise is approximately 24°C for a true strain of 0.47, or 11°C higher than the measured temperature at 0.1 s\(^{-1}\) for the same level of strain.

Figure 4-16 summarizes results of high-rate heating tests on a second amorphous polymer, PVC. As discussed in Chapter 7 (section 7.2), the PVC stress-strain behavior changes dramatically when spanning rates that provide isothermal to adiabatic conditions. In the high-rate curve of figure 4-16, the effects of thermal softening and entropic hardening appear to cancel. The measured temperature rise in PVC is slightly higher than that observed for PC, due in large part to the fact that more work is needed to deform it to large strains. Again, the four curves of temperature rise as a function of strain demonstrate the precision of this test method.
Figure 4-15: PC true stress-true strain behavior and corresponding temperature rise under uniaxial compression at an average true strain rate of approximately 2550 s\(^{-1}\). Plotted is a representative stress-strain curve and three measured curves of temperature rise, all under the same strain rate conditions.
Figure 4-16: PVC true stress-true strain behavior and corresponding temperature rise under uniaxial compression at an average true strain rate of approximately 3100 s$^{-1}$. Plotted is a representative stress-strain curve and four measured curves of temperature rise, all under the same strain rate conditions.
Figure 4-17: PC post-yield energies of deformation under high strain rate (2550 s\(^{-1}\)) compression: total work \((W_{p-y})\), dissipated energy \((\Delta Q_{p-y})\), and stored energy \((\Delta U_{p-y})\). Work and dissipation curves are calculated from the stress-strain and temperature rise data in figure 4-15, respectively; stored energy is calculated as the difference between the two. At strains prior to yield, data is not necessarily valid as dynamic equilibrium is yet to be achieved.

The test data obtained in high-rate experiments, where the thermodynamic condition is undoubtedly fully adiabatic, allows for a direct calculation of the amount of work which is dissipated as heat. Consequently, the amount of stored energy may be calculated, as the difference between the total work of deformation and this dissipated energy. In figure 4-17, the dissipative energy of high-rate PC deformation (2550 s\(^{-1}\)) is compared with that portion of the work which is stored; a corresponding figure for PVC is given as figure 4-18. In both cases, energy calculations prior to yield are not included, as the split-Hopkinson bar stress-strain data is not valid in this region. Once dynamic equilibrium is established – at a time approximately coincident with yield – data is assured of being valid.

In the case of PC (figure 4-17), significantly more energy is dissipated as heat than is stored, for all levels of strain beyond yield. Even at moderate strains the amount of work dissipated is greater than 75%. This result is in contrast to the published results of Oleynik and co-workers (Rudnev et al., 1991; Salamatine et al., 1992) which indicate that, for many
Figure 4-18: PVC post-yield energies of deformation under high strain rate (3100 s\(^{-1}\)) compression: total work (\(W_{p-y}\)), dissipated energy (\(\Delta Q_{p-y}\)), and stored energy (\(\Delta U_{p-y}\)). Work and dissipation curves are calculated from the stress-strain and temperature rise data in figure 4-16, respectively; stored energy is calculated as the difference between the two. At strains prior to yield, data is not necessarily valid as dynamic equilibrium is yet to be achieved.
amorphous polymers, nearly half of the work of deformation after yield is dissipated for strain levels up to 30-40%. For the case of PC (figure 4-3), the data of Rudnev et al. (1991) indicates that approximately 40% of the post-yield work is stored for a post-yield strain of 30%. According the high-rate data of this study (i.e. figure 4-17), only 20% of the work is stored for the same level of post-yield strain. However, the deformation calorimetry tests of Oleynik and co-workers were conducted at quasi-static strain rates ($\sim10^{-2}$ s$^{-1}$), where the intermolecular deformation resistance (resistance to chain translation/rotation) is much lower. If the energy storage during moderate strains is relatively insensitive to rate, then we would expect the ratio of energy stored/dissipated to be higher at the lower rates than at the high rates where restrictions on the $\beta$-motions significantly increases the overall deformation resistance (and dissipation).

Furthermore, the PC deformed under high strain rate exhibits significantly less softening than PVC. In fact, it exhibits less softening than even PC deformed at low and moderate strain rates. It is perhaps not coincidental that the PC and PVC have very different energy storage characteristics at low and moderate (<30%) strain levels. In the PVC (figure 4-18), there is more energy stored than dissipated up to a post-yield strain of approximately 15%, and the fraction of energy dissipated never exceeds 70%. Hasan and Boyce (1993) note that the secondary energy storage mechanism, that which occurs from small to moderate strains and is not related to entropic hardening, occurs over the same range of strains as the strain softening phenomenon. Nonetheless, by testing annealed and quenched specimens on a strain rate regime sampling the same basic process (for example, $\alpha$, or $\alpha + \beta$), they also note that the energy storage appears to be essentially independent of strain softening. It is expected that the secondary energy storage mechanism, that occurring mainly at low and moderate strain levels, as well as the strain softening phenomenon are both affected by the mobility and nature of the $\beta$-motions. This is a promising avenue of future research which is discussed in more detail in section 4.3.2.

4.3 Modelling

Following the techniques first proposed by Boyce et al. (1992b) and later applied by Arruda et al. (1995), the effects of energy storage and dissipation under adiabatic deformation are incorporated into the constitutive model of Chapter 2. The work of the entropic back stress
is taken to be stored, while the inelastic work associated with the viscoplastic dashpots is purely dissipative. From the first law of thermodynamics, the rate of change in temperature for the material under adiabatic conditions is given as:

$$\dot{\theta} = \frac{\text{trace}(T_{A\alpha} \dot{D}_{A\alpha}^p)}{\rho c_p} + \frac{\text{trace}(T_{A\beta} \dot{D}_{A\beta}^p)}{\rho c_p}$$  \hspace{1cm} (4.1)$$

where $T_{A\alpha}$ and $T_{A\beta}$ are the true stress tensors acting on the $\alpha$ and $\beta$ components of the model (defined in equations 2.19 and 2.20, respectively) and $\dot{D}_{A\alpha}^p$ and $\dot{D}_{A\beta}^p$ are the rates of viscoplastic stretching (defined in equations 2.15 and 2.16, respectively). All are defined with respect to the current (loaded) configuration. Appropriate values for the density $\rho$ and specific heat $c_p$ of PC, PMMA, and PVC, used in the model predictions of this section, are given in table 4.1. For the case of PC and PMMA, values were taken from the suppliers' datasheet$^6$; for the custom-made PVC, values were approximated from widely-available data for commercial brands of PVC.$^7$

<table>
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<tr>
<th></th>
<th>PC</th>
<th>PMMA</th>
<th>PVC</th>
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</thead>
<tbody>
<tr>
<td>$\rho \text{ [kg/m}^3\text{]}$</td>
<td>1200</td>
<td>1190</td>
<td>1380</td>
</tr>
<tr>
<td>$c_p \text{ [J/kg-°K]}$</td>
<td>1250</td>
<td>1470</td>
<td>1100</td>
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This modelling approach does *not* take into account the secondary energy storage mechanism described by Hasan and Boyce (1993) and also apparent in the data of Rudnev et al. (1991), thought to be associated with structural changes occurring during low and moderate strains (<30%). However, Arruda et al. (1995) found these methods to successfully capture the dramatic change in PMMA stress-strain behavior from isothermal to adiabatic strain rates. In this study, accurate temperature measurements for three different amorphous polymers over a range of strain rates allows for a more thorough evaluation of this approach.

### 4.3.1 Model Predictions

Following equation 4.1, the model predicts a significant rise in the polymer's temperature under adiabatic conditions. This temperature rise alters the predicted mechanical behavior,
as calculated through the thermal-activation model of yield together with the temperature-dependent elastic constants and shear resistance. The experimental results of this study allow the modelling techniques to be evaluated not only on their ability to predict the measured temperature rise, but also in terms of their ability to capture the corresponding changes in the stress-strain behavior.

The model is first evaluated for the case of PC deformed in uniaxial compression at 0.1 s\(^{-1}\), 2550 s\(^{-1}\), and 5050 s\(^{-1}\). Figures 4-19 and 4-21 show the experimentally-measured stress-strain response at these three rates in comparison with the model predictions under both an isothermal and an adiabatic assumption. As noted earlier, PC exhibits significantly less temperature sensitivity in its elasticity than does PMMA or PVC. Following the techniques described in Chapter 2, the model has already been properly calibrated for the temperature sensitivity of elasticity in PC, which ultimately determines the temperature sensitivity of the shear resistance ("s") through its relationship with the elastic constants. Thus the isothermal and adiabatic model predictions are very similar, despite the evolution of heat in the adiabatic case through viscoplastic dissipation.

For PC deformed at 0.1 s\(^{-1}\), the adiabatic model provides only a marginally better
Figure 4-20: PC specimen temperature rise in uniaxial compression at 0.1 s$^{-1}$ and 2550 s$^{-1}$: experiment and adiabatic model prediction.

Figure 4-21: PC true stress-true strain behavior in uniaxial compression at 5050 s$^{-1}$: experiment, isothermal model, and adiabatic model.
Figure 4-22: PC specimen temperature rise in uniaxial compression at 5050 s⁻¹: adiabatic model prediction.

prediction of the experimental curve than does the isothermal model. Under high-rate deformation, the isothermal model actually gives a closer prediction of the experimental curve than does the adiabatic model. This is demonstrated in both figure 4-19 and figure 4-21 for compression at 2550 s⁻¹ and 5050 s⁻¹, respectively. The agreement between the isothermal model prediction and the experimental curve measured under adiabatic conditions may be attributed to the fact that PC exhibits less intrinsic softening at high rates. This is a unique feature of the material response which is not incorporated into the constitutive model. It has been hypothesized that the need to activate backbone-type β-motions for yield – as in the case for PC under high-rate deformation – will decrease strain softening (Monnerie, Halary, & Kausch, 2005). This is an area of current research, and is discussed in more detail in section 4.3.2.

Due to the relative temperature-insensitivity of PC, the model predictions of the stress-strain response under adiabatic conditions provide little basis on which to evaluate the proposed modeling techniques. However, the adiabatic model predictions of temperature rise, compared against the experimental measurements in figure 4-20, provide validation for these techniques. In both cases, the model predicts the measured temperature rise to within
Figure 4-23: PVC true stress-true strain behavior in uniaxial compression at 3100 s\(^{-1}\): experiment, isothermal model, and adiabatic model.

3°C at all levels of strain. At 2550 s\(^{-1}\), it is expected that the agreement between model and experiment would be even better if the stress-strain curve were more accurately captured by the model. There is no experimental result corresponding to the model-predicted temperature rise at 5050 s\(^{-1}\), shown in figure 4-22.

The model is next evaluated for the case of PVC, which unlike PC exhibits significant thermal softening under high strain rate deformation. In figure 4-23, the isothermal and adiabatic model predictions are compared against the experimental result for a strain rate of 3100 s\(^{-1}\). Here clearly the adiabatic model provides a better prediction of the stress-strain response than does the isothermal model. While still under-predicting the stress by approximately 10% at all levels of strain, the adiabatic model captures well the character of the stress-strain curve and predicts the correct amount of post-yield softening. The isothermal model, on the other hand, incorrectly predicts the existence of significant hardening in the material, beginning at a true strain of 0.3. The effect is such that the stress at large strains is over-predicted by the isothermal model by as much as 30%.

In figure 4-24, the adiabatic model is also shown to capture well the magnitude of temperature rise in PVC under high-rate deformation. However, the character of the PVC
Figure 4-24: PVC specimen temperature rise in uniaxial compression at 3100 s\(^{-1}\): experiment and adiabatic model prediction.

Figure 4-25: PMMA true stress-true strain behavior in uniaxial compression at 0.1 s\(^{-1}\) and 1500 s\(^{-1}\): experiment, isothermal model, and adiabatic model.
temperature rise curve is slightly different than that predicted by the model. In the experimental curve, the rate of temperature increase continually increases through a range of intermediate strains, 0.10 to 0.35, before reaching an inflection point. The model, on the other hand, predicts a rate of temperature increase with strain which is continually decreasing. This discrepancy may be attributed to the secondary energy storage mechanism – that known to occur over low and moderate strains – which is not considered in the model formulation. For PC, there was no such discrepancy at intermediate strains, possibly because restrictions on the $\beta$-motions in that case have also limited the polymer’s ability to access the second energy storage mechanism. More discussion on this topic is given in section 4.3.2.

Finally, the model is used in predictions of PMMA behavior during adiabatic deformation. As shown in figure 4-25, again the adiabatic model provides a much better prediction of stress-strain response than does the isothermal model. At 0.1 s$^{-1}$, the agreement between the experiment and adiabatic model is excellent. The slight discrepancy in stress level at large strains, approximately 10% at a true strain of 0.75, could be captured by considering temperature dependence in the orientation-induced hardening as detailed by Arruda.
et al. (1995). At 1500 s$^{-1}$, however, the adiabatic model still does not capture well the dramatic softening observed experimentally. In this case the fit is not expected to improve significantly by considering temperature-dependence in the orientation hardening, as little orientation has developed over the strain region in which the discrepancy exists. Furthermore, the magnitude of the observed error is much larger than the changes in hardening response when temperature-dependence is considered.

The disparity between experiment and model prediction for the case of PMMA under high-rate compression may be attributed in large part to the fact that the parameters for the thermal activation model of yield have not been fully optimized for temperature dependence. As discussed in Chapter 2, appropriate values for the viscoplastic flow parameters ($\Delta G$ and $\gamma_0^s$) were determined from rate-dependent yield data. Ideally, values for these parameters would be determined from both rate- and temperature-dependent yield data. Also, the values of the shear resistances in the $\alpha$ and $\beta$ processes ($s_\alpha$ and $s_\beta$) were calculated from an analytical split of the measured storage modulus curve. For the case of PMMA, it was especially difficult to determine an appropriate split of the data due to the overlap of the two transitions. In Appendix B, a supplement to this chapter, it shown that in fact the particular parameters listed in Chapter 2 do not allow the model to capture the general trend in experimental temperature-dependent yield data available in the literature. The model significantly under-predicts the temperature sensitivity of PMMA yield; if captured correctly, the model would predict significantly more thermal softening under high-rate compression, where the expected temperature rise is 50-70°C for 50% strain.

The work of Monnerie et al. (2005) points towards yet another possible explanation for the disparity between experiment and model predictions of PMMA stress-strain behavior under high-rate compression. Monnerie suggests that PMMA exhibits increased strain softening corresponding to the degree to which $\beta$-motions are restricted, irrespective of the thermal softening effect (Monnerie et al., 2005). This unique behavior of PMMA is not considered by the current model, and is discussed in more detail in section 4.3.2.

Adiabatic model predictions of the PMMA temperature rise as a function of strain during deformation at rates of 0.1 s$^{-1}$ and 1500 s$^{-1}$ are given in figure 4-26. For this material, temperature measurements were not possible at high strain rates and thus only one experimental curve for a test at 0.1 s$^{-1}$ is given. This experimental curve is significantly over-predicted by the adiabatic model. Such disagreement is surprising, since the model
Figure 4-27: Model-predicted PC energies of deformation under high strain rate (2550 s⁻¹) compression: total work (W), dissipated energy (ΔQ), and stored energy (ΔU).

captured so well the observed stress-strain response at the same strain rate. As suggested earlier, several sources of experimental error existed in the temperature measurements at low and moderate strain rates. This discrepancy could merely be a manifestation of one or more of those possible sources of error. Otherwise, it is possible that the PMMA stores significantly more energy during low and moderate strains, as seems to be the case for PVC. The observed softening in the stress-strain response, then, would have to be explained not in terms of thermal softening, but rather in terms of changes in intrinsic softening behavior brought on by stress-activation of the β-motions (Monnerie et al., 2005).

The constitutive model’s success lies in its ability to discriminate work which is dissipative from work which is converted to stored energy. By considering together the measured stress-strain curves and observed temperature rise under adiabatic conditions, we were able to determine experimentally the relative contributions of energy storage and dissipation for both PC and PVC at high strain rates. These results were presented in figures 4-17 and 4-18. In figures 4-27 and 4-28, the corresponding model predictions are given. For the case of PC (figure 4-27), the model’s breakdown of stored versus dissipated energy closely resembles that calculated from the experimental results. At all levels of strain beyond yield,
at least 80% of the work of deformation is dissipated. For the case of PVC (figure 4-28), the model predicts a similar distribution of stored and dissipated energy. The model does not predict the additional energy storage at low and moderate levels of strains observed experimentally. This is a issue to be addressed in future iterations of the model, which incorporate a more sophisticated treatment of the energy storage phenomena.

4.3.2 Future Work

The modelling techniques employed here, which are an extension of those techniques first proposed by Boyce et al. (1992b), provide a first approximation in the effort to predict the effects of dissipated energy under adiabatic deformation at high strain rates. In many cases, the model predictions are adequate; in some cases, they are exceptional. Nonetheless there exists sufficient room for improvement.

It has been noted that many amorphous polymers exhibit a secondary energy storage mechanism which is distinct from the mechanisms associated with molecular alignment and the entropic back stress, as well as elasticity (see, for instance, Hasan and Boyce, 1993). This storage mechanism is thought to be related to structural changes on the molecular scale...
Figure 4-29: 1D rheological interpretation of the proposed constitutive model framework with revisions to account for additional low-strain energy storage.

which occur after yield and saturate at approximately 30% strain. It is an energy storage mechanism which is not considered in the current formulation of the model. However, the experimental results of this study suggest that it is an important effect at least in the case of PVC, and perhaps PMMA as well.

For those amorphous polymers in which secondary energy storage is important, an appropriate revision of the model formulation is suggested here. The revision is intended to provide a general framework which may be adapted to different polymers, but which is capable of capturing the most important feature of this mechanism: the mechanism is only operative at low and moderate strains (<30%); at larger strains, no additional energy is stored\(^8\) (Hasan & Boyce, 1993). A simple spring, linear or not, does not satisfy this need, as it would continue to store energy with increased deformation. However, in combination with a dashpot (figure 4-29) an additional spring can be used to store energy until the dashpot is activated. This dashpot will accommodate strains greater than 25-30%, while allowing the spring to continue to hold at the same stress level. As shown in figure 4-29, this Maxwell "storage" element is to be considered an extension of the \(\alpha\)-process, which in the present formulation is the component used to capture phenomena associated with large scale chain motions. Nonetheless, sufficient data has been presented in this study to suggest that \(\beta\)-motions also play a role in this energy storage mechanism, perhaps by

\(^{8}\)That is, no additional energy is stored by this particular mechanism. At strains greater than 30%, energy continues to be stored via elasticity and molecular alignment. These mechanisms are already considered by the model.
facilitating the large scale chain rotations/translations which locally store energy. To this end, an appropriate mathematical description of stress and thermal activation in this new element is yet to be determined.

In order to implement this strategy, it is first necessary that the model accurately captures the strain softening phenomenon, which also occurs over low and moderate strains (<30%), and which also seems to be affected by the accessibility of \( \beta \)-motions. While the techniques employed in this chapter allow the model to capture in most cases the thermal softening effect, there is need to better capture the rate-dependence of intrinsic strain softening, irrespective of the contributions of dissipative heat. The constitutive model predicts strain softening through an evolution in the shear resistance with plastic strain; the shear resistance is taken to decay to a "steady-state" value over the first 25-30% strain. Currently, this steady-state value of the shear resistance is defined as a constant ratio of its initial value, regardless of temperature or strain rate. However, for at least the case of PC, this assumption does not appear to hold over a wide range of strain rates. Significantly less softening is observed in PC deformed at high strain rates than at low strain rates, despite the increase in temperature associated with adiabatic deformation. In the case of PMMA, there appears to be more intrinsic strain softening at high rates than at low rates, though superposed thermal softening and model parameters which are not optimized for temperature-dependence make it difficult to draw conclusions.

