TEMPERATURE, STRAIN RATE AND STRAIN STATE
DEPENDENCE OF EVOLUTION
OF MECHANICAL BEHAVIOR AND STRUCTURE OF
POLY(ETHYLENE-Terephthalate)
WITH FINITE STRAIN DEFORMATION

by

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B.Sc., Mechanical Engineering, MIT (1992)
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Submitted to the Department of
Mechanical Engineering
in Partial Fulfillment of
the Requirements for the Degree of
Master's of Science in Mechanical Engineering

at the

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Abstract

Mechanical tests and Differential Scanning Calorimetry (DSC) analysis that characterize the effects of temperature, strain rate and strain state on the finite deformation and occurrence of strain induced crystallization of initially amorphous poly(ethylene-terephthalate) (PET) are presented. Uniaxial compression in the glassy (25°C–60°C) and glass transition (T_g) regime (60°C–76°C), over a wide range of strain rates (0.005/s – 0.5/s), shows the decrease in the yield stress, flow stress and a small decrease in strain hardening modulus with an increase in temperature and a decrease in strain rate. Post-deformation thermograms on specimens deformed to an imparted logarithmic strain of −1.5 show a decrease in the cold crystallization temperature (T_{cc}) with an increase in deformation temperature and imparted strain and no change in the cold crystallization exotherm (A_{cc}) and crystallinity from their pre-deformation values. It follows that uniaxial compression below and through the T_g region induces network orientation without strain-induced crystallization (SIC). However, uniaxial compression in the rubbery regime at 80°C, 0.5/s and imparted logarithmic strains up to −1.75 show a distinctively larger strain hardening from that observed at 0.005/s. DSC analysis on the specimens deformed at the rapid rate condition shows that the different strain hardening behavior may be the result of SIC. The plane strain deformation in the glassy and T_g region is characterized by an apparent increase in the yield stress and a larger strain hardening behavior than that observed in uniaxial compression. DSC analysis on the plane strain specimens shows the evolution of
both molecular orientation and crystallization which are expected to contribute to the strain hardening. It is not clear how much of the end crystallinity, of the order of 41%, is the result of SIC during straining or annealing of the stretched PET after deformation as it cools from the test temperature.

A constitutive model for the temperature, strain rate and strain state sensitive finite deformation behavior of initially amorphous Poly(ethylene-terephthalate) (PET) in the glass transition region is then presented. A thermal activation law is employed for modeling the onset of the flow processes where the flow stress decreases dramatically as the material goes through the glass transition. The Arruda and Boyce eight chain model is used to model the subsequent strain hardening. The strain softening behavior is found to have a strong dependence on deformation temperature when the material is tested in the glass transition region. A phenomenological law that correlates information from deformation tests to measurements from Differential Scanning Calorimetry (DSC) is proposed. The model is found to capture the rate and temperature dependent stress strain behavior in isothermal uniaxial compression and plane strain compression up to logarithmic strains of $-1.5$, even though DSC analysis reveals considerable crystallinity for the samples deformed in plane strain and the occurrence of crystallization is not included in the model. It is concluded that the dominant deformation mechanism of the strain hardening behavior in this temperature regime is the imparted orientation of the random macromolecular network and not the deformation resistance due to the developing crystallinity.

Thesis Advisor: M. C. Boyce
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The thesis is dedicated to the silent and powerful personality whose letters over the past six years have kept me going in times where the world was falling apart.
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Chapter 1

Introduction

Poly(ethylene-terephthalate) (PET) is a thermoplastic material found in numerous commercial applications in the form of films of different thickness, crystallinity and orientation. It is used frequently in photographic films, electrical applications (high quality electrical insulation cable wraps) and food packaging. The primary modes of PET processing are blow molding, vacuum forming, drawing, and biaxial stretching. During these processing modes, the polymer can take either an oriented amorphous or semicrystalline structural state. It thus exhibits the interesting feature of being able to undergo crystallization during processing; a phenomenon that is often termed strain or stress-induced crystallization. The occurrence of strain-induced crystallization provides increased stiffness and hardness as well as better dimensional stability or resistance to recovery.

Hence, the processing of PET near, in, or slightly above its glass transition temperature combined with its ability to crystallize during straining makes this material not only commercially viable but also of significant interest to the polymer scientist and mechanical engineer. PET has been the subject of numerous investigations over the past thirty years, some of which will be reviewed below. In the work of this paper we will present our recent research into the three dimensional rate and temperature dependent large strain deformation behavior of PET.

In Chapter 2, experiments are presented which sample the mechanical behavior
of the material under different states of large strain and over a wide range of temperatures spanning the glassy, the glass transition and the rubbery regime. The Differential Scanning Calorimetry Method (DSC) is then used to determine the crystallinity content as a function of the mechanical loading (strain state, magnitude of imposed strain, temperature of the imposed strain). The DSC together with the mechanical tests permit the assessment of any potential contribution of crystallization to the strain hardening process. Chapter 3 presents the constitutive model for the finite deformation of PET. The constitutive description of the flow process, strain softening, coupled with the constitutive description of the strain hardening via an entropic network-based model is the focus of the discussion. The model, with parameters reduced from isothermal and nearly isothermal uniaxial compression tests, is found to capture the experimentally observed deformation behavior of PET and can be used to simulate inhomogeneous deformations that occur in industrial-scale sheet stretching processes. Chapter 4 presents simulations of constrained stretching at elevated temperatures and high strain rates. The effects of non-homogeneous deformation temperature and initial film imperfections on the mechanical behavior and end state of the film are discussed and compared.
Chapter 2

Experimental Work

2.1 Background

Research on the mechanical behavior of PET starts, for example, with the early work of Marshall, Thompson [1]-[3] and Ward [4], and extends to current research e.g., [13]-[19]. A variety of experimental and analytical investigations, only a few of which are mentioned here, have examined the effects of temperature, deformation rate, state of deformation, material anisotropy and heat transfer on the elastic, plastic and finite deformation behavior of PET.

Early work by Marshall [1] on the continuous, heated drawing of initially amorphous PET examined the sensitivity of necking and the corresponding natural draw ratio (NDR) to deformation temperature (20°C to 80°C) and draw speed (5–70 cm/s). It was shown that NDR increases with decreasing temperature and increasing speed. In other work at deformation temperatures above $T_g$ (i.e. 100°C), Thompson [3] studied the stress-extension curves produced in roller drawing. It was found that rapid draw speed deformations result in large strain hardening of the material at extensions of the order of 300%. Subsequent X-ray analysis revealed high crystallinity in the drawn fibers; hence, strain hardening was attributed to the development of strain-induced crystallization. Ward [4] examined the cold drawing of PET at room temperature over a range of deformation conditions and for different polymer constitutions,
i.e., different values of cross linking, pre-orientation and initial crystallinity content. Birefringence and moduli of cold drawn fibers were fitted by a simple model which assumed that the drawn fiber consists of an aggregate of mechanically anisotropic units that were aligned by the drawing process. Also determination of the natural draw ratios and shrinkages of slightly pre-oriented fibers showed that the natural draw ratio could be regarded as equivalent to a network stretched to its limiting extension. In other work, Ward et al. [5], collected data over a variety of temperatures and rates in order to examine its pressure sensitivity.

In other work on strain-induced crystallization, Misra et al. [16] investigated the microstructure of PET films stretched both below and above Tg using small angle light scattering, optical microscopy and wide angle X-ray scattering. Annealing the necked portions of the samples that were stretched to 200% below $T_d$ (25°C) resulted in considerable crystallinity. For the samples tested above Tg and subsequently quenched to 0°C, crystallinity was found to increase considerably after a strain of 0.8 at a test temperature of 80°C and a strain rate of 300%/min. In relatively recent work, Jabarin et al. [11]-[12] have investigated extensively the strain-induced crystallization phenomenon in the rubbery region through the simultaneous and sequential biaxial stretching ¹ of initially amorphous films at temperatures above $T_p$ (80°C to 105°C) and strain rates that range from 5%/s to 200%/s up to limiting extension ratios of 4. It was shown that under these conditions PET undergoes strain-induced crystallization. The crystallization is manifested as a pronounced increase in strain hardening that commences at a temperature and strain rate dependent level of strain, termed the strain hardening parameter. When deformation is slow, however, strain-induced crystallization does not occur since relaxation phenomena dominate over orientation phenomena and the strain hardening modulus is low. The crystalline content of the deformed specimens are assessed from density measurements and the orientation from birefringence; both consistently show the structural evolution of PET from amorphous

¹The stretch state that is induced in the material from the simultaneous biaxial extension is very similar to that induced from the uniaxial compression mode
to semicrystalline with finite strain deformation.

Porter et al. [13] - [15] have conducted extensive tests on the deformation of PET and poly(ethylene2,6-naphthalate) (PEN) and subsequently have investigated the effects of extent of deformation and deformation temperature on the material microstructure. More specifically, Ghanem and Porter [13] performed isothermal solid state coextrusion tests on isotropic amorphous PEN below and above its $T_g$ and subsequently studied the behavior of the cold crystallization temperature ($T_{cc}$) with extrusion temperature and draw ratio. Their DSC analysis revealed that $T_{cc}$ decreases markedly with increasing draw ratio and goes through a minimum in the vicinity of the glass transition region. Also, strain-induced crystallization was found to increase with draw ratio and draw temperature to a saturation value. Guan, Wang and Porter [14] studied the planar deformation of PET in equal bi-axial stretching and forging at temperatures above $T_g$, i.e. 80°C to 110°C, and monitored the structural evolution of PET with DSC, wide angle X-ray scattering, density and recovery measurements. They observed that, as the biaxial draw ratio increases at 90°C, the area of the cold crystallization exotherm decreases, thus manifesting the presence of strain-induced crystallization upon large deformations. Their tests also demonstrated that thermal relaxation processes become more pronounced as the deformation temperature increases away from $T_g$, therefore, hindering crystallization. Sun, Pereira and Porter [15] conducted solid state coextrusion on initially amorphous PET below $T_g$, 50°C to 70°C, at various draw ratios and subsequently evaluated the cold crystallization behavior of the co-extrudates. They found that $T_{cc}$ decreases with extrusion draw ratio and also that for extrusion draw ratios up to 2.5, $T_{cc}$ decreases with extrusion temperature whereas above that value the trend is reversed. Finally, Buckley et al. [17] have recently conducted deformation tests on initially amorphous PET under conditions of biaxial stress at elongation rates ranging between 1 – 32/s and temperatures ranging between 75°C to 120°C. They found the yield stress to decrease with increasing temperature and/or decreasing elongation rate and large strain hard-

\[2\text{A tensile draw ratio of } 2.5 \text{ is analogous to a tensile logarithmic strain of } 0.92.\]
ening to initiate at nominal strains of the order of 1.5. Density measurements that were performed on biaxially deformed samples showed that crystallinity increases with maximum principal strain.

It is evident from the above review that a comprehensive set of mechanical tests with subsequent microstructural analysis on the deformed material can provide a picture of the structural evolution of PET; increasing the extent of deformation acts to orient the macromolecular network that under favorable conditions such as high temperature and rapid deformation rate, leads to strain-induced crystallization. The current work examines the mechanical behavior of initially amorphous PET in the glassy and glass transition regions where the effects of thermal aging and the relative importance of configurational to intermolecular energy barriers to deformation are still not well modelled. It also moves further in the rubbery region in the attempt to characterize strain-induced crystallization phenomena. The experimental part of the investigation, i.e. mechanical tests and microstructural analysis, is presented here in detail in this paper and thus serve as a basis for the constitutive modeling that is presented in the following sections.

2.1.1 Material/ Specimen Description

The material that was used in our experiments is amorphous isotropic PET supplied in sheet form from ICI Films of England; the average thickness of the sheet is 1.73\(mm\). The material appears optically clear, thus implying a very low crystallinity content; DSC measurements revealed a residual crystallinity of the order of 9%\(^3\). The small amount of residual crystallinity is a result of the practical difficulties encountered in quenching the polymer rapidly from the melt, i.e., controlling the film thickness, the temperature of the cooling drum, etc. in the effort to obtain an initially amorphous material. Birefringence measurements on similarly prepared ICI film indicate a high degree of isotropy [17] for the received film. Uniaxial and plane strain compression

\(^3\)Crystallinity was estimated from DSC analysis. From the measured enthalpies of cold crystallization and melting and a heat of fusion for PET crystals equal to 120\(kJ/kg\), the crystallinity content was estimated assuming a two phase model
tests were conducted in order to explore the material behavior. In previous compression tests on thermoplastics (see for example Arruda et. al [10]), test specimens were machined from bulk. Also, a specimen height to diameter ratio of unity, using Teflon sheet as a lubricant between the specimen and compression platen surface, was found to provide excellent conditions for obtaining homogeneous deformations and thus accurate true stress vs. true strain data. Typically, specimen heights were approximately 12\textit{mm}. In the current work, the sheet thickness is only 1.73\textit{mm} which poses the problem of specimen size, especially when considering that the material will be compressed to a true compressive strain of $-1.75$, therefore, causing a height reduction of the order of 85%.

