An Experimental and Numerical Study of the Film Casting Process

Kenneth Aniunoh
Clemson University, kaniuno@clemson.edu

Follow this and additional works at: https://tigerprints.clemson.edu/all_dissertations
Part of the Chemical Engineering Commons

Recommended Citation
https://tigerprints.clemson.edu/all_dissertations/148

This Dissertation is brought to you for free and open access by the Dissertations at TigerPrints. It has been accepted for inclusion in All Dissertations by an authorized administrator of TigerPrints. For more information, please contact kokeefe@clemson.edu.
AN EXPERIMENTAL AND NUMERICAL STUDY OF THE FILM CASTING PROCESS

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Chemical Engineering

by
Kenneth Kanayo Aniunoh
December 2007

Accepted by:
Dr. Graham M. Harrison, Committee Chair
Dr. Amod A. Ogale
Dr. Douglas E. Hirt
Dr. Christopher L. Cox
ABSTRACT

Film casting is a common industrial process used to produce polymeric films. During film casting, a polymer melt is extruded through a flat die before rapid cooling on a chill roll. The chill roll velocity is faster than the velocity at which the melt exits the die, thus the polymer melt is stretched and oriented in an extensional flow. The material properties and processing conditions have a significant impact on the process and the final thermal/mechanical properties of the film produced.

Optimization of industrial scale film casting processes is still greatly dependent on trial and error methods. Therefore, this work is motivated primarily by the vision of the Center for Advanced Engineering Fibers and Films (CAEFF) to provide industry partners with computer-aided simulation methods for the design and optimization of future film casting processes.

This work is unique in that it employs an integrated experimental and modeling research approach towards the investigation of the film casting process. Experimentally, we study the film development in the air-gap between the die and the chill roll, and the final film properties. The modeling uses parameters such that the physical conditions under which the film casting simulations are conducted are identical to the experiments. The model inputs are directly derived from the rheological and thermal characterization of the polymeric materials used in the experiments. Therefore, this work provides a comprehensive set of experimental data, coupled with some simulations, which contribute towards a more detailed understanding of the film casting process.
In this work, we experimentally investigate the impact of material properties (such as polymer viscosity) and process conditions (such as die temperature, draw ratio and air-gap length) on the film formation process in the region between the die exit and the chill roll. Experiments are conducted using polypropylene, and a full thermal and rheological characterization of these materials is used both to interpret the experimental results and to provide parameters for the subsequent simulations. The effect of secondary processing steps, such as uniaxial stretching, on film strength, orientation and crystallinity is also studied. Finally, the measured width, temperature and velocity profiles are compared to model predictions.

The machine direction ($v_x$) and transverse direction ($v_y$) velocity components are measured as a function of position in the air-gap. We believe that these are the first pointwise measurements of the $v_y$ velocity component in film casting using the LDV technique. The $v_y$ velocity component is a result of the film neck-in, and is seen to decrease from the film edges to the centerline. Calculated centerline strain rates are found to depend on the draw ratio due to the effects of the resistance to flow as the film cools near the chill roll and the tension applied to the film as draw ratio is increased.

An increase in the die temperature, or a decrease of the material molecular weight, causes an increase in film neck-in due to the reduced resistance to flow. Increasing the air-gap length also increases the neck-in. This is due to the reduction of the strain rate (Deborah number) as the air-gap length is increased.

Increasing the draw ratio results in an increase in the temperature drop in the air-gap region. This observation is due to improved heat transfer from the film as a result of the decrease in film thickness as draw ratio is increased. Temperature maps show a minimum
in the temperature in the central portions of the film, as the chill roll is approached, due to the formation of edge beads at the film edges.

The Primary film samples produced on the take-up roll are found to possess the mesomorphic crystalline morphology of isotactic polypropylene. This is attributed to the quenching action of the chill roll. Increasing the draw ratio slightly increases the crystalline content of the Primary film due to the decrease in the film temperature at the chill roll. Uniaxial stretching increases the moduli of the film due to the increase in film orientation and the effect on the film crystalline morphology. The stretching conditions also impact the film properties.

The wealth of experimental data generated during the course of this work is employed in the verification of the CAEFF FISIM 2D Cast Film Model. The experimental results are used as an indicator of the success of the model in capturing the primary physical characteristics of the film casting process. Using model parameters obtained directly from the thermal and rheological characterization of the polymer materials, and identical process variables to the experiments, we find that the model captures the qualitative effect of draw ratio, die temperature and polymer viscosity on the film geometry. The model also predicts the temperature drop and velocity profiles in the web.
DEDICATION

This dissertation is dedicated to the memory of my uncles; Emmanuel Aniunoh (Eze), Basil Aniunoh (Okwuoma) and Patrick Aniunoh (Ochudo).
ACKNOWLEDGMENTS

The completion of this work has been made possible by the assistance of many. I would like to thank those special people who have in no small measure contributed to the success of this work.

I would like to thank my parents Mr. and Mrs. Aniunoh for their support throughout my academic life. I would also like to express my appreciation to my siblings Chinedu, Ogugua, Chukwuma and Chike for all their brotherly love support.

I sincerely thank my advisor Dr. Graham M. Harrison for his guidance, motivation, understanding and patience. This work would not have been completed without his insightful comments and suggestions.

I would like to express my gratitude and appreciation for the cooperative efforts of my committee members, Dr. Amod A. Ogale, Dr. Douglas E. Hirt and Dr. Christopher L. Cox. I would also like to thank Dr. Cox for his time and expertise during the writing of the modeling section of this work.

I thank Dr. James B. von Oehsen for his work on the cast film model. I am grateful to all the post-doctoral fellows and fellow graduate students who have assisted me in some way during the course of this work. I also thank the employees of both the Chemical and Biomolecular Engineering Department and the Center for Advanced Engineering Fibers and Films (CAEFF) for their invaluable support.

Finally, I would like to thank the Center for Advanced Engineering Fibers and Films (CAEFF) for providing the funding for this research.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE PAGE</td>
<td>i</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>v</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xiii</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 The Film Casting Process</td>
<td>2</td>
</tr>
<tr>
<td>1.2 Numerical and Experimental Studies on Film Casting</td>
<td>7</td>
</tr>
<tr>
<td>1.3 Secondary Processing</td>
<td>11</td>
</tr>
<tr>
<td>1.4 Film Structure and Property Relationship</td>
<td>12</td>
</tr>
<tr>
<td>1.5 Objectives and Scope</td>
<td>14</td>
</tr>
<tr>
<td>2. EXPERIMENTS AND MATERIALS</td>
<td>15</td>
</tr>
<tr>
<td>2.1 Polymer Characterization</td>
<td>16</td>
</tr>
<tr>
<td>2.2 Film Casting Experiments</td>
<td>33</td>
</tr>
<tr>
<td>2.3 Film Processing and Testing</td>
<td>46</td>
</tr>
<tr>
<td>2.4 Film Morphology and Structure</td>
<td>58</td>
</tr>
<tr>
<td>2.5 Hypothesis Testing</td>
<td>66</td>
</tr>
<tr>
<td>2.5 Summary</td>
<td>70</td>
</tr>
</tbody>
</table>
Table of Contents (Continued)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3. EXPERIMENTAL INVESTIGATION OF FILM FORMATION</td>
<td>72</td>
</tr>
<tr>
<td>3.1 Effect of Draw Ratio on the Film Casting of Profax PH 835</td>
<td>73</td>
</tr>
<tr>
<td>3.2 Impact of Material Properties and Process Conditions on PP Film Casting</td>
<td>87</td>
</tr>
<tr>
<td>3.3 Conclusions</td>
<td>115</td>
</tr>
<tr>
<td>4. INFLUENCE OF PROCESS CONDITIONS ON FILM PROPERTIES</td>
<td>117</td>
</tr>
<tr>
<td>4.1 Wide Angle X-ray Diffraction</td>
<td>120</td>
</tr>
<tr>
<td>4.2 Differential Scanning Calorimetry</td>
<td>130</td>
</tr>
<tr>
<td>4.3 Dynamic Mechanical Analysis</td>
<td>138</td>
</tr>
<tr>
<td>4.4 Tensile Testing</td>
<td>144</td>
</tr>
<tr>
<td>4.5 Conclusions</td>
<td>148</td>
</tr>
<tr>
<td>5. MODEL VERIFICATION</td>
<td>150</td>
</tr>
<tr>
<td>5.1 Model Overview</td>
<td>150</td>
</tr>
<tr>
<td>5.2 Calculation of Model Parameters</td>
<td>156</td>
</tr>
<tr>
<td>5.3 Model predictions vs. Experimental Data</td>
<td>178</td>
</tr>
<tr>
<td>5.4 Conclusions</td>
<td>188</td>
</tr>
<tr>
<td>6. CONCLUSIONS AND FUTURE WORK</td>
<td>189</td>
</tr>
<tr>
<td>6.1 Conclusions</td>
<td>189</td>
</tr>
<tr>
<td>6.2 Recommendations for Future Work</td>
<td>192</td>
</tr>
</tbody>
</table>
Table of Contents (Continued)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>APPENDICES</td>
<td>195</td>
</tr>
<tr>
<td>A. Derivation of Calculation Method for the Transverse Velocity Component</td>
<td>196</td>
</tr>
<tr>
<td>B. Results of Research Hypothesis Testing</td>
<td>201</td>
</tr>
<tr>
<td>LITERATURE CITED</td>
<td>213</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Test cases for the Profax PH 835 film casting experiments.</td>
</tr>
<tr>
<td>2.2</td>
<td>Process conditions for the X171 and X172 film casting experiments.</td>
</tr>
<tr>
<td>3.1</td>
<td>Temperature drop and thermal gradients for PH 835 case I experiments.</td>
</tr>
<tr>
<td>3.2</td>
<td>Temperature drop and thermal gradients for PH 835 case II experiments.</td>
</tr>
<tr>
<td>3.3</td>
<td>Film half-width for the X171 and X172 samples (L = 9 cm).</td>
</tr>
<tr>
<td>3.4</td>
<td>Film widths for X171 and X172 samples produced at various DR and L.</td>
</tr>
<tr>
<td>3.5</td>
<td>Comparison of measured velocity, v60 to calculated z60-direction velocity component.</td>
</tr>
<tr>
<td>4.1</td>
<td>Processing conditions for Primary film samples.</td>
</tr>
<tr>
<td>4.2</td>
<td>Relative areas for the crystalline peaks Ic (110, 040, 130, 111, and mesomorphic peak) and the amorphous region Ia.</td>
</tr>
<tr>
<td>4.3</td>
<td>Crystalline axis Hermans orientation factors.</td>
</tr>
<tr>
<td>4.4</td>
<td>Degree of crystallinity and peak temperatures for X171 (Primary and Processed) films.</td>
</tr>
<tr>
<td>4.5</td>
<td>Degree of crystallinity and peak temperatures for X172 (primary and processed) films. The primary films are produced at $T_{die} = 200^\circ$C.</td>
</tr>
<tr>
<td>4.6</td>
<td>Degree of crystallinity and peak temperatures for X172 (primary and processed) films. The primary films are produced at $T_{die} = 220^\circ$C.</td>
</tr>
</tbody>
</table>
List of Tables (Continued)