As shown in figure 4-30, these effects might be captured by considering a steady-state value of the shear resistance and/or strain softening slope which are not constant in both temperature and strain rate. In particular, the PC behavior may be captured by adjusting the softening parameters for high rates such that there is no global softening in the isothermal model prediction. That is, intrinsic softening is just cancelled by the magnitude of entropic hardening. When the simulated thermodynamic condition is changed to adiabatic, softening appears through an increase in temperature (thermal softening). By comparing figures 4-30(a), 4-30(b), and 4-30(c) with figures 4-19, 4-20, and 4-21 respectively, it is obvious that this set of parameters provides a better fit of both the stress-strain and temperature rise curves, as compared to the parameters which were used to fit the low and moderate rate data. This result provides further credence to the suggestion that intrinsic softening is at least partially suppressed in the PC deformed at high strain rates.

For the case of PMMA, the high-rate softening behavior in the adiabatic case may
Figure 4-30: PC (a) stress-strain behavior at 2550 s⁻¹: experiment, isothermal model, and adiabatic model (b) temperature rise at 2550 s⁻¹, experiment and adiabatic model prediction (c) stress-strain behavior at 5050 s⁻¹: experiment, isothermal model, and adiabatic model (d) temperature rise at 5050 s⁻¹, adiabatic model prediction. For the model predictions, the softening parameters were adjusted such that global softening was suppressed in the isothermal case (sₘᵢₐₓ/s₀: 0.58 → 0.77, hₒ: 300 MPa → 500 MPa).
be better captured simply by optimizing the thermal activation model parameters for temperature-dependence. This minor item of future work is discussed in more detail in Appendix B. However, even after adjusting these parameters, the model may still under predict the high-rate softening behavior due to an increase in the intrinsic softening when $\beta$-motions are restricted. Such behavior has been suggested in a recent review article by Monnerie et al. (2005), who also note that intrinsic strain softening in PC seems to decrease when $\beta$-motions are restricted. Monnerie and co-workers theorize that the nature of the $\beta$-motion (i.e. side group versus main chain rotation) determines whether the strain softening amplitude will increase or decrease once the motions become restricted.

At the present time, very little attention has been paid to these changes in the softening behavior of amorphous polymers. It is only recently that more complete data sets, covering homogeneous stress-strain behaviors over a wider range of strain rates, have become available to theorists. Nevertheless, still more experimental data is necessary before corresponding model revisions can be proposed which are any more than phenomenological in nature. Because the rate-dependent data is clouded by the emergence of thermal softening under adiabatic deformation, it would be more useful to examine temperature-dependent stress-strain data spanning temperatures both above and below the $\beta$-transition temperature. Furthermore, this data is needed for a wide array of polymers with varying chemistry before connections may be drawn between macroscopic softening behavior and molecular dynamics.

The strategy going forward is to study these phenomena – moderate strain energy storage and strain softening – not independently, but rather in tandem. Both appear to be closely linked to the accessibility and the nature of the $\beta$-motions. In conjunction with the experiments described above, it may be elucidating to repeat the experiments of Hasan and Boyce (1993) on polymers which have been deformed at temperatures/rates both above and below the $\beta$-transition. These tests would provide information on the relative significance of moderate-strain energy storage as function of $\beta$-mobility. Furthermore, a test could be designed to better quantify any "backstress" associated with this secondary energy storage mechanism. Specimens would be loaded in compression to moderate strains, and then unloaded and re-loaded in tension in the same direction. The corresponding compressive and tensile yields, as well as stress achieved at maximum compressive strain, could together reveal this information. Again, the tests would be repeated on either side of $T_\beta$, in order
to determine how the magnitude of this backstress is affected by the polymer’s ability to access small-scale $\beta$-motions. All these tests need to be conducted on a variety of polymers with different types of $\beta$-motions (i.e. side-group versus backbone), as the trends seem to be highly dependent on the specific molecular mechanics.

4.4 Conclusion

An infrared technique for measuring specimen temperature rise during split-Hopkinson bar compression testing has been refined and applied here in the study of the thermomechanical behavior of amorphous polymers under high strain rates. Specifically, temperature measurements were used to directly calculate the fraction of input work which is dissipated as heat. Results of testing on both PC and PVC indicated that a non-negligible fraction of inelastic work is converted to stored energy in the polymer, though the magnitude is much less than that observed by Oleynik and co-workers at quasi-static rates (Rudnev et al., 1991; Salamatine et al., 1992). This discrepancy is attributed mainly to the fact that high-rate deformation induces significantly more resistance through the strength of intermolecular forces; work done against these forces is generally dissipative. The experimental results for PVC and, to a lesser extent, PMMA, also provide circumstantial evidence in support of the existence of a secondary energy storage mechanism occurring at low and moderate levels of strain.

In the second portion of this study, the constitutive model introduced in Chapter 2 is extended to predictions of specimen temperature rise under adiabatic deformation. This is accomplished by taking the work of the entropic back stress to be stored energy, whereas the inelastic work of the viscoplastic dashpots is purely dissipative. The secondary energy storage mechanism, occurring at low and moderate strains, is not considered. As a first approximation, this technique is shown to be successful. The model very closely predicts the temperature rise measured experimentally for both PC and PVC, simultaneously validating both the experimental methods and the modelling approach. Furthermore, the model captures the dramatic thermal softening observed in both PVC at high rates and PMMA at moderate (but still adiabatic) rates, as the predicted temperature rise is coupled to mechanical response through the thermal activation model of yield as well as the temperature-dependent elastic constants and shear resistance.
Avenues of future research have been suggested in order to capture even more accurately the complex thermomechanical behavior of amorphous polymers. A new model framework is proposed which shall be able to account for the additional energy storage occurring at low and moderate strains. Also, an experimental program is suggested in order to better understand the features of intrinsic rate-dependent strain softening, apart from heating effects. It is clear that the well-documented $\beta$-transition of many amorphous polymers plays an important role in the magnitude of strain softening, an effect which as of yet is not considered in any theoretical model mainly due to a lack of comprehensive data on the subject.
Chapter 5

Pressure Effects

During high-rate impact events, it is expected that large hydrostatic pressures will develop in the colliding materials. This notion is supported by figure 5-1, which shows both an experimental photograph and simulated pressure contours of a Taylor impact test on polycarbonate. In this particular test, a 76.2 mm PC cylinder impacted a steel plate at 277 m/s. Just after impact, the simulated pressure is shown to be in excess of 500 MPa, or about 25% of the room temperature Young’s modulus for this material. Both the elasticity and yield strength of polymers are known to be pressure-sensitive, and in the presence of such large pressures, these effects must be thoroughly considered. Pressure dependence in the elasticity is especially important because the material wave speed is determined by the elastic moduli. As shown by Sarva, Mulliken, and Boyce (2005), wave propagation and interaction plays a very important role in the response of polymeric cylinders in Taylor impact. In order to more accurately simulate impact events such as this, the constitutive model presented in Chapter 2 must be revised in order to consider pressure dependency in the elasticity as well. Here, this need is addressed along with a review of the treatment of pressure dependence in the shear yielding behavior.

5.1 Background

Beginning in the 1950s and continuing up to the 1970s, a limited number of studies examined specifically the pressure-dependence of elasticity, yield, and fracture in glassy polymers. These studies have been reviewed by Sauer, Pae, and co-workers (Sauer, Pae, & Bhateja, 1973; Pae & Bhateja, 1975; Sauer, 1977), who themselves were involved in many of the
Figure 5-1: Taylor impact test: polycarbonate rod (L=76.2mm, D=12.7mm) impacting a steel target at 277 m/s. High-speed photograph (left) and ABAQUS/Explicit FEM simulation pressure contours (right) 2.5 μs after impact (Sarva et al., 2005).
experiments. The experiments generally involved probing the uniaxial tension, uniaxial compression, or shear behavior of specimens subjected to a large superposed hydrostatic pressure (0-1000 MPa). The pressurizing was accomplished by surrounding a universal mechanical testing instrument with a sealed chamber, which could then be pumped with hydraulic fluid to the desired pressure. In every case tests were carried out at room temperature and quasi-static strain rates ($10^{-5}$ s$^{-1}$ to $10^{-3}$ s$^{-1}$). Experiments of this kind were conducted on a wide range of semicrystalline and amorphous polymers. Upon collecting this data for the first time, Sauer et al. (1973) notes that for most polymers, both the modulus and yield strength will increase several hundred percent with the application of high (>500 MPa) hydrostatic pressure. In general, the pressure sensitivity was found to be greater in semicrystalline polymers than in amorphous polymers. It was also noted that, for most polymers, both the axial modulus and the yield strength increase linearly with increases in pressure (Pae & Bhateja, 1975; Sauer, 1977). Furthermore, it is recognized that whether linear or not, the pressure dependence in the yield strength mimics the pressure dependence in the modulus (Sauer, 1977).

Deviation from linear pressure dependence is consistently observed for polymers which exhibit a glass transition close to, but below, room temperature. Figure 5-2, reprinted from Silano, Pae, and Sauer (1976), shows the pressure dependence of both the shear modulus and shear yield stress of semicrystalline polypropylene (PP; $T_g$=-20°C). A kink is observed in both curves at a pressure of approximately 2.5 kbar (250 MPa). This kink is thought to be the consequence of a pressure-dependent shift of $T_g$. At pressures below 250 MPa, the amorphous domain of PP would exhibit rubbery behavior; at pressures above 250 MPa, the amorphous domain of PP would exhibit glassy behavior. It is noted here, and elsewhere for other polymers (Sauer et al., 1973; Sauer, 1977), that the pressure-sensitivity of both the modulus and yield strength is much greater in the rubbery regime than in the glassy regime.

This portion of the literature provides important insight into the specific pressure-dependence of the two exemplary amorphous polymers investigated in this thesis, PC and PMMA. Three studies report specifically on the pressure-dependent modulus and yield strength of PC: Sauer, Mears, and Pae (1970), Christiansen, Baer, and Radcliffe (1971), and Spitzig and Richmond (1979). Christiansen et al. (1971) conducted their tests in uniaxial tension under large superposed hydrostatic pressure, whereas Sauer et al. (1970)
and Spitzig and Richmond (1979) conducted both uniaxial tension and compression under pressure. The data from these three studies has been compiled and presented in a consistent manner in figures 5-3 and 5-4. Similarly, three studies focused specifically upon the pressure-dependent modulus and yield behavior of PMMA: Rabinowitz, Ward, and Parry (1970), Harris, Ward, and Parry (1971), and Matsushige, Radcliffe, and Baer (1976). Both Rabinowitz et al. (1970) and Harris et al. (1971) conducted torsional tests under pressure, providing data on the pressure-dependent shear modulus and shear yield strength, whereas the uniaxial tension tests of Matsushige et al. (1976) provide data on pressure-dependent Young's modulus and axial yield strength of PMMA. The data from the three studies on PMMA is compiled in figures 5-5 and 5-6. For both polymers, the modulus and yield strength are shown to be highly pressure-dependent.

It is expected that the bulk behavior of amorphous polymers is also pressure-dependent. Again, this would have important ramifications in the simulation of high-rate impact events, where pressures may be as large as a few GPa. However, experimental data on the subject of bulk modulus pressure-dependence in the glassy state is extremely limited, especially for pressures on the order of 500 MPa. Carter and Marsh (1995) at Los Alamos have studied the relationship between pressure and volume for a variety of amorphous polymers at pressures from 1 GPa to 50+ GPa via shock wave techniques. In figure 5-7, their data for PC and

Figure 5-2: Polypropylene pressure-dependent shear modulus and shear yield strength (Silano et al., 1976).
Reference values for the modulus data in figure 5-3

<table>
<thead>
<tr>
<th>E(p=atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sauer et al.</td>
</tr>
<tr>
<td>Spitzig and Richmond</td>
</tr>
</tbody>
</table>

Figure 5-3: PC Young's modulus as a function of pressure; experimental data compiled from the literature.

PMMA are reproduced. In both cases, the relationship between pressure and normalized volume is strongly nonlinear, indicating a pressure-dependent bulk modulus. For the case of PC, there is a substantial drop-off in normalized volume at a pressure of approximately 25 GPa; a similar phenomenon is observed for polystyrene (Carter & Marsh, 1995). Carter and Marsh attribute this drop-off to the collapse of ring structures in the polymer chain. PMMA, which has no ring structures in either its main chain or side groups, does not exhibit the same behavior (figure 5-7). These phenomena observed by Carter and Marsh – strong pressure dependence in the bulk modulus over the range 0-60 GPa, a significant drop in volume at ~25 GPa for polymers with a ring structure – will have important consequences in regards to material behavior under extreme blast loading conditions. Nonetheless, in the impact events of interest in the study, pressures are expected to be much lower than even investigated by Carter and Marsh.¹

Warfield (1966) studied the pressure-volume behavior of amorphous polystyrene at more

¹The first data points reported by Carter and Marsh (1995) and reproduced in figure 5-7 correspond to pressures ≥1.5 GPa. In Taylor impact simulations, pressures reached a maximum of ~500 MPa (Sarva et al., 2005).
Reference values for the yield data in figure 5-4

<table>
<thead>
<tr>
<th>Reference</th>
<th>Yield Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sauer et al.</td>
<td>90.0 MPa</td>
</tr>
<tr>
<td>Christiansen et al.</td>
<td>63.9 MPa</td>
</tr>
<tr>
<td>Spitzig and Richmond</td>
<td>78.0 MPa</td>
</tr>
<tr>
<td>Mulliken and Boyce</td>
<td>63.9 MPa</td>
</tr>
</tbody>
</table>

Figure 5-4: PC axial yield strength as a function of pressure; experimental data compiled from the literature compared with predictions from the Mulliken-Boyce constitutive model (Chapter 2).
Reference values for the modulus data in figure 5-5

<table>
<thead>
<tr>
<th></th>
<th>$\mu E(p=\text{atm})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rabinowitz et al. (shear)</td>
<td>675 MPa</td>
</tr>
<tr>
<td>Matsushige et al. (tensile)</td>
<td>2850 MPa</td>
</tr>
</tbody>
</table>

Figure 5-5: PMMA Young's modulus and shear modulus as a function of pressure; experimental data compiled from the literature.
Reference values for the yield data in figure 5-6

<table>
<thead>
<tr>
<th></th>
<th>(\tau_y(p=\text{atm}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rabinowitz et al.</td>
<td>50.0 MPa</td>
</tr>
<tr>
<td>Harris et al.</td>
<td>47.5 MPa</td>
</tr>
<tr>
<td>Mulliken and Boyce</td>
<td>49.8 MPa</td>
</tr>
</tbody>
</table>

Figure 5-6: PMMA shear yield strength as a function of pressure; experimental data compiled from the literature compared with predictions from the Mulliken-Boyce constitutive model (Chapter 2).
relevant pressures (0-1115 MPa), and essentially found there to be insignificant changes in
the bulk modulus over the range 0-400 MPa. That is, the pressure-volume relationship in
this range is very nearly linear, as shown in the 25°C curve of figure 5-8. Additional insight
may be garnered from the rubber elasticity literature, where, in a few limited studies, ex-
periments have been conducted on the compressibility of rubbery polymers. This data was
recently summarized by Bischoff, Arruda, and Grosh (2001) and modelled with a compress-
able rubber elasticity theory. Figure 5-9 shows the Bischoff model fit to three independent
sets of pressure-volume data, corresponding to three different rubbery polymers. Here, too,
it may be seen that the pressure-volume relationship is nearly linear for pressures less than
300-400 MPa.

Yet another way to evaluate the pressure-dependent mechanics of amorphous polymers
is to examine pressure-dependent shifts of the relevant material transitions (e.g. \( \alpha \), \( \beta \),
etc.). This method has direct analogy to the dynamic mechanical spectroscopic techniques
utilized in quantifying the rate-dependent shifts of the viscoelastic transitions (Chapter 2).
In the literature, a limited number of studies have focused on the pressure-dependent shift
of the glass transition (\( T_g \)) in amorphous polymers, using predominately pressure-volume-
temperature (PVT) measurements. The PVT test yields data on the specific volume of a
polymer as a function of both temperature and imposed hydrostatic pressure; at \( T_g \), there
Figure 5-8: Pressure-volume data for polystyrene at three temperatures. Figure reproduced from Warfield (1966).

Figure 5-9: Bischoff model fit to pressure-volume data for three rubbery materials (Boyce & Arruda, 2000).
is a distinct "kink" in the volume-temperature curve. By tracking the temperature location of this kink as a function of pressure, the pressure-dependence of \( T_g \) may be determined. Other techniques for examining the pressure dependence of material transitions include differential thermal analysis (DTA) and dielectric analysis (DEA), both of which may be optionally conducted under superposed hydrostatic pressure. In table 5.1, data on the pressure dependence of \( T_g \) in amorphous polymers has been compiled from three studies: Bianci, Turturro, and Basile (1967), Zoller (1982), and Schouten, Scholten, Nelissen, and Nies (1991). In these studies, the pressure applied never exceeded 150 MPa, but still significant shifts of the glass transition were observed. The glass transition of amorphous polymers is observed to shift approximately 30-50°C/100 MPa pressure.

Table 5.1: Pressure-dependent shift of \( \alpha \)-transition (\( T_g \)); data compiled from the literature.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( \frac{dT_g}{dP} ) [°C/100 MPa]</th>
<th>Max. Pressure Tested</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>53.1</td>
<td>100 MPa</td>
<td>Zoller (1982)</td>
</tr>
<tr>
<td>PVAc</td>
<td>35.5</td>
<td>30 MPa</td>
<td>Bianchi et al. (1967)</td>
</tr>
<tr>
<td>PVC</td>
<td>37.5</td>
<td>30 MPa</td>
<td>Bianchi et al. (1967)</td>
</tr>
<tr>
<td>PS</td>
<td>28.0</td>
<td>150 MPa</td>
<td>Schouten et al. (1991)</td>
</tr>
</tbody>
</table>

As for the pressure dependence of secondary transitions (e.g. \( \beta \)), even less research has been conducted. Koppelmann and Gielessen (1961) report that the temperature location of the dielectric \( \beta \)-peak of PVC is insensitive to pressure, for tests in the pressure range 0-100 MPa. Similar pressure insensitivity has been observed for the \( \beta \) transitions of both polyethylene terephthalate (PET) (Williams, 1966) and poly-n-butyl methacrylate (PBMA) (Williams & Edwards, 1966). Through dielectric testing under imposed pressure, Williams (1966) found the PET \( \beta \)-peak to shift approximately one decade in frequency with 200 MPa of imposed pressure. Williams notes that this pressure-dependent shift is about four times less than the pressure-dependent shift of the \( \alpha \)-transition observed for other polymers: polymethyl acrylate (PEMA), polypropylene oxide, and polyvinyl acetate (PVA). Williams and Edwards (1966) found the PBMA \( \beta \)-peak to shift only 0.1 decade in frequency for 100 MPa in pressure, whereas the \( \alpha \)-peak of this same polymer shifted 1.2 decades in frequency for the same amount of pressure. There is no experimental data for any amorphous polymer to suggest that the pressure-sensitivity of the \( \beta \)-transition is greater than the pressure-sensitivity of the \( \alpha \)-transition. Thus the correspondence between pressure-sensitivity and
rate-sensitivity is minimal, at least with regards to the molecular mechanisms of deformation resistance.