Trial experiments on commercially available bulk polycarbonate (PC) guided the compression specimen design for the PET sheet. Room temperature uniaxial compression tests at a strain rate of 0.001/s were conducted with PC samples of variable height to diameter ratio. It was found that samples with an initial height to diameter ratio in the range of 0.4 – 1.1 provided identical stress vs. strain results indicating little influence of sample size and/or friction on the measurement thus providing a sound basis for subsequent material testing. Given those results, an initial height to diameter ratio of 0.45 was chosen for the PET sheet. The specimens were then prepared in a series of steps: Initially, disks of 19.05\textit{mm} diameter were stamped out of the polymer film with a sharp punch that was fitted to a manual press. Owing to the shape of the punch, the cutting operation did not result in any noticeable plastic deformation around the disk circumference. The disks were then machined down in a lathe to a final diameter of 12.7\textit{mm}. The machining operation increased the dimensional accuracy considerably and eliminated any effects of the cutting operation. In order to provide the desired initial height to diameter ratio of .45 a stack of three disks was used as a test specimen. Finally, in order to eliminate the possibility of slippage between the disks in the course of the experiment, the two disk to disk interfaces were roughened with coarse grid sand paper \(^4\). A photograph of an undeformed and one

\(^4\)Increasing the number of disks per sample from three to four in order to achieve a sample less
deformed (to a logarithmic strain of \(-1.5\)) specimen is shown in Fig. 2.1.1-1.

A similar rationale, but a different cutting process, was used to produce specimens for the plane strain compression tests: Rectangular pieces of width \(w = 9.53\text{mm}\) and length \(l = 8.64\text{mm}\) were cut in a horizontal milling machine with the use of a fine-tooth blade: a \(0.5\text{m} \times 0.5\text{m}\) piece of the PET sheet bolted on a polymeric frame was clamped on the horizontal milling machine and cut. The cutting operation did result in some plastic deformation at the edges of the produced rectangles; the specimen irregularities were carefully removed with the use of razor blade and fine grid sand paper. As in the case of the uniaxial compression sample, each plane strain compression sample consisted of a stack of three rectangles in order to keep the possible effect of the interfaces the same for both experimental conditions and, more importantly, achieve a height to diameter ratio in the size and friction free limits mentioned above. With the above described process an initial height to length ratio of the order of 0.56 was achieved. The samples produced with the above procedures, were found to give nearly homogeneous deformations to a final (uniaxial and plane strain) true strain of \(-1.3^5\).

### 2.1.2 Description of Mechanical Tests

Uniaxial and plane strain compression tests over a range of strain rates and temperatures were conducted in order to measure the stress vs. strain behavior of PET as a function of strain state, strain rate and temperature. The temperature range spans from \(25^\circ C\) to \(80^\circ C\) where the glass transition temperature is approximately \(73.5^\circ C^6\). The strain rate range spans from the slow isothermal rate of \(-0.005/s\)

---

5Some inhomogeneous deformation occurred at the ends of the plane strain specimen due to the one layer locally rolling over the other layer. This end effect did not affect consistency or repeatability of stress versus strain results prior to strains of \(-1.3\); some effects were observed from strains of \(-1.3\) to \(-1.5\).

6As measured from DSC analysis at \(10^\circ C/min\).
to a fast adiabatic rate of \(-0.5/s\). Compression modes were chosen over the tensile mode, since at some temperatures tension typically results in inhomogeneous deformations at finite strains (i.e. necking). In addition to the necking inhomogeneity, PET has been shown to craze when stretched in tension at temperatures right below the glass transition. Also a uniform specimen temperature is more easily maintained in compression tests; therefore, a set of compression experiments provides excellent conditions for examining the inherent material constitutive behavior.

The mechanical tests were performed on an Instron 1350 servohydraulic machine using a Macintosh for control and real time data acquisition via a Keithley 550 D/A and A/D interface. The tests were performed in the strain control mode with an 2620-824 extensometer in order to eliminate the Instron load train compliance errors and obtain best accuracy in the measurement of deformation at high levels of true strain. During experimental time, strain (a logarithmic strain measure is used) was monitored as a function of time and fed back to the controller in order to alter the actuator displacement rate to provide constant strain rate conditions during the large strain tests. For the elevated temperature tests, a radiant furnace was used to bring the sample to the desired experimental temperature. The time required for the environment of the furnace to reach thermal equilibrium was between 20 and 30min\(^7\).

The sensitivity of the mechanical properties of the material at test temperatures near \(T_g\) motivated a careful temperature control for the mechanical tests. In the uniaxial compression mode the specimen temperature was monitored prior to and during the course of the experiment with three type-K thermocouples that were positioned in different positions on the sample circumference and extra thermocouples welded on the stationary (top) compression platen of the Instron. The latter thermocouple allowed the monitoring of temperature in the course of the experiment when all other thermocouples were no longer in contact with the sample. Furthermore, in the plane

\(^7\)According to Imai et al. [20], the induction period for crystallization of melt quenched PET due to annealing at 80°C is \(\approx 100\)min. Having annealed our samples in the thermal environment of the furnace for much shorter times and at lower temperatures we argue that we have not crystallized our samples prior to testing. This is evident from the DSC results presented later in the paper.
strain compression mode, thermocouples were welded on the plane strain fixture and some were positioned in the fixture in contact with the specimen. Our method allowed us to obtain reasonably consistent results over a wide range of temperatures. For further details on our experimental procedure the reader is referred to [8],[9],[10],[22].

Due to the range of the strain rates, the duration of the tests varied from approximately 3 sec for the $-0.5/s$ rate to 300 sec for the $-0.005/s$ rate. We note that the inelastic nature of the deformation results in heat dissipation which may or may not produce a temperature rise in the specimen during the test depending on the strain rate and the experimental temperature of the test. It should be apparent that the faster the rate, the less time for heat transfer hence the more important the adiabatic effects. Also the higher the experimental temperature, the smaller is the value of the plastic work input to the sample and hence the lower the temperature rise under heating conditions. We classify a test as isothermal, thermo-mechanically coupled or adiabatic by comparing the duration of the loading part of the test, $t_{exp}$ to the time required for heat to transfer out of the specimen $t_{cond}$ with the following first order analysis: If $h_i$ is the instantaneous height of the sample and the dominant mode of heat transfer in the course of the experiment is conduction of heat from the uniaxially compressed sample to the compression platens, then, the characteristic length that controls the heat transfer is the distance from the platen to the center of the sample; namely half the current sample height, $h_i$. It follows that the time required for heat to escape the sample, $t_{cond}$ is given as,

$$t_{cond} = \frac{(h_i/2)^2}{2k/\rho c}$$

(2.1)

where, $k = 0.218 W/mK$, is the thermal conductivity, $\rho = 1330 g/cm^3$, is the density of amorphous PET and, $c = 1300 J/kgK$, is the specific heat capacity\(^8\). For a constant strain rate test the loading time required to reach the final strain $t_{exp}$ is given

\(^8\)Property values extracted from the Polymer Handbook [24]
by the ratio of the imparted strain \( \varepsilon_f = -1.5 \) to the strain rate \( \dot{\varepsilon} \). The calculations presented in Table 1 show that the experimental time is much shorter than the heat transfer time for the \(-0.5/s\) rate, hence, the heat transfer conditions during the latter rate are expected to be adiabatic.

<table>
<thead>
<tr>
<th>strain rate(1/s)</th>
<th>-0.005</th>
<th>-0.01</th>
<th>-0.1</th>
<th>-0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_{exp}(s) )</td>
<td>300</td>
<td>150</td>
<td>15</td>
<td>3.0</td>
</tr>
<tr>
<td>( t_{cond}(s) )</td>
<td>10.349</td>
<td>10.349</td>
<td>10.349</td>
<td>10.349</td>
</tr>
<tr>
<td>( \frac{t_{exp}}{t_{cond}} )</td>
<td>28.98</td>
<td>14.49</td>
<td>1.449</td>
<td>0.289</td>
</tr>
<tr>
<td>heat transfer condition</td>
<td>isothermal</td>
<td>isothermal</td>
<td>coupled</td>
<td>adiabatic</td>
</tr>
</tbody>
</table>

Table 1: Comparison of unsteady conduction time to experimental time.

The same first order analysis can be applied for the plane strain compression tests that were performed at the \(-0.01/s\) rate. In the latter case, conduction occurs in two directions namely to the sidewalls and simultaneously to the top and bottom of the steel plane strain fixture. The dominant heat transfer time for the latter experiment is the largest of the two conduction times and, therefore, corresponds to the maximum between the two controlling dimensions, namely, the specimen width and height. It is apparent that the width of the sample which remains constant through the experiment is the controlling characteristic length. Calculations with the use of eqn.(2.1) show the time required for heat to escape is \( \approx 90\,\text{sec} \) hence the rate is isothermal.

2.1.3 Description of DSC Measurements

Differential Scanning Calorimetry monitors the rate of change of enthalpy of the material as a function of increasing temperature at a given heating rate. Information on the microstructure and internal energy content of the material can be obtained from the DSC scan through proper data reduction and interpretation. We note that aspects of the DSC scan, e.g. the exact location of the glass transition temperature, are somewhat dependent on the imposed heating rate and that the kinetic effects cannot be eliminated from the DSC readings. Therefore, care must be taken in choosing a
heating rate and only thermograms with the same rate should be compared with one another when interpreting the enthalpy content in the polymer. Furthermore, a compromise should always be sought between a fast rate that would cause non-uniform heating of the sample and a very slow rate that could cause aging of the sample in the DSC pan. For that purpose our work was performed at a rate of $10^\circ C/min$ and with sample weights ranging from 10 to $20\text{mg}$. This is a set of experimental conditions that have been shown to give repeatable results and is typical for polymer samples [6]. All DSC measurements were performed on a Perkin-Elmer DSC-7A with ice as the cooling medium. The instrument was initially calibrated with two known calibrants, Zinc and Indium. A baseline run was then conducted at the same heating rate in order to measure the residual enthalpy rate between the reference and sample pans. The baseline was subtracted from the subsequent thermograms of the polymer samples during real time. DSC thermograms were taken on the as-received material as well as on samples deformed at different temperatures, strain rates, strain states and to different final strains in order to assess the effects of deformation conditions on crystallization.

2.2 Experimental Results

In this section, results from the mechanical tests and the DSC measurements are presented. Effects of temperature, strain rate and imparted strain are discussed separately for the mechanical tests. For the DSC results glass transition phenomena are discussed first and cold crystallization phenomena follow.

2.2.1 Mechanical Tests

Uniaxial compression and plane strain compression tests were conducted from $25^\circ C$ to $80^\circ C$ and strain rates of $-0.005/s$, $-0.01/s$, $-0.1/s$ and $-0.5/s$. The results of the

---

6DSC specimens were cut carefully from the deformed sample centers, with the help of a Buehler Isomet low speed saw, in order to eliminate any end effect phenomena from the compression tests on the subsequent DSC readings.
tests are presented in terms of true stress vs. true strain. The true strain, $\epsilon$, is defined as the natural logarithm of the current height, $h_i$, to the initial height $h_o$, namely, $\epsilon = ln(h_i/h_o)$. The true stress is the ratio of the current force $F$ to the current area $A$, namely, $\sigma = F/A$, where the current area is computed using the measured current height and assuming incompressibility of inelastic deformation.

Fig.2.2.1-1 shows a set of isothermal uniaxial compression loading - unloading curves at a temperature of $25^\circ C$, strain rate of $-0.01/\text{s}$, to final strains of $-0.3$, $-0.6$, $-0.9$, $-1.2$ and $-1.5$ respectively. Initially, the deformation is linear elastic with the stress increasing proportionally with strain. Then, there is a nonlinear region prior to yield where the stress reaches a maximum with a corresponding yield strain of approximately $-0.07$. After yield, the stress is observed to decrease with increasing strain (i.e. strain soften) to a minimum which we term the flow stress. This is the strain softening phenomenon also observed in poly(methyl-methacrylate) (PMMA), polystyrene (PS), and PC, for example, by Arruda and Boyce [10] and then Hasan and Boyce [7]. After strain softening, a monotonic increase in the true stress with true strain is observed and the material is said to strain harden. The strain hardening is observed to be nonlinear with the hardening slope increasing with strain. The unloading profiles of the tests show that during unloading the material initially behaves in a linear elastic manner followed by nonlinear recovery. The degree of nonlinear recovery increases with increasing strain and some additional recovery occurs after unloading. The amount of additional recovery is shown in Table 2, where, for each test shown in Fig.2.2.1-1, the imparted strain, final strain after unloading and measured residual strain after 48hrs are reported. The residual strain is a manifestation of plastic deformation locked in the material at that particular deformation temperature.
<table>
<thead>
<tr>
<th>imparted strain</th>
<th>res. strain after unloading</th>
<th>res. strain after 48 hrs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>0.26</td>
<td>0.20</td>
</tr>
<tr>
<td>0.6</td>
<td>0.55</td>
<td>0.45</td>
</tr>
<tr>
<td>0.9</td>
<td>0.83</td>
<td>0.72</td>
</tr>
<tr>
<td>1.2</td>
<td>1.1</td>
<td>0.96</td>
</tr>
<tr>
<td>1.5</td>
<td>1.32</td>
<td>1.17</td>
</tr>
</tbody>
</table>

Table 2: Imparted strain, residual strain immediately after unloading and residual strain after 48 hrs for the uniaxial compression at 25°C and -0.01/s.