Table                                                                                                    Page

4.7  Tensile properties for unstretched samples at \(L = 5\) cm and \(T_{\text{die}} = 220\) °C. The value in ( ) is the standard deviation. All other values are average values. .................. 145

4.8  Tensile properties for unstretched samples at \(L = 8\) cm and \(T_{\text{die}} = 220\) °C. The value in ( ) is the standard deviation. All other values are average values. .................. 145

4.9  Tensile properties for stretched samples with \(L = 5\) cm and \(T_{\text{die}} = 220\) °C. The value in ( ) is the standard deviation. All other values are average values. .................. 147

4.10 Tensile properties for stretched samples with \(L = 5\) cm and \(T_{\text{die}} = 200\) °C. The value in ( ) is the standard deviation. All other values are average values. .................. 148

5.1  Carreau model parameters for the X171 and X172 samples. ...................................................... 162

5.2  Arrhenius constants......................................................................................................................... 162

5.3  Giesekus model parameters for the X171 and X172 samples. ...................................................... 164

5.4  Crystallization parameters. ........................................................................................................... 178

B-1  Comparing centerline velocities for the Profax PH-835 sample. .................................................. 202

B-2  Comparing effect of air-gap length on the thickness profile for the X172 sample.......................... 203

B-3  Comparing Temperature Profiles for X171 and X172. .............................................................. 204

B-4  Centerline velocity comparison for draw ratio of 8.6. ................................................................. 205

B-5  Centerline velocity comparison for draw ratio of 10.7............................................................... 205

B-6  Heat of melting for the X171 sample films. .................................................................................... 207
List of Tables (Continued)

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-7</td>
<td>208</td>
</tr>
<tr>
<td>Heat of melting for X172 films produced using ( T_{\text{die}} = 200 , ^\circ\text{C} ).</td>
<td></td>
</tr>
<tr>
<td>B-8</td>
<td>209</td>
</tr>
<tr>
<td>Heat of melting for X172 films produced using ( T_{\text{die}} = 220 , ^\circ\text{C} ).</td>
<td></td>
</tr>
<tr>
<td>B-9</td>
<td>210</td>
</tr>
<tr>
<td>Comparing Heat of melting for X171 and X172 at ( T_{\text{die}} = 220 , ^\circ\text{C} ).</td>
<td></td>
</tr>
<tr>
<td>B-10</td>
<td>211</td>
</tr>
<tr>
<td>Comparing Tensile properties for different stretch rates.</td>
<td></td>
</tr>
<tr>
<td>B-11</td>
<td>212</td>
</tr>
<tr>
<td>Comparing Yield stress as function of DR and L for X171.</td>
<td></td>
</tr>
<tr>
<td>B-12</td>
<td>212</td>
</tr>
<tr>
<td>Comparing Yield stress as function of DR and L for X172.</td>
<td></td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Schematic of a film casting line.</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>Film neck-in and thickness draw down in the air gap.</td>
<td>4</td>
</tr>
<tr>
<td>2.1</td>
<td>The DSC thermogram for PH 835 showing the reheating step. Melting peak occurs at about 168 °C.</td>
<td>20</td>
</tr>
<tr>
<td>2.2</td>
<td>The DSC thermogram for X171 and X172 showing the reheating steps for both samples. The melting peaks occur at about 148 °C.</td>
<td>21</td>
</tr>
<tr>
<td>2.3</td>
<td>Isotactic polypropylene (a) defect free chain</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>(b) regio 2,1-erythro defect.</td>
<td></td>
</tr>
<tr>
<td>2.4</td>
<td>Dynamic rheology properties for Profax PH 835 at 180 °C and 210 °C.</td>
<td>24</td>
</tr>
<tr>
<td>2.5</td>
<td>Dynamic viscosity and moduli for X171 and X172 at 200 °C as functions of frequency. Solid points (●) are for the X171 plots while unfilled points (○) are for the X172 sample.</td>
<td>26</td>
</tr>
<tr>
<td>2.6</td>
<td>Dynamic viscosity and moduli for X171 and X172 at 220 °C as functions of frequency. Solid points (●) are for the X171 plots while unfilled points (○) are for the X172 sample.</td>
<td>27</td>
</tr>
<tr>
<td>2.7</td>
<td>Front and plan view of the extensional viscosity fixture. The extensional flow is provided by cylinder A rotating about its axis while also rotating around cylinder B (reproduced with permission of the Harrison group at Clemson University).</td>
<td>29</td>
</tr>
<tr>
<td>2.8</td>
<td>Extensional rheology data for PH 835 at 170 °C.</td>
<td>32</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.9</td>
<td>Extensional viscosity at 170°C for X171 at various extension rates</td>
</tr>
<tr>
<td>2.10</td>
<td>A digital image showing the film neck-in occurring between the Die exit and the Chill roll</td>
</tr>
<tr>
<td>2.11</td>
<td>Infrared image of the polymer film in the air-gap. The temperature color scheme is shown in the right edge of the figure</td>
</tr>
<tr>
<td>2.12</td>
<td>Schematic of laser head/detector used in the LDV technique. The frequency of the scattered rays is proportional to the velocity of the moving surface</td>
</tr>
<tr>
<td>2.13</td>
<td>The deviation angle between the operating position and the ideal position</td>
</tr>
<tr>
<td>2.14</td>
<td>Schematic of the laser head as observed from the rear of the instrument. The arrows indicate the direction of the velocity component being measured, for the shown laser head position</td>
</tr>
<tr>
<td>2.15</td>
<td>Biaxial stretching machine installed at the Center for Advanced Engineering Fibers and Films (CAEFF)</td>
</tr>
<tr>
<td>2.16</td>
<td>Tensile fixtures and sample for a DMA test</td>
</tr>
<tr>
<td>2.17</td>
<td>Schematic of test sample and grips</td>
</tr>
<tr>
<td>2.18</td>
<td>Characteristic Stress-strain plots for brittle (1) and ductile (2) plastic samples (adapted from Fried (2002))</td>
</tr>
<tr>
<td>2.19</td>
<td>Example of crystal planes and their indices for cubic lattices</td>
</tr>
<tr>
<td>2.20</td>
<td>Incident and reflected X-rays for a stack of planes</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.21</td>
<td>WAXD diffractogram for X171 film stretched to 2X its initial length. Diagram shows the crystalline and amorphous areas.</td>
</tr>
<tr>
<td>3.1</td>
<td>PH 835 width profiles as a function of draw ratio (test case I).</td>
</tr>
<tr>
<td>3.2</td>
<td>Centerline temperature profile for PH 835 as a function of draw ratio (test case I).</td>
</tr>
<tr>
<td>3.3</td>
<td>Centerline temperature profile for PH 835 as a function of draw ratio (test case II).</td>
</tr>
<tr>
<td>3.4</td>
<td>Temperature field for PH 835 at DR = 12.8 (test case I).</td>
</tr>
<tr>
<td>3.5</td>
<td>Draw direction velocity map for PH 835 at DR = 8.6 (test case I).</td>
</tr>
<tr>
<td>3.6</td>
<td>Draw direction velocity maps for PH 835 at DR = 6.5 and DR = 12.8 (test case II).</td>
</tr>
<tr>
<td>3.7</td>
<td>Centerline velocity profiles for PH 835 as a function of draw ratio (test case I).</td>
</tr>
<tr>
<td>3.8</td>
<td>Centerline strain rates as a function of DR (test case I).</td>
</tr>
<tr>
<td>3.9</td>
<td>Half-width profiles as functions of viscosity and draw ratio at die temperature of 220 °C.</td>
</tr>
<tr>
<td>3.10</td>
<td>Half-width profile as a function of temperature for X171 at DR = 8.6.</td>
</tr>
<tr>
<td>3.11</td>
<td>Thickness profile for X171 and X172 films at T_{die} = 220 °C.</td>
</tr>
<tr>
<td>3.12</td>
<td>Thickness profile for X172 films at T_{die} = 200 °C and 220 °C.</td>
</tr>
<tr>
<td>3.13</td>
<td>Half-width profile as a function of air-gap for the X171 and X172 samples at a die temperature of 220 °C.</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

Figure                                                                                       Page

3.14  Thickness profile for X171 films at T_{die} = 220 °C................................................ 96

3.15  Temperature profile in web for the X171 and X172 samples at DR = 8.6 and die temperature of
       220 °C................................................................................................................. 97

3.16  Centerline temperature profile for X171 and X172 at a die temperature of 220 °C. Air-gap lengths of
       5 cm and 8 cm are used for these experiments. ...................................................... 99

3.17  Centerline velocity as functions of draw distance and draw ratio for X172 at a die temperature of 220 °C
       and L = 9 cm. ........................................................................................................ 101

3.18  Centerline velocity as functions of draw distance and draw ratio for X171 at a die temperature of 220 °C
       and L = 9 cm. ........................................................................................................ 102

3.19  Centerline strain rates for X171 and X172 at a die temperature of 220 °C and L = 9 cm. .................. 103

3.20  Velocity map showing velocity as a function of transverse distance for X171 and X172
       (DR = 8.6, L = 9 cm, T_{die} = 220 °C).................................................................. 104

3.21  Relative velocity vector directions for the experiments set-up used in the determination of v_y............................................................... 106

3.22  Plot of the magnitude of the v_x and v_60 velocity components for X172 at DR = 8.6, L = 8 cm
       and a die temperature of 220 °C........................................................................ 108

3.23  Calculated v_y component velocity magnitude for X172 at DR = 12.8, L = 8 cm and a die temperature of
       220 °C.................................................................................................................. 109