5.2 Modelling

Original Method

In the constitutive model of Chapter 2, pressure dependence of the elastic constants, including the bulk modulus, was not taken into account. Pressure-dependence of the shear resistance to inelastic deformation is given as:

\[
\tilde{s}_\alpha = s_\alpha + \alpha_\alpha p \quad (5.1)
\]

\[
\tilde{s}_\beta = s_\beta + \alpha_\beta p \quad (5.2)
\]

where \( \alpha_\alpha \) and \( \alpha_\beta \) are the \( \alpha \) and \( \beta \) process pressure coefficients, respectively, and the pressure-independent athermal shear resistances (\( s_\alpha \) and \( s_\beta \)) are given as functions of the rate- and temperature-dependent elastic moduli:

\[
s_\alpha = \frac{0.077\mu_\alpha}{1 - \nu_\alpha} \quad (5.3)
\]

\[
s_\beta = \frac{0.077\mu_\beta}{1 - \nu_\beta} \quad (5.4)
\]

Thus, the shear resistance values used in the plastic strain rate equations (equations 2.29 and 2.28) are implicitly rate- and temperature-dependent and explicitly pressure-dependent. The process-specific pressure coefficients are determined from available data in the literature, as described in the "Material Parameters" section appended to Chapter 2. As shown in figures 5-4 and 5-6, these methods accurately capture observed pressure dependence in the yield strength of both PC and PMMA. Nonetheless, the pressure dependence in elasticity has been neglected. The pressure-dependent elasticity determines the material wave speed, which is important in high rate loading conditions. Furthermore, pressure dependence in the bulk modulus is not considered, which may or may not play an important role in the bulk response of polymers under impact.
Proposed Methods

**Method 1** The first proposed method is to use pressure-dependent shifts of the storage modulus \(\alpha\)-component to capture the pressure dependence of both the elastic shear moduli and the shear yield strength. In this manner, pressure-dependence would conveniently be incorporated into the decompose-shift-reconstruct techniques described in Chapter 2 (section 2.3.2). These techniques were shown to be successful in capturing the rate- and temperature-dependence of both the elastic moduli and yield strength. In this method, pressure dependence of the shear yield strength will arise through implicit dependence on pressure of the \(\alpha\) shear resistance \((s_\alpha)\), which is calculated from the elastic moduli (equation 5.3). Unlike the original methods, pressure-dependence is implemented only through the \(\alpha\)-process. Available literature data seems to indicate that the pressure-dependence of the \(\beta\)-transition is either nonexistent or negligible in comparison to the pressure-dependence of the \(\alpha\)-transition \((T_g)\). The inherent assumption is that a polymer's ability to access the small-scale \(\beta\)-motions is largely unaffected by the presence of hydrostatic pressures up to 500 MPa. This assumption is accepted here as only a first approximation in the absence of more thorough data.

This method considers primarily the pressure-dependence of the Young's modulus. Other \(\alpha\)-process elastic constants are calculated from the pressure-dependent Young's modulus as well as a pressure-independent bulk modulus. The calculation of the bulk modulus is left unchanged from the methods described in Chapter 2 (section "Material Parameters"), despite indications in the literature to suggest that this parameter too is pressure-dependent. At this time, there is insufficient data to determine even the magnitude of the pressure-dependence of the bulk modulus, though it is expected that the effect is small at least for pressures less than 100 MPa. Further research on this topic is needed, as discussed in section 5.3.

In order to test this method in the cases of PC and PMMA, an appropriate value for the \(\alpha\)-component pressure-dependent shift factor is required. In the original decompose-shift-reconstruct methods, the rate-dependent shift factors for the \(\alpha\) and \(\beta\) storage modulus components were taken directly from experimentally-observed rate-dependent shifts of the corresponding transitions. Here we draw off of available literature data on the pressure-dependent shift of \(T_g\) to determine a pressure-dependent shift factor for the storage modulus.
Figure 5-10: PC Young's modulus as a function of pressure; model method 1 compared to experimental data from the literature (Sauer et al., 1973; Spitzig & Richmond, 1979). Method 1 is a pressure-dependent shift of the modulus α-component, 50°C/100 MPa.

Figure 5-11: PC yield strength as a function of pressure; model method 1 compared to experimental data from the literature (Sauer et al., 1973; Christiansen et al., 1971; Spitzig & Richmond, 1979). Method 1 is a pressure-dependent shift of the modulus α-component, 50°C/100 MPa.
Figure 5-12: PMMA Young's modulus as a function of pressure; model method 1 compared to experimental data from the literature (Matsushige et al., 1976). Method 1 is a pressure-dependent shift of the modulus $\alpha$-component, $50^\circ$C/100 MPa.

Figure 5-13: PMMA shear yield strength as a function of pressure; model method 1 compared to experimental data from the literature (Rabinowitz et al., 1970; Harris et al., 1971). Method 1 is a pressure-dependent shift of the modulus $\alpha$-component, $50^\circ$C/100 MPa.
α component. As summarized in Table 5.1, the T_g of various amorphous polymers has been observed to shift approximately 30-50°C per 100 MPa of pressure applied. Simply for the purposes of testing this method, the α-component pressure shift factor is taken to be 50°C per 100 MPa pressure, for both PC and PMMA.

The method is first tested against literature data for PC. As shown in figures 5-10 and 5-11, the method severely under-predicts the pressure dependence of both the Young’s modulus (figure 5-10) and the axial yield strength (figure 5-11). In order to capture just the pressure-dependence of the Young’s modulus, a shift factor of approximately 150°C per 100 MPa pressure would be required. Based on available data (Table 5.1), such a shift factor seems physically unreasonable. Furthermore, the pressure-dependent yield strength would still be under-predicted, as it exhibits a greater pressure sensitivity than does the Young’s modulus. For PMMA, the pressure-dependence of the Young’s modulus is very nearly captured by this method, as shown in figure 5-12. However, as was the case for PC, the yield stress appears to have a greater pressure-sensitivity than the Young’s modulus, and still the pressure-dependent yield is well under-predicted (figure 5-13).

These disappointing results provide motivation for establishing a more accurate method for capturing pressure-dependence in the elasticity and yield strength of amorphous polymers.

**Method 2** Here, a second, more general method of capturing pressure-dependent effects in the elasticity and yield of amorphous polymers is suggested. The method is to modify the α shear modulus for explicit pressure dependence:

\[
\mu_\alpha = \mu(\dot{\varepsilon}, \theta) + mp
\]  

(5.5)

where \( m \) is the shear modulus pressure coefficient. To accurately capture pressure dependence in the yield strength as well, the pressure-dependence must be "amplified" through an additional explicit pressure-dependence on the α shear resistance:

\[
\bar{s}_\alpha = s_\alpha + np
\]  

(5.6)

where \( n \) is the amplification factor. In this method, the final shear resistance \( \bar{s}_\alpha \) is implicitly rate-, temperature-, and pressure-dependent through its relationship with the elastic
Figure 5-14: PMMA shear modulus as a function of pressure; model method 2 compared to experimental data from the literature (Rabinowitz et al., 1970). Method 2 is explicit pressure dependence in both the shear modulus and the shear resistance, as defined by equations 5.5 and 5.6.

Figure 5-15: PMMA shear yield strength as a function of pressure; model method 2 compared to experimental data from the literature (Rabinowitz et al., 1970; Harris et al., 1971). Method 2 is explicit pressure dependence in both the shear modulus and the shear resistance, as defined by equations 5.5 and 5.6.
Figure 5-16: PC Young’s modulus as a function of pressure; model method 1 compared to experimental data from the literature (Sauer et al., 1973; Spitzig & Richmond, 1979). Method 2 is explicit pressure dependence in both the shear modulus and the shear resistance, as defined by equations 5.5 and 5.6.

Figure 5-17: PC axial yield strength as a function of pressure; model method 2 compared to experimental data from the literature (Sauer et al., 1973; Christiansen et al., 1971; Spitzig & Richmond, 1979). Method 2 is explicit pressure dependence in both the shear modulus and the shear resistance, as defined by equations 5.5 and 5.6.
constants, and now also explicitly pressure-dependent. This method is motivated by the fact that experimental data for most polymers demonstrates a linear pressure-dependence in both elasticity and yield (Pae & Bhateja, 1975; Sauer, 1977). Again, it is assumed that the pressure-dependence is an α-process phenomenon, and also that the bulk modulus may be taken to be constant in pressure. Both of these are approximations, and further research is needed to determine whether or not they are justified. The two parameters – m and n – are determined by fitting available data presented in figures 5-3 to 5-6; optimal values for PC and PMMA are given in table 5.2.

In figures 5-14 to 5-17, Method 2 is shown to capture well the available data for both PC and PMMA. The success of this method lies in its generality and simplicity. With future research into the pressure-dependent effects, it is expected that this method will be replaced by techniques which are more physical than phenomenological in nature.

Table 5.2: PC and PMMA pressure coefficients, following proposed method #2

<table>
<thead>
<tr>
<th></th>
<th>PC</th>
<th>PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>m</td>
<td>1.30</td>
<td>0.95</td>
</tr>
<tr>
<td>n</td>
<td>0.059</td>
<td>0.257</td>
</tr>
</tbody>
</table>

5.3 Future Work

In this chapter, a particular implementation of pressure-dependence is suggested which, in a phenomenological manner, captures existing experimental data for the pressure-dependent modulus and yield strength of PC and PMMA. However, this experimental data is severely limited in scope. Further research is needed in order to understand more clearly the effects of pressure-dependence coupled with rate- and temperature-dependence in polymeric materials. Specifically, very little is known in regards to the role of the β-process in this pressure dependence, which has been shown to have a significant effect on both the rate- and temperature-dependence of glassy polymers. To address this need, an experimental program could be designed in which pressure-dependent elastic and yield behavior is probed both above and below $T_\beta$. These experiments could also be conducted at varying strain rates, in order to better understand the coupling between rate, temperature, and pressure in determining the mechanical behavior of amorphous polymers. Finally, in order to most accurately capture pressure-dependence in the elastic behavior, more experimental data is
needed in regards to the pressure dependence of the bulk modulus of glassy polymers.
Chapter 6

Model Summary

This chapter provides a brief summary of the final constitutive model, including the revisions proposed in Chapter 3 (thermal expansion), Chapter 4 (adiabatic heating), and Chapter 5 (pressure effects). For more detailed discussion on these individual topics and their corresponding implementation in the model, the reader is referred to the previous chapters. In the final sections of this chapter, additional modifications are proposed for future implementations of the model. These modifications include the addition of linear viscoelasticity, discussed briefly in Chapter 2, as well as the addition of a secondary energy storage component, as discussed in Chapter 4.

Throughout the derivations of this chapter, terms relating to the combined thermo-elasto-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 2-13). All quantities specific to the $\alpha$ and $\beta$ components will be given those subscripts as well. Boldface type indicates tensorial quantities in this three-dimensional formulation.

6.1 Kinematics

The total deformation gradient $F$ acts in full on each of the three main components of the model:

$$F_{A\alpha} = F_{A\beta} = F_B = F$$  \hspace{1cm} (6.1)

In the $\alpha$ and $\beta$ components of the model, decomposition of the deformation gradient into elastic, thermal expansion, and plastic components is considered, following Weber and Boyce...
Figure 6-1: Schematic representation of the thermo-elasto-plastic kinematic framework. Starting at the far left and continuing clockwise, the configurations are labelled as the reference, the loaded, and the unloaded. The configuration at the bottom is an intermediate configuration not explicitly referred to in this chapter.
and described schematically in figure 6-1. The multiplicative decomposition of the deformation gradients is given as:

\[ F_{A\alpha} = F_{A\alpha}^e F_{A\alpha}^{th} F_{A\alpha}^p \quad (6.2) \]
\[ F_{A\beta} = F_{A\beta}^e F_{A\beta}^{th} F_{A\beta}^p \quad (6.3) \]

It is assumed that all plastic deformation is volume preserving, i.e. \( \det F_{A\alpha}^p = \det F_{A\beta}^p = 1 \).

The rate of deformation is described by the velocity gradient \( L = L_{A\alpha} = L_{A\beta} \equiv \dot{F} \dot{F}^{-1} \). By substituting the expressions 6.2 and 6.3 into this definition, the velocity gradient too is expressed in terms of elastic, thermal, and plastic components:

\[ L_{A\alpha} = L_{A\alpha}^e + F_{A\alpha}^e \left[ L_{A\alpha}^{th} + F_{A\alpha}^{th} L_{A\alpha}^p \left( F_{A\alpha}^{th} \right)^{-1} \right] (F_{A\alpha}^e)^{-1} \quad (6.4) \]
\[ L_{A\beta} = L_{A\beta}^e + F_{A\beta}^e \left[ L_{A\beta}^{th} + F_{A\beta}^{th} L_{A\beta}^p \left( F_{A\beta}^{th} \right)^{-1} \right] (F_{A\beta}^e)^{-1} \quad (6.5) \]

where \( L_{A\alpha}^e \equiv \dot{F}_{A\alpha}^e (F_{A\alpha}^e)^{-1} \), \( L_{A\alpha}^{th} \equiv \dot{F}_{A\alpha}^{th} (F_{A\alpha}^{th})^{-1} \), and \( L_{A\alpha}^p \equiv \dot{F}_{A\alpha}^p (F_{A\alpha}^p)^{-1} (i = \alpha, \beta) \). We also introduce the thermo-plastic velocity gradient, \( L^{thp} \):

\[ L_{A\alpha}^{thp} = \dot{F}_{A\alpha}^{thp} \left( F_{A\alpha}^{thp} \right)^{-1} = L_{A\alpha}^{th} + F_{A\alpha}^{th} L_{A\alpha}^p \left( F_{A\alpha}^{th} \right)^{-1} = D_{A\alpha}^{thp} + W_{A\alpha}^{thp} \quad (6.6) \]
\[ L_{A\beta}^{thp} = \dot{F}_{A\beta}^{thp} \left( F_{A\beta}^{thp} \right)^{-1} = L_{A\beta}^{th} + F_{A\beta}^{th} L_{A\beta}^p \left( F_{A\beta}^{th} \right)^{-1} = D_{A\beta}^{thp} + W_{A\beta}^{thp} \quad (6.7) \]

where \( D_{A\alpha}^{thp} \) and \( D_{A\beta}^{thp} \) (symmetric tensors) represent the rates of thermo-plastic stretching; similarly, \( W_{A\alpha}^{thp} \) and \( W_{A\beta}^{thp} \) (skew tensors) are the rates of thermo-plastic spin. Here, the thermo-plastic flow is taken to be irrotational, i.e. \( W_{A\alpha}^{thp} = W_{A\beta}^{thp} = 0 \). It follows, then, that

\[ \dot{F}_{A\alpha}^{thp} = D_{A\alpha}^{thp} F_{A\alpha}^{thp} \quad (6.8) \]
\[ \dot{F}_{A\beta}^{thp} = D_{A\beta}^{thp} F_{A\beta}^{thp} \quad (6.9) \]

The expressions above are integrated explicitly to obtain \( F_{A\alpha}^{thp} \) and \( F_{A\beta}^{thp} \); the elastic portion of the deformation gradients are then obtained via

\[ F_{A\alpha}^e = F_{A\alpha} \left( F_{A\alpha}^{thp} \right)^{-1} \quad (6.10) \]
\[ F_{A\beta}^e = F_{A\beta} \left( F_{A\beta}^{thp} \right)^{-1} \quad (6.11) \]
$F_{A_{\alpha}}^{'th}$ and $F_{A_{\beta}}^{'th}$ are constitutively prescribed, allowing for the calculation of $F_{A_{\alpha}}^p$ and $F_{A_{\beta}}^p$:

$$F_{A_{\alpha}}^p = \left( F_{A_{\alpha}}^{'th} \right)^{-1} F_{A_{\alpha}}^{'thp}$$  \hspace{1cm}(6.12)

$$F_{A_{\beta}}^p = \left( F_{A_{\beta}}^{'th} \right)^{-1} F_{A_{\beta}}^{'thp}$$  \hspace{1cm}(6.13)

In general, the rate of thermo-plastic stretching is considered to be the sum of two contributions:

$$D_{A_{\alpha}}^{'thp} = \dot{\hat{D}}_{A_{\alpha}}^p (T_{A_{\alpha}}, \theta, A_i) + \tilde{\hat{M}}_{A_{\alpha}} (\theta, A_i) \dot{\theta}$$  \hspace{1cm}(6.14)

$$D_{A_{\beta}}^{'thp} = \dot{\hat{D}}_{A_{\beta}}^p (T_{A_{\beta}}, \theta, A_k) + \tilde{\hat{M}}_{A_{\beta}} (\theta, A_k) \dot{\theta}$$  \hspace{1cm}(6.15)

Where $\hat{D}_{A_{\alpha}}^p$ and $\tilde{\hat{M}}_{A_{\alpha}} \dot{\theta}$ ($i = \alpha, \beta$) primarily capture the rate of plastic stretching and the rate of thermal stretching (thermal expansion) in the unloaded configuration, respectively.\footnote{Note, however, that in general $\hat{D}_{A_{i}} = \hat{F}_{A_{i}}^{'th} L_{A_{i}}^p (F_{A_{i}}^{'th})^{-1}$ and $\tilde{\hat{M}}_{A_{i}} = L_{A_{i}}^{'th} (i = \alpha, \beta)$.}

Both contributions depend upon the current temperature $\theta$ and a list of tensorial internal variables, $A_i$ or $A_k$. The rate of plastic stretching depends also on the driving stress $(T_{A_{\alpha}}$ and $T_{A_{\beta}}$).

The rate of plastic stretching in this thermo-elasto-plastic framework can itself be considered the sum of two components:

$$\bar{D}_{A_{\alpha}}^p = \text{sym} \left( F_{A_{\alpha}}^{'th} L_{A_{\alpha}}^p (F_{A_{\alpha}}^{'th})^{-1} \right) + \text{sym} \left( \frac{\partial F_{A_{\alpha}}^{'th} (T_{A_{\alpha}}, \theta, A_i)}{\partial A_i} F_{A_{\alpha}}^{'th} \right)$$  \hspace{1cm}(6.16)

$$\bar{D}_{A_{\beta}}^p = \text{sym} \left( F_{A_{\beta}}^{'th} L_{A_{\beta}}^p (F_{A_{\beta}}^{'th})^{-1} \right) + \text{sym} \left( \frac{\partial F_{A_{\beta}}^{'th} (T_{A_{\beta}}, \theta, A_k)}{\partial A_k} F_{A_{\alpha}}^{'th} \right)$$  \hspace{1cm}(6.17)

In these expressions, the first term is simply the symmetric part of the convected plastic velocity gradient; the second term represents that part of the thermal velocity gradient which evolves with a changing internal state. Both terms are framed in the unloaded configuration.

The second contribution to the rate of thermo-plastic stretching is taken as the portion
of the thermal velocity gradient which evolves with changing temperature:

\[
\mathbf{M}_{A_\alpha} \dot{\theta} = \text{sym} \left( \frac{\partial \mathbf{F}_{A_\alpha}^{th}}{\partial \theta} (\mathbf{F}_{A_\alpha}^{th})^{-1} \right) \dot{\theta} \quad (6.18)
\]

\[
\mathbf{M}_{A_\beta} \dot{\theta} = \text{sym} \left( \frac{\partial \mathbf{F}_{A_\beta}^{th}}{\partial \theta} (\mathbf{F}_{A_\beta}^{th})^{-1} \right) \dot{\theta} \quad (6.19)
\]

Combining equations 6.18 and 6.19 with equations 6.16 and 6.17, along with the irrotational constraint, the total thermo-plastic velocity gradients are in general given as:

\[
\mathbf{L}_{\alpha \beta}^{\text{thp}} = \mathbf{D}_{\alpha \beta}^{\text{thp}} = \text{sym} \left( \mathbf{F}_{A_\alpha}^{th} \mathbf{L}_{A_\alpha}^{\text{th}} (\mathbf{F}_{A_\alpha}^{th})^{-1} + \frac{\partial \mathbf{F}_{A_\alpha}^{th}}{\partial A_i} \mathbf{F}_{A_\alpha}^{th} + \frac{\partial \mathbf{F}_{A_\alpha}^{th}}{\partial \theta} (\mathbf{F}_{A_\alpha}^{th})^{-1} \right) \quad (6.20)
\]

\[
\mathbf{L}_{\alpha \beta}^{\text{thp}} = \mathbf{D}_{\alpha \beta}^{\text{thp}} = \text{sym} \left( \mathbf{F}_{A_\beta}^{th} \mathbf{L}_{A_\beta}^{\text{th}} (\mathbf{F}_{A_\beta}^{th})^{-1} + \frac{\partial \mathbf{F}_{A_\beta}^{th}}{\partial A_k} \mathbf{F}_{A_\beta}^{th} + \frac{\partial \mathbf{F}_{A_\beta}^{th}}{\partial \theta} (\mathbf{F}_{A_\beta}^{th})^{-1} \right) \quad (6.21)
\]

In this thermo-elasto-plastic framework, the constitutive model requires explicit constitutive description of both the plastic velocity gradient \( \mathbf{L}_{A_\alpha}^{\text{th}} \) and \( \mathbf{L}_{A_\beta}^{\text{th}} \) and the thermal expansion component of the deformation gradient \( \mathbf{F}_{A_\alpha}^{th} \) and \( \mathbf{F}_{A_\beta}^{th} \), as well as the stresses which arise from deformation.