<table>
<thead>
<tr>
<th>Temperature (C)</th>
<th>-0.005/s</th>
<th>-0.01/s</th>
<th>-0.1/s</th>
<th>-0.05/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>1.26</td>
<td>1.21</td>
<td>1.16</td>
<td>1.18</td>
</tr>
<tr>
<td>76</td>
<td>0.79</td>
<td>0.56</td>
<td>0.79</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Table 3: Residual strain measured 48 hrs for the uniaxial compression to an imparted strain of -1.5 at 60°C, 76°C and -0.005/s to -0.5/s.

Below the effects of temperature, strain rate and strain state on the distinctive features of the mechanical behavior, elasticity, onset of plastic deformation, strain softening, strain hardening are examined.

**Effects of deformation temperature:** Fig. 2.2.1-2 shows the isothermal uniaxial compression in the glassy region at 25°C, 50°C and 60°C at a strain rate of -0.01/s, thus, demonstrating the effect of temperature in the glassy region. It is evident, that as the temperature increases, the elastic modulus, yield stress and flow stress decrease. Strain softening \(^{10}\) is insensitive to temperature and occurs over the same level of true strain for all three temperatures. Subsequent to strain softening, strain hardening decreases moderately with temperature.

Figs. 2.2.1-3 through 2.2.1-6 show the isothermal uniaxial compression in the glass transition region over the temperature range of 60°C to 76°C at strain rates of -0.01/s and -0.1/s thus demonstrating the effects of deformation temperature on the mechanical behavior in that region. From the two figures it is observed that:

\(^{10}\)decrease in the difference between the yield stress and the flow stress with strain
1. As the deformation temperature increases, the elastic compressive modulus \(^{11}\) decreases monotonically with temperature.

2. As the deformation temperature increases, the yield stress and flow stress decrease. However, the yield stress decreases more rapidly with increasing deformation temperature than the flow stress.

3. The height of the aging peak (percent difference in peak stress vs. flow stress), which was insensitive to experimental temperature up to 60\(^\circ\)C, decreases at a rapid rate in the vicinity of \(T_p\) \(^{12}\). Strain softening from the yield to the flow stress occurs over the same level of true strain for both strain rates.

4. The strain hardening subsequent to yield is not sensitive to deformation temperature between 60\(^\circ\)C and 76\(^\circ\)C.

Fig.2.2.1-7 shows the adiabatic uniaxial compression in the rubbery region at 80\(^\circ\)C at a strain rate of \(-0.5/s\) to final imparted strains of \(-1.25, -1.5\) and \(-1.75\) respectively. PET flows without any apparent yielding under these conditions since the experimental temperature is above the glass transition; however, the strain hardening modulus is much more pronounced than that observed in tests at temperatures between 60\(^\circ\)C to 76\(^\circ\)C range at the same deformation rate.

Effects of strain rate: Equally interesting are the effects of strain rate on the mechanical behavior: Fig.2.2.1-8 shows the uniaxial compression results at a temperature of 25\(^\circ\)C, to a final true strain of \(-1.5\) and strain rates \(-0.005/s, -0.01/s, -0.1/s\) and \(-0.5/s\). The tests for the three slowest rates exhibit nearly identical elastic plastic and subsequent strain hardening behavior indicating low strain rate sensitivity at this temperature. However, the test at \(-0.5/s\) that has been shown

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\(^{11}\)The elastic modulus was measured as the steepest slope of the stress strain curve at each experimental condition. Comparison of companion Dynamic Mechanical Analysis (DMA) modulus measurements with the above method were found in reasonable agreement

\(^{12}\)The fact that it is slightly higher for the 60\(^\circ\)C data than for the 25\(^\circ\)C and 50\(^\circ\)C could be attributed to the heating prior to testing in the thermal environment of the furnace resulting in some additional aging; these effects are discussed in greater detail in the Differential Scanning Calorimetry Section.
in the previous first order analysis to be adiabatic exhibits a lower flow stress. The decrease in flow stress can be explained from the increase in temperature that results in the thermal softening of the material due to the adiabatic condition of the test. That effect leads to a lower apparent flow stress for the rapid test when compared to the slower strain rates. Hence the finding proves to be consistent with the first order analysis presented earlier \textsuperscript{13}. PET should therefore be expected to exhibit thermal softening when tested at rapid rates in the glassy regime. Fig. 2.2.1-9 shows the uniaxial compression results at a temperature of 76\textdegree{}C to a final true strain of $-1.5$ and strain rates $-0.005/s$, $-0.01/s$, $-0.1/s$ and $-0.5/s$. The results show that the elastic modulus, yield and flow stress exhibit a pronounced sensitivity to strain rate in the $T_g$ region.

The most interesting result appears to come from the deformation of PET in the rubbery regime. Fig. 2.2.1-10 shows the uniaxial compression at 80\textdegree{}C and strain rates of $-0.005/s$ and $-0.5/s$. In the rubbery regime the plasticity mechanism is inactive and hence the related phenomena, i.e. yield, strain softening, are absent. The distinctive difference between the rapid and slow rate occurs in the strain hardening behavior: the $-0.5/s$ rate deformation exhibits large strain hardening behavior much greater than that of the $-0.005/s$, suggesting the presence of strain-induced crystallization at $-0.5/s$. The hardening rate at $-0.005/s$ is lower than that observed in the 76\textdegree{}C data suggesting a molecular relaxation process dominating as temperatures get higher and strain rates lower. The result is consistent with the experimental observations of Jabarin et al. [12].

Figs. 2.2.1-11 through 2.2.1-14 summarize the effects of temperature and strain rate on the mechanical behavior in the glassy and glass transition region as they are reduced from the stress vs. strain data. The variation of the elastic modulus with temperature and strain rate is shown in Fig. 2.2.1-11. The variation clearly shows that the material is in the glassy region from 25\textdegree{}C to 50\textdegree{}C and in the glass transition region from 60\textdegree{}C to 76\textdegree{}C. It also shows that the rate of deformation

\textsuperscript{13}the apparent decrease in the flow stress is also observed in other polymers (see Arruda et al. [24])
clearly affects the precise value of the glass transition temperature as is well known: $T_g$ increases with increasing strain rate. Furthermore, Figs. 2.2.1-12 and 2.2.1-13 show the decrease in yield and flow stress with increasing temperature and decreasing strain rate. Note the nearly linear variation of the flow stress data with the natural logarithm of the plastic strain rate \(^{14}\) as shown in Fig.13: This type of variation suggests the exponential dependence of the flow stress to the plastic strain rate over a wide range of temperatures in the glass transition regime, a finding which is consistent with data from other polymers. Finally, our data show that as the temperature increases the amount of recovery upon unloading increases. This is evident from the variation of the specimen residual strain with temperature (see Table 3) which demonstrates that uniaxial compression below $T_g$ does not result in full recovery even at 76°C.

**Effects of state of strain:** Plane strain compression tests were performed at an isothermal constant strain rate of $-0.01/s$ in the same range of temperatures; results for the $-0.01/s$ rate and deformation temperatures of 60°C to 76°C are presented in Fig.2.2.1-15. When compared to the uniaxial compression results, the latter results differ from the former in the initial yield, strain softening and the finite strain behavior. Direct comparison can be seen in Fig. 2.2.1-16 for glassy and glass transition region behavior respectively. Both figures show that the yield stress is slightly higher in plane strain compression than in the uniaxial compression tests. The trend can be explained partly from the apparent increase in yield stress due to the state of strain (if we employ the von Mises criterion.) and partly from the hydrostatic pressure effect on the yield stress \(^{15}\). The different strain hardening behavior observed here under the two states of strain where the plane strain is much harder, has also been observed in PMMA and PC by Arruda et al. [22] where it was found that the difference can be attributed to the evolution in molecular orientation with state of strain for poly-

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\(^{14}\)The plastic shear strain rate $\dot{\gamma}_p$ is related to the experimental compression strain rate $\dot{\epsilon}_p$ by the von Mises relation: $\dot{\gamma}_p = \dot{\epsilon}_p \sqrt{3}$ and the flow stress $\sigma$ is related to the shear flow stress $\tau$ by: $\tau = \frac{\sigma}{\sqrt{3}}$

\(^{15}\)The pressure effect has been thoroughly investigated by Ward et. al [5] who noted a pressure, $p$, dependence on the yield of PET of the order of $a = 0.175$ in $\tau = \tau_o + ap$ if $\tau$ and $\tau_o$ are the pressure modified and unmodified shear yield stresses respectively.
mers which remain amorphous after deformation. In the case of PET, this difference on strain hardening may also be due to strain-induced crystallization. The effects of deformation on both energy storage and crystallization are evident from the DSC measurements that follow.

2.2.2 Differential Scanning Calorimetry Tests

DSC scans were performed on samples in the as-received condition as well as samples which were deformed in uniaxial and plane strain compression to different levels of imparted strain at different temperatures and strain rates in their unloaded condition. The DSC results enable the assessment of physical aging phenomena through analysis of the glass transition behavior, as well as percent crystallinity content through analysis of the cold crystallization behavior.

Fig. 2.2.2-1 shows a standard thermogram, i.e., the variation of heat flow into the sample as a function of increasing temperature, at a constant heating rate of 10°C/min on the as-received PET. At that particular heating rate, the glass transition temperature $T_g$ is observed at approximately 73.5°C. The observed value is consistent with our mechanical tests which show the rapid decrease in the yield and flow stress and the erasure of the aging effect when the deformation (uniaxial / plane strain compression) temperature approaches $73 \pm 1°C$. The glass transition does not exhibit a smooth enthalpic transition indicating that the material has undergone physical aging, where aging manifests itself as the well known endothermic overshoot at $T_g$. Furthermore, as the temperature is increased beyond $T_g$ the material begins to crystallize in the DSC pan, where the onset of the cold crystallization exotherm, $(T_{cc})$ is observed at $137°C$ at this rate of heating and the area of cold crystallization $(A_{cc})$ equals $32J/g$. As the temperature is increased further, the crystals begin to melt at an approximate temperature of $239\pm1°C$. The melting of the crystals manifests itself as a wide endotherm whose peak is approximately at $252 \pm 1°C$ and its area $(A_m)$ equals $45J/g$.

Based on a two phase (crystalline-amorphous) model, the weight percent crys-
tallinity of the as-received material can be estimated. The weight percent crystallinity $p_c$ is given as,

$$p_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_f}$$  \hspace{1cm} (2.2)

where $\Delta H_{cc}$ is the enthalpy released during cold crystallization, $\Delta H_m$ is the enthalpy required for melting and $\Delta H_f$ is the enthalpy of fusion of PET crystals, taken to be equal to $120J/g$.\(^{16}\)

Eqn.(2.2) gives an initial crystallinity content for the received material of the order of 9%. It should be noted that this kind of quantitative analysis from DSC data requires fully corrected data i.e. elimination of residual enthalpy readings from the signal and appropriate choice of integration limits since the accuracy of the method depends heavily on the measurement of the crystallization and melting areas with respect to the fully corrected baseline\(^{17}\). Furthermore, in order to ascertain the possible effects of the furnace thermal environment on the material prior to mechanical testing, we heated as-received PET at $65^\circ C$ and $75^\circ C$ for 30min and then cooled to room temperture in the furnace. The temperatures chosen are characteristic of the temperatures at which mechanical deformation was later imparted and the heating time chosen far exceeds the characteristic residence time of the sample in the furnace prior to and in the course of testing. For the two thermal treatments, the glass transition behavior is slightly different, namely, the endothermic overshoot is pushed to a lower temperature. At the same time, the imposed thermal history does not change the onset temperature and energy magnitude of the cold crystallization exotherm, therefore indicating that heating the material to the desired test temperature maintains the amorphous structure of the sample.

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\(^{16}\)Private communication with Dr. D.P. Jones of ICI Films, England.