3.24  Calculated magnitude of the velocity vector as a function of position in the web for X172 at
       DR = 8.6, L = 8 cm and a die temperature of 220 °C.......................................... 113
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figures</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.25</td>
<td>Direction vectors for X172 at DR = 8.6, L = 8 cm and a die temperature of 220 °C.</td>
</tr>
<tr>
<td>4.1</td>
<td>WAXD patterns for X171 film samples produced at $T_{\text{die}} = 220$ °C and DR = 8.6. (a) unstretched sample (b) sample stretched to 3X the initial length.</td>
</tr>
<tr>
<td>4.2</td>
<td>X172 film at $T_{\text{die}} = 200$ °C and DR = 8.6.</td>
</tr>
<tr>
<td>4.3</td>
<td>X172 film at $T_{\text{die}} = 200$ °C and DR = 8.6. The film is stretch to 3X the initial length at 100 mm/s/s.</td>
</tr>
<tr>
<td>4.4</td>
<td>WAXD diffractogram for X171 film stretched to 2X its initial length. Diagram shows the crystalline and amorphous areas.</td>
</tr>
<tr>
<td>4.5</td>
<td>The 040 and 110 crystal planes with respect to the a, b, and c crystallographic axes.</td>
</tr>
<tr>
<td>4.6</td>
<td>Heating curve for X172 films with $T_{\text{die}} = 200$ °C and L = 5 cm.</td>
</tr>
<tr>
<td>4.7</td>
<td>Heating curve for processed X171 films with $T_{\text{die}} = 220$ °C and L = 5 cm and DR = 8.6. Stretcher acceleration used is 100 mm/s/s.</td>
</tr>
<tr>
<td>4.8</td>
<td>Stress and modulus as functions of percent strain for X172 film produced using $T_{\text{die}} = 200$ °C, DR = 12.8 and L = 5 cm.</td>
</tr>
<tr>
<td>4.9</td>
<td>Modulus as a function of temperature for X172 films. The processing conditions for the primary film are $T_{\text{die}} = 200$ °C and L = 5 cm.</td>
</tr>
<tr>
<td>4.10</td>
<td>Modulus as a function of temperature for X171 processed films. The processing conditions for the primary film are $T_{\text{die}} = 200$ °C, DR = 8.6 and L = 5 cm.</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.11</td>
<td>Modulus as a function of temperature for X172 processed films. The film samples are stretched at two different rates. The processing conditions for the primary film are $T_{\text{die}} = 200, ^\circ\text{C}$, DR = 8.6 and $L = 5, \text{cm}$ while the films were stretched to 3X the initial length.</td>
<td>143</td>
</tr>
<tr>
<td>5.1</td>
<td>Film neck-in and thickness draw down in the air gap region.</td>
<td>151</td>
</tr>
<tr>
<td>5.2</td>
<td>Shear and complex viscosity for X171 at 200 °C.</td>
<td>161</td>
</tr>
<tr>
<td>5.3</td>
<td>Carreau model predictions for the X171 sample complex viscosity.</td>
<td>163</td>
</tr>
<tr>
<td>5.4</td>
<td>Giesekus model predictions for the X171 sample storage and loss moduli at 200 °C.</td>
<td>165</td>
</tr>
<tr>
<td>5.5</td>
<td>Giesekus model predictions for the X172 sample storage and loss moduli at 200 °C.</td>
<td>166</td>
</tr>
<tr>
<td>5.6</td>
<td>Giesekus model predictions for the X171 and X172 sample complex viscosities at 200 °C.</td>
<td>167</td>
</tr>
<tr>
<td>5.7</td>
<td>DSC cooling curves for the X171 sample at cooling rates of 5 °C/min, 10 °C/min and 20 °C/min.</td>
<td>169</td>
</tr>
<tr>
<td>5.8</td>
<td>DSC cooling curves for the X172 sample at cooling rates of 5 °C/min, 10 °C/min and 20 °C/min.</td>
<td>170</td>
</tr>
<tr>
<td>5.9</td>
<td>Reciprocal half-time as a function of temperature.</td>
<td>172</td>
</tr>
<tr>
<td>5.10</td>
<td>DSC cooling curves for the crystallization of the X171 sample at various temperatures.</td>
<td>173</td>
</tr>
<tr>
<td>5.11</td>
<td>DSC Thermogram for the X171 sample at 95 °C. The crystallization curve is extrapolated to the zero heat flow line.</td>
<td>175</td>
</tr>
<tr>
<td>5.12</td>
<td>Degree of crystallinity as a function of time, for the X171 sample at various temperatures.</td>
<td>176</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.13</td>
<td>Plot of reciprocal half-time vs. Temperature for X172. This plot is used for determining model parameters for the energy equation. 177</td>
</tr>
<tr>
<td>5.14</td>
<td>Model verification of the prediction for the width profile. 179</td>
</tr>
<tr>
<td>5.15</td>
<td>Model verification of the prediction for the temperature profile. 181</td>
</tr>
<tr>
<td>5.16</td>
<td>Model verification of the prediction for the velocity profile. 182</td>
</tr>
<tr>
<td>5.17</td>
<td>Model prediction vs. experiment for PH 835 at T_{die} = 220 °C, DR = 8.6, and L = 8.8 cm for the velocity profile. 184</td>
</tr>
<tr>
<td>5.18</td>
<td>Model prediction for X172 width profiles at L = 5 cm and 8 cm. Here T_{die} = 220 °C, DR = 8.6, and L = 8 cm. 185</td>
</tr>
<tr>
<td>5.19</td>
<td>Model prediction for X172 centerline temperature profiles at L = 5 cm and 8 cm. Here T_{die} = 220 °C, DR = 8.6, and L = 8 cm. 186</td>
</tr>
<tr>
<td>5.20</td>
<td>Model prediction for X172 centerline temperature profiles at L = 5 cm and 8 cm. Here T_{die} = 220 °C, DR = 8.6, and L = 8 cm. 187</td>
</tr>
</tbody>
</table>
CHAPTER 1
INTRODUCTION

The polymer industry continues to grow, and worldwide the industry was projected to increase production from 101 million metric tons in 1993 to 123 million metric tons in 1998 (Kanai and Campbell, 1999). This represents about a 4% yearly growth rate. Prnewswire.com (2007) reports that the U.S. polymer industry is expected to grow at 3-4% per year, worldwide, until 2020 (www.prnewswire.com). This is three times the growth rate for other basic materials. The polymer industry in Ohio is said to generate up to 49 billion dollars in revenue annually (www.polymerohio.org). By some measures, the polymer industry is reported as the 4th largest industry in the United States (Baumann, 2005). Some of the more popular production processes used in the polymer industry include blow and injection molding, sheet and film extrusion and vacuum forming (Kanai and Campbell, 1999).

Film casting is one of two major methods for the production of industrial films. The other major production method is film blowing. The film blowing process is a more rapid and economical means for film production, while the film casting method usually produces better quality film in terms of thickness variation and clarity (Pearson, 1985; Giles et al., 2005). Polymer films produced from film casting are used in the making of geomembranes, stretch wraps, embossed and normal films in diapers, and for the packaging of food and disposable medical supplies (Giles et al., 2005).
Optimization/design of industrial scale film casting processes still depends greatly on trial and error methods. A major focus of this work is an experimental investigation of film casting, followed by a numerical analysis of the process. The ultimate goal is then to combine process modeling and experimental verification in order to develop process optimization/design methods based on computer-aided design.

In this chapter we present a description of the parts of the film casting process that are relevant to this work, and review of some of the previous work found in the literature on film casting.

1.1 The Film Casting Process

A representative sketch of a film casting line is shown in Figure 1.1. Essential components of the line include a hopper, an extruder screw/housing, a melt pump, a die and a chill roll. During operation, polymer pellets are introduced to the extruder through the hopper. The extruder has different zones in which the temperature can be set independently (depending on the melting characteristics of the polymer being used). The extruder screw serves to melt the polymer and also as a feed pump to the die. A melt pump is placed between the die inlet and the extruder outlet to maintain steady polymer flow to the die.
In film casting a polymer melt is extruded through an (approximately) rectangular flat die and cooled on a chill roll or in a water bath (Pearson, 1985). In this work a chill roll is utilized as the means for cooling the polymer melt. The polymer melt undergoes a predominantly elongational flow field in the region between the die and the chill roll (in subsequent chapters in this dissertation, we will refer to this as the air-gap region) because the chill roll is run at a higher velocity than the velocity of the polymer melt at the die exit. This stretching induces some orientation in the film, and the chill roll serves to freeze in this orientation. Thus, films produced using film casting tend to have

Figure 1.1 Schematic of a film casting line.
different tensile and tear properties in the machine and transverse directions (Kanai and Campbell, 1999; Elias et al., 2000). The air-gap lengths employed in this work range from 5-9 cm (to allow for more measurement space) and are typically higher than those (air-gap lengths) encountered in industrial film casting lines (typically 2-5 cm). Figure 1.2 shows how the flow process in the air-gap causes a draw down in film width (neck-in) and thickness due to mass conservation. Films produced using the cast film process have less thickness variation (due to the die and cooling method used) and greater clarity, due to the rapid quenching on the chill roll which minimizes crystal growth and crystal size (Giles et al., 2005).

**Figure 1.2** Film neck-in and thickness draw down in the air gap.
After passing off the chill roll, the primary film obtained can be subjected to secondary processing steps such as biaxial stretching. Secondary processing helps impart the desired end-use properties (Baird and Collias, 1995). For polyolefin films a flame treatment stage may be added to the secondary processing steps if the film is to have a printable surface (Giles et al., 2005). This allows for better adhesion to inks and coatings. The success of secondary processing is impacted by the quality of the primary film. Some of these important end-use film properties include toughness, transparency and flexibility (Pearson, 1985).

Some problems typically encountered experimentally in film casting are the edge-bead formation and draw resonance (Silagy et al., 1999). The edge-bead formation results in the edges of the final film being thicker than the central portions of the film (Smith and Stolle, 2000; Dobroth and Erwin, 1986). In industry, the film edges are usually trimmed-off before further processing of the film and the waste material is recycled (Pearson, 1985). Draw resonance is an instability whereby there is a periodic variation in the film neck-in (Silagy et al., 1999; Yeow, 1974; Smith and Stolle, 2000). This occurs at high draw ratios and places a limit on the draw ratio for a particular film casting operation. The draw ratio at which this instability sets in depends on the polymer material.