### 6.2 Material Description

#### 6.2.1 Thermal Expansion

As a first approximation, the thermal expansion behavior is assumed to be *isotropic*. Any functional dependence of \( \mathbf{F}_{A_\alpha}^{th} \) on network orientation is neglected. With this assumption, the thermal expansion tensor is taken to be purely volumetric:

\[
\mathbf{F}_{A_\alpha}^{th} = \mathbf{F}_{A_\beta}^{th} = \hat{\beta}(\theta) \mathbf{1} \quad (6.22)
\]

where \( \beta \) is a scalar-valued function. The description of thermal expansion in the \( \alpha \) and \( \beta \) processes is taken to be the same, so that the material will expand uniformly in both a macroscopic and a local sense. With this isotropic description, there is no component of the thermal velocity gradient which evolves with the internal state of the material. The second term in equations 6.20 and 6.21 (last term in equations 6.16 and 6.17) vanishes. The rate
of thermo-plastic stretching simplifies then to:

\[
D_{A\alpha}^{thp} = \text{sym} \left( F_{A\alpha}^{th} L_{A\alpha}^p (F_{A\alpha}^{th})^{-1} \right) + \text{sym} \left( \frac{\partial F_{A\alpha}^{th}}{\partial \theta} (F_{A\alpha}^{th})^{-1} \right) \tag{6.23}
\]

\[
D_{A\beta}^{thp} = \text{sym} \left( F_{A\beta}^{th} L_{A\beta}^p (F_{A\beta}^{th})^{-1} \right) + \text{sym} \left( \frac{\partial F_{A\beta}^{th}}{\partial \theta} (F_{A\beta}^{th})^{-1} \right) \tag{6.24}
\]

Without loss of generality, the first term in equations 6.23 and 6.24 – the symmetric portion of the convected plastic velocity gradient – is described as the product of a magnitude \(\gamma_p^\alpha\) or \(\gamma_p^\beta\) and a direction tensor \(N_{A\alpha}^p\) or \(N_{A\beta}^p\):

\[
\bar{D}_{A\alpha}^p = \text{sym} \left( F_{A\alpha}^{th} L_{A\alpha}^p (F_{A\alpha}^{th})^{-1} \right) = \gamma_p^\alpha N_{A\alpha}^{thp} \tag{6.25}
\]

\[
\bar{D}_{A\beta}^p = \text{sym} \left( F_{A\beta}^{th} L_{A\beta}^p (F_{A\beta}^{th})^{-1} \right) = \gamma_p^\beta N_{A\beta}^{thp} \tag{6.26}
\]

where \(N_{A\alpha}^{thp}\) and \(N_{A\beta}^{thp}\) are taken to be coaxial with the deviatoric stresses (convected back to the unloaded configuration) acting on the \(\alpha\) and \(\beta\) components of the intermolecular network \(A\), respectively:

\[
N_{A\alpha}^{thp} = \frac{(F_{A\alpha}^e)^{-1} T_{A\alpha}^e F_{A\alpha}^e}{|T_{A\alpha}|} \tag{6.27}
\]

\[
N_{A\beta}^{thp} = \frac{(F_{A\beta}^e)^{-1} T_{A\beta}^e F_{A\beta}^e}{|T_{A\beta}|} \tag{6.28}
\]

Section 6.2.2 provides constitutive laws for \(T_{A\alpha}\) and \(T_{A\beta}\); section 6.2.3 provides constitutive laws for \(\gamma_p^\alpha\) and \(\gamma_p^\beta\).

The second term in equations 6.23 and 6.24 – the portion the thermal velocity gradient which evolves with changing temperature – is calculated from the suggested form of \(F^{th}\) (equation 6.22):

\[
\text{sym} \left( \frac{\partial F_{A\alpha}^{th}}{\partial \theta} (F_{A\alpha}^{th})^{-1} \right) = \text{sym} \left( \frac{\partial F_{A\beta}^{th}}{\partial \theta} (F_{A\beta}^{th})^{-1} \right) = \hat{\alpha}(\theta) \hat{\theta} \hat{1} \tag{6.29}
\]

where \(\alpha (= d\ln \beta/d\theta)\) is the temperature-dependent coefficient of thermal expansion. Thus
the final expression for the thermo-plastic velocity gradient is given as:

\[
\mathbf{L}^{thp}_{A\alpha} = \mathbf{N}^{thp}_{A\alpha} \mathbf{A}^{\alpha} + \alpha \dot{\mathbf{A}} \mathbf{I} \\
\mathbf{L}^{thp}_{A\beta} = \mathbf{N}^{thp}_{A\beta} \mathbf{A}^{\beta} + \alpha \dot{\mathbf{A}} \mathbf{I}
\]

(6.30)

(6.31)

The scalar function \( \beta(\theta) \) (equation 6.22) is determined through its relationship with the coefficient of thermal expansion. As a first approximation, the CTE (\( \alpha \)) is taken as a constant, independent of temperature. It follows, then, that

\[
\mathbf{F}^{th}_{A\alpha} = \mathbf{F}^{th}_{A\beta} = \exp[\alpha(\theta - \theta_0)] \mathbf{I}
\]

(6.32)

The description of thermal expansion (in the glassy regime) requires just one parameter – the coefficient of thermal expansion, \( \alpha \). Appropriate values for \( \alpha \) may be determined experimentally, as described in section 3.2, and are also available in the literature for many common amorphous polymers.

6.2.2 Elasticity

The intermolecular (element A) contribution to the material stress state is related to the deformation by the constitutive laws for the linear elastic springs:

\[
\mathbf{T}_{A\alpha} = \frac{1}{J_{A\alpha}} \mathbf{L}_5 \ln \mathbf{V}_{A\alpha} \\
\mathbf{T}_{A\beta} = \frac{1}{J_{A\beta}} \mathbf{L}_5 \ln \mathbf{V}_{A\beta}
\]

(6.33)

(6.34)

Where \( \mathbf{T}_{A\alpha} \) is the Cauchy (true) stress; \( J_i = \det \mathbf{F}_{A\alpha} \) is the elastic volume change; \( \mathbf{L}_5 \) is the fourth-order modulus tensor; and \( \ln \mathbf{V}_{A\alpha} \) 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 are formed from the process-specific shear moduli (\( \mu_\alpha \) and \( \mu_\beta \)) and bulk moduli (\( \kappa_\alpha \) and \( \kappa_\beta \)):

\[
\mathbf{L}_5 = 2\mu_\alpha \mathbf{I} + \left( \kappa_\alpha - \frac{2}{3}\mu_\alpha \right) \mathbf{I} \otimes \mathbf{I} \\
\mathbf{L}_5 = 2\mu_\beta \mathbf{I} + \left( \kappa_\beta - \frac{2}{3}\mu_\beta \right) \mathbf{I} \otimes \mathbf{I}
\]

(6.35)

(6.36)
where $I$ and $\mathcal{I}$ are the fourth-order and second-order identity tensors, respectively. Experimental DMTA data provides values for the rate- and temperature-dependent process-specific Young's moduli, following the techniques described in Chapter 2. To determine the rate- and temperature-dependent process-specific bulk moduli, the relative contributions of the $\alpha$ and $\beta$ processes are taken to scale in accordance with the Young's modulus data, while maintaining a constant value for the overall bulk modulus of the polymer:

$$\frac{\kappa_\alpha(\theta, \dot{\varepsilon})}{\kappa_\beta(\theta, \dot{\varepsilon})} = \frac{E_\alpha(\theta, \dot{\varepsilon})}{E_\beta(\theta, \dot{\varepsilon})} \quad (6.37)$$

$$\kappa_\alpha(\theta, \dot{\varepsilon}) + \kappa_\beta(\theta, \dot{\varepsilon}) = \kappa^o \quad (6.38)$$

where $\kappa^o$ is the (constant) total bulk modulus, with value given by the material's reported bulk modulus at standard rate ($10^{-3}$ s$^{-1}$), temperature ($25^\circ$C) and pressure (1 atm) conditions. The process-specific Young's moduli and bulk moduli are then used to calculate the rate- and temperature-dependent process-specific shear moduli:

$$\mu_\alpha(\theta, \dot{\varepsilon}) = \frac{3\kappa_\alpha(\theta, \dot{\varepsilon})E_\alpha(\theta, \dot{\varepsilon})}{9\kappa_\alpha(\theta, \dot{\varepsilon}) - E_\alpha(\theta, \dot{\varepsilon})} \quad (6.39)$$

$$\mu_\beta(\theta, \dot{\varepsilon}) = \frac{3\kappa_\beta(\theta, \dot{\varepsilon})E_\beta(\theta, \dot{\varepsilon})}{9\kappa_\beta(\theta, \dot{\varepsilon}) - E_\beta(\theta, \dot{\varepsilon})} \quad (6.40)$$

Finally, the $\alpha$-process shear modulus is modified to capture pressure-dependence in the elastic behavior:

$$\bar{\mu}_\alpha = \mu(\dot{\varepsilon}, \theta) + mp \quad (6.41)$$

where $p$ is the external pressure and $m$ is a pressure coefficient. In this study, appropriate values for $m$ were determined from experimental data in the literature.

### 6.2.3 Viscoplasticity

The constitutive laws for the magnitude of plastic flow in the $\alpha$ and $\beta$ processes are given as:

$$\dot{\gamma}_\alpha^p = \dot{\gamma}_{0,\alpha} \exp \left[ -\frac{\Delta G_\alpha}{k\theta} \left( 1 - \frac{\tau_\alpha}{\delta_\alpha} \right) \right] \quad (6.42)$$

$$\dot{\gamma}_\beta^p = 2\dot{\gamma}_{0,\beta} \exp \left( -\frac{\Delta G_\beta}{k\theta} \right) \sinh \left[ \tau_\beta \left( \frac{\Delta G_\beta}{s_\beta} \right) \right] \quad (6.43)$$
where \( \gamma_{0,i}^P \) \((i = \alpha, \beta)\) is the pre-exponential factor proportional to the attempt frequency; \( \Delta G_i \) is the activation energy; and \( s_i \) is an internal variable. The shear stresses \( \tau_\alpha \) and \( \tau_\beta \) are scalar equivalent stress measures, calculated as:

\[
\tau_\alpha = \sqrt{\frac{1}{2} T'_A \cdot T'_A} \\
\tau_\beta = \sqrt{\frac{1}{2} T'_B \cdot T'_B}
\]  

where \( T'_A = T_A - \frac{1}{3} \text{trace}(T_A) \) \((i = \alpha, \beta)\) is the deviatoric part of the stress tensor.

It has been assumed that the stresses in the \( \alpha \) process are sufficiently high such that the reverse progress of plastic flow may be neglected. In the \( \beta \)-process, this assumption is not appropriate for many of the applications of the model and thus the flow rule retains the full hyperbolic sine form.

In both processes, the initial value of the internal variable \( s_i \) is related to the shear modulus and Poisson ratio, as first described by Argon (1973):

\[
s_{0,\alpha} = \frac{0.077 \mu_\alpha}{1 - \nu_\alpha} \quad (6.46) \\
s_{0,\beta} = \frac{0.077 \mu_\beta}{1 - \nu_\beta} \quad (6.47)
\]

In the \( \alpha \)-process only, the shear strength \( s \) is taken to evolve to a preferred state with plastic straining:

\[
\dot{s}_\alpha = h_\alpha \left(1 - \frac{s_\alpha}{s_{ss,\alpha}}\right) \gamma_{0,\alpha}^P \quad (6.48)
\]

where \( h_\alpha \) is the softening slope and \( s_{ss,\alpha} \) describes 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 in the \( \alpha \)-process captures the strain softening phenomenon. Furthermore, the \( \alpha \)-process value of \( s \) is modified to capture pressure dependence of the yield strength:

\[
\tilde{s}_\alpha = s_\alpha + np \quad (6.49)
\]

where \( n \) is a second pressure coefficient. The final shear resistance \( \tilde{s}_\alpha \) inserted into equation 6.42 is implicitly rate-, temperature-, and pressure-dependent through its relationship with the elastic constants, and also explicitly pressure-dependent following equation 6.49.
Experimental yield data is used to solve for the pre-exponential factors $\gamma_{0,\alpha}$ and $\gamma_{0,\beta}$ and the activation energies $\Delta G_\alpha$ and $\Delta G_\beta$. Following a technique originally developed in association with the Ree-Eyring yield model, the experimentally-measured yield values are decomposed into $\alpha$ and $\beta$ contributions, assuming that the two processes individually exhibit characteristic Eyring behavior. For each process, the parameters are calculated through a pair of simultaneous equations which are developed by applying either equation 6.42 or 6.43 at the point of yield. The pressure coefficient $n$ is determined from pressure-dependent yield data, available in the literature for a number of amorphous polymers. Finally, the softening parameters $h_\alpha$ and $s_{ss,\alpha}$ are determined by fitting the model to experimental stress-strain curves.

### 6.2.4 Entropic Hardening

The stress in the non-linear hardening component, the network "back stress" due to entropic resistance to molecular alignment, is taken to be deviatoric and is defined as in the earlier models using the Arruda-Boyce 8-chain approximation:

$$TB = \frac{CR}{3} \frac{\sqrt{N}}{\lambda_{chain}^p} L^{-1} \left( \frac{\lambda_{chain}^p}{\sqrt{N}} \right) B'$$

(6.50)

where $\lambda_{chain}^p = \sqrt{\text{trace}(\bar{B})}/3$ is the stretch on a chain in the eight-chain network; $L$ is the Langevin function defined by $L(\beta) \equiv \coth \beta - \frac{1}{\beta}$; $B'$ is the deviatoric part of the isochoric left Cauchy-Green tensor, $\bar{B} = (\det F)^{-2/3} FF^T$; $\sqrt{N}$ is the limiting chain extensibility; and $CR \equiv nk\theta$ is 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 magnitude of this back stress increases asymptotically as the chain stretch approaches its limiting extensibility.

Two model parameters are needed to define the Langevin spring behavior: the rubbery modulus $CR$ and the limiting chain extensibility $\sqrt{N}$. Both of these parameters are taken to be constants, and are determined by fitting the model to experimental stress-strain data over the region dominated by strain hardening.

### 6.2.5 Adiabatic Heating

Under rate conditions which are known to be adiabatic, heat is evolved in the system through the dissipative work of the viscoplastic dashpots. As a first approximation, only
the elasticity and inelastic work of the entropic spring are taken to be stored. Following the first law of thermodynamics, a corresponding temperature rise is predicted by the model:

$$
\dot{\theta} = \frac{\text{trace}(\bar{T}_{Aa}^f \bar{D}^b_{Aa})}{\rho c_p} + \frac{\text{trace}(\bar{T}_{A\beta}^f \bar{D}^b_{A\beta})}{\rho c_p}
$$

(6.51)

where $\bar{T}_{Ai}^f$ ($i = \alpha, \beta$) is the deviatoric stress convected back to the unloaded configuration (i.e. $\bar{T}_{Aa}^f = (F_{Aa}^e)^{-1}T_{Aa}^e F_{Aa}^e$), $\rho$ is the material density and $c_p$ is the specific heat. This predicted temperature rise is coupled with the predicted mechanical response of the polymer through the implementation of thermal expansion, the thermal activation model of yield, as well as the temperature-dependent elastic constants and shear resistance. Values for the two material properties required for implementation of adiabatic heating – $\rho$ and $c_p$ – are widely available in the literature, and also may be readily measured with existing commercial laboratory equipment.
6.3 Model Parameters and Material Constants

elasticity

\[ \mu_\alpha(\theta, \dot{\varepsilon}) \quad \mu_\beta(\theta, \dot{\varepsilon}) \]  
\text{process-specific shear moduli}

\[ \kappa_\alpha(\theta, \dot{\varepsilon}) \quad \kappa_\beta(\theta, \dot{\varepsilon}) \]  
\text{process-specific bulk moduli}

\[ m \]  
\text{shear modulus pressure coefficient}

viscoplasticity

\[ \dot{\gamma}_0^{\alpha} \quad \dot{\gamma}_0^{\beta} \]  
\text{pre-exponential factors}

\[ \Delta G_\alpha \quad \Delta G_\beta \]  
\text{activation energies}

\[ h_\alpha \quad h_\beta \]  
\text{softening slope}

\[ s_{ss,\alpha} \quad s_{ss,\beta} \]  
\text{preferred state of athermal shear strength}

\[ n \]  
\text{shear strength pressure coefficient}

entropic hardening

\[ C_R \]  
\text{rubbery modulus}

\[ \sqrt{N} \]  
\text{limiting chain extensibility}

thermal expansion

\[ \alpha \]  
\text{linear coefficient of thermal expansion}

adiabatic heating

\[ \rho \]  
\text{material density}

\[ c_p \]  
\text{specific heat}
As detailed above, the constitutive model described in this thesis requires definition for 17 model parameters and material constants in order to simulate complex events of high-rate impact. However, it is expected that in many other applications, not all aspects of the model will need to be considered, thus significantly reducing the number of parameters/constants to be defined. For instance, a simulation of PC in uniaxial compression at quasi-static strain rate and room temperature would require knowledge only of the α-process elasticity and viscoplasticity parameters, as well as the entropic hardening parameters (total of 8 constants).

6.4 Implementation of Linear Viscoelasticity

As discussed briefly in Chapter 2, it may be advantageous to implement a form of viscoelasticity in the constitutive model rather than the discrete rate-dependent elasticity (stiffness tensor that depends on strain rate) originally proposed. For one, viscoelasticity provides a mathematical framework which is more appropriately descriptive of the true material behavior at small strains, although small strain behavior is not the primary interest in this thesis. The viscoelastic techniques also offer a solution for potential numerical problems associated with the current model framework and its implementation in the finite element method.

As originally proposed, the model calculates the current elastic moduli and shear resistances from an estimate of the strain rate. If there is a simulation in which there is a large gradient in strain rate, then there will correspondingly be a strong gradient in elastic moduli and shear resistance. Also, if there is a jump in strain rate, there would be a corresponding jump in the value of the modulus since we are using a hyperelastic relationship (relating stress to the current total elastic strain) rather than a hypoelastic relationship (relating the increment in stress to the current increment in elastic strain). The current technique can inadvertently generate discontinuous jumps and fluctuations in the material wave speed due to the changing elastic moduli. These spatially- and temporally-varying wave speeds have potential to cause numerical difficulties especially in simulations of high-rate impact where either the mesh is too coarse or the time step too large. It is expected that an alternate implementation of rate-dependent elasticity, based on linear viscoelasticity theory, would eliminate any of these potential problems.
An alternate model framework, incorporating instead a linear viscoelastic description of time-dependent elasticity, is suggested here. A one-dimensional rheological depiction of the suggested model is given as figure 6-2. In place of the rate-dependent $\alpha$ and $\beta$ elastic springs, there is now a Maxwell element in series with each of the viscoplastic dashpots. The mathematical description of the elastic springs is the same as before (equations 6.33 and 6.34), except now the material description is such that the modulus tensors are formed from constant values of $\mu$ and $\kappa$ – there is no variation with either rate or temperature. The corresponding dashpots are taken as linear, Newtonian dashpots, with rates of shear straining $\dot{\gamma}_\alpha^L$ and $\dot{\gamma}_\beta^L$:

\begin{align}
\dot{\gamma}_\alpha^L &= \frac{\tau_\alpha}{\eta_\alpha} \\
\dot{\gamma}_\beta^L &= \frac{\tau_\beta}{\eta_\beta}
\end{align}

(6.52)  (6.53)

where $\tau_\alpha$ and $\tau_\beta$ are the equivalent shear stresses acting on the $\alpha$ and $\beta$ components (as defined in equations 6.44 and 6.45), and $\eta_\alpha$ and $\eta_\beta$ are the viscosities to be defined.