\(^{17}\)There are several methods for the measurement of crystallinity such as N.M.R. X- Ray, density etc. For a comprehensive review of these methods see ref.[19]. For other applications of the above method see refs. [13],[14],[18].
Glass transition phenomena in the glassy and glass transition regions:

The results from the mechanical tests demonstrate that the finite strain mechanical behavior of the amorphous PET is characterized by elastic followed by inelastic deformation. As in the case of other initially amorphous polymers, we expect that the active deformation mechanisms will affect the enthalpy temperature profile on the DSC thermogram. Fig. 2.2.2-2 shows the effects of different levels of imparted strain on the glass transition behavior at an experimental temperature of 25°C and a rate of \(-0.01/s\). It can be seen that as the imparted strain increases the endotherm related to aging diminishes and in turn two exotherms appear in the \(T_g\) region (one just prior and one just after \(T_g\)) that evolve with imparted strain. These exotherms indicate the occurrence of energy storage in the polymer due to inelastic deformation [6].

A further effect to be investigated is that of the deformation temperature ranging from 60°C to 76°C on the \(T_g\) region when the samples are deformed to an imparted strain of \(-1.5\). Figs. 2.2.2-3 through 2.2.2-6 show the effect of test temperature on uniaxially compressed samples at rates of \(-0.01/s\) and \(-0.1/s\) respectively. Two interesting signatures occur: The exotherm only appears at temperatures beyond the test temperatures, as should be expected, and, therefore, the broad pre-\(T_g\) exotherm which appeared in the 25°C deformed samples is absent in these cases. With the post-\(T_g\) exotherm still present, an endotherm appears in the vicinity of \(T_g\). The energy of the endotherm \(^{18}\) increases and its onset shifts to the right with test temperature therefore indicating that it is related to the annealing effect of the furnace on the sample prior to and during the course of testing. Therefore, any erasure of this endotherm (as in the 25°C data) due to inelastic deformation is undone by the annealing effect during testing.

Cold crystallization phenomena in the glassy, glass transition and rubbery region:

Deformation is also observed to impact the crystallization in the DSC analysis. Fig. 2.2.2-7a shows the effects of different levels of imparted strain on \(T_{cc}\) for samples

\(^{18}\)The energy of the peak is equal to its area in units of J/g
strained in uniaxial compression at $-0.01/s, 25^\circ C$. It can be seen that as the imparted strain increases, $T_\infty$ decreases markedly; a result most likely due to the orienting of the macromolecular network creating a more favorable structure for crystallization. Also, the area of the cold crystallization exotherm remains invariant to strain ($\approx 31 J/g$) thus showing that the microstructure of the deformed and then unloaded samples is still amorphous. Fig 2.2.2-7b shows the effects on $T_\infty$ of the different levels of imparted strain at the same deformation rate and temperature for samples strained in plane strain compression. The more pronounced strain hardening of the plane strain condition can, in part, be attributed to stronger network orientation that in turn manifests itself as lower $T_\infty$ in the DSC thermogram. However, not only are the onset temperatures of the exotherms lower in plane strain, but the cold crystallization area of the sample strained to $-1.3$ is now smaller than $\approx 32 J/g$, about $\approx 21 J/g$, indicating an estimated crystallinity of the order of 23%. It is not clear whether the crystallinity is concurrent with deformation or occurs immediately after, however, it appears that the amount of stretching is sufficient for macromolecules to lock in a stable crystalline configuration even when deformation is imparted at $25^\circ C$.

Figs. 2.2.2-8 through 2.2.2-11 show the effects of imparted strain of the order of $-1.5$ applied at different deformation temperatures from $60^\circ C$ to $76^\circ C$ at $-0.01/s$ and $-0.1/s$ strain rates respectively in uniaxial compression: Comparing the thermograms of the samples deformed under these conditions to that of undeformed PET we see that:

1. $T_\infty$ after an applied strain of $-1.5$ is significantly lower than that of the undeformed sample for all deformation temperatures. We also note $T_\infty$ decreases with deformation temperature and that the cold crystallization exotherm area may become more diffuse as the temperature at which strain was imparted increases.

2. The area of the crystallization exotherm is practically constant $\approx 32 J/g$ for the uniaxial compression temperatures considered ($25^\circ C$ to $76^\circ C$). The areas of the corresponding melting endotherms, not shown here, are also constant as
one would expect, where their onset is observed at \( \approx 239 \pm 1^\circ C \) and their areas are constant and equal to \( \approx 44J/g \). Our melting endotherm characteristics are consistent with the values reported by Guan et al. [14].

3. From eqn.(2.2) and the conditions examined above it follows that strain-induced crystallization is absent at temperatures below and in the glass transition region over the rates examined when the material is deformed in uniaxial compression.

4. As deformation temperature increases the onset of cold crystallization exotherm decreases. However, no marked difference in strain hardening was observed for the mechanical tests at the range of deformation temperatures.

The results of the DSC scans on the samples deformed in plane strain compression in the same temperature range of 60°C to 76°C and at a strain rate of \(-0.01/s\) are shown in Fig. 2.2.2-12: The following trends should be noted:

1. \( T_\infty \) after an applied strain of \(-1.5\) is significantly lower than that of the undeformed sample for all deformation temperatures as well as the \( T_\infty \) values of samples deformed in uniaxial compression under the same deformation conditions. Owing to the very diffuse nature of the cold crystallization phenomenon and its proximity to \( T_g \), it is very difficult to measure exact values for \( T_\infty \) and \( A_\infty (\approx 0) \).

2. The areas of the corresponding melting endotherms do not change considerably with deformation temperature: Their onset is observed at \( \approx 241 \pm 1^\circ C \) and their areas are constant and equal to \( \approx 52J/g \). Onset and peak values are the same as in the uniaxial compression, however, the areas of the melting peaks are significantly higher in plane strain than in uniaxial compression.

3. From eqn.(2.2) and the conditions examined above it follows that crystallization is present at temperatures below and in the glass transition region over the rates examined when the material is tested in plane strain compression. The end
crystallinity for the samples tested in plane strain compression is of the order of 41%.

The plane strain DSC results show considerable increase in crystallinity with imparted strain at deformation temperatures ranging from 25°C to 76°C. However, as deformation temperature increases, the effect of heat setting the strained amorphous phase in the plane strain fixture becomes a possibility. Separating the crystallization contribution of heat setting and strain is not possible from the DSC readings since crystallinity was measured on the sample after cooling.

Furthermore, the effects of temperature, strain rate and imparted uniaxial strain on $T_{ce}$ are equally interesting when the material is tested in the rubbery region: the microstructural state of the samples deformed to final strains of $-1.25, -1.5, -1.75$, at $-0.5/s$ and $80°C$ are shown in Fig. 2.2.2-13a: $T_{ce}$ is depressed as the imparted strain increases. Unlike the uniaxial compression tests below the glass transition, however, as imparted uniaxial strain increases, the area of the cold crystallization exotherm decreases. It can be inferred that strain induced crystallization evolves in the material during uniaxial compression. The end crystallization of the sample strained to a final uniaxial strain of $-1.75$ is of the order of 18%. Fig.2.2.2-13b shows the thermograms of samples deformed to final strains of $-1.5, -1.75$, at $-0.005/s$ and $80°C$. The depression of $T_{ce}$ is significant, indicating network orientation due to deformation, and the depression of $A_{ce}$ indicates strain-induced crystallization. The end crystallization of the samples strained to final strains of $-1.5$ and $-1.75$ are of 15% and 19% respectively.

2.3 Discussion, Conclusions

Both the mechanical tests and the post deformation microstructural analysis show that the mechanical behavior of PET is a strong function of deformation temperature.

- For a fixed deformation temperature, as the imparted strain increases the material deforms elastically then yields and eventually strain hardens. As the
deformation temperature increases and the strain rate decreases, the elastic modulus, yield stress and flow stress decrease to the point where aging effects vanish when the deformation temperature is just above $T_g$. Uniaxial compression tests show the linear dependence of the flow stress to the logarithm of the plastic strain rate. This linear dependence suggests the modeling of the flow process with a diminishing energy barrier thermal activation law.

- The uniaxial compression tests over a wide range of temperatures below and through the glass transition and a wide range of slow to rapid strain rates have shown that deformation of the order of $-1.5$ in true strain does not result in strain induced crystallization. This is evidenced by an essentially temperature invariant cold crystallization exotherm area. The evolution of the microstructure, was also monitored as a function of imparted strain. At a moderate isothermal strain rate $-0.01/s$ and $25^\circ C$ deformation temperature, the macromolecular orientation becomes more pronounced as the imparted strain increases (demonstrated by the depression of $T_{cc}$), while the cold crystallization area remained constant indicating no strain-induced crystallization.

- The same trends in mechanical behavior are observed in the results of the plane strain compression tests. The strain hardening behavior is moderately depressed as deformation temperature approaches the glass transition; however, consistent with the behavior observed in other amorphous polymers, it is always much greater than that observed in the uniaxial compression. The more severe strain hardening observed in plane strain compression than in uniaxial is, at least in part, the result of more severe macromolecular orientation. Indeed, the $-0.01/s$, $25^\circ C$ deformations at various levels of imparted strain show a higher depression of $T_{cc}$, with imparted strain than in uniaxial compression hence validating the above hypothesis. At the same time however, $A_{cc}$ is depressed considerably with imparted strain which shows that strain-induced crystallization occurs in plane strain compression even at $25^\circ C$. The strain-induced crystallization may also contribute to the higher hardening rate. Furthermore, a high value of end
crystallinity (41%) of samples deformed in plane strain at $-0.01/s$ tested from 60°C to 76°C indicates that in plane strain below Tg the polymer deforms as an amorphous structure that crystallizes in the plane strain fixture either during or after the course of deformation. Thus, precise material structure evolution during plane strain compression cannot be quantitatively assessed from subsequent DSC analysis on the deformed specimens since there may be a post stretch annealing effect. However, some crystallization was observed at 25°C where no annealing occurred.

- The mechanical behavior of the material above $T_g$ at 80°C is characterized by the extreme sensitivity of the strain hardening behavior to strain rate. Rapid strain rates favor orientation and possible strain-induced crystallization manifested as pronounced strain hardening; whereas, very slow rates favor relaxation phenomena manifested as weak strain hardening. The extreme sensitivity of the material to the deformation conditions in the rubbery region impedes accurate control of the imparted deformations resulting in experimental results of low repeatability. Strain-induced crystallization estimates are difficult to obtain in that temperature region. The material can crystallize rapidly in the mechanical test upon unloading due to temperature and time; that additional crystallinity is measured in the DSC thermogram in that way impeding the correlation of the temperature and strain rate sensitive strain hardening to developing crystallinity.

The similarity of the mechanical behavior of PET in the transition to that of strictly amorphous polymers motivates the modeling of the above deformations in the transition region with a modified Arruda and Boyce constitutive model [22]. The phenomenological basis, mathematical formulation of the model as well as the results are presented in the following chapters of the thesis.
References


23. Boyce M.C., Montagut E.L., Argon A.S., The effects of thermo-mechanical coupling in the cold drawing process of glassy polymers. *Polymer Engineering and

Fig. 2.1.1-1: Uniaxial compression specimens undeformed, deformed to an imparted true strain of -1.5
Fig. 2.2.1-1: Isothermal uniaxial compression at 25°C, 0.01/s, at different levels of imparted strain.
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Fig. 2.2.1-4: Isothermal uniaxial compression at 60°C – 76°C and -0.01/s: effect of deformation temperature on mechanical properties in the glass transition region.
Fig. 2.2.1-5: Isothermal uniaxial compression at 60°C – 76°C and -0.1/s: effect of deformation temperature on mechanical properties in the glass transition region
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Fig.2.2.2-9: Cold crystallization behavior as a function of temperature (60°C to 76°C), uniaxial compression, −0.01/s.
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Chapter 3

Constitutive Model

3.1 Background

The elastic-viscoplastic behavior of amorphous polymers has been modeled by several investigators by assuming that two physically based deformation resistances must be overcome prior to any finite strain deformation. When the polymer is deformed below its glass transition temperature it must first be stressed to exceed the barrier to chain segment rotation and/or translation. That energy barrier is primarily a function of intermolecular interactions. Once the material begins to flow, molecular alignment occurs altering the configurational entropy of the macromolecular network: This orientation of the molecular network is the second source of deformation resistance in the material. Recent DSC work by Hasan and Boyce [7] strongly supports the existence of these two distinct deformation mechanisms. Chang and Li [29] obtained similar experimental results from their DSC experiments on Poly(carbonate) and have thus postulated the existence of two independent "defect structures" resulting from plastic deformation. In our work we follow the concept of the two barriers to deformation. Below, we first provide relevant background on modeling each barrier.