The response of polymeric fluids to flow processes like film casting is significantly dependent on the polymer material properties such as viscosity (shear and/or elongational) and molecular weight as well as the process conditions such as draw ratio and die temperature (Baird and Collias, 1995; Pearson, 1985).
1.1.1 Process Conditions

The film formation process in the air-gap region is dependent on several process conditions including the **draw ratio** (DR), which is defined as the ratio of the polymer film velocity at the chill roll to the polymer melt velocity at the die exit:

\[
DR = \frac{v_L}{v_0}.
\]  

In Equation 1.1, \(v_L\) represents the velocity at the chill roll and \(v_0\) represents the velocity at the die exit. The draw ratio can be varied by maintaining a constant chill roll velocity while the polymer throughput is varied or by keeping the throughput constant while the chill roll velocity is adjusted. Changing both the film velocity at the chill roll, and the polymer throughput, can also vary the draw ratio. The draw ratio affects both the amount of neck-in, the draw down in film thickness, orientation etc. obtained in the air-gap (Smith and Stolle, 2000; Silagy et al., 1999). Other important process variables include the **air-gap length** \(L\) and the **die** and the **chill roll temperatures**. The air gap length is the distance between the die exit and the point of contact between the film and the chill roll. The film formation process is affected by the air gap length by virtue of its effect on the flow geometry and the strain rate experienced by the polymer film. Some studies show that increasing the air-gap length can increase the amount of neck-in obtained (Acierno et al., 2000). An increase in the film neck-in (at constant throughput and DR) may also lead to an increase in the film thickness (Rajagopalan, 1999). This is due to mass conservation. Since the increase in neck-in implies a decrease in film width, this
should lead to an increase in film thickness in order for the film cross-sectional area to remain approximately constant.

### 1.1.2 Material Properties

The properties of the film produced using the film casting process are significantly affected by the properties of the starting raw material. Polymer material properties influence the film formation process in the air-gap (Acierno et al., 2000; Seyfzadeh et al., 2005) due to the role played by shear and extensional viscosity in determining the response of the polymer to thermal (temperature) and mechanical (draw ratio, air-gap length) process variables. For example, changing the polymer molecular weight (or viscosity) may lead to changes in the final film properties such as film width and thickness uniformity due to the effect of viscosity on the resistance to flow in the air-gap region.

### 1.2 Numerical and Experimental Studies on Film Casting

The literature on film casting contains works that deal with the subject from both an experimental viewpoint and a numerical/theoretical approach. The theoretical works currently make up the bulk of the studies on film casting. These two approaches ideally should work in a complementary fashion because experimental data is necessary for model verification.
1.2.1 Process Modeling

Modeling of the Cast Film Process is primarily focused on developing accurate and efficient models for predicting the film formation process in the region between the die and the chill roll. The 3-D, non-isothermal, viscoelastic and extension-dominated nature of the film casting process makes it a complex, though interesting, process to model. Availability of adequate sets of experimental data aids the model development process. In addition, the selection of a constitutive equation for the stress function and subsequent evaluation of process models relies on the availability of experimental rheological data. This dissertation is motivated in part by the need to bridge the gap between the amount of theoretical work on film casting and the relative lack of complete experimental data available in the literature for model verification.

A significant amount of the previous simulation work on film casting has been devoted to predicting the film formation process in the air-gap. Some studies have employed isothermal Newtonian models (Silagy et al., 1999; Yeow, 1974); however, models that account for non-isothermal conditions and/or viscoelasticity (Alaie and Papanastasiou, 1991; Smith and Stolle, 2000; Satoh et al., 2001) are physically more representative of the observed experimental results. Yeow (1974) employed an isothermal Newtonian model in studying the stability of the film casting process. He determined that above a critical DR the film flow becomes unstable (draw resonance). Silagy et al. (1999) were able to predict the edge-beads using an isothermal Newtonian membrane (two dimensional, 2D) model. They also used their model to study the draw resonance in the film and determined that increasing the air-gap improves the stability of the film casting process. In their model, Alaie and Papanastasiou (1991) account for
viscoelasticity by using an integral constitutive equation of the BKZ type. They assumed that the film temperature is invariant over the film cross-section. Thus their model only predicts temperature variations in the machine direction. Smith and Stolle (2000) employed a non-isothermal 2-D viscoelastic model to study factors responsible for neck-in reduction and improved thickness uniformity. Satoh et al. (2001) used a quasi-3D model with the Larson equation for the viscoelastic stress to predict both the thickness profile of the final film and the film width as a function of distance from the die. They compared these predictions to experimental results obtained for a laboratory scale process and an industrial scale process, and found good agreement between the experimental and predicted results for the lab scale process, but not for the industrial scale process. Dobroth and Erwin (1986) studied the causes of edge bead formation. They concluded that edge stress effects, not surface tension or die swell, are primarily responsible for edge-beads. The edge stress effects result from the film edge undergoing uniaxial elongation while the central regions of the film experience planar elongation.

Other modeling works on film casting include that of Rajagopalan (1999), which studies the effect of variable thickness die lips on the final film width. A 2-D Giesekus model is used for the study. The study showed that using variable thickness (parabolic) dies could help reduce edge beads.

In this work a pseudo 3-D model that accounts for viscoelasticity through the Giesekus constitutive equation (Giesekus, 1982; Morrison, 2001; Bird et al., 1987) is used to predict the width, temperature and velocity profile in the air-gap region. The model predictions are also compared to experimental data accumulated in the course of this study.
1.2.2 Experimental Results in the Literature

In addition to the modeling efforts, there are some experimental studies available in the literature on film casting. Canning et al. (2001) studied the film tension, velocity and width profile for a low-density polyethylene melt and found that the film tension increases with increasing draw ratio (at a point on the film centerline). Lamberti et al. (2002) and Lamberti and Brucato (2003) investigated crystallinity and orientation in the film as a function of draw ratio. They found that increasing the draw ratio increases polymer orientation. Lamberti et al. (2001; 2002) also studied temperature and width profiles for polypropylene. They compared their experimental results to model predictions obtained using a 1-D model that incorporates the effects of crystallization. Acierno et al. (2000) studied the temperature profiles for film casting of PET. They found that increasing the draw ratio increases the temperature drop in the air-gap and that the central portion of the film cool more rapidly than the film edges. This is due to the decreasing film thickness as the draw ratio is increased and the extra heat generated from the thicker edge-beads. Seyfzadeh et al. (2005) made point-wise measurements of the velocity, width and temperature profiles for film casting of PET. They found that, under their experimental conditions, the centerline strain rate decreased with an increase in distance from the die.

In this work we measure the width, temperature and velocity profiles in the air-gap region as functions of position in the air-gap. These measurements are conducted while systematically varying process variables including the draw ratio, the die temperature and the air-gap length. We generate a complete set of experimental film casting data that can be used in model development and verification.
1.3 Secondary Processing

Due to the wide variety and diversity of end-use properties required for polymer films, secondary processing of the primary film (which is the film obtained immediately after the chill roll) is an integral part of industrial film production. Biaxial stretching helps impart molecular orientation to the film, thus improving the thermomechanical stability of the final film (Adams et al., 2000).

The two methods predominantly used for the production of biaxially oriented film are the tentering process and the double bubble tubular film process (Kanai and Campbell, 1999). The tentering method is further divided into the step-by-step or sequential stretching method and the simultaneous stretching method. The type of tentering process employed depends on the polymer material. The sequential stretching process can be performed as a single-stretching method which involves stretching the primary film first in the machine direction (MD) and then in the transverse direction (TD). It can also be operated as a multistretching method which consists of three or more stretching steps e.g. MD → TD → MD or MD → TD → MD → TD (Elias et al., 2000; Kanai and Campbell, 1999).

Elias et al. (2000) studied the effect of uniaxial/biaxial stretching on the morphology of polypropylene films (using Differential Scanning Calorimetry and Wide Angle X-ray Diffraction) and found that uniaxial stretching increases orientation in the machine direction, while subsequent stretching in the transverse direction (to produce a biaxially oriented film) tends to improve property uniformity in both the machine and transverse directions. Adams et al. (2000) studied entanglement slippage in biaxially drawn PET films with the aim of extending a glass-rubber constitutive model to incorporate features
such as stress-induced crystallization. Vigny et al. (1999) investigated the stretching of PET plates and determined that the strain induced crystallization proceeds at a faster rate with increasing strain rate. Sweeney et al. (1997) developed a hyper-elastic model for the prediction of the stress-strain response of polymer sheets to uniaxial deformation. The inaccuracies of the model in predicting experimental results were attributed to the purely elastic nature of the model.

1.4 Film Structure and Property Relationship

During the design of film products for a particular end-use application it is of great importance to determine the response of the film samples to applied mechanical stresses. The response of the film samples to the applied stress depends on the film structure developed during processing (Sperling, 2001). This response (to deformation) determines its design window or application range and can also be used as feedback in improving the film formation process.

Some methods used in studying the evolution of film structure in terms of crystallinity and orientation include Wide Angle X-ray Diffraction (WAXD), Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA). Tensile testing can be employed in elucidating the mechanical response of film samples to loading conditions (Choi and White, 2004; Diez et al., 2005; Sadeghi et al., 2007).

Diez et al. (2005) investigated the crystalline morphology of biaxially oriented polypropylene films using WAXD, DMA and tensile testing. By studying the peak intensities of the 110, 040 and 130 diffraction planes (obtained from WAXD experiments), they determined that biaxial stretching increases the molecular orientation
in the draw direction. The modulus values determined from the DMA studies and tensile testing of the films (in machine and transverse directions) were used to confirm the preferential orientation in the draw direction. Sakurai et al. (2005) showed that structure evolution during hot drawing of isotactic-polypropylene (i-PP) depended on the process conditions, polymer molecular weight distribution (MWD) and isotacticty (IT). They conducted simultaneous WAXD and Small Angle X-ray Scattering (SAXS) tests on film samples undergoing tensile testing. The results from the WAXD and SAXS experiments were correlated to the stress-strain response. Sadeghi et al. (2007) investigated the effect of different polypropylene grades on the development of micro-porous membranes obtained using films made from cast film extrusion and annealing. The film morphology was characterized using DSC, WAXD and tensile testing. The membrane performance (determined from permeability and porosity studies) was found to be significantly affected by the polymer molecular weight. Chen et al. (2006) studied the nucleation effect of SiO\(_2\) on the crystallization kinetics of i-PP and co-PP using DSC. They used a modified Avrami equation to describe the non-isothermal crystallization kinetics. They found that SiO\(_2\) increased the crystallization rate of i-PP but had the opposite effect on co-PP. This was attributed to the heterogeneous nucleating effect of SiO\(_2\) on i-PP. Mishra et al. also used the DSC technique to study the effect of nano-particles on the non-isothermal crystallization of PP/Ca\(_3\)(PO\(_4\))\(_2\) composites. Reducing the size of the Ca\(_3\)(PO\(_4\))\(_2\) nano-particles and increasing the amount of the nano-particles was found to accelerate the non-isothermal crystallization of the composites. Thermal characterization techniques like DSC can be used in obtaining model parameters for film casting models that incorporate crystallization effects on the flow field in the air-gap.
1.5 Objectives and Scope

The current work is aimed at understanding the effect of material properties such as viscosity, and process variables such as die temperature and draw ratio, on the film casting process. We focus on three polypropylene samples with different molecular weights (and hence different zero-shear viscosities), and interpret our film casting results in terms of the differences in rheological behavior. The width, the temperature and the velocity profiles of the polymer web in the air-gap are measured during the steady film casting process.