In incorporating this description of linear viscoelasticity into the constitutive model previously defined, the viscoelastic (linear in $\tau$) shear straining is taken to be coaxial with the viscoplastic (non-linear in $\tau$) shear straining, which itself is defined as coaxial with the stress convected back to the unloaded configuration. In this manner, viscoelastic straining
is considering merely by an extra term in the definitions of $\overline{D}_{A\alpha}^p$ and $\overline{D}_{A\beta}^p$:

\[
\overline{D}_{A\alpha}^p = (\dot{\gamma}_\alpha^L + \dot{\gamma}_\alpha^{NL}) N_{A\alpha}^{thp} \\
\overline{D}_{A\beta}^p = (\dot{\gamma}_\beta^L + \dot{\gamma}_\beta^{NL}) N_{A\beta}^{thp}
\]  

(6.54)  

(6.55)

where $\dot{\gamma}_\alpha^L$ and $\dot{\gamma}_\beta^L$ are defined as in equations 6.52 and 6.53, $\dot{\gamma}_\alpha^{NL}$ and $\dot{\gamma}_\beta^{NL}$ are defined exactly as $\dot{\gamma}_\alpha^P$ and $\dot{\gamma}_\beta^P$ in equations 6.42 and 6.43 (only the nomenclature has changed), and $N_{A\alpha}^{thp}$ and $N_{A\beta}^{thp}$ are defined as in equations 6.27 and 6.28.

Appropriate values for the elastic constants ($\mu_\alpha$ and $\mu_\beta$, $\kappa_\alpha$ and $\kappa_\beta$) and viscosities ($\eta_\alpha$ and $\eta_\beta$) are determined by considering the model in the case of uniaxial stress relaxation. The Maxwell element (linear spring-dashpot combination) used in both the $\alpha$ and $\beta$ components predicts an exponential decay of the axial modulus with time:

\[
E(t) = E_0 \exp \left(-\frac{E_0}{\eta} t\right)
\]  

(6.56)

where $E_0$ is the initial (short time) modulus, dictated by the elastic spring, and the ratio $E_0/\eta$ describes the ensuing exponential decay afforded by the linear dashpot. The inverse of $E_0/\eta$ is also defined as the time constant, $\bar{\tau} \ [s]$ (not to be confused with the shear stresses $\tau_\alpha$ and $\tau_\beta$).

The experimental DMTA measurements and corresponding analytical techniques presented in Chapter 2 provide data to which this simple viscoelastic model may be fit, for the case of stress relaxation. As reprinted in figure 6-3 for the case of PC, the analytical techniques of Chapter 2 led to a description of the rate- and temperature-dependent axial moduli specific to the $\alpha$ and $\beta$ processes. In lieu of high strain rate measurements of the axial modulus, the short time values may be approximated with low temperature values. That is, $E_0$ for the $\alpha$ process (equation 6.56) is set to $E_\alpha$ at -140°C ($\sim$2000 MPa for PC; figure 6-3) and $E_0$ for the $\beta$ process is set to $E_\beta$ at -140°C ($\sim$1000 MPa for PC; figure 6-4). From these short time values of the axial moduli, the necessary (constant) shear moduli may be calculated, again assuming a constant total bulk modulus with $\alpha$ and $\beta$ components that scale with the ratio $E_\alpha/E_\beta$. In this manner, the axial behavior of the elastic springs is generalized to three dimensions.

In order to calculate appropriate values for the viscosities $\eta_\alpha$ and $\eta_\beta$, it is necessary to
Figure 6-3: PC storage modulus components (analytical) as a function of temperature. Vertical dashed lines mark the lowest temperature achieved in experiments (-140°C) and room temperature (25°C).

Figure 6-4: Time-dependent PC elastic modulus components following the implementation of linear viscoelasticity in the \( \alpha \) and \( \beta \) processes.
Figure 6-5: PC effective axial modulus components as a function of strain rate, following the implementation of linear viscoelasticity in the $\alpha$ and $\beta$ processes. The effective modulus is estimated as the modulus value for a time corresponding to the inverse of the strain rate.

define long time values of $E_\alpha$ and $E_\beta$, as well as the time it takes for the modulus to decay from its short time value to these long time values. One method, employed here, is to take the room temperature values of the storage modulus components as the long time values, as denoted in figure 6-3. Then the time to decay to this value is taken as the inverse of the DMA instrument’s imposed strain rate: $1/10^{-3} = 1000$ s. With these values, the viscosities $\eta_\alpha$ and $\eta_\beta$ are calculated as $1.05\times10^{13}$ Pa-s and $1.45\times10^{11}$ Pa-s, respectively. The corresponding time constants are 5250s and 145s for the $\alpha$ and $\beta$ processes, respectively. Figure 6-4 shows the model’s predicted behavior in axial stress relaxation, following implementation of linear viscoelasticity with these values for the constants. Figure 6-4 provides an estimate of the "effective" modulus components predicted by the viscoelastic formulation as a function of strain rate. As in the original implementation of rate-dependent elasticity, the two processes act in tandem to provide resistance to elastic deformation. At long times (slow strain rates), the $\beta$ contribution becomes negligible in comparison with the $\alpha$ resistance. Extensive validation and investigation of this linear viscoelasticity implementation is given in Appendix C, a supplement to this chapter. The model with viscoelasticity incorporated is compared against the original model formulation in simulations of creep, stress-relaxation,
The method of implementing linear viscoelasticity in place of the rate-dependent elasticity originally posed provides perhaps a more accurate description of the small-strain, time-dependent behavior of amorphous polymers, as well as a more thermodynamically appropriate description of the hyperelastic constitutive relation between stress and total elastic strain. In the above-described methods, both the entropic hardening and the viscoplastic shear resistance are unchanged from the original implementation. The shear resistances $s_\alpha$ and $s_\beta$ are still calculated from the current strain rate and temperature in a discrete and sometimes discontinuous manner. The intent of the suggested model changes is mainly to be more physically precise and to smooth out any numerical difficulties associated with rapidly fluctuating wave speeds. In simulations of high-rate Taylor impact, such as those reported on in Sarva et al. (2005), it is has been found there are no appreciable changes in the predicted highly inhomogeneous and dynamic structural response when linear viscoelasticity is used in place of the original rate-dependent elasticity. However, these suggested changes may allow for larger time steps and/or a more coarse mesh to be employed without difficulty, thereby reducing computation time.

6.5 Future Work: Viscoelasticity + Energy Storage

As discussed in Chapter 4, future iterations of the constitutive model may include also the effects of a secondary energy storage mechanism not captured in the current framework. In order to also consider rate-dependence in the elastic behavior through an implementation of
linear viscoelasticity – motivated either by a desire to more accurately capture small strain behavior or a need to eliminate potential numerical difficulties in high rate simulations – the methods proposed in the future work section of Chapter 4 may be combined with the linear viscoelasticity implementation discussed in the previous section. A one-dimensional spring-dashpot representation of this proposed combined model is given as figure 6-6. In this model, an additional spring-dashpot combination is added in parallel to the $\alpha$ and $\beta$ components, though it may be considered an extension of the $\alpha$-process. This storage element is to be defined mathematically such that stress builds up in the spring, either in a linear or non-linear manner, over low and moderate strain levels (<30%); beyond approximately 30% strain, further deformation is accommodated by the dashpot while the stored energy remains constant. In this manner, the storage element will be able to capture at least the phenomenological features of the secondary energy storage mechanism described by Hasan and Boyce (1993), among others. Further researcher is needed to understand the molecular physics behind this storage mechanism, and specifically the role of the small-scale $\beta$-motions. In the combined model, the viscoelasticity and viscoplasticity in the $\alpha$ and $\beta$ processes may be defined just as before, accounting mainly for that work which is dissipated in the polymer.
Chapter 7

Application to Polymer Composite Material Systems

Introduction

In the second chapter of this thesis, it was suggested that the elastic, yield, and post-yield behavior of amorphous polymers may be explained in terms of multiple activated processes, each with their own unique rate-, temperature-, and pressure-dependence, and each associated with a particular segmental motion of the polymer's macromolecules. Specifically, it was postulated that the restriction of certain small-scale secondary ($\beta$) molecular mobilities enhances both the stiffness and strength of the bulk material. An experimental procedure was outlined which allowed for a precise description of the rate and temperature conditions under which this restriction would occur. Finally, a new constitutive model was proposed, in an attempt to capture the observed behaviors in a way that is congruent with the molecular theory. In this model, two separate activated processes compose the total intermolecular deformation resistance; these processes are assumed to be sufficiently de-coupled such that their contributions are independent. Throughout Chapter 2, these methods were successfully applied to the rate-dependent behavior of two exemplary amorphous polymers, PC and PMMA.

In this last installment of the thesis, the generality of the experimental and theoretical methods introduced in Chapter 2 are examined. The methods are applied in three separate studies, each one focusing on a different polymer-based composite material system and its
neat counterpart. In all three cases, special attention is paid to the material behavior under high rates of deformation.

**Experimental Program**

The experimental program applied in all three studies is the same as that which was designed to investigate the rate-dependent behavior of PC and PMMA, as detailed in Chapter 2. Dynamic mechanical analysis and uniaxial compression testing techniques are used together in order to better understand the connections between molecular-level motions and macroscopic mechanical behavior.

**Dynamic Mechanical Thermal Analysis**

Dynamic mechanical thermal analysis (DMTA) testing was performed on a TA Instruments Q800 Dynamic Mechanical Analyzer. Rectangular specimens (approximately 20 mm x 3 mm x 1.6 mm) 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 total 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 was calculated. The materials were then tested at frequencies of 1 Hz, 10 Hz, and 100 Hz, over small ranges in temperature around identified material transitions. The particular frequencies of these tests corresponded to strain rates over the range $10^{-3}$ s$^{-1}$ to $10^{-1}$ s$^{-1}$, depending on the exact specimen gage length and displacement amplitude prescribed. Again, storage modulus and loss modulus information was recorded, and corresponding loss tangent calculations were made.

**Uniaxial Compression**

In each study, uniaxial compression tests were conducted over a span of at least five decades in strain rate, ranging from $3 \times 10^{-4}$ s$^{-1}$ to 3000 s$^{-1}$. Low to moderate rate testing ($3 \times 10^{-4}$ s$^{-1}$ to $3 \times 10^{-1}$ s$^{-1}$) was conducted on a Zwick servo-hydraulic testing machine at constant engineering strain rates. For lubrication, thin Teflon sheets were placed between the Zwick platens and specimen surfaces, and WD-40 was used between the Teflon sheets and platens.
All specimens were of right circular cylinder geometry, with a height-to-diameter ratio of 1:2 in order to be consistent with the geometry of the high rate specimens.

High strain rate testing (800 s\(^{-1}\) to 3000 s\(^{-1}\)) was performed on a compressive split-Hopkinson bar test apparatus designed in cooperation with and built by Physics Applications, Inc. of Dayton, Ohio. This apparatus employs solid aluminum pressure bars, both with a length of approximately 2.3 meters and a diameter of 19.05 millimeters. Specimens for split-Hopkinson bar testing were also of right circular cylinder geometry, with a diameter of 5.0 millimeters and a length of 2.5 millimeters. All specimens were lubricated with a thin layer of petroleum jelly on both faces, and little to no barrelling was ever observed.
7.1 Polycarbonate and a Polycarbonate-POSS Nanocomposite

7.1.1 Background

Over the past decade, advances in polymer chemistry have allowed for the introduction of nano-scale particles into homopolymers, creating a new subclass of materials called polymer nanocomposites (see, for instance, Vaia and Giannelis, 2001). The nano-scale particles have at least one dimension that is on the same length scale (1-10 nm) as those chain segments involved in secondary molecular motions. It may be expected, then, that the presence of these particles will alter the accessibility of particular secondary chain motions for a given polymer matrix. Consequently, the science associated with polymer nanocomposite material systems represents a significant opportunity to tailor the rate-dependent mechanical behavior of polymers for specific applications. By focusing attention on the interactions between the nano-scale particles and secondary molecular motions in particular, it may be possible to design new lightweight, polymer-based material systems with exceptional high-rate behavior and impact-resistant capabilities.

For the case of POSS-based polymer nanocomposites, most of the research has involved investigations into synthesis techniques, structure-property relationships, and mechanical behavior enhancements in thermosetting resins which have been augmented with POSS particles; this line of work is summarized in the review articles of Li, Wang, Hanli, and Pittman (2001) and Haddad, Tomczak, and Phillips (2004). In preliminary investigations, the POSS particles have been shown to significantly change the mechanical properties of amorphous thermoplastics, including polyurethane (Fu et al., 2001; Liu & Zheng, 2005), PET (Yoon, Polk, Park, Min, & Schiraldi, 2005), and PS-PMMA blends (Zhang et al., 2002). A more thorough testing program, covering the mechanical behavior of a variety of PMMA-POSS composites over a wide range of strain rates, has recently been conducted by Kopesky and co-workers (Kopesky, Haddad, Cohen, & McKinley, 2004; Kopesky, 2005). Depending on the tethered vs. untethered/blended nature of the POSS in the PMMA and the corresponding state of POSS dispersion, they found the POSS to act either as a plasticizer or as a traditional filler. In particular, the plasticizer effect is a strong indicator of the ability of POSS to locally interact with and alter molecular mobility of the polymer chains. Capaldi and co-workers (Capaldi, 2005; Capaldi, Rutledge, & Boyce, 2005) have used atom-
istic simulations to study the interactions between POSS particles and polyethylene (PE) chains in untethered blends. In the Capaldi PE-POSS system, the POSS was found to alter polymer structure and dynamics in a directional manner in a boundary layer regime around the POSS particle. Clearly, nanoscopic particles such as POSS provide a potential avenue to manipulate the polymer structure, dynamics, and end macroscopic properties. Despite the ongoing efforts to understand the changes in mechanical behavior induced by POSS particles, no constitutive model for this class of polymer nanocomposite has yet been suggested.

In this study, we investigate the rate-dependent mechanical properties of one particular POSS-based polymer nanocomposite and its homopolymer counterpart. The experimental and analytical methods described in Chapter 2 are used to help understand how the POSS nano-particles - introduced in very small amounts - affect both the primary ($\alpha$) and secondary ($\beta$) molecular mobilities of the matrix polymer. The results summarized here are also presented in detail in Mulliken and Boyce (2006b).

### 7.1.2 Materials

The matrix polymer for this study was chosen as Lexan® 9034 polycarbonate (PC), distributed by GE Polymershapes.\(^1\) PC is an optically-transparent amorphous polymer which is glassy at room temperature. It is used extensively in applications where it is intended to resist impact, including eyeglasses, visors, and vehicle headlights. This particular PC – Lexan 9034 – includes additives which make it especially impact-resistant.

The nano-scale particles used in this study belong to a family of organic-inorganic hybrid molecules known as Polyhedral Oligomeric Silsesquioxanes (POSS). POSS molecules feature an inorganic cage-like structure made of silicon and oxygen atoms, with different unreactive and/or functional organic groups connected to the corner silicon atoms. The TriSilanolPhenyl-POSS® used in this study (figure 7-1) has phenyl rings connected to seven of the cage corners, making it compatible with the PC chains. The eighth corner has no silicon atom, leaving three Si-OH (silanol) groups exposed for increased interactions between the POSS molecules and the PC chains. The largest dimension of the TriSilanolPhenyl-POSS molecule is approximately 2-3 nanometers.

\(^1\)This is the same brand of PC used in the experiments of Chapter 2. However, the thermal history prior to mechanical testing was slightly different, and thus the experimental results – both DMA and compression – are expected to be slightly different.
Figure 7-1: TriSilanolPhenyl-POSS: $C_{42}H_{38}O_{12}Si_7$ (www.hybridplastics.com)

The polymer nanocomposite was formed by mechanically mixing pellets of Lexan 9034 with TriSilanolPhenyl-POSS powder in a DACA co-rotating twin screw microextruder at a mass ratio of 95:5. The extruded material was pelletized and then dried in a vacuum oven at 60°C for 8-12 hours. Finally, the dried pellets were compression molded into 50 millimeter disks and machined into both rectangular and cylindrical specimens for DMTA and compression testing.\(^2\) The control specimens (pure Lexan 9034 PC) were machined directly from sheet stock. Although the nanocomposite and control specimens did not have the same processing history, they were annealed together at approximately 5°C above $T_g$ and then oven cooled, so that they would have the same relevant thermal history at the time of mechanical testing.

7.1.3 Experimental Results and Discussion

Key DMTA results on the neat PC and PC-POSS nanocomposite are summarized in figures 7-2 and 7-3. The temperature-dependent storage modulus curve (figure 7-2) has the same character for both material systems. Traversing from high to low temperature, the storage modulus increases by three orders of magnitude at approximately 160°C as the material passes through its glass transition; at approximately -15°C, there is a significant upturn in the curve, corresponding to the onset of restrictions on the $\beta$-motions. The two curves

\(^2\)When blended with a polymer, POSS can tend to aggregate and/or crystallize into larger-scale particles. The dispersed vs. aggregated nature of the POSS within the polymer strongly influences the properties of the nanocomposite. In this study, the clarity of the PC-POSS nanocomposites indicate that the POSS particles were well dispersed.
are in quantitative agreement at temperatures above -15°C; the storage moduli are seen to overlap, and the glass transition temperatures are nearly identical. Below -15°C - in the region where the \( \beta \)-motions are restricted - the neat polymer exhibits a significantly greater stiffness than does the nanocomposite, indicating that the POSS interaction with the PC chains somewhat alleviates the restriction of the \( \beta \)-motions.

The rate-dependent shift of the \( \beta \)-transition in these two materials was explored by changing the frequency of the DMA load program, as reported in figure 7-3. By tracing the temperature location of the peak in the loss tangent (tan \( \delta \)) curves with increasing frequency, the \( \beta \)-transition was found to shift approximately 15°C per decade increase in strain rate, for both the neat polymer and the nanocomposite. However, at every frequency, the temperature location of the \( \beta \)-transition was found to be consistently 4-5 degrees higher in the case of the polymer nanocomposite. Limited data on the \( \alpha \)-transition revealed similar behavior: while the actual temperature location of \( T_g \) differed by a couple degrees between the two material systems, the rate dependent shift was the same (~4°C per decade increase in strain rate).

By applying the DMTA analytical techniques introduced in Chapter 2, it is found that the \( \alpha \)-contribution to the overall modulus value is nearly identical in the two material systems, for all temperatures and strain rates. The \( \beta \)-contribution, on the other hand, is always...
less for the case of the polymer nanocomposite, and the difference increases with either increasing strain rate or decreasing temperature. It is this decreased deformation resistance in the \#process of the nanocomposite which accounts for the low temperature discrepancy between the two storage modulus curves in figure 7-2. This decreased deformation resistance is postulated to also manifest itself in the yield strength of the nanocomposite under high rate conditions. Under low strain rate and moderate temperature conditions, the DMTA data analysis suggests that both the polymer nanocomposite and its homopolymer counterpart will exhibit the same mechanical response.

The results of all uniaxial compression testing on the PC-POSS nanocomposite are summarized in figures 7-4 to 7-5. Figure 7-4 contains representative stress-strain curves for the PC-POSS, at strain rates ranging from $10^{-3}$ s$^{-1}$ to 2200 s$^{-1}$. As with neat PC (figure 2-9), the flow stress of the nanocomposite is highly rate-dependent, while the general character of the stress-strain curve remains the same over the entire range of strain rates tested. In figure 7-5, the stress-strain behavior of the nanocomposite is compared directly with that of the PC homopolymer. At $10^{-3}$ s$^{-1}$, the stress-strain curves are nearly identical. If mechanical characterization were limited to quasi-static testing, one may be led to believe that the POSS particles had no effect upon the mechanics of this polymer. However, it is clear from the high rate curves in figure 7-5 that the POSS does in fact alter the mechanics.
Figure 7-4: PC-POSS nanocomposite true stress-true strain behavior at four low, moderate, and high strain rates. The reported high strain rate is an approximate average over the course of the test.

Figure 7-5: PC and PC-POSS nanocomposite true stress-true strain behavior at low ($10^{-3}$ s$^{-1}$) and high ($\sim$2400 s$^{-1}$) strain rates. Reported high strain rates are approximate averages over the course of the tests.
of PC. Under high rate compression, the PC-POSS yield stress and post-yield stress-strain response is significantly lower than that of the neat PC.