One attempt to explain the temperature dependent yield behavior of amorphous polymers in the glass transition regime was made by Robertson [1],[2] who considered the deformation resistance to arise from intramolecular interactions. The basic concept of the Robertson model is that of the applied shear stress acting to decrease
the intramolecular energy barrier amplitude. In the Robertson model, the work by
the shear stress decreases the energy amplitude between the undeformed and inelast-
ically deformed states each of which are characterized by a different concentration of
cis (flexed) and trans (preferred) conformational states. The maximum shear strain
rate, $\dot{\gamma}$, induced by the shear stress, $\tau$, is given by,

$$
\dot{\gamma} = \tau \eta_g \exp \left[-2.303 \frac{C_1 C_2 T_1}{(T_1 - T_2 + C_2)(T) - C_1}\right]
$$

(3.1)

where $\eta_g$ is a glassy state viscosity; $C_1, C_2$ are the WLF constants; $T_1$ is a fictive,
structure dependent temperature; and $T_2$ is the glass transition temperature. Pressure
sensitive versions of the model of Robertson by Ward et al. [3] with optimized values
for $C_1$ and $C_2$ have fitted the yield behavior of isotropic amorphous Poly(methyl-
methacrylate) (PMMA) and PET, over deformation temperature ranges of 23°C to
90°C and $-25$°C to 60°C respectively. It should be noticed that the temperature
ranges covered in that work are below the transition region for both polymers. Even
if successful in its predictions, this model does not account for any intermolecular
interactions that are the major source of deformation resistance well below the glass
transition.

Recognizing the dominant role of intermolecular over intramolecular interactions
well below $T_g$, Argon [4],[5], based his intermolecular theory on thermally-activated
local molecular kinks located in an elastic matrix initiating inelastic transformations.
The finite amplitude of the activation energy that is substituted in an Arrhenious
form of a thermal activation law, was modelled from the intermolecular energy barrier
resulting from the stress fields of the wedge disclination loops extending at the point
of rotation of two neighboring molecular kinks. The expression suggested by Argon
for the plastic shear rate $\dot{\gamma}_p$ is,

$$
\dot{\gamma}_p = \gamma_0 \exp \left[-\frac{\Delta G}{kT}\right]
$$

(3.2)

with the energy barrier given as (e.g., Kocks, Argon and Ashby[16]),

$$
\Delta G = \Delta F \left[1 - \left(\frac{T}{T_g}\right)^p\right]^q
$$

(3.3)
where, $\gamma_0$ is a pre-exponential factor; $\Delta G$ is the amplitude of the free energy barrier to inelastic transformation; $\Delta F$ is the stress unbiased Helmholtz Free Energy; $k$ is Boltzmann's constant; $T$ is the absolute deformation temperature; $\tau$ is the applied equivalent shear stress; $s$ is the athermal shear resistance; and $p, q$ are experimentally fitted or theoretically derived coefficients. In the Argon model, $p=5/6$, $q=1$. The theory, in the form presented above, has been successful in predicting the yield behavior of amorphous polymers such as PET, PMMA, Polycarbonate (PC), Polystyrene (PS) over temperatures lower and up to $(T_g - 15)K$ and decades of strain rates. However, in the immediate vicinity of the glass transition temperature, the Robertson model has been found to provide a better fit to experimental data (Argon et al. [5]).

In recent experimental developments, the mechanical tests and subsequent Positron Annihilation Lifetime Spectroscopy (PALS) and DSC tests by Hasan, Boyce Li and Berko [23] and Hasan and Boyce [25], respectively, has allowed them to isolate the effects of thermal prehistory on the viscoplastic behavior and in that way distinguish between the upper yield stress, that depends heavily on the thermo-mechanical history, and the flow stress that is practically independent of that history. As also postulated by other investigators, macroscopic inelastic deformation was considered to be a distributed process on a macroscopic scale where regions with a low local resistance to inelastic arrangement is low, cooperatively produce global macroscopic flow. The PALS measurements on PMMA showed that the aged structure has a smaller so called free volume content than the quenched structure, while at the same time the DSC showed the difference in enthalpic content between the two structures at their undeformed and deformed states. From these findings it followed that the resistance to inelastic deformation is lower for the quenched polymer owing to lower energy barriers due to locally higher free volume content. Hasan [25] succeeded in modelling the distributed nature of the transformed regions for plastic deformation with a distributed (Gaussian-type) activation energy. In the simulations of the non-linear viscoelastic-viscoplastic behavior of glassy PMMA the following activation law was assumed,

---

1. Best fits typically provide $0 < p < 1$ and $1 < q < 2$ for a wide range of materials.
2. Here, only the forward component of the transformation rate is considered.
\[ \dot{\gamma}_p = \dot{\gamma}_0 \int \Psi(\Delta F) \exp \left[ -\frac{(\Delta F - \tau_0(T))}{kT} \right] d\Delta F \] (3.4)

In eqn. (3.4), the term, \( \Psi(\Delta F) \), expresses the distribution of the activation Helmholtz free energy \( \Delta F \) and \( v \) expresses the activation volume for the process. The activation volume, work conjugate to the shear stress, expresses quantitatively the extent of the cooperative motion of the macromolecules required for the initiation of irrecoverable deformation of the polymer. The activation volume can be more formally expressed as the product of the physical volume of the transformation site, \( \Omega \), and the resulting shear strain, \( \Delta \gamma^T \), of the transformation site (Mott[10]).

Recently, Argon, Mott and Suter [10], [11] have reported molecular level, computer simulations of the inelastic deformation of polypropylene (PP) based on the early model introduced by Theodorou and Suter [17]. This model assumes the rigidity of the macromolecular structure and shows the presence of substantial stresses in the undeformed equilibrated structure. The computational approach is based on energy minimizations in a small periodic cell that pictures a molecular environment. These results indicate that plastic deformation is a result of repeated nucleation of shear transformations in a very large group of segments acting in a cooperative manner. The local transformation shear strains were found to be of the order of \( \Delta \gamma^T = 1.7\% \). More specifically, for PET, the volume of transforming sites was found to be of the order of \( 9.77 \times 10^{-25} m^3 \), thus, giving a product of 17, 200 \( \AA^3 \) for the activation volume.

Furthermore, the work on modeling the strain hardening behavior of polymers has also been extensive: An excellent review of this field up to the late 70’s can be found in the text of Treloar [13],[14]. It is apparent today that the invariant based models of, for example, Odgen [19], Rivlin [18], Valanis [20] lack a direct physical connection to the mechanisms of deformation, i.e., lack the connection to real structural descriptors which can enable them to be predictive under conditions of complex thermal and mechanical loading conditions. The alternative approach to the description of the finite deformation resistance in amorphous polymers, are network based models built on Gaussian statistics of chain configuration (such as the ones suggested by Flory and Rehner [21]), and more advanced models based on Langevin statistics such as
the ones suggested by Wang and Guth [30] and more recently by Arruda and Boyce [9]. These statistical models have found considerable success in modeling both rubber elastic materials as well as strictly amorphous glassy thermoplastics deformed in a variety of states of strain.

Given accurate constitutive descriptions of the two deformation resistances, combinations of them in a single kinematic framework can be used in simulations of polymer deformation in the glassy and glass transition region. The work of Boyce et al. [6] is already in that direction. A similar approach with emphasis in the glass transition region is that of Buckley et al. [22]. In the Buckley work they have employed a model based on Eyring type plastic flow to explain viscoelasticity and the Edwards and Vilgis network model to describe strain hardening during stretching of initially amorphous PET at high strain rates and temperatures above the glass transition.

In the following sections, the finite strain kinematics of the model are presented, followed by the constitutive description of the isotropic resistance to inelastic flow, then the description of the strain softening from the yield to the flow stress and finally the description of the anisotropic resistance to network orientation. The model results are compared directly to experimental data, where constant strain rate uniaxial and plane strain compression tests are modelled at several temperatures and strain rates. In what follows, a bold face upper case indicates a second order tensor, while scalars are presented in plain notation as before.

3.2 Constitutive model formulation

3.2.1 Kinematics of deformation

The reference configuration of an initially amorphous non-oriented polymer is an isotropic state, i.e., randomly oriented physically entangled macromolecules. We can express the deformed state of the material with respect to the reference state in terms of the deformation gradient \( F \). In our model, we decompose \( F \) in the following multiplicative way \( F = F^e F^p (\text{Lee [27]}) \), where \( F^e \) is the elastic and \( F^p \) the plastic deformation gradient. Plasticity is assumed to preserve volume, hence, \( \text{det}(F^p) = 1 \).
The multiplicative decomposition of the deformation gradient can be further manipulated with the polar decomposition theorem: \( F = (VR) = (RU) \) where \( R \) denotes the rotation tensors and \( U \) and \( V \) the left and right stretch tensors respectively. Similarly, \( F^e = (V^eR^e) = (R^eU^e) \) and \( F^p = (V^pR^p) = (R^pU^p) \). From the decomposition it follows that \( R^e, R^p \) are not necessarily unique and, hence, must be defined in some manner. If we chose \( R^e = I \) then the elastic deformation gradient is unique and symmetric: \( F^e = F^{eT} \).\(^8\)

The rate quantities corresponding to this formulation begin with the velocity gradient tensor \( L \),

\[
L = \dot{F}F^{-1} = D + W = \dot{F}^eF^{e-1} + F^eL^pF^{e-1}
\]

(3.5)

where \( D \) is the symmetric rate of deformation and \( W \) is the skew symmetric spin. The velocity gradient \( L^p \) of the relaxed configuration is given as,

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

(3.6)

In eqn.(3.6), the rate of shape change \( D^p \) must be described in a constitutive way while \( W^p \) is to be described in an algebraic way due to the constraint \( F^e = F^{eT} \); the magnitude of \( D^p \) is given by the scalar plastic strain rate \( \dot{\gamma}_p \) (see the next section) and the tensorial direction of \( D^p \) is specified by \( N = T^e/\sqrt{2}r \), the normalized portion of the activation stress tensor \( T^e \); this assignment gives rise to an associative flow rule. The activation stress tensor, \( T^e \), is given by the total Cauchy stress \( T \) minus the orientation stress tensor \( B \) (where \( B \) will be defined later):

\[
T^e = T - \frac{1}{\text{det}F}F^eBF^{eT}
\]

(3.7)

We refer to \( T^e \) in eqn.(3.7) as the activation stress tensor because it is only this portion of the stress that continues to activate inelastic flow. The network orientation stress tensor \( B \), which will be defined constitutively later, is an internal stress which

\(^8\)A second option for the glassy polymer is given in [12]: instead of defining the rotations, a relaxed configuration which is not spinning is chosen \( W^p = 0 \).
evolves due to macromolecular orientation and acts as a resistance to chain alignment. Since $B$ is defined in the relaxed configuration, it is here convected in the current configuration. The effective equivalent shear stress $\tau$ for activating flow is then given by the following modified von Mises criterion,

$$\tau = \sqrt{\frac{1}{2} T' \cdot T'}$$  \hspace{1cm} (3.8)

where in the above $T'$ is the deviatoric component of the activation stress. Finally, the Cauchy stress is given by the hyperelastic relation [28]

$$T = \frac{1}{\text{det}(V^\circ)} \mathcal{L}(\ln V^\circ)$$ \hspace{1cm} (3.9)

where $\mathcal{L}$ is the fourth order isotropic elasticity tensor. Complete analysis of the finite strain kinematics are given in Boyce, Parks and Argon [6] and Boyce and Weber [12]. The constitutive descriptions of the deformation resistances to chain rotation and alignment follow.

### 3.2.2 Flow rule

As discussed earlier, when an initially amorphous polymer deforms, it must first be stressed to exceed the resistance to macromolecular rotation and/or translation in order for yield to occur. This yield phenomenon can be observed in a constant strain rate compression test. At the first stages of the imposed deformation, the stress increases proportionally with strain, i.e., the material behaves in a linear elastic manner. With further deformation, the stress-strain behavior becomes non-linear and then reaches a maximum level which we term the yield stress, and marks the onset of irreversible inelastic transformations. As deformation is increased further, the stress level falls, i.e., the material strain softens, to a level which we term the flow stress. The flow stress is independent of the pre-deformation thermo-mechanical history (Hasan and Boyce [23]).