In Chapter 2 we introduce the polymer materials used in this work and discuss their rheological characterization. We then present a description of the laboratory scale film casting line employed in this study. Also discussed in Chapter 2 are the experimental methods used in studying the effect of processing conditions on the film formation process and in obtaining structure-property relationships of the primary and processed films. Chapter 3 reports an experimental study of the temperature, geometry and velocity in the air gap region as functions of die temperature, draw ratio, air-gap length and polymer viscosity/molecular weight. In Chapter 4, we report on the mechanical testing of the cast films, and the relationship between processing conditions (DR, air gap length and die temperature) and film properties (mechanical and morphological). We also study the effect of secondary processing steps like uniaxial stretching on the film properties. Chapter 5 develops a predictive model for the film casting process, and shows direct comparisons between our experimental results and numerical simulations. Chapter 6 is dedicated to Conclusions and Recommendations for future work.
CHAPTER 2

EXPERIMENTS AND MATERIALS

In this chapter, we report on the experimental methods and materials employed in this work. First, results of the thermal and rheological characterization of the polymer materials used in this study are presented. Next we describe the lab scale film casting apparatus and the process conditions employed for the film casting experiments. We also present information on the uniaxial stretching of the cast films and the test parameters used in the Dynamic Mechanical Analysis (DMA) and Tensile Testing studies of the polymer films. We will discuss two classes of film in this thesis. Primary film refers to the film samples obtained immediately after the chill roll stage. Processed films are those films that have undergone uniaxial orientation. Finally, the Differential Scanning Calorimetry (DSC) and Wide Angle X-ray Diffraction (WAXD) experiments used in studying the film morphology are discussed. The Tensile Testing, DMA, DSC and WAXD experiments help in determining the effect of processing conditions on the final film properties.
2.1 Polymer Characterization

Polypropylene (PP) is a low cost, semi-crystalline polymer resin. It has a versatile range of applications which include fibers, glass reinforced sheets, automotive interiors, medical applications and packaging (Giles et al., 2005). Polypropylene is produced by free-radical/addition polymerization (Sperling, 2001) and exhibits good chemical, heat and impact resistance.

The three polypropylene samples used in this work were all obtained from Basell Polyolefins (USA). The samples are; Profax PH 835 (MFR = 34 g/10 min); X11291-37-1 (MFR = 15 g/10 min), and hereafter referred to as X171; and X11291-37-2 (MFR = 25 g/10 min), and hereafter referred to as X172. The three samples are polypropylene homopolymers and all contain stabilizers (less than 5%). The PH 835 sample is produced using the traditional Ziegler-Natta catalysts while the X171 and X172 samples are metallocene catalyzed polypropylenes.

Polypropylene metallocene technology is fairly recent. Metallocene catalysts are single-site catalysts and allow for close control of the polymer molecular weight and molecular weight distribution (Benedikt, 1999). The use of single-site catalysts during polymerization of polypropylene also allows for control of the polymer stereochemistry and stereoregularity. The molecular weight, molecular weight distribution, stereochemistry and stereoregularity all impact the polymer morphology and thus affect the final properties of the polymer resin. It should be expected that the metallocene catalyzed samples may show thermal and rheological property trends that differ from the traditional property trends exhibited by polypropylene (due to the difference in stereoregularity and stereochemistry). For example metallocene catalyzed polymers may
exhibit melting point temperatures and shear thinning behavior that differ from the corresponding properties exhibited by Ziegler-Natta catalyzed polymers of similar molecular weight (Sakurai et al., 2005).

2.1.1 Differential Scanning Calorimetry

In this section we discuss the thermal characterization of the polypropylene samples obtained using the Differential Scanning Calorimetry (DSC) technique. This thermal characterization method provides information on the melting point and degree of crystallinity for the polypropylene samples. It can also be used in the study of the crystallization kinetics of the samples. Knowledge of the polymer thermal properties (e.g. melting point, heat capacity and heat of fusion) could aid in film process modeling, as accounting for crystallization in models may lead to better numerical predictions (Lamberti et al., 2001; Lamberti et al, 2002). The information obtained is also relevant in selecting processing temperatures (e.g. extruder and die temperatures).

Differential Scanning Calorimetry (DSC) is a thermal analysis technique which measures the difference in energy required to maintain a zero temperature difference between a test sample and a reference material while both sample and reference material are being subjected to identical heat treatment procedures i.e. identical heating or cooling rates.

The equipment used in this work is a PerkinElmer Pyris 1 DSC. The weight of the PP samples used for this thermal characterization ranged from 3-8 mg. An empty sample pan is weighed, the sample is introduced into the pan and then the sample and pan are weighed again. This allows for the determination of the sample mass. The sample pan is
then inserted into the calorimeter. A reference pan in the calorimeter is kept empty. The DSC experiment is controlled by software in which the initial sample weight, the heating/cooling rate and the temperature range are inputted before the experiment start-up. The experimental procedure involves heating the samples from 30 °C to 200 °C, cooling the samples from 200 °C to 30 °C, followed by the reheating of the samples from 30 °C to 200 °C. The heating/cooling rates used are 5 °C/min, 10 °C/min and 20 °C/min. Before the start of each step the samples are held at the initial temperature for 1 minute. The initial quenching and subsequent reheating steps are introduced so as to reduce or eliminate the effect of the sample thermal history on the DSC results. At least 5 different runs were conducted on the samples to ensure reproducibility. The reported data are average values from the different experimental runs.

Figure 2.1 shows the DSC thermogram for the Profax PH 835 sample. The thermograms for the X171 and X172 samples are shown in Figure 2.2. From the DSC curves the PH 835 sample has a $T_m = 168 °C$ while the metallocene catalyzed samples melt at about $T_m = 148 °C$. Benedikt (1999) reports that this reduced melting point temperature exhibited by PP samples produced using single-site catalysts may be due to a 2-1 insertion defect that occurs during polymerization. The regio 2,1-erythro defect results from the disruption of the predominantly head-to-tail (1-2) monomer addition (exhibited during polymerization of polypropylene) by a head-to-head monomer insertion. This defect is reported to be present only in metallocene catalyzed polypropylenes (Benedikt, 1999). Figure 2.3 shows examples of a defect free isotactic polypropylene chain and a chain containing a regio defect (Nyden et al., 2001). The
melting point temperatures determined here using the DSC technique are similar to the values reported in the material data sheets provided by Basell Polyolefins.
Figure 2.1 The DSC thermogram for PH 835 showing the reheating step. Melting peak occurs at about 168 °C.
Figure 2.2 The DSC thermogram for X171 and X172 showing the reheating steps for both samples. The melting peaks occur at about 148 °C.
2.1.2 Shear Rheology

Shear and dynamic rheological characterization of the materials was performed using a TA Instruments ARES rheometer equipped with a 25 mm cone and plate geometry. The cone angle was 0.1 radians, and the distance between the truncated cone (upper plate) and the flat, lower plate is specified as 0.056 mm. The frequency sweep tests were conducted using a frequency range of 0.1 rad/s to 500 rad/s at 5 % strain. This strain is within the experimentally determined linear viscoelastic regime for the polymers. Due to the shear rate limitations on the ARES rheometer, the step shear rate tests were run using shear rates of 0.1 s\(^{-1}\) to 10 s\(^{-1}\). High shear rate tests (i.e. 10 s\(^{-1}\) to 1000 s\(^{-1}\)) were conducted using an ACER capillary rheometer. The rheological data is important for numerical modeling of the process because it facilitates the selection of the constitutive equations and the model parameters used in the simulations.
Figure 2.4 shows the storage modulus $G'$, the loss modulus $G''$, and the complex viscosity $\eta^*$ for the Profax PH 835 sample at two representative temperatures of 180 °C and 210 °C. These temperatures are in the range of temperature encountered in the film casting experiments presented in this work. Increasing the temperature decreases both the polymer complex viscosity and the storage and the loss moduli. Because of the temperature dependence of the polymer rheology, it is apparent that the die temperature, and the changes in film temperature as the polymer web approaches the chill roll, will have a significant effect on the film formation process between the die and the chill roll. Over the 30 °C variation in temperature (which lies within that observed in the cast film web) there is a change in complex shear viscosity from approximately 200 Pa-s to 600 Pa-s. There is also an increase in the onset frequency for shear thinning as temperature is increased. This can be explained by a decrease in the relaxation time for the polymer as the temperature is increased.
Figures 2.5 and 2.6 show the complex viscosity, $\eta^*$, storage modulus, $G'$, and loss modulus, $G''$ for the X171 and X172 samples at 200 °C and 220 °C. The filled points (●) indicate results for the X171 sample, while unfilled points (○) indicate the results for the X172 sample. The X171 sample is seen to have a higher complex viscosity, over the frequency range tested, than the X172 sample. Both materials demonstrate shear thinning behavior at high frequencies. The slope of the shear thinning region of the X171 sample is greater than that shown by the X172 sample. This may indicate that the X171 sample exhibits a lower molecular weight distribution (MWD) than the X172 sample (Morrison, 2001). Observing the cross-over frequency ($\omega_c$) between $G'$ and $G''$, in Figures 2.5 and 2.6, shows that the X172 sample has a lower relaxation time than the X171 sample and
that the relaxation times for both samples decrease with increase in temperature. This is due to the inverse relationship between frequency and time (Morrison, 2001). The Generalized Linear Viscoelastic Equation (GLVE) predicts the following relationship between the cross-over frequency and the longest relaxation time $\lambda_L$, for a polymer:

$$\lambda_L = \frac{1}{\omega_c}.$$  \hspace{1cm} (2.1)

Therefore, an increase in the frequency at which $G'$ crosses $G''$ indicates a decrease in the polymer relaxation time.
Figure 2.5 Dynamic viscosity and moduli for X171 and X172 at 200 °C as functions of frequency. Solid points (●) are for the X171 plots while unfilled points (○) are for the X172 sample.
Figure 2.6 Dynamic viscosity and moduli for X171 and X172 at 220°C as functions of frequency. Solid points (●) are for the X171 plots while unfilled points (○) are for the X172 sample.
The shear and extensional rheology data presented in this chapter are average values obtained from at least three separate experimental runs. For reference, Figure 2.5 also shows error bars plotted using the standard deviation of the data.