The yield stress as a function of strain rate for the PC-POSS nanocomposite is presented in figure 7-6, in comparison with that of the neat PC. Both materials are observed to transition between two distinct regimes of strain rate sensitivity, over the range of strain rates tested. The data trend lines indicate that, in both cases, the transition is centered at a strain rate of approximately 100 s\(^{-1}\). Assuming that these yield behavior transitions are related to the \(\beta\) transitions in the viscoelastic behavior, this alignment was to be expected; the \(\beta\) transitions in the two material systems were found to have equivalent shift factors. The small differences in the temperature location of the transitions proved to be relatively insignificant in comparison with the large temperature range over which the transitions shifted under high-rate loading. At strain rates below the yield transition, the strengths of the neat polymer and the nanocomposite are found to coincide quite well. Seemingly, the mechanical behavior of PC in the quasi-static regime is unaffected by the inclusion of POSS particles. However, at high strain rates, the yield strength of the nanocomposite is approximately 10% less than that of the homopolymer. As predicted by DMTA analysis, this reduced strength is a manifestation of the decreased deformation resistance in the \(\beta\)-process. In general, a lower yield stress helps avert stress levels which may give premature brittle failure, and thus provides for greater ductility and toughness. Therefore this ability to selectively lower the yield stress under high rates of loading may increase the energy absorption of PC under impact conditions. Large strain tension and notched tension behavior remain to be explored.

While the precise molecular-level mechanics which explain the macroscopic mechanical behaviors can not be assessed from these results, the experimental data allows us to speculate on their origins. The inclusion of the POSS particles in this particular material system affects only the \(\beta\)-process, and the effect is to reduce the deformation resistance. We suggest that the POSS locally interacts with the PC molecules to enhance the mobility of the \(\beta\)-motions. The fact that the \(\alpha\)-process is left unaffected at this level of POSS loading (5 weight percent) suggests a very local effect in this case, as opposed to a more typical, large-scale plasticizer effect observed with diluent molecules. The nature of this POSS particle and its phenyl ring R-groups is such that it only very locally interacts with the polymer chains. Thus the POSS does not create enough additional free volume to enhance
the mobility of large chain segment rotations and/or translations. By these means, the dispersed nanoparticles acted to target the β-process of PC alone, altering the macroscopic mechanical behavior only within certain temperature and/or rate regimes.

### 7.1.4 Constitutive Modelling

As a final step in this study, the constitutive model described in Chapter 2 (section 2.5) is extended to capture the behavior of the PC nanocomposite. Like the Ree-Eyring yield model, this constitutive model makes no assumptions in regards to the specific molecular interactions which control the thermally-activated processes of intermolecular deformation resistance. Thus the framework is general enough that it may be applied to other material systems, such as this polymer nanocomposite, which exhibit the same type of phenomenological behaviors as seen with amorphous homopolymers.

In this particular case, the constitutive model has already been shown to accurately predict the rate-dependent finite-strain behavior of the neat homopolymer PC. Thorough experimental and analytical investigation of the corresponding polymer nanocomposite has revealed that the nano-scale particles only serve to reduce the deformation resistance in the β-process, by measurable amounts. The general stress-strain behavior is identical to the neat polymer at low and moderate strain rates, indicating that the strain softening and entropic hardening phenomena are not significantly altered by the introduction of this specific nano-scale particulate phase. Furthermore, the rate-dependent shifts of the α and β transitions are unchanged, as is the α-process contribution to the rate- and temperature-dependent elastic moduli. The only model parameters which are unique to the PC-POSS are the β-component elastic moduli and the β-process activation energy ($\Delta G_\beta$).

In figures 7-6 and 7-7, the constitutive model – with appropriate adjustments in the material parameters – is shown to accurately capture the rate-dependent yield and stress-strain behavior of the PC-POSS. Many of the model parameters common to the PC and PC-POSS are the same as those given in Chapter 2, for the PC data of a different study. Table 7.1 details the model parameters for both materials. The rate- and temperature-dependent elastic constants for the β-process were derived from the sub-$T_\beta$ storage modulus data in figure 7-2, as well as the rate-dependent shift of the β-transition. The β-process activation energies were calculated from the split-Hopkinson bar (high rate) yield data in figure 7-6. In both material systems, the β-process activation energy ($\Delta G_\beta$) is significantly less than
Figure 7-6: PC and PC-POSS nanocomposite true yield stress as a function of strain rate (logarithmic scale); low to high strain rates, model and experiment. Each data point represents the average of at least three tests. The model-predicted yield curves are developed from discrete predictions spaced at semi-decade intervals.

Figure 7-7: PC-POSS nanocomposite true stress-true strain behavior in uniaxial compression at low, moderate, and high strain rates: model prediction (dotted lines) and experiment (solid lines).
that of the α-process, due to the greater strain rate and temperature sensitivity observed in both DMTA testing (sub-Tₐ) and compression testing (above 100 s⁻¹). Further details on the determination of model parameters can be found in the section "Model Parameters" appended to Chapter 2.

Table 7.1: PC and PC-POSS model parameters

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<td>1900 MPa</td>
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<tr>
<td>E₁</td>
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<td>4.26e10 s⁻¹</td>
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<tr>
<td>ΔG₀</td>
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<td>3.21e-19 J</td>
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<td>ΔG₁</td>
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<td>h₀</td>
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<td>300 MPa</td>
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<tr>
<td>sₚ₀/ₚ₀</td>
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</tr>
<tr>
<td>C₀</td>
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</tr>
</tbody>
</table>

7.1.5 Conclusion

A novel polymer nanocomposite has been developed by blending impact-resistant Lexan® 9034 PC with TriSilanolPhenyl-POSS®, at a mass ratio of 95:5. In this particular material system, the POSS was found to enhance the mobility of secondary (β) molecular motions, without affecting the large chain rotations and/or translations associated with the PC α-process. This "local plasticization" effect reduces the overall deformation resistance of the polymer at low temperatures and high strain rates. By lowering the stress levels under these conditions, the POSS may suppress certain brittle failure modes and increase the overall ductility of the polymer, thereby enhancing its energy absorption capabilities during impact. Furthermore, the unique behaviors of this material system should help to guide the design of other polymer nanocomposites for specific high-rate applications. It may be possible to select a different nano-scale particle which restricts rather than enhances the
mobility of secondary molecular motions in PC, while still not affecting the \( \alpha \)-motions. One could then construct a microscale composite of these versions of PC, i.e. the neat, the ductility enhanced, and the strength enhanced, to provide an assembly with interactive and complementary deformation and failure mechanisms. As a final step in this study, a new multi-process thermoplastic constitutive model (Chapter 2) was extended to capture the behavior of the PC-POSS. The accurate predictions given by this model validate the assumption that the model framework is in fact transferable to polymer nanocomposite material systems, for the case where the nano-particles are of order nanometer lengthscale in all dimensions and are well-dispersed within the polymer. In the future, it will be possible to use this model in optimizing the design of polymer nanocomposite components for impact applications.
7.2 Poly(vinyl chloride) and a Plasticized Poly(vinyl chloride)

7.2.1 Background

Poly(vinyl chloride) (PVC) is an amorphous polymer which is used as a structural and/or packaging material in many industries, with applications ranging from construction and building supplies to medical devices to electronics packaging. For many of these engineering applications, the PVC is blended with a plasticizing agent such as dioctyl phthalate (DOP). The plasticizing agent is intended to decrease the stiffness and yield stress of the PVC, as well as enhance its ductility by suppressing brittle failure modes. PVC and its plasticized variants, like most polymeric materials, are known to exhibit strong rate- and temperature-dependent mechanical properties, including elastic modulus, yield strength, and post-yield flow stress. Furthermore, the particular rate and temperature sensitivities are known to change through different temperature and strain rate regimes, as various primary and secondary molecular mobilities are accessed. Like PC and PMMA, PVC exhibits enhanced stiffness and strength under conditions of high strain rate and/or low temperature, a phenomenon which has been attributed to the restriction of certain small-scale (β) motions (Bauwens et al., 1969; Walley & Field, 1994). This rate-dependent behavior is further complicated by the adiabatic nature of high-rate plastic deformation, coupled with the strong temperature sensitivity of the material.

This study represents just a portion of a larger investigation into the mechanical behavior of a variety of PVC variants, led by S. Soong and advisor R.E Cohen (Department of Chemical Engineering). This work was conducted in collaboration with S. Soong; related publications include Soong, Cohen, Boyce, and Mulliken (2006) and Mulliken, Soong, Boyce, and Cohen (2006).

7.2.2 Materials

The poly(vinyl chloride) (PVC) used in this study was custom-made by Scientific Polymer Products, Inc. (Ontario, NY) with an approximate molecular weight of 90,000 grams per mole. Neat PVC and 20wt% dioctyl phthalate (DOP, Sigma-Aldrich) in PVC were prepared for this study. After the targeted percentage of DOP was mixed into PVC powders, the mixture was melt-blended in a lab scale extruder (DACA Instruments). Both materials con-
tained 3wt% of thermal stabilizer (Thermolite 890S, Atofina) to minimize degradation. In order to prepare the specimens for both DMTA and compression testing, extruded polymer strands were first pelletized and then compression molded into 50 millimeter disks. These disks were then machined to the specified geometries: rectangular specimens 20 mm x 3 mm x 1.6 mm for DMTA testing; cylindrical specimens of diameter 5 mm and height 2.5 mm for compression testing.

7.2.3 Experimental Results and Discussion

The results of all DMTA tests are summarized in figures 7-8 and 7-9 and table 7.2. Both the storage modulus (figure 7-8) and loss modulus (figure 7-9) curves for the two materials are markedly different at all temperatures, -120°C to 120°C. The PVC homopolymer exhibits two distinct viscoelastic transitions, α and β. As the PVC storage modulus is traced with decreasing temperature, there is a sharp jump from 5 MPa to nearly 2.5 GPa through the material α (glass) transition. There is a corresponding narrow and intense peak in the loss modulus curve, centered at approximately 76°C. For the β-transition, the change in storage modulus is much more gradual, from 3.0 GPa at -15°C to 4.2 GPa at -90°C. Furthermore, the broad β-peak in the loss modulus curve, centered at -56°C, describes an event which is much more distributed in nature than the primary transition. In PVC, a polymer whose molecular chains have no side groups, the β-transition is generally attributed to restricted rotations of small main-chain segments (Pezzin, Ajroldi, & Garbuglio, 1967).

For the case of the 20wt% diluent compound, only one transition is observed over the range of temperatures accessed by the DMA. As noted by Soong et al. (2006), and observed earlier by other researchers (see, for instance, Vilics, Schneider, Manoviciu, Manoviciu, 1996), the β-motions are heavily suppressed in this blend, as compared to the PVC homopolymer, and the β-peak in the loss modulus has become unrecognizable. Furthermore, the plasticization has reduced the temperature location of the glass transition so much that the material can no longer be considered glassy at room temperature. The now-broad glass transition begins at approximately -20°C and extends to 40°C (in the neat PVC, the glass transition occurs over a range of only 15°C). At temperatures above 40°C, the compound exhibits fully rubbery behavior. The addition of dioctyl phthalate has induced an increase in free volume around the PVC molecules such that the primary chain motions are able to occur with significantly less stress-assistance. Even in the glassy state, the PVC-DOP
Figure 7-8: PVC and DOP-plasticized PVC storage modulus as a function of temperature at 1 Hz ($\sim 5 \times 10^{-3}$ s$^{-1}$).

Figure 7-9: PVC and DOP-plasticized PVC loss modulus as a function of temperature at 1 Hz ($\sim 5 \times 10^{-3}$ s$^{-1}$).
Figure 7-10: PVC-DOP predicted storage modulus as a function of temperature at 0.0001 s\(^{-1}\) and 1000 s\(^{-1}\). The vertical dotted line represents room temperature.

Figure 7-11: PVC predicted storage modulus as a function of temperature at 0.0001 s\(^{-1}\) and 1000 s\(^{-1}\). The vertical dotted line represents room temperature.
compound exhibits less resistance to elastic deformation at all temperatures.

The temperature locations of the viscoelastic transitions are known to shift to higher temperatures with increasing strain rate. By testing the material at higher frequencies (10 Hz, 100 Hz) in the DMA, the strain rate experienced by the sample is increased. Since the PVC \( \beta \)-transition has a much lower activation energy than the \( \alpha \)-transition, its associated peak shifts faster than the \( \alpha \)-peak. In neat PVC, the loss modulus \( \beta \)-peak shifted at a rate of approximately 17.5°C per decade increase in strain rate, over the range 1 Hz to 100 Hz, whereas the \( \alpha \)-peak only shifted 3°C per decade increase in strain rate. The single distributed peak observed in the PVC-DOP compound shifted at rate of approximately 4°C per decade increase in strain rate. The exact temperature locations of the various peaks at different frequencies are given in table 7.2.

### Table 7.2: Frequency-dependent temperature locations of PVC and PVC-DOP viscoelastic transitions.

<table>
<thead>
<tr>
<th></th>
<th>PVC</th>
<th>PVC-DOP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 Hz</td>
<td>100 Hz</td>
</tr>
<tr>
<td>( \alpha )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>76°C</td>
<td>82°C</td>
</tr>
<tr>
<td></td>
<td>-56°C</td>
<td>-21°C</td>
</tr>
</tbody>
</table>

Following the analytical techniques described in Chapter 2, these rate-dependent shifts may be used in conjunction with the storage modulus "reference curves" (figure 7-8) to predict the storage modulus at strain rates well beyond those accessed by the DMA instrument. For the PVC-DOP compound, these predictions are especially elucidating. Figure 7-10 shows the predicted storage modulus curves of PVC-DOP at both 0.0001 s\(^{-1}\) and 1000 s\(^{-1}\). For a strain rate of 0.0001 s\(^{-1}\), the modulus value at room temperature is approximately 250 MPa; when the strain rate increases to 1000 s\(^{-1}\), the transition is predicted to shift through room temperature such that the modulus value is almost an order of magnitude higher (2000 MPa). For neat PVC (figure 7-11), the material is already in the glassy regime at 0.0001 s\(^{-1}\) and the modulus at room temperature is 2500 MPa. For a strain rate of 1000 s\(^{-1}\), the \( \beta \)-transition shifts through room temperature and the modulus is predicted to increase to 3500 MPa.

The results of uniaxial compression tests on both the neat PVC and the PVC-20wt% DOP blended compound are summarized in figures 7-12, 7-13, and 7-14. In all compression tests, the deformation was homogenous; little to no barrelling was ever observed, and no
Figure 7-12: PVC true stress-true strain behavior in uniaxial compression at low, moderate, and high (engineering) strain rates. Reported high-rate strain rates are averages over the duration of the test.

Figure 7-13: DOP-plasticized PVC true stress-true strain behavior in uniaxial compression at low, moderate, and high (engineering) strain rates. Reported high-rate strain rates are averages over the duration of the test.
cracks or other fracture events were seen. In the high-rate experiments, dynamic equilibrium was achieved before yield in all tests due to the short specimen lengths.

The stress-strain curves for PVC (figure 7-12) exhibit glassy polymer response at all strain rates: initial elasticity transitioning into non-linear elasticity and global yield, followed by strain softening, and finally strain hardening. The rate-dependence is clear, as both the global yield stress and plastic flow stress increase monotonically with increasing strain rate. At 0.03 s\(^{-1}\), the thermodynamic condition is transitioning between isothermal and adiabatic, and thus thermal softening contributes to the stress-strain behavior such that the apparent hardening is less than that observed at 0.003 s\(^{-1}\). In the high rate curves, the thermodynamic condition is fully adiabatic, and the strain hardening of the material is masked by thermal softening. The PVC-20wt% DOP blend (figure 7-13) does not exhibit a glassy stress-strain response at all strain rates. Following the DMTA data and associated analytical predictions, rubber-like deformation behavior was expected and observed in low and moderate rate testing (0.0003 s\(^{-1}\) – 0.03 s\(^{-1}\)). In the case of the high rate compression tests, the \(\alpha\)-transition shifted to a higher temperature, above room temperature, and glassy polymer behavior was observed. The glassy stress-strain response of the PVC-DOP compound, however, is still different in character from the stress-strain response of the PVC homopolymer, as the inclusion of dioctyl phthalate has changed both the strain softening

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**Figure 7-14:** PVC and DOP-plasticized PVC true yield stress as a function of strain rate (logarithmic scale).
and hardening attributes of the material, in addition to the general rate-dependence.

The yield data obtained from compression tests on PVC and PVC-20wt% DOP is summarized in figure 7-14. For neat PVC, the yield stress increases linearly with the logarithm of strain rate in both the low-rate and high-rate regimes. However, in the high-rate regime the rate sensitivity is much greater. The transition location, at approximately 10 s⁻¹, is consistent with that predicted by the rate-dependent shifting of the viscoelastic \( \beta \)-transition. In may be concluded, then, that the observed bi-linear character of the rate-dependent yield curve of PVC is a manifestation of restricted secondary \( \beta \) molecular mobilities under high-rate conditions. Once these motions are restricted, an additional contribution to the overall material deformation resistance arises in both the elasticity and yield. The rate-dependent yield data for the PVC-DOP blend also shows two distinct regimes of rate sensitivity. However, in this case, the transition in the rate-dependent yield behavior is governed by a shift of the \( \alpha \)-transition rather than the shift of a secondary transition.

### 7.2.4 Constitutive Modelling

Using the experimental data of this study, predictive capabilities have been established within the framework of the constitutive model introduced by Mulliken and Boyce (Chapter 2). This model was devised specifically for capturing the rate-dependent mechanical behavior of two exemplary amorphous polymers, PC and PMMA, which both exhibit an enhanced stiffness and strength under conditions of moderate and high strain rate related to restricted \( \beta \) molecular motions. Here, the model is extended to another amorphous homopolymer, PVC, whose high-rate mechanical response is also thought to be partially dictated by restricted secondary molecular mobilities. In fact, the temperature location, distributed nature, and rate-dependent shifting of the PVC viscoelastic transitions are very similar to those observed in PC. In a second case, the model is extended to a plasticized variant of PVC, a material which exhibits rubbery behavior at low and moderate strain rates and glassy behavior at high strain rates. For the PVC-DOP compound, the transition in the rate-dependent mechanical behavior is controlled by a shift of the primary \( \alpha \) transition.

In fitting the constitutive model to the PVC data, two elastic-viscoplastic molecular processes \( \alpha \) and \( \beta \) are considered, as was the case for PC and PMMA. The unique definitions of rate- and temperature-dependent elasticity in these two processes were de-
Figure 7-15: PVC true stress-true strain behavior in uniaxial compression at low, moderate, and high strain rates: model prediction (dotted lines) and experiment (solid lines).

Figure 7-16: DOP-plasticized PVC true stress-true strain behavior in uniaxial compression at low, moderate, and high strain rates: model prediction (dotted lines) and experiment (solid lines).
terminated from a analytical decomposition of the storage modulus data, as described in Chapter 2. Similarly, a component-wise split of the yield data is used to calculate the activation parameters for the $\alpha$ and $\beta$ component dashpots. Like PMMA, PVC exhibited strong temperature dependence in DMTA tests, and also significant thermal softening at moderate and high strain rates. Therefore, the model here considers also the heat evolved under adiabatic deformation, in accordance with the methods detailed in Chapter 4. Under adiabatic conditions, the dissipative work of the viscoplastic dashpots leads directly to a temperature rise in the polymer. This resulting temperature rise alters the predicted mechanical behavior of the polymer, as calculated through the thermal-activation model of yield together with the temperature-dependent elastic constants and shear resistance.

For the case of the PVC-DOP compound, a variant of the constitutive model introduced in Chapter 2 is employed. This version of the model accounts for the rate and temperature dependence of just a single, lumped activated process which we call $\alpha$. The model parameters, also determined from the DMTA and yield data, are such that this $\alpha$-process provides negligible resistance at the lowest strain rates. Under these conditions, the only contribution to the total material deformation resistance is the entropic hardening predicted by the Langevin spring. This entropic hardening model alone has been used to successfully capture the mechanical behavior of rubbery materials (Arruda & Boyce, 1993b). Under high-rate conditions, the $\alpha$-process is active (i.e. requires stress assistance), and again the heat evolved through dissipative viscoplastic work is considered. The model parameters used for both PVC and the DOP-plasticized PVC are given in table 7.3.