The general expression for the shear strain rate for a constant structure material given in eqn.(3.4), as suggested for example in [4], serves as a basis for the formu-
lation of a modified plasticity flow rule for non-constant structure materials that is used in our finite deformation model. Manipulation of the expanded form given in eqn.(5), shows that for a wide set of temperatures, the plastic shear stress \( \tau \) should be linearly proportional to the natural logarithm of the plastic strain rate, \( \dot{\gamma}^p \). This trend is consistent with our findings from isothermal and nearly isothermal uniaxial compression tests that were presented in the companion paper [24] in the form of the commonly termed Eyring plot \(^4\). The variation of the shear flow stress versus the logarithm of the plastic strain rate, for samples tested in uniaxial compression over a range of temperatures from \( 60^\circ C \) to \( 76^\circ C \) and a range of strain rates from \( -0.005/s \) to \( -0.5/s \), is linear as shown in Fig.3.2.2-1. The better agreement of the flow stress variation to an Eyring-type kinetic law than that of the upper yield stress variation, makes physical sense since the upper yield stress bears already the signature of active relaxation mechanisms that drive the material towards thermodynamic equilibrium. Returning to the generic form of the activation law, the plastic shear strain rate, \( \dot{\gamma}^p \) is given as,

\[
\dot{\gamma}^p = \dot{\gamma}_0 \exp \left[ -\frac{\Delta G(\tau, T, \text{structure})}{kT} \right]
\]

(3.10)

As previously mentioned, the predictive capabilities of eqn.(10) have been used extensively for many amorphous polymers for deformations well below their respective glass transition temperatures. It remains to be shown, however, whether an activation law similar to the one above is able to capture the rapidly diminishing magnitude of yield in the vicinity of \( T_g \), i.e., in the region where structural relaxations occur and give rise to a non-constant structure. The distinctive feature of the plastic strain rate expression used in the proposed constitutive model from the ones suggested earlier, is the explicit dependence of the activation free energy, \( \Delta G \), on the deformation temperature \( T \). Here, in an Eyring type format, the shear stress decreases the activation energy by a work amount equal to \( \tau \nu \), where \( \nu \) is the shear stress activation volume. However, we also postulate that in the vicinity of the glass transition temperature,

\(^4\)The flow stress \( \sigma \) is related to the shear flow stress \( \tau \) by the von Mises rule: \( \tau = \sigma/\sqrt{3} \) and the plastic strain rate \( \dot{\gamma}^p \) to the compression rate \( \dot{\varepsilon} \) by \( \dot{\gamma} = \dot{\varepsilon}\sqrt{3} \)
where structure is not constant, the stress free energy barrier is a monotonically decreasing function of temperature: This reflects the physical picture that as the temperature approaches the glass transition \(^5\), the amplitude of the energy barrier to initiate flow diminishes to zero because the sum of intermolecular and intramolecular interactions becomes smaller. According to this hypothesis, the barrier should be zero at a temperature slightly above \(T_g\) when the plasticity mechanism is fully inactive and the material behaves in a rubbery manner. For purposes of clarity, we review our first order approximations:

1. **The activation barrier to the initiation of the flow processes is assumed single valued.** The distributed nature of the polymer structure motivates its statistical representation in the process of formulating a constitutive model for plastic flow. Earlier attempts by Hasan et al. [25] to use a structure-energy distribution in investigating the role of thermo-mechanical history on yield have been successful in capturing nonlinear yield and post-yield behavior for glassy PMMA. For the purposes of simplicity, we intentionally choose to model flow with a single energy barrier.

2. **The amplitude of the activation barrier decreases monotonically with absolute deformation temperature.** As the material goes through the glass transition, a monotonic decrease in the upper yield stress is observed until reaching a value of zero, when the material is then in the rubbery region. The flow stress is also decreasing monotonically with increasing deformation temperature as shown in Fig. 3.2.2-2. This erasure of the intermolecular energy barrier as the material goes through the glass transition will be modeled as a decrease in the activation free enthalpy with increasing deformation temperature.

3. **The pre-exponential factor \(\gamma_0\) is taken to be constant and equal to \(1.0 \times 10^{13}/s\).**

4. **The effective shear stress \(\tau\) decreases the amplitude of the energy barrier.**

Based on these four statements, the proposed flow rule can be written as,

---

\(^5\)Kinetic effects on the exact value of \(T_g\) are being neglected in this first order analysis.
\[
\gamma^p = \gamma_0 \exp \left[ -\frac{(\Delta F_{\text{flow}}(T) - \Delta W(\tau, p))}{kT} \right]
\]

(3.11)

where in eqn. (3.11) \(^6\), the activation free energy is expressed as the difference between the structure dependent activation Helmholtz Energy \(\Delta F_{\text{flow}}(T)\) and a work term \(\Delta W(\tau)\). The work term can be expressed as \(\tau v_T\) and can also include the pressure effect via the work term \(p v_P\). With the pressure work included, the work term becomes,

\[
\Delta W(\tau, p) = \tau v_T - p v_P
\]

(3.12)

where in eqn. (3.12), \(p = (1/3)tr(T)\), is the applied pressure and \(v_p\) is the work conjugate pressure activation volume.

### 3.2.3 Strain softening model

The diminishing role of any prior thermo-mechanical history on the yield stress when the material is deformed at temperatures approaching the glass transition is evident from our isothermal uniaxial and plane strain compression tests in that region. Figs. 3.2.3-1(a),(b) show the difference between the yield and flow stress vs. equivalent plastic strain \(^7\) at 0.005/s and 0.01/s respectively. It is apparent that as the deformation temperature approaches \(T_g\) the difference between the yield stress and the flow stress decreases gradually to zero. The yield stress softens to the flow stress level over an equivalent plastic strain of 0.2 \(^8\).

With the above experimental observations as a basis, the strain-softening process can be modelled using an energy barrier to deformation which is taken to decrease with strain; The energy barrier prior to any inelastic transformations is dependent on previous thermo-mechanical history only. The evolution with respect to strain can be algebraically expressed as,

---

\(^6\) For a detailed discussion of the choice of thermodynamic potential see Kocks et al.\([16]\).

\(^7\) The equivalent plastic strain is given as \(\varepsilon_p = \sqrt{\frac{1}{3}[(\varepsilon_{11} - \varepsilon_{22})^2 + (\varepsilon_{22} - \varepsilon_{33})^2 + (\varepsilon_{11} - \varepsilon_{33})^2]}\), where \(\varepsilon_{ij}\) are principal components of plastic strain.

\(^8\) which is essentially independent of temperature, strain rate and strain state.
\[
\frac{\partial[\Delta F_{\text{soften}}(T, \gamma^p)]}{\partial \gamma^p} = -\frac{1}{\gamma_{ss}} \Delta F_{\text{soften}}(T, \gamma^p)
\]  
(3.13)

where, \(\Delta F(T, \gamma^p)_{\text{soften}}\) is the difference between the temperature and strain dependent Helmholtz free energy of the aged structure that yields and the quenched structure that flows. \(\gamma_p\), is the shear equivalent plastic strain and \(\gamma_{ss}\) is the shear plastic strain over which complete strain softening occurs, a constant. Notice that in this first order approximation rate effects on softening are omitted\(^9\). The solution of eqn.(3.13) with \(\Delta F_{\text{soften}}(T, \gamma^p = 0) = \Delta F_o(T)\) \(^{10}\) as the initial condition is:

\[
\Delta F_{\text{soften}}(T, \gamma^p) = \Delta F_o(T) \exp \left(-\frac{\gamma^p}{\gamma_{ss}}\right)
\]  
(3.14)

Eqn.(3.14) predicts an exponential decrease of the energy barrier with plastic strain.

Mechanical tests provide quantitative information about the yield stress, the flow stress and also the level of plastic strain over which complete strain softening occurs. Additional information regarding the effects of aging and the difference between the yield stress and the flow stress can be found from DSC. In DSC analysis, the energy difference between the aged and the quenched (unaged) structural states is apparent in the different thermograms. The energy information reduced from these thermograms can be correlated to the mechanical tests. The different heat flow profiles at a temperature increase rate of 10°C/min of PET aged at 75°C for 30min \(^{11}\) and that quenched in liquid Nitrogen after equilibration at 90°C(= \(T_g + 15°C\)) are shown in Fig.3.2.3-2. The following observations are interesting:

- The instantaneous heat flow rate, \(\dot{H}\), at every level of temperature is higher for the aged (equilibrated) than for the quenched (non equilibrated) polymer (a well known phenomenon).

- Complete erasure of the thermo-mechanical history is observed over 16°C: In

\(^9\)Consequently, rate effects on yield come only from the kinetic description of flow

\(^{10}\)\(\Delta F_o(T)\) expresses the pre-deformation difference of Helmholtz energy of the aged and quenched structure.

\(^{11}\)A temperature and time heat treatment very similar to that imposed on the material during deformation tests.
the deformation tests erasure occurs in the range from \(60^\circ C\) to \(76^\circ C\); in the DSC thermograms it occurs in the range from \(70^\circ C\) to \(85^\circ C\), i.e. over the same temperature difference shifted by \(10^\circ C\).

Integration of the thermograms over temperature (hence time) gives the total enthalpy difference between the aged and the quenched state\(^{12}\) as,

\[
\Delta H_{a/q} = \int_{T=T_{\text{min}}}^{T=T_{\text{max}}} \left[ \left( \frac{\partial Q}{\partial t} \right)_a - \left( \frac{\partial Q}{\partial t} \right)_q \right] \left( \frac{\partial T}{\partial t} \right)^{-1} dT
\]

(3.15)

where \(T_{\text{min}}\) and \(T_{\text{max}}\) are the low and high temperatures in the range of which the difference in heat flow rates non zero . Fig.3.2.3-2 gives values for \(T_{\text{min}} \approx 70^\circ C\) and \(T_{\text{max}} \approx 85^\circ C\). The dependence of the enthalpy difference on the kinetic rate explicitly through the DSC temperature increase rate and implicitly through the heat flow profile is clear. In that same argument, the enthalpy difference between the aged structure and the quenched one at an arbitrary absolute temperature \(T_i\) is given as,

\[
\Delta H(T_i)_{a/q} = \int_{T=T_i}^{T=T_{\text{max}}} \left[ \left( \frac{\partial Q}{\partial t} \right)_a - \left( \frac{\partial Q}{\partial t} \right)_q \right] \left( \frac{\partial T}{\partial t} \right)^{-1} dT
\]

(3.16)

In eqn.(3.16), \(\Delta H(T_i)_{a/q}\) has a maximum value when \(T_i = T_{\text{min}}\) and is zero when \(T_i = T_{\text{max}}\). The variation of \(\Delta H(T_i)_{a/q}\) vs. \(T_i\) is measured for a given mass during DSC analysis; it should, however, be normalized per particle in order to be used in the proposed flow rule. For that purpose we normalize the enthalpy using the weight average molecular weight \(^{13}\). The resulting variation of \(\Delta H(T_i)_{a/q}\) per molecule with \(T_i\) is shown in Fig. 3.2.3-3. The values are superimposed with a fitted \(\Delta F_o(T)\) which is backed out from the mechanical tests \(^{14}\). Our measurements from independent mechanical tests and DSC thermal analysis with the subsequent calculations show that the decrease of \(\Delta H_{a/q}(T_i)\) with temperature reduced from the DSC tests correlates

\(^{12}\)Recall that in DSC analysis \(\dot{Q} = \dot{H}\).

\(^{13}\)By definition, the latter is given as the product of the average number molecular weight \(M_n = 19,000g/mol\) and the poly-dispersion index \(PDI = 1.8\).

\(^{14}\)To obtain \(\Delta F_o(T)\) the flow rule is backsolved in one case using shear yield stress values and in the other case using shear flow stress values from the isothermal/nearly isothermal uniaxial compression tests (see eqn.(12)). Same values for the parameters \(\gamma_0, \nu_T, \alpha\) are used in both cases.
clearly with the decrease of $\Delta F_s(T)$ with temperature reduced from the uniaxial compression tests. Hence, both experiments agree in the decrease of the internal (structure) energy measure with temperature. In view of the above finding, eqn.(4) can be written as,

$$\Delta F_{\text{soften}}(T, \gamma_p) \approx \Delta H(T)/e \exp \left[-\frac{\gamma_p}{\gamma_{ss}}\right]$$  \hspace{1cm} (3.17)

Including the thermo-mechanical history and plastic strain dependent energy barrier to capture the strain softening phenomenon in eqn.(3.14), the flow rule to be used in the subsequent deformation simulations is given by,

$$\dot{\gamma}^p = \gamma_0 \exp \left[-\frac{(\Delta F_{\text{flow}}(T) + \Delta F_{\text{soften}}(T, \gamma_p) - \Delta W(\tau))}{kT}\right]$$  \hspace{1cm} (3.18)

Finally, since aging does not affect the value of the elastic modulus at any given deformation temperature, the law can be further simplified by introducing: $\frac{\Delta F_{\text{flow}}(T_1)}{\Delta F_{\text{flow}}(T_2)} = \frac{E(T_1)}{E(T_2)}$ in eqn.(3.18).