2.1.3 Extensional Rheology

The extensional viscosity of the polymer samples are measured using a TA Instruments ARES rheometer fitted with the Extensional Viscosity Fixture (EVF). This fixture, as shown in Figure 2.7, consists of two cylinders to which a molded 17mm x 10 mm rectangular sample is attached. The fixture applies an extensional flow to the sample by rotating the bottom fixture cylinder about its axis while simultaneously rotating the bottom fixture cylinder round the upper fixture cylinder. The ARES-EVF employs the same concept as the Meissner rheometer (Meissner and Hostettler, 1994; TA Instruments ARES-EVF manual) in that the sample is elongated, uniaxially, within a confined space. In the ARES-EVF the confined space is determined by the distance between the top and bottom fixture cylinders. The initial length of the sample, \( L_0 \), is the distance between the initial points of contact between the sample and the fixture cylinders. The maximum accessible Hencky strain is \( \varepsilon_h = 4 \), because at that condition the sample begins to wrap onto itself on the cylinder. The torque required to apply a constant extension rate to the sample is measured, from which a stress is calculated. The transient startup extensional viscosity, as a function of time, is then reported at the given strain rate.
Figure 2.7 Front and plan view of the extensional viscosity fixture. The extensional flow is provided by cylinder A rotating about its axis while also rotating around cylinder B (reproduced with permission of the Harrison group at Clemson University).

The sample is elongated equally in both directions; therefore the sample strain rate is given by;

\[ \dot{\varepsilon}_0 = \frac{\varepsilon(t)}{t} = \frac{2v_{end}}{L_0} \quad . \]  

(2.2)

In equation 2.2 $v_{\text{end}}$ is the velocity of the rotating bottom fixture cylinder and is the product of the cylinder radius ($r_b$) and the angular speed of the cylinder ($\Omega(t)$) i.e.
The Hencky strain is $\varepsilon_h = \ln\left[\frac{L(t)}{L_0}\right]$, where $L(t)$ is measured from the rotation of the bottom cylinder. The top fixture is fixed and measures the torque applied to the sample. The force response of the sample is then calculated from the torque. The stress on the sample is calculated as;

$$\sigma_E(t) = \frac{F(t)}{A(t)}.$$

(2.4)

The sample is assumed to be incompressible, therefore, the change in the sample cross-sectional $A(t)$ is written as (TA Instruments ARES-EVF manual);

$$A(t) = A_0 e^{-\dot{\varepsilon}_0 t}.$$

(2.5)

Finally, the uniaxial elongation viscosity of the sample is calculated as;

$$\eta_E(t) = \frac{\sigma_E(t)}{\dot{\varepsilon}_0}.$$

(2.6)

Figure 2.8 reports the extensional viscosity for PH 835 for two different strain rates. The strain rates shown are of the same magnitude as strain rates encountered in the film casting experiments presented in this dissertation. At the low strain rates investigated, the steady elongational viscosity achieved remains approximately constant. The elongation viscosity in the steady state region is approximately $\eta_e = 3500$ Pa.s, whereas the zero shear rate viscosity is approximately $\eta_0 = 1100$ Pa.s. The Trounton ratio is therefore
close to the theoretical value for a Newtonian fluid of $T_R = 3$. Figure 2.8 also shows error bars plotted using the standard deviation of the viscosity data from the average values. At least 95% of the standard deviation values fall within 0.6% - 6% of the average values.

Figure 2.9 shows extensional viscosity as a function of elongation time, at different extension rates, for X171. This polymer exhibits strain hardening. The onset of the strain hardening region is seen to occur at lower elongation times as the extension rate is increased. Strain hardening occurs when the polymer molecules are fully aligned in the stretching direction, and begin to offer resistance to any further elongation. Increasing the extension rate reduces the time required for the polymer molecules to be fully aligned in the extensional flow direction. The elongation viscosity in the steady state region is approximately $\eta_e = 6700$ Pa.s, while zero shear viscosity at 170 °C is $\eta_0 = 2200$ Pa.s. These viscosity values indicate that the Trounton ratio in the plateau region is close to the Newtonian value of $T_R = 3$. 
Figure 2.8 Extensional rheology data for PH 835 at 170°C.
Figure 2.9 Extensional viscosity at 170 °C for X171 at various extension rates.

2.2 Film Casting Experiments

A laboratory scale cast film line developed and maintained by the Center for Advanced Engineering Fibers and Films (CAEFF) at Clemson University was used in this work. The film casting schematic shown in Figure 1.1 is again presented here to simplify the discussion.
Figure 1.1 Schematic of a film casting line.

A lab scale extruder (1.27 cm screw) coupled to a 10.16 cm x 0.1 cm slit die is used. The chill roll is 30 cm wide with a diameter of 19.95 cm. The gap between the die and the chill roll can be varied. In this work, air-gap lengths of 5 cm, 5.5 cm, 8 cm, 8.8 cm and 9 cm are used for the film casting experiments. Typical air-gap lengths used in industry are generally much smaller than those employed in this work. However, the chosen dimensions allow velocity and temperature measurements to be made over a wide range
of positions within the web, enabling a large amount of experimental data to be collected pointwise for the verification of model predictions.

The die temperature as well as the die throughput and the chill roll velocity are computer controlled. Thus, process variables such as the draw ratio and die temperature can be systematically varied and investigated. For the work discussed in this study, the process conditions for the cast film experiments are shown in Tables 2.1 and 2.2. Table 2.1 details the process conditions and test cases for the film casting experiments conducted using the Profax PH 835 sample and Table 2.2 presents the process conditions applied in the film casting experiments for the X171 and X172 samples. The chill roll temperature was kept constant at 18 °C (65 °F) for all the experiments reported in this work.
Table 2.1 Test cases for the Profax PH 835 film casting experiments.

<table>
<thead>
<tr>
<th>Test</th>
<th>Air-gap length ,L (cm)</th>
<th>Chill roll speed (cm/s)</th>
<th>Mass flow rate (g/s)</th>
<th>Draw ratio, DR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case I</td>
<td>8.8</td>
<td>2.5</td>
<td>0.35</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.3</td>
<td>0.35</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.1</td>
<td>0.35</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.9</td>
<td>0.35</td>
<td>12.8</td>
</tr>
<tr>
<td>Case II</td>
<td>8.8</td>
<td>3.3</td>
<td>0.46</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.3</td>
<td>0.35</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.3</td>
<td>0.28</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.3</td>
<td>0.24</td>
<td>12.8</td>
</tr>
</tbody>
</table>

For test case I, in Table 2.1, the mass flow rate is maintained constant at 0.35 g/s and the draw ratio varied by changing the chill roll speed. The air gap distance for this case is 8.8 cm. In test case II the chill roll speed is kept constant at 3.3 cm/s while the draw ratio is varied by manipulating the mass flow rate. The die temperature is maintained at 220 °C for all of the test cases reported in Table 2.1. Film casting tests on this polymer sample were designed to determine the effect of draw ratio on the width, temperature and velocity profiles in the air-gap.
For the process conditions listed in Table 2.2 the experiments were performed at die temperatures of 200 °C and 220 °C. The draw ratio was varied from 6.5 to 12.8 by maintaining a constant throughput (0.35 g/s) while changing the chill roll velocity. The air-gap length is also varied from 5 cm to 9 cm as shown in Table 2.2. This set of experiments probes the effect of process variables such as die temperature, draw ratio and air-gap distance, and the material property of viscosity (molecular weight) on the film formation process in the air-gap.

**Table 2.2** Process conditions for the X171 and X172 film casting experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Air-gap length, L (cm)</th>
<th>Mass flow rate, g/s</th>
<th>Draw ratio, DR</th>
<th>Die temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>X171</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.35</td>
<td>6.5, 8.6, 12.8</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>0.35</td>
<td>8.6, 12.8</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.35</td>
<td>6.5, 8.6, 10.7, 12.8</td>
<td>200, 220</td>
</tr>
<tr>
<td>X172</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.35</td>
<td>8.6, 12.8</td>
<td>200, 220</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>0.35</td>
<td>8.6, 12.8</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.35</td>
<td>6.5, 8.6, 10.7, 12.8</td>
<td>200, 220</td>
</tr>
</tbody>
</table>
2.2.1 On-Line Width profile and Film Thickness

For the experimental measurements of the film properties and characteristics in the air-gap, instruments were mounted on a tripod equipped with translation stages to probe the entire polymer web between the die and the chill roll.

The film width, temperature and velocity were measured for the PP samples as functions of the draw direction (x) and the transverse direction (y) in the air-gap. The film neck-in, as a function of distance from the die, was measured using images obtained from a SONY DSC-S90 digital camera. The digital images were analyzed with the aid of Image-Pro PLUS software. The die width was used as the reference length scale and the measured values were verified by comparing film widths at the chill roll obtained using the software to the measured widths for the produced films. At least 3 different runs were conducted for each of the experimental conditions utilized, and the plotted width profiles are average values from these experiments. Figure 2.10 shows a representative image. Note the film neck-in which is a direct result of the chill roll being run at a higher velocity than the velocity at which the polymer melt exits the die. The neck-in is a direct result of conservation of mass and the increased velocity on the chill roll relative to the die.
Figure 2.10 A digital image showing the film neck-in occurring between the Die exit and the Chill roll.
2.2.2 On-Line Temperature profile

Temperature profiles were determined by infrared thermography using a MIKRON TH5104 infrared camera. Figure 2.11 shows a representative infrared image used in determining the temperature profile in the web. The rectangular bar in the right edge of this figure displays the temperature colorscale legend. The TH5104 calibration software is used to determine the temperature locally throughout the infrared image. The temperature profiles depend on the inputted emissivity value. The emissivity values for the experiments were set by varying the emissivity until the temperature of a point, on the film centerline, at the die exit was equal to the die temperature. For the temperature measurement experiments, the results shown are average values from at least 3 different runs.
Figure 2.11 Infrared image of the polymer film in the air-gap. The temperature color scheme is shown in the right edge of the figure.