The PVC model predictions of stress-strain behavior are given in figure 7-15. At the low rates (0.0003 s$^{-1}$ and 0.003 s$^{-1}$), where only the $\alpha$-component requires stress-assisted activation and the deformation is considered fully isothermal, the model predictions coincide with the experimental curves. The model also predicts the dramatic increase in stress associated with high-rate deformation, by accounting for the deformation resistance of restricted $\beta$-motions. Without this consideration, the model would under-predict the yield stress at 1750 s$^{-1}$ by almost 50 MPa. The model predicts the high-rate softening behavior observed at large strains by considering deformation to be fully adiabatic. As shown in figure 7-17, the temperature of the PVC is predicted by the model to increase by over 20°C for a true strain of 55%. In figure 7-16, the model is shown to also capture the rubbery-to-glassy transition of the PVC-20wt% DOP blend stress-strain behavior over low to high
Figure 7-17: PVC and PVC-DOP model-predicted temperature rise under high-rate deformation. Model predictions correspond to the high-rate stress-strain curves in figures 7-15 (PVC) and 7-16 (PVC-DOP).

strain rates. Again, the low rate (0.003 s⁻¹) is taken to be isothermal, while the high rates (850 s⁻¹ and 1550 s⁻¹) are assumed to be adiabatic. At all strain rates, the stress-strain curve is well predicted by the model, including observed high-rate thermal softening.

7.2.5 Conclusion

The experimental and theoretical methods of Chapter 2 have been successfully extended to two additional material systems: PVC (amorphous homopolymer) and a DOP-plasticized PVC. Over a wide range of temperatures and strain rates, the neat PVC was found to exhibit two significant material transitions, α and β. The temperature location of the α-transition is sufficiently far enough above room temperature such that PVC exhibits characteristic glassy stress-strain behavior at all strain rates. Under conditions of high strain rate, the β-transition too shifts above room temperature as the associated molecular motions become inhibited. Consequently, the PVC yield and flow stress is enhanced at high (>100 s⁻¹) strain rates. This rate-dependent behavior is similar to that observed in PC and PMMA, as described in Chapter 2.

With the addition of 20wt% DOP, the PVC β-transition was almost completely suppressed, and only a single, broad transition is observed. This "α" transition begins well below room temperature, such that the PVC-DOP compound exhibits rubbery stress-strain
Table 7.3: PVC and PVC-DOP model parameters.

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<tr>
<th>Parameter</th>
<th>PVC</th>
<th>PVC-DOP</th>
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<td>2200 J/kg$\cdot^\circ$C</td>
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</table>

behavior at low and moderate strain rates. Under conditions of high strain rate, the primary transition shifts through room temperature and the material exhibits glassy stress-strain behavior. Such material response could be utilized in applications which require flexibility under normal rates and temperatures, and rigidity under impact.

For both the PVC and DOP-plasticized PVC, the constitutive model described in Chapter 2 was found to accurately predict stress-strain behavior at all strain rates. The model predicts the enhanced rate sensitivity at high strain rates observed experimentally through a shift of the $\beta$-transition in the case of neat PVC and a shift of the $\alpha$-transition in the case of the PVC-DOP compound. Furthermore, by considering the effects of dissipative work under adiabatic conditions, following the techniques outlined in Chapter 4, the model predicts the post-yield thermal softening seen at high strain rates.
7.3 Polycarbonate and a Polycarbonate-Triptycene Copolymer

7.3.1 Background

In sections 7.1 and 7.2, the rate-dependent mechanical behavior of two polymer-based composite material systems were investigated, in comparison with the rate-dependent mechanical behavior of their neat counterpart. In both cases, a secondary phase was introduced into an amorphous polymer via mechanical blending. The polymer retained its chemical identity, but its ability to access various primary and secondary molecular mobilities was altered. In this study, the modifying particles are substituted into the main chain of the neat polymer at measured intervals. This technique is expected to alter not only the polymer's ability to access various molecular mobilities, but also perhaps alter the molecular motions themselves. The work presented in this section has been conducted in collaboration with N. Tsui and advisor E.L. Thomas (Department of Materials Science and Engineering).

The substituting particle used in this study is an aromatic hydrocarbon known as triptycene. The triptycene (figure 7-18) has a rigid "paddlewheel" structure composed of three benzene rings. When incorporated into a polymer chain, the triptycene is attached at multiple points to the neighboring chain segments and hence is limited in its rotational freedom. Long and Swager have studied extensively the effects of introducing triptycene into liquid crystal polymers (Long & Swager, 2001, 2002). In general, they found the triptycene to minimize free volume in the polymer by encouraging additional orientation around the rigid, three-dimensional triptycene frame. More recently, Tsui and co-workers (Tsui, Paraskos, Torun, Swager, & Thomas, 2006) have substituted triptycene into polyester molecules and measured the associated changes in mechanical behavior of the bulk polymer. For a 21wt% triptycene content, the enhancement in mechanical properties was enormous: a three-fold increase in both stiffness and strength, and a twenty-fold increase in strain to failure. In this study, the triptycene is incorporated into the molecular chains of polycarbonate (PC), which is already known to exhibit excellent mechanical properties. The commercial applications of PC are widespread, and any improvement on this material would garner significant interest from a wide range of industries.
7.3.2 Materials

Table 7.4 lists the three PC variants that were used to prepare the materials characterized in this study. PC1 is a high viscosity grade bisphenol-A polycarbonate supplied by Mitsubishi Engineering Plastics under the commercial name Lupilon® E2000. PC2 and PC-Trip were both supplied by Triton Systems, Inc. of Chelmsford, Massachusetts. PC2 is a low molecular weight bisphenol-A polycarbonate that served as a baseline for PC-Trip, a polycarbonate-triptycene copolymer. The chemical structure of the PC-Trip is given as figure 7-19. In this copolymer, there is a 9:1 ratio of bisphenol-A PC monomers to triptycene monomers.

Table 7.4: Molecular weight characteristics of the three PC variants, as determined by gel permeation chromatography.

<table>
<thead>
<tr>
<th></th>
<th>(M_n) [g/mol]</th>
<th>(M_w) [g/mol]</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC1</td>
<td>31,700</td>
<td>82,400</td>
<td>2.6</td>
</tr>
<tr>
<td>PC2</td>
<td>14,900</td>
<td>30,000</td>
<td>2.0</td>
</tr>
<tr>
<td>PC-Trip</td>
<td>12,900</td>
<td>26,500</td>
<td>2.1</td>
</tr>
</tbody>
</table>

From these three PC variants, three different polymers were made for mechanical characterization. The first polymer was pure PC1, commercial-grade PC. The second polymer was prepared as a blend of PC1 (high molecular weight) and PC2 (low molecular weight),
at a mass ratio of 3:1. The third polymer was prepared as a blend of PC1 with PC-Trip, also at a mass ratio of 3:1, yielding overall an approximate 2.75wt% triptycene. The blends were prepared by solvent mixing with a spinner in dichloromethane at room temperature overnight. Solutions were allowed to evaporate in a fume hood for 2-3 days in Teflon dishes, leaving behind highly crystallized thick films. These films were ground into a fine powder and then stored in a vacuum oven, along with pellets of PC1, at 120°C overnight before melt processing. For all three polymers, disks of approximately 50 millimeters in diameter and 3 millimeters in thickness were compression molded at 265°C. Finally, compression molded disks were machined into specified geometries for DMTA and compression testing.

7.3.3 Experimental Results and Discussion

The dynamic mechanical testing of these three polymers is summarized in figures 7-20 and 7-21. In general, the character of the storage modulus curve (figure 7-20) is the same for all three polymers. All three curves exhibit a high temperature (~150°C) glass transition, through which the storage modulus changes by three orders of magnitude, and also a low-temperature secondary transition which gives a more gradual change in the storage modulus. Both polymer 2 and polymer 3 show a decreased glass transition temperature relative to that of the commercial-grade PC – this may be attributed to the low molecular weight portion of the blends, as the effect is the same in both polymers. It is unusual to note that, despite the decreased glass transition temperature and the presence of a large amount (25 weight percent) of low molecular weight PC, both polymer 2 and polymer 3 show an enhanced stiffness at most temperatures, relative to the commercial grade PC (polymer 1). At all temperatures above -75°C, polymer 2 has a modulus which is 5-10% higher than the commercial grade polymer’s modulus, while the modulus of polymer 3 is 15-20% higher. The increase in stiffness from polymer 2 to polymer 3 may be attributed to the presence of triptycene, which acts as a steric hindrance to large-scale chain motions by inducing an increase in physical entanglements. The increase in stiffness from polymer 1 to polymer 2 remains unclear. Based on the storage modulus data alone, the analytical methods introduced in Chapter 2 suggest that, for all strain rates, the yield strength of polymer 2 will be slightly higher than that of polymer 1, and the yield strength of polymer 3 will be still higher than that of polymer 2.

The loss modulus curves for the three polymers are given in figure 7-21. The α-peak
Figure 7-20: Storage modulus as a function of temperature at 1 Hz ($\sim 10^{-3}$ s$^{-1}$) for commercial PC and the two PC blends.

Figure 7-21: Loss modulus as a function of temperature at 1 Hz ($\sim 10^{-3}$ s$^{-1}$) for commercial PC and the two PC blends.
is found to be slightly broader and decreased in temperature for polymers 2 and 3, with respect to polymer 1 (commercial grade). The presence of triptycene in polymer 3 does not appear to change the intensity, distributed nature, or temperature location of this α-peak, though the changes in the secondary (β) transition are pronounced. For the case of polymer 2, the β-peak is nearly identical to that of polymer 1 (commercial grade), save for a shoulder which has appeared on the high-temperature side. This is obviously induced by the presence of a significant amount of lower molecular weight PC, though again the exact mechanism is unclear. It is possible that low molecular weight PC has a β-transition which is located at a higher temperature, as the molecular chains are able to pack more tightly together; when combined at a mass ratio of 1:3 with high molecular weight PC, the β-transitions of the two constituent materials can both be observed. With the addition of triptycene, two distinct peaks of equal intensity are observed in the place of the original, broad β peak of the commercial PC. One of these peaks is at approximately the same temperature location as the shoulder peak observed in polymer 2, while the other is located at a temperature lower than the traditional T_β of PC. This dramatic change in the secondary transition of PC, induced by the substitution of triptycene along the PC backbone, provides further evidence that the PC β-transition is governed by the rotational freedom of main chain segments (Jho & Yee, 1991; Xiao & Yee, 1992; Floudas et al., 1993).

Due to the limited amount of material available for testing, it was not possible to fully characterize the rate-dependent shifts of the secondary transitions observed in the three polymers. It is expected that the dominant β-peak in both polymer 1 (commercial PC) and polymer 2 (blend of molecular weights) shifts at approximately the same rate for the two materials. However, the rate-dependent shift of the two secondary peaks exhibited by the third polymer – PC with triptycene – is of the greatest interest. Preliminary testing indicated that the two peaks shift at approximately the same rate, though more corroborating data is needed.

The results of uniaxial compression testing on the commercial PC and the two PC blends are summarized in figures 7-22 to 7-24. Figure 7-22 provides a comparison of the materials' stress-strain response at a low strain rate (0.001 s⁻¹), while figure 7-23 provides the same for a high strain rate (2000 s⁻¹). In both cases, the initial stiffness and yield strength of polymer 2 is greater than that of polymer 1, while the stiffness and yield stress of polymer 3 (with triptycene) is greater still. This observed behavior follows exactly the trend predicted.
Figure 7-22: True stress-true strain behavior at 0.001 s$^{-1}$ for commercial PC and the two PC blends.

Figure 7-23: True stress-true strain behavior at approximately 2000 s$^{-1}$ for commercial PC and the two PC blends.
by DMTA analysis. At both strain rates, the advantage of the polymer with triptycene is lost by a strain level of approximately 50% (true strain); at strains higher than 50%, the stress in polymer 3 is equal to or less than that measured in polymer 2. Consequently, over very large deformation the energy absorption characteristics of the polymer with triptycene would be the same as those of the molecular weight blend. The benefit of the triptycene is most pronounced at initial yield, as detailed in figure 7-24. At all strain rates measured, the yield strength of the polymer blend with triptycene is at least 6% higher than the yield strength of the baseline blend, and at least 12% higher than the yield strength of commercial grade PC. Further testing is needed to determine if there is any loss in ductility associated with the substitution of triptycene into the PC chains. This could be accomplished with large strain tensile testing, by comparing the strain to failure of polymer 2 (blend without triptycene) and polymer 3 (blend with triptycene).

7.3.4 Conclusion

A series of experiments has been conducted on commercial PC and two PC blends, following the experimental protocol described in Chapter 2 of this thesis. The study was focused specifically upon the changes in the rate-dependent mechanical behavior brought about by the substitution of triptycene along the PC main chain. Through DMTA techniques, the
presence of triptycene at very low loading (2.75wt%) was found to enhance the stiffness of the PC at all temperatures. Similarly, the triptycene enhanced the yield strength of the PC by at least 6% at all strain rates. While the exact mechanism(s) of these enhancements are unclear, loss modulus data revealed that the PC $\beta$-transition was significantly altered by the inclusion of triptycene, creating two distinct low-temperature loss peaks where there had only been one before. A more thorough experimental program, including DMTA and compression experiments on a series of polymer homologues with a smooth gradient in triptycene content is needed to understand better the molecular mechanics of this material system. With additional material, this DMTA data will be collected for a variety of frequencies, in order to better understand also the molecular dynamics of these material systems. Additional experiments are also needed to determine whether or not the ductility of PC remains with the substitution of triptycene along the main chain. Nevertheless, with enhanced stiffness and strength at all strain rates, this material offers significant potential to replace traditional PC in impact applications.
Summary

Through the short studies of this chapter, the experimental protocol, analytical techniques, and constitutive model framework introduced in Chapter 2 are shown to be sufficiently universal such that they may be extended to a wide variety of polymer-based material systems. In every case, new insight was garnered into the rate-dependent mechanical behavior of the materials of interest.

In the first study, a small amount of POSS particles (5wt%) was found to enhance the mobility of β-motions in PC, significantly reducing the resistance to high-rate and low-temperature deformation only. As for the case of PC and PMMA homopolymer, viscoelastic data was correlated with large-strain compression data through novel analytical techniques. The constitutive model was able to capture the stress-strain response of the PC-POSS nanocomposite by accounting for decreased deformation resistance in the β-process.

In the second study, plasticization effects in PVC were observed. The introduction of 20wt% DOP significantly reduced the glass transition temperature of the PVC, as well as the stiffness and strength measured at all temperatures and strain rates. Furthermore, the PVC β-transition was completely suppressed, the α-peak was broadened, and the characteristic glassy stress-strain behavior was altered. The constitutive model was shown to capture the rubbery to glassy transition in the DOP-plasticized PVC stress-strain behavior by considering the rate-dependent shifting of a just a single activated process.

In the final study, we observed the changes in the mechanical behavior of PC induced by a substitution of triptycene every tenth monomer unit into the PC macromolecules. The presence of triptycene served to increase both the stiffness and strength of PC by measurable amounts, for nearly all temperatures and strain rates tested. The triptycene also significantly altered the character of the PC β-transition, providing further evidence that the associated motion is cooperative and intramolecular in nature. Again, a strong correlation was found between DMTA data and uniaxial compression data.

As a whole, the methods introduced in Chapter 2 and utilized again here provide a toolkit for polymer scientists and structural engineers alike. The experimental protocol and associated analytical techniques shall allow for efficient design and evaluation of polymer-based material systems for applications in targeted rate and/or temperature regimes. The constitutive model, completed by the treatment of thermal expansion (Chapter 3), adiabatic
heating (Chapter 4), and pressure dependency (Chapter 5), may be implemented numerically and used in finite element simulations to optimize the design of polymeric engineering components. The tools have been designed specifically for high-rate applications, but have sufficient generality such that they may be applied more broadly, as is the case here.
Chapter 8

Concluding Remarks

This thesis has been motivated by a desire to better understand and predict the mechanical behavior of amorphous polymers, generally in their glassy state, under high (impact) rates of deformation. The knowledge developed here is to be used in the material selection and design of engineering components which are intended to resist impact, spanning a wide range of civilian and military applications.

At the outset, significant research in the field of polymer mechanics had already been conducted, with studies relevant to the current work dating as far back as fifty years ago. In Chapter 1, these relevant studies are thoroughly reviewed, serving as both a backdrop and a foundation for the original research described in ensuing chapters. In particular, research in the areas of macroscopic mechanical testing of polymers at high strain rates, mathematical modelling of the rate-dependent yield and stress-strain behavior of amorphous polymers, and experimental and theoretical molecular dynamics are discussed in detail. In Chapter 2 of this thesis, generally representing work presented in a preceding thesis (Mulliken, 2004) by the author, historical techniques, results, and theories are woven together and built upon in order to deliver a more complete and comprehensive picture of the rate-dependent mechanical behavior of amorphous polymers. In later chapters, a constitutive model proposed in Chapter 2 is revised and appended to more accurately account for various complexities in the material behavior, including: thermal expansion, adiabatic heating, pressure effects, and small-strain time-dependent creep and stress relaxation. In the final content chapter, the experimental protocols and theoretical interpretations introduced in Chapter 2 are extended to the study of a variety of polymer composite material systems.
8.1 Summary of Accomplishments

Foremost in the list of accomplishments for this thesis work is the development of a large body of experimental data. This data is relevant to the rate-dependent thermomechanical behavior of amorphous polymers in general, but is focused upon the behavior of two exemplary amorphous polymers in particular: polycarbonate (PC) and poly(methyl methacrylate) (PMMA). PC and PMMA rate-dependent behavior was first probed through dynamic mechanical thermal analysis (DMTA) techniques, covering small strain viscoelastic response over a wide range of both temperatures (-140°C to 160°C) and frequencies (1 Hz to 100 Hz). Later, large strain inelastic behavior was investigated via uniaxial compression experiments. These compression tests employed both a servo-hydraulic machine, covering low and moderate strain rates (10^-6 s^-1 to 1 s^-1), as well as a split-Hopkinson pressure bar apparatus covering high strain rate behavior (500 s^-1 to 5000 s^-1). In conjunction with the high rate compression test, an experimental set-up and corresponding test methods were established to accurately measure the specimen surface temperature rise during deformation by infrared radiation detection. This measurement was successfully obtained for both PC and poly(vinyl chloride) (PVC) under high-rate (>1000 s^-1) compression. Finally, experiments were devised in order to investigate the orientation dependence of the coefficient of thermal expansion (CTE) of PMMA. The experimental results of this thesis may be found in Chapters 2, 3, and 4.

In conjunction with the DMTA experiments, new analytical techniques were proposed and tested against the data for homopolymer PC and PMMA. The techniques are based upon the same postulate as that which underlies the Ree-Eyring yield model (Ree & Eyring, 1955; Bauwens et al., 1969): total deformation resistance may be decomposed into the contributions from multiple thermally-activated processes (α, β, etc.), each of which is associated with a distinct molecular motion. The analytical methods proposed here allow for predictions of the temperature-dependent elastic modulus at rates (frequencies) well beyond those accessible in the laboratory. Furthermore, these methods allow one to predict at what rate and temperature conditions certain small-scale ("β") molecular motions will become restricted, significantly altering the macroscopic mechanical response of the polymer. Through these techniques, transitions in the rate-dependent yield behavior were successfully predicted from DMTA data alone, for both PC and PMMA. Chapter 2 provides
a detailed explanation of these analytical methods.

The thesis also provides a framework for a fully three-dimensional constitutive model to predict the large strain mechanical behavior of amorphous polymers. This model considers rate-dependence (10^{-6} \text{s}^{-1} to 10^4 \text{s}^{-1}), temperature-dependence (-140^\circ \text{C} to T_g), and pressure-dependence (0 to 500 \text{MPa}) in the mechanical behavior. Furthermore, the model has capability to predict isotropic thermal expansion, as well as heating under adiabatic conditions. Issues related to the application and numerical implementation of the model are addressed in the thesis. In finite element simulations, the constitutive model is shown to capture PC and PMMA uniaxial stress-strain behavior under both isothermal and adiabatic conditions, PC temperature rise under adiabatic conditions, and PMMA post-deformation thermal expansion and recovery (all measured experimentally in this same thesis). The model is first introduced in Chapter 2, and revised and appended throughout chapters 3 through 6.