### 3.2.4 Strain hardening model

Details for the basis and derivation of a statistical network model for the finite deformation of the macromolecular network are given in [6], [8] and [9]. In this paper some of the basic constitutive expressions of the model are reviewed. The undeformed polymer in the reference configuration can be modeled as a network of entangled macromolecules. The chain density is expressed as $n$ and the number of rigid links between two physical entanglements as $N$. The orientation stress is derived from the change in entropy of that network with imparted strain. The Arruda and Boyce eight chain model is comprised of eight non Gaussian macromolecular chains that originate from the center of a cube and each end at a corresponding corner; each chain is modelled using Langevin statistics thus accounting for the finite extensibility of the network. The advantage of this approach is its demonstrated ability to simulate a true network response of cooperative strain stretching which represents a clear picture of the deformation process. The principal components of the orientation stress
tensor, \( B \), as these are computed from the eight chain model are,

\[
B_i = \frac{nKT}{3} \sqrt{\frac{N}{L^2}} \left[ \frac{\lambda_{\text{chain}}}{\lambda_{\text{chain}}} \right] \frac{\lambda^2 i - \frac{1}{3} I_1}{\lambda_{\text{chain}}} \tag{3.19}
\]

In eqn.(19) \( \lambda_{\text{chain}} = \sqrt[3]{(\lambda^2_1 + \lambda^2_2 + \lambda^2_3)} \); \( \lambda_i \) are the principal values of the plastic stretch tensor; \( I_1 \) is its first invariant of the stretch tensor and \( L^{-1} \) is the inverse Langevin function \(^{15}\). Eqn.(19) captures the deformation of the macromolecular network in different strain states using only two parameters, the initial rubbery modulus, \( C_R = nKT/3 \), and the number of rigid links between entanglements \( N \).

### 3.2.5 Model parameters

The discussion that follows presents the parameters required in the numerical implementation of the model:

1) **FLOW RULE**: The shear and pressure activation volumes can be determined experimentally. The shear stress activation volume is proportional to the slope of the \( \ln(\dot{\gamma}^p) \) vs. \( \tau \) (Eyring plot) at each deformation temperature,

\[
\nu_T = kT \left[ \frac{\partial \ln(\dot{\gamma}^p)}{\partial \tau} \right]_{p,T}
\tag{3.20}
\]

Even though the dependence of \( \nu_T \) on absolute deformation temperature as obtained from eqn.(3.20) is explicit, for the uniaxial compression tests presented in the companion paper, eqn.(3.20) gives an essentially constant shear stress activation volume equal to 8800 A³.

The strong temperature dependence of the structure in the \( T_g \) region was modeled as the decreasing Helmholtz free enthalpy \( \Delta F_{\text{flow}}(T) \) with temperature. Rearrangement of eqn.(3.12) gave \( \Delta F_{\text{flow}}(T) \) in terms of pertinent parameters and subsequent substitution of numerical values for them as well as values from shear flow stress from the uniaxial compression tests from 60°C to 76°C. The coefficients of the fitted polynomial for the activation free enthalpy

\(^{16}\)The Langevin function is defined as \( L(x) = \coth(x) - (1/x) \).
\[ \Delta F_{\text{flow}}(T) = AT^2 + BT + C \]  

(3.21)

are also shown in Fig. 5 are \( A = -16.73 \times 10^{-22}(J/K^2), B = 10.9 \times 10^{-20}(J/K), C = -1.78 \times 10^{-17}(J) \). With the above parameters, \( \Delta F_{\text{flow}}(T) \) ranges from \( 2.5 \times 10^{-19}(J) \) at \( 60^\circ C \) to \( 1.6 \times 10^{-19}(J) \) at \( 76^\circ C \) in the temperature range of interest. Thus eqn.(3.12) 
together with eqn.(3.15) can capture the strain rate, temperature and stress dependence of inelastic flow as the structure goes through the glass transition.

2) PRESSURE DEPENDENCE: Similarly, the pressure activation volume is given as,

\[ v_p = kT \left[ \frac{\partial \ln(\dot{\gamma})}{\partial p} \right]_{\tau,T} = kT \left[ \frac{\partial \ln(\dot{\gamma})}{\partial \tau} \right]_{\tau,p} \left[ \frac{\partial \tau}{\partial p} \right]_{\tau,p} = v_T \left[ \frac{\partial \tau}{\partial p} \right]_{\tau,p} = v_T a_p \]  

(3.22)

Pressure dependence is typically apparent through the pressure sensitivity of the shear flow stress. However, pressure sensitivity of flow was not examined in the experimental part of the investigation. For the purposes of simulating plane strain compression behavior, and capturing more general state of strain effects, a value of \( a_p = (\partial \tau/\partial p)_{\tau,p} = 0.175 \) obtained by Ward et al. [3] was used.

3) AGING AND STRAIN SOFTENING: Mechanical tests in uniaxial compression were sufficient for obtaining values for \( \gamma_{as} \) the characteristic equivalent plastic strain. A value of \( \gamma_{as} = 0.075 \) was found to capture strain softening. The initial amplitude of the energy barrier was correlated to the DSC tests (see previous section).

4) STRAIN HARDENING: Isothermal tests in uniaxial compression were sufficient for obtaining values for the strain hardening model: Numerical values for the rubbery modulus \( C_R = 4.2\text{MPa} \) and the number of rigid links between entanglements \( N = 15 \) were reduced from curve fitting the strain hardening behavior of isothermal and nearly isothermal uniaxial compression tests at a strain rate of \( 0.01/s \). Since strain hardening appears insensitive to temperature as that appears from the experiment, temperature sensitivity of \( n \) and \( N \) was omitted.

Finally, the following table reviews all the parameters that were used in the sim-
ulations:

<table>
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<tr>
<th>Behavior</th>
<th>Property</th>
<th>Value:</th>
<th>Source:</th>
</tr>
</thead>
<tbody>
<tr>
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<td>$E (MPa)$</td>
<td>Polynomial fit</td>
<td>Uniaxial compression</td>
</tr>
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<td>$\nu$</td>
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<td></td>
</tr>
<tr>
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<td>Uniaxial compression</td>
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<tr>
<td></td>
<td>$\nu (A^3)$</td>
<td>8,800</td>
<td>Uniaxial compression</td>
</tr>
<tr>
<td>Pressure Dependence</td>
<td>$a_p$</td>
<td>0.175</td>
<td>Ward (1970)</td>
</tr>
<tr>
<td>Strain Softening</td>
<td>$\Delta F_{soften}(T)$</td>
<td>Polynomial fit</td>
<td>DSC analysis or compression</td>
</tr>
<tr>
<td></td>
<td>$\gamma_{ss}$</td>
<td>0.075</td>
<td>Isothermal uniaxial compression</td>
</tr>
<tr>
<td>Strain Hardening</td>
<td>$C_R (MPa)$</td>
<td>4.2</td>
<td>Isothermal uniaxial compression</td>
</tr>
<tr>
<td></td>
<td>$N$</td>
<td>15</td>
<td>Isothermal uniaxial compression</td>
</tr>
</tbody>
</table>

Table 1: List of properties used in simulations.

3.3 Model results

Results of simulations superposed with experiments are shown in Figs. 3.3-1 and 3.3-2 for the cases of isothermal uniaxial compression over the temperature range 60°C to 76°C, at 0.005/s and 0.01/s. It can be seen that our simulation captures elastic behavior, yield, strain softening\(^ {16}\) and strain hardening: The rate and temperature dependence of initial yield are well modelled by our flow rule that determines the value of stress at which the material yields (at that deformation temperature). The thermal history dependent energy barrier to inelastic transformations decreases exponentially giving rise to the strain softening which is also found to be in good agreement with the tests. Further increase of the uniaxial compressive strain aligns macromolecules in the plane perpendicular to the axis of compression; the macromolecular orientation strain hardens the material.

The model captures similar characteristics of deformation behavior for the case of isothermal plane strain compression at 0.01/s as shown in Fig. 3.3-3. The experiment

\(^ {16}\)The assumption of an rate independent $\Delta F_{soften}$ introduces some error.
shows that the plane strain yield stress is higher than the uniaxial yield stress, owing to state of strain and pressure effects. Strain softening is nearly exponential \(^{17}\) and finally strain hardening as observed from the experiment is much greater than in uniaxial compression: In the case of plane strain the macromolecules orient in a nearly uniaxial manner in the flow direction, perpendicular to the axis of compression, i.e., to a much larger extent than in uniaxial compression. The model captures yield and strain softening is overpredicted—this may be due to some inhomogeneity in testing at early stages of the deformation as explained in the companion paper. Moreover, the model captures successfully the state of strain dependent strain hardening, using evolution of macromolecular orientation without incorporating any crystallization effects.

What is also interesting is the evolution of structure with strain hardening when the material is deformed in these two states of strain. Crystallinity estimates from DSC thermograms of samples deformed to an imparted logarithmic strain of \(-1.5\), have shown that the material remains amorphous when deformed in uniaxial compression, but develops considerable crystallinity when deformed in plane strain compression. It would be reasonable, therefore, to expect the strain-induced crystallization to impact the finite deformation resistance in plane strain. The good agreement of simulation to experiment for both states of strain as shown again in Figs. 3.3-4 and 3.3-5 suggests that the dominant deformation mechanism in the strain hardening of initially amorphous unoriented PET in the temperature region is the orientation of the underlying macromolecular network and not strain-induced crystallization.

3.4 Conclusions

We have simulated the deformation of an initially amorphous, unoriented, crystallizable grade of PET, through its glass transition. For that purpose we have used:

- a scalar thermal activation law for the temperature, pressure, strain rate, strain state onset of inelastic flow: The foundation of the law is the decreasing energy

\(^{17}\)It exhibits a stress plateau due to non-homogeneous zones that develop at the early stages of deformation but do not seem to affect overall deformation later.
barrier with deformation temperature owing to the decreasing magnitude of the intermolecular and intramolecular interactions.

- a scalar phenomenological law for capturing the temperature and strain sensitive softening from the yield to the flow stress. The law is based on the gradual erasure of the energy difference between the aged and quenched structure with evolving plastic strain. The strain at which complete softening occurs is independent of temperature, state of strain and moderately dependent on strain rate as revealed from a series of isothermal deformation tests. The initial magnitude of the energy barrier between the yield and flow stress correlates to the enthalpy difference between the two structures as measured from DSC thermal analysis.

- the Arruda and Boyce eight chain model that was originally suggested for explaining the orientation-induced strain hardening in amorphous polymers. Even though thermal analysis has shown that crystallization may occur when the material is deformed in plane strain, the model predicts strain hardening well both in the state of plane strain compression and that of uniaxial compression without incorporating the effects of crystallization.
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26. Raha, S., Bowden, P.D., Birefringence of plastically deformed Polymethylmethacrylate Polymer 13 174-183


Fig. 3.2.2-1: Eyring plot: variation of shear flow stress vs. plastic shear strain rate for uniaxial compression tests 60°C to 76°C and strain rates 0.005/s – 0.5/s.
Fig. 3.2.2-2: Variation of compressive flow stress vs. deformation temperature for uniaxial compression tests 25°C to 76°C and strain rates 0.005/s – 0.5/s.
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Fig. 3.3-1: Isothermal constant strain rate uniaxial compression at \(-0.005/s\) from 60°C to 76°C: Experiments and simulations.
Fig. 3.3-2: Isothermal constant strain rate uniaxial compression at -0.01/s from 60°C to 76°C: Experiments and simulations.
Fig.3.3-3: Isothermal constant strain rate plane strain compression at $-0.01/s$ from 60°C to 76°C: Experiments and simulations.
Fig. 3.3-4: Comparison of uniaxial and plane strain compression at 73°C, 0.01/s.
Fig. 3.3-5: Comparison of uniaxial and plane strain compression at $60^\circ C, 0.01/s$. 
Chapter 4

Simulations of Constrained Stretching

4.1 Description of the process

Fig. 4.1 shows the stages of the stretching operation that produces biaxially oriented films from initially amorphous unoriented PET. First, the polymer chips must be dried. Water that is absorbed during the chemical processing stages acts as a copolymer and therefore shifts the value of the glass transition temperature by a couple of degrees Celcius. This shift has a direct impact on the mechanical properties of the film. Dried chips are then fed into an extruder; as the extruder turns, chips are taken in and compressed. Melting of the chips is the result of both mechanical loading and heating. The molten polymer is then filtered and cast on a water cooled drum. Cooling time of the film from its melting temperature to well below room temperature (≈ 10°C) is very small and therefore gives the film an initially amorphous non-oriented structure. Zero crystallinity is possible to achieve only if heat transfer times are indeed very small. Heat transfer time depends on two factors: the mechanism that controls the temperature of the drum and the initial thickness of the melt cast on the drum. If the cast film is thicker than 2 – 3mm, then the heat transfer time at the center of the film is slow enough to allow for an initial crystallinity of the order of 5 – 10% to develop.
During the next stage, the cast film travels through a forward draw unit where it is heated to 90°C that is 15°C above the glass transition temperature and stretched to roughly three times its original length. The drawn film is fed into two sets of continuous chains which grip it on each side and carry the film into special ovens where it is heated again to about 90°C and stretched by the same amount in the transverse direction. The biaxially oriented film is then passed through a heat setting region and exposed to a temperature of 220 – 240°C. In that region the oriented macromolecular structure locks into a crystalline one and thus the film become partly crystalline. The semicrystalline structure has better dimensional stability and more uniform mechanical properties. It is apparent that the dimensional quality and the structural uniformity of the end product depends heavily on all stages of production of the semi-crystalline film.