2.2.3 On-Line Velocity profile

The online velocity profiles were measured using the Laser Doppler Velocimetry (LDV) technique (see, for example: Bourke et al., 1970; Cummins and Pike, 1977; Kramer and Meissner, 1980; Kaufman, 1986). A BETA LaserMike laser head/detector was used as the laser source for measuring the velocity field in the web as a function of position in both the machine direction (MD) and the transverse direction (TD). Due to the transparent nature of the polymer film in the web a 0.03 % w/w seeding of TiO₂ particles
was used to provide scattering centers for the laser beam. This is necessary for the velocity measurements. The TiO$_2$ particles range in size between 10 and 45 microns.

Figure 2.12 shows a typical LDV set-up. The Laser Doppler Velocimetry method involves directing two intersecting laser beams at a moving surface. The laser beams intersect at an angle of 2φ. The laser head is placed 12 inches from the moving surface so that the two beams intersect at the point for which the velocity is being measured. The surface scatters the laser beams as it passes through the intersection point. The laser head also contains a detector that picks up the frequency of the scattered rays. The frequency of the scattered rays, as shown in equation 2.7, is proportional to the velocity of the moving surface. In equation 2.7 $f$ is the frequency of the scattered rays while $\lambda$ is the laser wavelength.

$$ v = \frac{f\lambda}{2 \sin \varphi}.$$  \hspace{1cm} (2.7)
Figure 2.12 Schematic of laser head/detector used in the LDV technique. The frequency of the scattered rays is proportional to the velocity of the moving surface.

The laser head/detector measures the velocity in a direction along the plane of the intersecting laser beams. Ideally the laser head should be positioned such that the face of the laser head is parallel to the moving surface. If the face of the laser head deviates from this ideal position the measured velocity values can be corrected for with the aid of the deviation angle. The deviation angle (θ) as shown in Figure 2.13 is the angle between the axis of the laser head, in the operating position, and the laser head axis in the ideal position.
The true velocity is determined using equation 2.8, where $v_T$ is the true velocity and $v_M$ is the measured velocity (BETA LaserMike LS205 GUAGE Instruction Handbook; TSI Model LS50M Multiplexed LaserSpeed System Instruction Manual).

$$v_T = \frac{v_M}{\sin(90 - \theta)}.$$  \hspace{1cm} (2.8)

For velocity measurements in this work the laser head was initially set up to measure the x-direction velocities ($v_x$) as a function of transverse ($y$) and machine ($x$) direction
positions. The majority of the velocity measurements in this study are therefore for \( v_x \) as a function of \( x \) and \( y \).

At least three runs were performed for each set of experimental conditions. For each experimental run the measured velocity is an average value since the LDV method used in this work reads the velocity at 0.002 s intervals. Measurements for each data point were taken for 10 s. The collected data was filtered by deleting all zero readings and using those velocity readings with the required quality factor (i.e. Q.F = 15). The quality factor indicates the strength of the velocity signal (BETA LaserMike LS205 GAUGE Instruction Handbook). The averaged values in this case also show standard deviations in the range 0.013 to 0.08 m/min.

In order to measure the y-direction component of the velocity, the laser head was set up to additionally measure velocities in a direction 60 degrees \((v_{60})\) from the horizontal as shown in Figure 2.14. This test was conducted for the X171 and X172 samples at a die temperature of 220 °C and air-gap length of 8 cm. The measured velocity values \( v_x \) and \( v_{60} \) values were then used to calculate the y-direction velocity component \( v_y \).
2.3 Film Processing and Testing

Secondary processing of film products is being driven by the need to obtain film with the desired molecular orientation and thickness uniformity required to meet property requirements (Kanai and Campbell, 1999). In this work a biaxial stretcher designed and operated at the CAEFF is used for the film stretching experiments. In the biaxial stretching mode, the apparatus requires the use of 75 mm x 75 mm film. Due to the lab
scale nature of the film casting apparatus used in this work (die width of 10.16 cm or 4
inches) the maximum film width obtained is approximately 6 cm. Therefore, the
produced film were only stretched and oriented in the machine direction (e.g. a uniaxial,
rather than biaxial, deformation). The polymer films were tested both before and after
orientation in order to determine the effect of processing conditions (both during film
casting and uniaxial stretching) on the film mechanical properties.

Figure 2.15 Biaxial stretching machine installed at the Center for Advanced Engineering
Fibers and Films (CAEFF).
2.3.1 Uniaxial Stretching

The biaxial stretcher used for this work (shown in Figure 2.15) has capabilities for both sequential and simultaneous film stretching. The machine consists of an oven for heating the film sample to the desired processing temperature while the stretching rate and distance are controlled using a computer software (Pesce, 2005).

The film samples were cut to 7.6 cm in length by 3.8 cm in width. In order to minimize the effect of the variations in film thickness along the film cross-section (the thickness of the produced films varies, symmetrically, from the film centerline to the edges) samples were cut from the central portion of the film. The film samples were stretched in the machine direction (MD) at 100 °C to 2X (100 mm) and 3X (150 mm) the tenter gage length (approximately 50 mm). The stretching operation was conducted at accelerations of 50 mm/s/s and 100 mm/s/s. These experiments probe the effect of stretching rates and deformation on the film mechanical properties.

2.3.2 Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) is a material characterization technique that provides information about material properties that directly affect the performance of the polymeric material (Menard, 1999). Dynamic Mechanical Analysis helps provide information on the relationship between the material’s chemical structure/morphology and the mechanical properties. It can also provide information about primary (melting), secondary (glass transition) and tertiary (chain relaxation) thermal transitions occurring in a material.
In a DMA test a sample is subjected to an oscillatory stress or strain and the material response is measured (Menard, 1999; Sepe, 1998; Fried, 2002). The applied stress/strain can be tensile, compressive, torsional etc. The DMA equipment used in this study is a TA Instruments RSA III with tensile testing fixtures. With this instrument, an oscillating strain is applied to the sample and the stress response is measured. Figure 2.16 is a digital image showing a test sample attached to the tensile testing fixtures of the RSA III analyzer.

Figure 2.16 Tensile fixtures and sample for a DMA test.
In tensile testing the storage modulus $E'(\omega)$ and the loss modulus $E''(\omega)$ are measured. The quantity $\tan \delta = E'' / E'$ is the damping coefficient or loss tangent and is an indication of how efficiently a material dissipates energy (Menard, 1999; Sepe, 1998).

The film samples were tested in tensile mode both before and after uniaxial orientation, using a gage length of 23 mm. A temperature ramp test was run with an initial temperature of 30 °C, a final temperature of 130 °C and a heating rate of 5 °C/min. Testing was conducted at 0.5 % strain and a frequency of 1 Hz. The strain used is determined by running a strain sweep at a frequency of 1 Hz and a temperature of 30 °C. The chosen strain is within the linear viscoelastic limit for the sample (usually less than 1 %). For MD tests, film samples were cut (from the central portions of the primary and processed film) to 35 mm length and 5-7 mm width. The primary film samples were also tested in the transverse direction (TD) in order to determine the effect of draw ratio on the level of film orientation obtained in the air-gap. The reported DMA data are average values from at least 5 test specimens for each batch of films.

2.3.3 Tensile Testing

During the design of film products for a particular end-use application it is of great importance to determine the response of the film samples to applied mechanical stresses. The response of the film samples to the applied stress determines its design window or application range.

Several methods are available for elucidating the mechanical response of film samples to loading conditions. These methods may be classified as cyclic, impact, transient or static (Fried, 2002). Static testing refers to mechanical testing modes that
impose a constant deformation rate (with respect to time) on a sample (Fried, 2002). These modes can be tensile, compressive or shear but the tensile mode is the most common.

During tensile testing a sample of given dimensions is deformed at a constant rate and the applied force required to achieve this constant deformation rate is measured as a function of the sample extension. The sample response is shown as a plot of stress against strain. Figure 2.17 shows an illustration of the film sample and the grips. One grip (in this work the bottom grip) is kept stationary while the other grip moves at a constant rate (away from the stationary grip) until sample failure is achieved. In Figure 2.17 \( L_0 \) is the gage length (in this case the initial grip separation), \( w_0 \) is the sample width and \( h_0 \) is the sample thickness.
Figure 2.17 Schematic of test sample and grips.
The stress ($\sigma$), is calculated as

$$\sigma = \frac{F}{A_0} \tag{2.9}$$

While the strain ($\varepsilon$), is given by

$$\varepsilon = \frac{\Delta L}{L_0} \tag{2.10}$$

In equation 2.9, $A_0$ is the cross-sectional area of the sample prior to deformation and in equation 2.10, $\Delta L$ is the change in sample length ($L - L_0$) due to deformation. In this study the change in sample length (extension) is measured from the grip separation. For ideal solids the stress developed during deformation is related to the sample strain by Hooke’s law.

$$\sigma = E \varepsilon \tag{2.11}$$

The proportionality factor in equation 2.11 is the tensile (or Young’s) modulus of elasticity. For an ideal, elastic solid the Young’s modulus is a constant and is independent of the stress. Polymers are not ideal solids and as such only the initial portion of the stress-strain plot for plastics may be expected to show Hookean behavior (Sperling, 2001).

Figure 2.18 shows representative stress-strain curves for brittle and ductile plastic samples (Fried, 2002). Curve 1 is representative of brittle polymers (e.g. polystyrene) and oriented film samples. At normal use temperatures ductile polymers (e.g.
polypropylene) exhibit the behavior depicted by curve 2. From curve 1, brittle polymers show rapid increase in stress with increasing strain until failure. In curve 2 the stress increases with strain and reaches a maximum called the yield stress \( \sigma_y \). The yield point represents the point of permanent damage for the sample. Upon further increase of the strain, the stress begins to decrease. This is called strain softening. After strain softening, the material may undergo extensive elongation at almost constant stress (i.e. cold drawing). This is the plastic flow region (Sperling, 2001). The sample then experiences orientation or strain hardening before failure. The cold drawing at constant stress and the subsequent orientation hardening results from the polymer chains being stretched and aligned in the draw direction (Sperling, 2001; Fried, 2002). This chain orientation enhances crystallization and causes a resistance to further stretching. This resistance ultimately shows up as an increase in stress. The samples tested in this work show orientation hardening. The samples are also observed to exhibit draw induced crystallization during the cold drawing stage.
Figure 2.18 Characteristic Stress-strain plots for brittle (1) and ductile (2) plastic samples (adapted from Fried (2002)).