Finally, as presented in Chapter 7, the experimental protocols, DMTA analytical techniques, and constitutive model framework are successfully extended to a variety of polymer composite material systems, including: a PC-POSS® nanocomposite, a plasticized PVC, and a PC-Triptycene co-polymer. The experimental methods revealed rate-dependent phenomena in the mechanical behavior consistent with those observed in PC and PMMA, the DMTA analysis successfully predicted the rate/temperature location of transitions in the yield behavior, and the constitutive model was able to capture stress-strain behavior over a wide range of strain rates. This success proves the generality of the methods proposed in the thesis, and also lends validation to the accompanying theory and interpretations.

8.2 Future Work

This thesis work has generally been motivated by a desire to understand better the high-rate mechanical behavior of amorphous polymers. Through a series of experiments and analysis, it was discovered that, for many amorphous polymers, behavior in this regime is at least partially dictated by restrictions on small-scale secondary ("\beta") molecular motions. In the analytical and theoretical methods introduced in this thesis, it was assumed that these \beta-motions are sufficiently distinct and independent of the large-scale \alpha-motions such that their relative contribution to the macroscopic mechanical behavior may be de-coupled.
Furthermore, both the strain softening phenomena and the pressure-dependence are mod-elled as features of the $\alpha$-process alone; that is, they are assumed to be not influenced by the mobility (or lack thereof) of the $\beta$-motions. In both cases, this approach is merely a first approximation. Further research is needed in order to determine the role of the $\beta$-motions in both the macroscopic pressure dependence of the polymer as well as the strain softening phenomena. There is significant evidence to suggest that the strain softening in particular is strongly influenced by the accessibility of small-scale molecular motions.

In all of the material systems investigated, only the mobility of the $\alpha$ and $\beta$ motions is considered. However, the model framework may be generalized to material systems with three or more thermally-activated processes of intermolecular deformation resistance. Additional processes may be significant even in these same material systems (e.g. PC, PMMA) when larger ranges of temperature or strain rate are considered. For instance, when examining material behavior under blast loading, where strain rates may be many decades higher in magnitude than those observed under ballistic impact, it is possible that additional molecular motions ($\delta$, $\gamma$, etc.) are restricted. To predict behavior under blast loading, an experimental program must be devised to probe molecular dynamics and/or macroscopic mechanical behavior at either much higher strain rates or equivalent low temperatures.

The constitutive model described in this thesis has been designed especially for predicting polymer mechanical behavior under high strain rates. However, before it may be fully utilized in finite element simulations of structural impact, it is finally necessary to incorporate material failure considerations. Amorphous polymers are known to fail through both brittle and ductile modes, depending on the environment and loading conditions as well as the specific polymer chemistry. It is expected that the accessibility of the $\beta$-motions will also influence local failure modes, though little research has thus far been devoted to the topic.
Appendix A

Direct Comparison of the Richeton-Ahzi and Mulliken-Boyce Models

The intent of this Appendix is to provide a direct comparison of the cooperative yield model, as formulated by Richeton, Ahzi, and co-workers (Richeton et al., 2005a, 2005b, 2006), with the two-process model of Mulliken and Boyce (2006a) summarized in Chapter 2 of this thesis. While the Mulliken-Boyce model is a fully three-dimensional constitutive model capable of predicting stress-strain behavior up to large strains, here we consider only the viscoplasticity definition and its predictions of yield strength. Recent publications have demonstrated the ability of both models to accurately predict the rate- and temperature-dependent yield behavior of various amorphous polymers important in engineering applications, including PC and PMMA. While these two models give similar predictions, the supporting theoretical foundations and specific mathematical formulations are unique.

In Chapter 1, the theory behind various forms of the cooperative model is described in detail. In short, this model assumes that plastic flow will occur in solid polymers only when \( n \) identical chain segments simultaneously transition from one energy state to another, via stress-assisted activation. Thus the yielding process requires the cooperative motion of polymer segments. In the Richeton-Ahzi formulation, the past thermal history of polymer is also considered through an internal stress, which provides additional resistance to yielding (Richeton et al., 2005b).
The Mulliken-Boyce model, on the other hand, assumes that there are multiple rate-activated processes involved with yield, and that each of these processes is associated with a unique molecular motion of specific length scale. The theory never assumes that the molecular motions of these processes are not cooperative, only that they are distinct and that they are restricted under unique rate, temperature, and pressure conditions. More on the theoretical foundations of this model is given in Chapters 1 and 2.

In the following sections, mathematical details will be given for both models, so as to allow a more direct comparison. As stated before, only the viscoplasticity definition of the Mulliken-Boyce model is considered; this portion of the constitutive model is directly analogous to the cooperative yield model of Richeton and Ahzi. Furthermore, the pressure dependence and behavior close to \( T_g \) are left out of both models, for simplicity.

### A.1 Richeton-Ahzi Cooperative Model Summary

In the Richeton-Ahzi formulation of the cooperative model, the rate of plastic straining is given by:

\[
\dot{\epsilon} = \dot{\epsilon}^* \sinh^n \left( \frac{\sigma^* V}{2kT} \right) \tag{A.1}
\]

where \( \sigma^* = \sigma_{\text{applied}} - \sigma_i \) is the effective stress driving viscoplastic flow, and where the characteristic strain rate \( \dot{\epsilon}^* \) and internal stress \( \sigma_i \) are given by:

\[
\dot{\epsilon}^* = \dot{\epsilon}_0 \exp \left( \frac{-\Delta H_\beta}{kT} \right) \tag{A.2}
\]

\[
\sigma_i(T) = \sigma_i(0) - mT \tag{A.3}
\]

Note that equations A.2 and A.3 are only valid for \( T < T_g \); alternate expressions, described in section ??, are provided for \( T \geq T_g \).

Combining equations A.1-A.3 and setting \( \sigma_{\text{applied}} = \sigma_y \), the cooperative yield model (Richeton et al., 2005a) is given as:

\[
\sigma_y = \sigma_i(0) - mT + \frac{2kT}{V} \sinh^{-1} \left[ \frac{\dot{\epsilon}}{\dot{\epsilon}_0 \exp \left( \frac{-\Delta H_\beta}{kT} \right)} \right]^{1/n} \tag{A.4}
\]
Cooperative Model Parameters (6)

- $n$ number of segments moving cooperatively
- $V$ activation volume [m$^3$]
- $\dot{\varepsilon}_0$ pre-exponential strain rate (frequency factor) [s$^{-1}$]
- $\Delta H_\beta$ $\beta$-process activation energy [J/mol]
- $\sigma_i(0)$ athermal internal stress [Pa]
- $m$ unspecified material parameter [Pa/K]

Cooperative Model Variables (3)

- $\sigma_y$ polymer yield strength [Pa]
- $\dot{\varepsilon}$ axial strain rate [s$^{-1}$]
- $T$ absolute temperature [K]

A.2 Mulliken-Boyce Model Summary

Considering the two-process formulation of the Mulliken-Boyce model (Chapter 2), there are two relevant plastic strain rate equations: one for the $\alpha$-process (equation A.5) and one for the $\beta$-process (equation A.6). As described in Chapter 2, we consider both the forward and reverse progress of the $\beta$-process; in the $\alpha$-process, the reverse progress is assumed to be negligible.

$$\dot{\gamma}_\alpha = \dot{\gamma}_{0,\alpha} \exp \left( -\frac{\Delta G_\alpha}{kT} \left( 1 - \frac{\tau_\alpha}{s_\alpha} \right) \right) \quad (A.5)$$

$$\dot{\gamma}_\beta = \dot{\gamma}_{0,\beta} \exp \left( -\frac{\Delta G_\beta}{kT} \right) \sinh \left( \frac{\tau_\beta \left( \frac{\Delta G_\beta}{s_\beta} \right)}{kT} \right) \quad (A.6)$$

In the constitutive model, the above equations fully define the behavior of the viscoplastic dashpots. In order to develop a yield model from these equations, we first assume uniaxial deformation, making a change of stress and strain rate variables ($\tau \to \sigma/\sqrt{3}$, $\dot{\gamma} \to \sqrt{3}\dot{\varepsilon}$),
and re-arrange to give expressions for stress in the individual processes:

\[
\sigma_\alpha = \sqrt{3}s_\alpha + \frac{\sqrt{3}kT}{(\Delta G_\alpha/s_\alpha)} \ln \left( \frac{\dot{\epsilon}_\alpha}{\sqrt{3}\gamma_{0,\alpha}} \right) \quad (A.7)
\]

\[
\sigma_\beta = \frac{\sqrt{3}kT}{(\Delta G_\beta/s_\beta)} \sinh^{-1} \left[ \frac{\dot{\epsilon}_\beta}{\sqrt{3}\gamma_{0,\beta} \exp \left( -\frac{\Delta G_\beta}{kT} \right)} \right] \quad (A.8)
\]

Finally, these equations are applied at the point of yield, where \(\dot{\epsilon}_\alpha = \dot{\epsilon}_\beta = \dot{\epsilon}\) (global), and the respective contributions of the \(\alpha\) and \(\beta\) processes are summed to give an expression for the total polymer yield stress:

\[
\sigma_y = \sqrt{3}s_\alpha + \frac{\sqrt{3}kT}{(\Delta G_\alpha/s_\alpha)} \ln \left( \frac{\dot{\epsilon}}{\sqrt{3}\gamma_{0,\alpha}} \right) + \frac{\sqrt{3}kT}{(\Delta G_\beta/s_\beta)} \sinh^{-1} \left[ \frac{\dot{\epsilon}}{\sqrt{3}\gamma_{0,\beta} \exp \left( -\frac{\Delta G_\beta}{kT} \right)} \right] \quad (A.9)
\]

Note that in the full Mulliken-Boyce constitutive model, there will also be a stress contribution from network orientation (the Langevin spring). However, at yield the polymer chain network has only evolved slightly from its initial random configuration, and the magnitude of this contribution is less than 2 MPa. For the purposes of this discussion, we shall disregard this contribution.

**Mulliken-Boyce Model Parameters (6)**

- \(\dot{\gamma}_{0,\alpha}\) \(\dot{\gamma}_{0,\beta}\): pre-exponential shear strain rates (frequency factors) \([s^{-1}]\)
- \(\Delta G_\alpha\) \(\Delta G_\beta\): activation energies \([J/molecule]\)
- \(s_\alpha(T,\dot{\epsilon})\) \(s_\beta(T,\dot{\epsilon})\): internal shear resistances \([Pa]\)

**Mulliken-Boyce Model Variables (3)**

- \(\sigma_y\): polymer yield strength \([Pa]\)
- \(\dot{\epsilon}\): axial strain rate \([s^{-1}]\)
- \(T\): absolute temperature \([K]\)
Appendix B

Chapter 4 Supplement: Temperature-Dependent Yield

In the constitutive model described in Chapter 2, and later modified in Chapter 4 to capture the effects of adiabatic heating, temperature-dependent mechanical behavior is considered through the thermal activation model of yield, the temperature-dependent shear resistances ($s_\alpha$ and $s_\beta$), and the temperature-dependent elastic constants. However, due to a lack of relevant temperature-dependent experimental data, the model parameters for both PC and PMMA have thus far only been optimized to accurately capture rate-dependence. As shown in Chapter 2, the model does an excellent job of predicting the experimental data for the rate-dependent yield behavior of both PC and PMMA. In this section, a supplement to Chapter 4, these parameters are evaluated in terms of their ability to also predict temperature-dependent yield behavior reported in the literature.

Using the parameters listed in table 2.2, the model is first evaluated for the case of PC (figure B-1). Here, the model-predicted temperature-dependent yield behavior is compared against experimental data taken from the doctoral thesis of E.M. Arruda (1992). Over a wide range of temperatures, extending from room temperature to 120°C (approximately 25°C below $T_g$), the model predictions are in excellent agreement with the experiments. Temperature-dependent yield data was never used to calibrate the model parameters; this behavior is captured simply by calculating the viscoplastic model parameters ($\Delta G$ and $\tilde{\gamma}_0$) from rate-dependent yield data and using an analytical split of the temperature-dependent storage modulus curve to determine the relative shear resistances in the $\alpha$ and $\beta$ pro-
cesses. This agreement confirms that the model parameters are properly calibrated for temperature-dependent effects in the thermal activation model of yield, at least over the range of temperatures investigated here. Discrepancy between model and experiment in regards to the stress-strain behavior under high (adiabatic) rates, then, must be attributed to a change in intrinsic softening behavior, as suggested in section 4.3.2.

For the case of PMMA (figure B-2, the model parameters listed in table 2.2 clearly do not allow for accurate predictions of temperature-dependent behavior. The model severely under-predicts the temperature sensitivity of yield, such that the discrepancy between model and experiment increases monotonically with increasing temperature. At room temperature, the model correctly predicts the yield strength; at 50°C, the model is off by 20%; at 75°C, the model is off by almost 100%. This shortcoming of the PMMA model parameters has important ramifications in the prediction of thermal softening behavior. Under high-rate compression, PMMA is expected to heat 50-70°C with 50% strain. As the thermal activation model of yield is obviously not properly calibrated for temperature-dependent effects, the associated changes in softening/flow behavior will not be captured. If the model parameters were properly calibrated for temperature-dependence, then significantly more thermal softening would be predicted. This correction would likely close the gap between the model predictions and experimental measurements of stress-strain behavior under adiabatic conditions (figure 4-25). Nonetheless, more experimental data is required in order to properly optimize the PMMA parameters for temperature dependence. The data given in figure B-2 only provides information in regards to temperature dependence in the α-process, and even then the data set is less than comprehensive.
Figure B-1: PC true yield strength as function of temperature at 0.001 s\(^{-1}\), Mulliken-Boyce model (Chapter 2 parameters) and experiment. Experimental data from Arruda (1992).

Figure B-2: PMMA true yield strength as function of temperature at 0.001 s\(^{-1}\), Mulliken-Boyce model (Chapter 2 parameters) and experiment. Experimental data from Arruda (1992).
Appendix C

Chapter 6 Supplement:
Viscoelastic Model Predictions

A series of simulations have been conducted in order to verify and examine the implementation of linear viscoelasticity in the constitutive model, as described in Chapter 6 (section 6.4). The viscoelastic formulation is proposed as an alternative to the rate-dependent elasticity presented in Chapter 2. This alternate formulation is suggested as a more accurate physical description of the material behavior, especially in the small-strain regime, and also as a means to smooth out numerical difficulties associated with fluctuating wave speeds. Here, the predictions of the viscoelastic model formulation described in section 6.4 are compared against the predictions of the original model formulation given in Chapter 2. Note that only the definition of elasticity differs in these two models; viscoplasticity and entropic hardening are left unchanged in the revised (viscoelasticity) formulation.

Creep Response

The model is first tested in its ability to predict creep at room temperature. The simulated load history consists of two steps: 1) load in uniaxial compression to an axial stress of 20 MPa over a time period of two seconds 2) hold at constant stress (20 MPa) for one hour (3600 seconds). The model-predicted strain response is given in figure C-1. First, it is noted that the initial strain value differs slightly between the two model formulations; this is attributed to the fact that there is a difference in the value of the modulus, as both are loaded to 20 MPa. For the original model formulation ("rate-dependent elasticity"),
the strain output remains constant at its initial value – no creep is predicted. Even the viscoelastic model predicts a negligible amount of creep over this time period when the parameters given in Chapter 6 are used (i.e. \( \eta_a=1.05 \times 10^{13} \text{ Pa-s} \)). However, it is expected that either an elevated temperature or a longer time period would lead to a prediction of creep. To prove this notion, the same simulation is run with a lower value of viscosity in the \( \alpha \)-process. This change in viscosity – an order of magnitude decrease – serves to exaggerate the viscoelastic effects of the alternate model formulation. As shown in figure C-1, the lower viscosity in the \( \alpha \)-process linear dashpot yields a prediction of creep which is significant in magnitude. The predicted creep response is generally linear.

**Stress Relaxation**

The model formulation is next tested in its ability to predict stress relaxation at room temperature. The imposed strain history again consists of two steps: 1) deform in uniaxial compression to a true strain of 1% over a time period of two seconds 2) hold at constant strain (1%) for one hour (3600 seconds). The model-predicted axial stress response is given
Figure C-2: PC simulated stress relaxation: original constitutive model with rate-dependent elasticity formulation vs. modified constitutive model with viscoelasticity formulation.

in figure C-2. Initially, the two different models predict a slightly different stress level; as in the initial strain response predicted in the creep simulations, this discrepancy is attributed to the fact that the two models use a different initial value of elastic modulus. In the simulation using the original model, no change in stress is observed beyond the initial loading – stress relaxation is not captured. The viscoelastic model formulation, on the hand, shows a significant change in stress over this time period even with the higher value of viscosity. When the viscosity is decreased in the α-process to exaggerate the viscoelastic effects, the stress relaxation is observed to be exponential in character. This predicted exponential decay is consistent with the time-dependent changes in elastic modulus predicted analytically (equation 6.56), and is also expected to be observed in the case with the higher viscosity, given a longer time period.

Post-Yield Stress Relaxation

The revised model is finally examined in its prediction of post-yield stress relaxation. That is, what behavior does the viscoelastic component predict when the non-linear viscoplastic
dashpot is activated also? The imposed strain history here is similar to that in the previous simulation, except that this time the material is initially strained to just over 40% true strain – well beyond yield – at a constant true strain rate of 0.001 s\(^{-1}\). As before, the strain is then held constant. The relative time periods of these two phases of the simulation are given in figure C-3, a diagram of the strain load program. The model-predicted stress response is given in figure C-4, alongside the response predicted by the original constitutive model.

During the loading phase (0 to 410s), both models predict characteristic stress-strain response to uniaxial deformation. The curves are slightly different, for two reasons. First, the initial modulus predicted by the two models differs by approximately 20%. In the original formulation, this modulus is determined by the calculated strain rate (0.001 s\(^{-1}\)); in the revised viscoelastic formulation, the modulus always has the same value (2 GPa) at very short times. Secondly, the model with a viscoelastic formulation is shown to predict slight stress relaxation even during the loading phase. There is sufficient time for the modulus to appreciably decrease as the linear dashpot opens and relieves some of the stress on the linear spring. In the original model, the modulus does not change over the course of the loading phase because the strain rate remains constant. By the end of the loading phase, the viscoelastic model predicts a stress which is 1-2 MPa lower than that predicted by the original model formulation for the same amount of strain. This effect would be magnified if the simulated strain rate were lower, but would be negligible at high strain rates.

Once the loading is halted and strain is held constant, the stress level predicted by the original model drops slightly. This is due to the fact that there is no appreciable strain rate, and the modulus – now calculated from a nominal strain rate of 0.0001 s\(^{-1}\) – instantaneously decreases. Thereafter, the predicted stress remains constant. The alternate model formulation, on the other hand, predicts a more realistic continued decrease in stress with time. This decrease again appears to be exponential, but in this case quickly saturates due perhaps to the large value of viscosity. In a laboratory experiment, this stress would continue to decrease with time as elastic strain was relieved.
Figure C-3: PC post-yield stress-relaxation simulation: strain load program.

Figure C-4: PC post-yield stress-relaxation simulation: predicted stress response, original constitutive model with rate-dependent elasticity vs. modified constitutive model with viscoelasticity formulation.
Summary

The model revisions proposed in Chapter 6, in which the original definition of rate-dependent elasticity is replaced with a linear elastic formulation, are shown here to capture important phenomenological features of the small-strain, long-time behavior of amorphous polymers. In particular, the model is shown to successfully predict both creep and stress relaxation effects in the elastic regime, whereas the original constitutive model formulation can do neither. The viscoelastic model formulation is also shown to predict slightly different behavior in a simulation which extends through yield, though these differences are unlikely to appear during simulations of high-rate impact events, due to the very short loading times. In general, it may be expected that these revisions will in fact help to smooth numerical difficulties associated with fluctuating wave speeds (as predicted by the original model formulation), without appreciably changing quantitative predictions of deformation and/or stress states. Furthermore, the revisions allow for a more physically realistic description of material behavior in the elastic regime, if such behavior is of interest.
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