Control of the following parameters is critical for accurate prediction of the state of the end product:

- deformation temperature, both as a function of deformation time and position of the material point on the film,
- deformation speed,
- initial thickness uniformity of the cast film.

It is interesting to examine the sensitivity of the final product to the parameters just mentioned. In that effort, simulations of constrained stretching process were performed in order to demonstrate the effects of non-uniform deformation temperature and non-uniform initial thickness on the mechanical behavior of the film in the course of deformation as well as the final thickness uniformity of the stretched film. A schematic of a constrained stretching process is shown in Fig.4.1.2: The initially amorphous non-oriented sheet is constrained in the z direction while it is stretched in the x direction; this is essentially a plane strain condition since all the components of the strain tensor in the z direction are zero. The final stretch of the film is four, that

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1That deformation is equivalent to a final stretch of four, or a logarithmic strain of 1.38

98
is, the final extension equals three times the initial length. The speed of deformation is a nominal strain rate of 0.1/s, that corresponds to a final stretch of four in 30 seconds.

The discussion that follows examines the effects of poor temperature control and film thickness non-uniformity on the deformation history and the dimensional quality of the final product. The discussion includes also details about the finite element model used in each case. Deformation is monitored in each case through,

- the plastic shear strain rate history,
- the accumulated shear plastic strain history,
- the film thickness history,
- the film final thickness,
- and the nominal stress vs. strain behavior.

4.2 Effects of non-uniform deformation temperature

As mentioned before, poor temperature control is often the case during stretching operations. A primary component of that problem is the difficulty to accurately measure temperature as a function of time and position on the film. Isothermal uniaxial and plane strain compression tests that were performed in the experimental part of the project and were presented in the first chapter, showed that temperature differences of the order of 3°C have considerable effects on the overall deformation behavior.

4.2.1 Model description

Fig. 4.2.1-1 presents a model that was used to simulate the effects of a constant temperature difference along a film deformed in constrained stretch at 0.1/s to a
final stretch of four. The meshed portion isolates a quarter of the sheet thickness: \( x=0 \) is the center of the film at \( 73^\circ C \) while \( x=1 \) is the end of the film away from the center at \( 69^\circ C \). Also, \( y = 0 \) is the mid-thickness and \( y = -h \) is the surface of the film exposed to the ambient air. The constant element density mesh consists of element type CPE4 \(^2\) elements that are available in the FE package ABAQUS [1]. The deformation temperature range used in the simulations are lower than the ones used during the actual industrial process. The choice of the deformation temperature range is such simply because the experimental and modeling analysis was performed in that region. Also, the assumption of a constant temperature difference along the film is very close to the stretching process since the primary source of heat transfer during deformation is conduction from the roller to the film. The constant temperature difference condition is modeled by assigning rows of elements to a fixed and constant temperature during the simulation.

### 4.2.2 Results

Figs. 4.2.2-1(a),(b) shows the evolution of plastic strain rate with time. At first, inelastic deformation initiates at the warmer end favored by high local thermal activation. As deformation continues the deformed material hardens and plasticity advances towards the cold end. It is interesting to note that the plastic strain rate reaches a maximum at \( 45^\circ \) angle to the stretch direction at 0.812\(s\). This is a direct consequence of the associative nature of the plastic rule incorporated in the finite deformation model. The rule correlates the direction of the maximum effective equivalent shear stress to the maximum plastic strain rate. With further deformation the shear band vanishes because the material in the band has strain hardened, thus, increasing the barrier to further plastic flow. Plasticity now advances towards the cold end. It is interesting to note that during the final stages of the deformation after the cold end has strain hardened, the plastic rate maximizes again at the warm end. Equally interesting is the evolution of the accumulated plastic strain with time shown in Figs. 4.2.2-2(a),(b). As deformation advances, plastic strain increases always being

\(^2\text{CPE4 is a four node bi-linear plane strain element.}\)
higher at the warm end than at the cold end.

The history of the displacement in the y direction at set distances from \( x = 0.0 \) is shown in Fig. 4.2.2-3. At the first stages of the deformation, film contraction is maximum close to the warm end \((x = 0)\) and minimum close to the cold end \((x = 1.0)\). As deformation time progresses, the difference in contraction diminishes, however, at the end of the stretch there is still contraction non-uniformity. The final thickness non-uniformity is shown in Fig.4.2.2-4. In this case, a temperature difference of 4\(^\circ\)C produced a thickness variation of the order of 3\%. That final non-uniformity is prohibitive at high end MELINEX applications, e.g., in photographic films where the quality of the application depends heavily on the film itself.

Fig.4.2.2-5 shows the nominal stress vs. strain behavior of the stretched film as that is measured at the cold end \((x = 1.0)\). Since the deformation temperature range is slightly below the glass transition, the material behaves elastically, then yields, strain softens and finally strain hardens due to the orientation of the molecular network. The nominal stress vs. strain behavior of the cast film is compared with three other deformation conditions, i.e. homogeneous constrained stretching at constant temperatures of 69\(^\circ\)C, 71\(^\circ\)C and 73\(^\circ\)C respectively. Comparing the constant temperature cases to the non-homogeneous temperature case we observe that:

- The elastic behavior is the same for both cases of uniform and non-uniform deformation temperature.

- Since yielding occurs at the warm end, the initial yield stress of the non-homogeneous deformation is closest to the 73\(^\circ\)C yield stress.

- The apparent softening is irregular during the non-homogeneous deformation. The post yield stress level has the form of a steady plateau unlike the homogeneous deformations where the stress level falls exponentially.

- Strain hardening is the same for both deformations. The initial deformation localization does not affect the direction and amount of orientation on the molecular network.
4.3 Effects of dimensional imperfections

Often times, the cast film includes dimensional imperfections, e.g., its initial thickness may be locally non-uniform. That problem may arise from the inhomogeneous cooling of the melt on the drum and/or the irregular spreading of the melt from the extruder on the drum. The following discussion examines the sensitivity of the deformation behavior of the film on the local inhomogeneity.

4.3.1 Model description

Fig. 4.3.1-1 shows the mesh that was used to model a non-homogeneous film. A constant density, square mesh was used. As before, since this is a plane strain deformation condition, element type CPE4 was used. A local inhomogeneity was introduced by decreasing the thickness of the film locally by 1%. The imperfection is positioned at $x = 0.5$ and modeled by locating the node at that position slightly closer to the mid-thickness. Apparently, the deformation behavior depends heavily on the size and shape of the local non-homogeneity and its position relative to the rollers. The purpose of this simulation, however, is not a thorough study of local defects of films; rather, the interest lies in investigating the effects of a local non-homogeneity on the global deformation behavior.

4.3.2 Results

Figs. 4.3.2-1(a),(b) show the evolution of the plastic strain rate with deformation time when the film is stretched at 69°C. During the early stages of the deformation, two zones of maximum plastic rate appear that originate from the imperfection and evolve at a 45° angle to the direction of stretch. As deformation time advances the material strain hardens, the barrier to inelastic deformation increases and as a result the rate becomes lower. Similar effects on the plastic rate history are observed when the material is stretched at a deformation temperature 4°C higher, namely at

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3In contrast to imperfection simulation, in the temperature gradient simulation that was presented earlier only one maximum plastic rate zone was present.
$73^\circ C$. Results are shown in Figs. 4.3.2-2(a),(b). As before, the two zones originate at the imperfection, however, soon after, the rate becomes constant in the material. It follows that the effect of the imperfection on deformation localization is smaller as deformation temperature increases.

Figs. 4.3.2-3(a),(b) shows the history of accumulated plastic strain when the material is stretched at $69^\circ C$. The plastic strain is always maximum at the imperfection and around it at the zones of maximum plastic rate. As deformation time advances, elliptic contours of maximum strain appear, that gradually evolve into regions of maximum strain. At the same time plastic strain maxima continue to nucleate at the imperfection. Similar behavior is observed for the stretch at $73^\circ C$, results of which are shown in Figs. 4.3.2-4(a),(b). During that latter case, however, plastic strain in the material is more uniform at all deformation times.

Furthermore, Fig.4.3.2-5 clearly shows that the initial imperfection has a lesser effect on the thickness history of the film than the constant temperature gradient. Unlike the temperature gradient case where at the initial stages of the deformation thickness contraction is non-uniform, the contraction of the thickness is very close to uniform along the film throughout the latter simulation. Fig. 4.3.2-6 shows the final contraction vs. position. The thickness contraction is higher only by 0.6% at the position of the initial imperfection. Finally, the most important effect of the imperfection appears to be shear on the film surface. The final stages of the stretch, that essentially give the state of the end product, show that the material at the film surface is sheared away from the imperfection while the material close to the mid-thickness of the film shows no shear at all.

Finally, Figs. 4.3.2-7(a),(b) show the nominal stress vs. strain behavior of the stretched film at the two deformation temperatures $69^\circ C$ and $73^\circ C$. It is apparent that:

- The elastic behavior is the same both for the homogeneous and non-homogeneous film.

- The yield stress of the homogeneous and non-homogeneous film are approximately the same ($\pm 2MPa$).
• Strain softening is irregular in the deformation of the non-homogenous film. Strain softening does not appear as exponential decrease of the stress level but as an stress plateau after yield. For the deformation at 73°C, however, the effect of the imperfection diminishes, i.e., the plateau disappears.

• Strain hardening is the same for both cases; the initial deformation localization at the imperfection does not affect the direction and amount of orientation on the molecular network.

4.4 Rapid stretching: model predictions vs. experimental results

As a conclusion to this work, it is interesting to compare the ability of the current model to capture the results of mechanical tests of other workers. Fig. 4.3.4-8 shows recent experimental results obtained by Buckley et al. from the constrained stretching of initially amorphous PET stretched at a nominal extension rate of 1/s. On the same figure are superposed model predictions of our finite-strain model with parameters reduced from our mechanical tests. Results are plotted as the variation of true stress vs. nominal strain. The agreement is satisfactory, but not perfect. The model captures the level of yield at about 15MPa as well as the subsequent strain hardening. Even though there is about 5MPa difference between theory and experiment at a nominal strain of 1.5, the difference becomes less as the strain approaches a level of 1.75. Structure differences between the grades of PET tested by the two groups and adiabatic heating effects are two reasons that contribute to the disagreement.

4.5 Conclusions

Simulations of rapid, uniaxially constrained stretching of initially amorphous, un-oriented PET under conditions of a) either non-homogeneous initial thickness or b)

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4 The tests were presented in the second chapter of the thesis.
non-homogeneous deformation temperature have shown that,

- The plastic strain rate maximizes locally at regions of high deformation temperature as well as in the presence of local imperfections.

- As a result, accumulated plastic strain is always higher locally when conditions such as the ones mentioned above favor a high plastic rate.

- For the conditions examined, i.e., a constant temperature difference of 4°C and a initial thickness imperfection of 1% the temperature difference resulted in larger thickness non-uniformity of the end product. A more thorough understanding of the effects of imperfections requires a complete parametric analysis.

- Both the dimensional imperfection and the temperature difference impact on the global mechanical behavior of the film during stretching. Nominal stress vs. strain results showed that strain softening is irregular when the film incorporates a local imperfection and/or is stretched at a non-uniform temperature.

- When the film is stretched in non-homogeneous temperature, the material close to the surface of the film is sheared towards the cold end. On the other hand, when the film stretched includes a local dimensional imperfection, the shear close to the surface of the film is always away from the imperfection. In both cases, the amount of shear decreases as the distance to the mid-thickness of the film decreases.

References

1. ABAQUS Manuals, Hibbitt, Karlson Sorensen, Pawtuckett R.I..

Fig. 4.1-1: Production stages of PET based biaxially oriented sheet (From the MELINEX production guide [2]).
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Fig. 4.2.1-1: Finite element model of a constrained stretching process with a constant temperature difference along the sheet. The mesh isolates one quarter of the film in stretch.
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Fig. 4.2.2-1(b): Plastic strain rate ($\dot{\gamma}^p$) contours at sampled deformation times.

$t = 4.31 - 29.3$ s
Fig.4.2.2-2(a): Accumulated plastic strain ($\gamma^p$) contours at sampled deformation times.

t=0.812 - 9.81s
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$t=22.0 - 30\ s$
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