In Figure 2.18 it is seen that only the initial part of the curves obeys Hooke’s law. The “proportional limit” is used to describe the point at which the stress ceases to follow Hookean behavior and usually occurs before 1 % strain (Fried, 2002). Hence the elastic modulus is calculated as the slope of the tangent to the initial (linear) portion of the stress-strain plot. A second form of modulus normally reported for plastic samples is the secant modulus (shown on curve 1). This is calculated by drawing a line from the origin of the plot to a designated point on the curve and the secant modulus is the slope of this secant line. The secant modulus is normally reported in conjunction with the percentage
strain at which it is determined. For instance a 1 % secant modulus means that the secant was drawn from the origin to a point on the plot corresponding to 1 % strain. The modulus is a material property and is affected by the testing temperature and time rate (time scale) of deformation. Brittle polymers normally have a higher modulus than their ductile counterparts. But the ductile polymers require a greater amount of energy for deformation to the point of failure. This is referred to as the tensile energy and is calculated by the area under the stress-strain curve. A higher tensile energy implies that a sample can absorb more energy upon contact.

As shown in curve 1 of Figure 2.18, the stress and strain at the point of failure are referred to as the ultimate stress ($\sigma_u$) and the ultimate strain ($\varepsilon_u$). Other tensile properties calculated from the stress-strain curve include (ASTM D882);

1. **Tensile strength**- calculated by dividing the maximum load by the undeformed cross-sectional area of the specimen (MPa).

2. **Yield strength**- Calculated by dividing the load at the yield point by the undeformed cross-sectional area of the specimen (MPa).

3. **Percent elongation at yield**- Calculated by dividing the extension at the yield point by the initial gage length of the specimen and then multiplying by 100.

The film samples collected during film casting of the X171 and X172 samples were tested in tensile mode in order to study the influence of air-gap length, draw ratio and material properties on the tensile properties of the films. The X171 and X172 film samples were also subjected to uniaxial stretching under various processing conditions and then mechanically tested in tensile mode. This allowed for determination of the effect of the processing conditions on the tensile properties of the films. All tensile tests were
conducted at 73 °F and 43 % relative humidity. The tensile samples were cut to 7.62 cm in length and 1.27 cm in width. The thickness of the samples varied from batch to batch due to earlier discussed effects of processing conditions on film neck-in in the air-gap. For each batch 5 specimens were tested at an initial strain rate of 20 in./in.min. The initial strain rate (C), is calculated according to the ASTM D 882 standards using equation 2.12 below

\[
C = \frac{A}{B}.
\]  

In equation 2.12 above A = 20 inches/min is the rate of grip separation and B = 1 inch is the gage length. Mechanical grips were used in testing the stretched samples while air-actuated grips were used in testing the unstretched samples. The stretched samples were tested with adhesive tapes attached to the grip regions of the sample. This was done to prevent sample slippage at the grips. The unstretched samples were tested without any adhesive tapes attached since the samples only slipped from the grips at high elongations. The unstretched samples were observed to undergo large extensions before failing. The failure mode for the unstretched samples was mostly by slipping from the bottom grip. Since the slippage occurred during the strain hardening region of the stress-strain curve, only a number of the tensile properties calculated from the ensuing stress-strain curve can be used in any mechanical design. The stretched samples mainly failed by sample breakage near the bottom grip. Some of the samples were however observed to fail by splitting. The stress-strain curves for the stretched samples are observed to show no strain hardening or a cold-draw region.
2.4 Film Morphology and Structure

The film formation process in the air-gap is affected by the mechanical process conditions. Secondary processing of the primary film will also affect the film properties, orientation and morphology. Thus, experimental techniques like DSC and Wide Angle X-ray Scattering (WAXD) were used to elucidate the film orientation and crystallinity (in terms of crystalline species and percent crystallinity) in order to quantify the effect of the processing conditions for both the film formation process in the air-gap and the uniaxial stretching.

2.4.1 Differential Scanning Calorimetry

DSC tests were performed on the film samples before and after stretching in order to determine the crystalline content of the film samples. Tests were conducted by heating the samples from an initial temperature of 30 °C to a final temperature of 200 °C at a rate of 20 °C/min. The samples were then quenched and reheated. At least 7 specimens were tested for each batch of film samples, and the reported data are average values from the tested specimens. The operating procedure for these DSC experiments is similar to that described in section 2.1.1. The fast heating rate used here is to prevent any recrystallization that may occur during heating of the sample (Elias et al., 2000).

The area under the melting peak indicates the amount of heat absorbed in melting the crystalline portions of the sample. Since polymers are semi-crystalline, by comparing the heat of melting per unit mass for a (semi-crystalline) sample to the heat of melting for a 100 % crystalline sample we can determine the degree of crystallinity for that sample (Mishra et al., 2006; Chen et al., 2006). An expression for the degree of crystallinity is
\[ X_c = \frac{\Delta H_m}{\Delta H^0_m} \quad . \quad (2.13) \]

In equation 2.13, \( \Delta H_m \) is the heat of melting in J/g for the semi-crystalline sample, \( \Delta H^0_m \) is the heat of melting for a 100% crystalline sample in J/g and \( X_c \) is the degree of crystallinity. In this work we employ \( \Delta H^0_m = 209 \) J/g for a fully crystalline polypropylene sample (Chen et al, 2006, Sperling, 2001).

**2.4.2 Wide Angle X-ray Diffraction**

The crystalline morphology and mechanical properties developed by polymer films, as a result of processing are significantly influenced by the polymer material properties. These material properties include the molecular weight (MW), the molecular weight distribution (MWD), tacticity (whether the polymer is isotactic, syndiotactic or atactic) and the degree of stereo-regularity (Sakurai et al., 2005). During the film casting process, the amount of crystalline content developed in the polymer film, as a result of polymer orientation and flow-induced crystallization, affects the film mechanical strength (Alberty, 1983; Zhang and Ajji, 2005). An understanding of the relationships between processing conditions, film crystalline structure and film mechanical properties is essential for process optimization (Diez et al., 2005; Sakurai et al., 2005).

The Wide Angle X-ray Diffraction (WAXD) technique provides an important tool for determining/investigating the crystalline content and crystal structure obtained during processing. WAXD is an analytical method that can provide information on crystal form and the arrangement of atoms within the crystal (Alberty, 1983; Sperling, 2001). It can
also be used for determining crystalline orientation and degree of crystallinity (Choi and White, 2004; Sadeghi et al., 2007). In this work the WAXD technique is used to study the film orientation and crystallinity in conjunction with the DSC and DMA experiments. Diez et al. (2005) used the DSC and WAXD methods to study the percent crystallinity values for both Primary and Processed polypropylene films. The reported percent crystallinity values obtained using WAXD were shown to be consistently higher than the corresponding values obtained using the DSC method.

A crystal is made up of lattice points arranged in an ordered three-dimensional pattern such that each point in the crystal lattice experiences the same environment as the other points in the crystal (Albery, 1983). In crystalline materials these lattice points may represent atoms, molecules, ions or groups of these species (i.e. atoms, molecules or ions). A given crystal lattice can be generated by the repetition of its unit cell in three dimensions (Albery, 1983). The unit cell consists of atoms, molecules or ions and possesses the same geometric shape as the crystal (Sperling, 2001).

The crystal dimensions are defined by the intercepts of the crystal faces on a set of three coordinate axes \((a, b, c)\) and the angles between these axes \((\alpha, \beta, \gamma)\). The axes are chosen such that the faces of the crystal will either be parallel to some of the axes or intercept these axes at definite distances from the origin (Sperling, 2001). The angle; \(\alpha\) is the angle between \(b\) and \(c\), \(\beta\) is the angle between \(a\) and \(c\), and \(\gamma\) is the angle between \(a\) and \(b\).

All crystal types can be classified into 6 crystal systems (Sperling, 2001); namely Triclinic, Monoclinic, Orthorhombic, Tetragonal, Hexagonal, and Isometric (Albery,
1983). These crystal systems are based on the geometry of their unit cells as defined by the dimensions of the unit cell along the axes $a$, $b$, and $c$ and the angles $\alpha$, $\beta$, $\gamma$.

Interpretation of WAXD results is aided by the concept of crystal planes. Crystal planes are planes passing through crystal lattice points and may represent crystal faces (Alberty, 1983). A set of crystal planes is described by their indices. The indices are written as $(xyz)$ and are determined by the number of planes crossed in moving one lattice spacing along the coordinate axis $a$, $b$, and $c$. A lattice spacing is the distance between two lattice points. The index $x$ corresponds to the $a$-axis, $y$ corresponds to the $b$-axis, and $z$ corresponds to the $c$-axis. Figure 2.19 shows examples of 100, 110 and 111 planes (Alberty, 1983). The 100 planes, for example, are parallel to both the $b$ and $c$ axes; thus no planes are crossed in moving one lattice spacing in either the $b$ or $c$ direction.
When X-rays are directed at a crystal the electrons in the crystal scatter the x-rays. Bragg introduced the concept of considering X-rays as being reflected from a stack of planes in the crystal (Sperling, 2001). The reflected X-rays from a given stack of planes occur only at a particular angle which is determined by the perpendicular distance between planes and the wavelength of the incident X-rays (see Figure 2.20).
The Bragg equation provides the relationship between the incident X-rays of wavelength $\lambda$, the angle of incidence $\theta$, and the inter-planar distance $d$. That is

$$2d \sin \theta = n\lambda.$$  \hspace{1cm} (2.14)

Where $n$ is a whole number. This equation gives the relationship between the inter-planar distance and the angle at which the reflected radiation, from incident x-rays at a given wavelength, has a maximum intensity. This maximum intensity occurs when all the x-rays are in phase. In discussing X-ray reflections it is customary to set $n = 1$ in equation 2.14 (Alberty, 1983). Photographic plates are used to detect the intensity and pattern (spots, arcs or circles) of the reflected beams and the angle at which this occurs. The reflection from the crystal planes in a unit cell are used to determine the crystal structures present in a material (Sperling, 2001).
The crystalline content is calculated from the X-ray diffractogram (i.e. a plot of intensity as a function of $2\theta$) in terms of the crystallinity index $CI$ (Sperling, 2001). This is given as

$$CI = \frac{I_c}{I_c + I_a}. \tag{2.15}$$

In equation 2.15 $I_c$ and $I_a$ represent the contributions, to the area under the diffractogram, of the crystalline and amorphous portions of the material, respectively. Figure 2.21 shows a representative plot of a WAXD diffractogram for the X171 sample. The crystalline contributions and the amorphous curve is calculated using the method of Weidinger and Hermans (1961). The crystalline orientation is calculated using the Herman’s orientation factor $f_j$ and is given as (Choi and White, 2004)

$$f_j = \frac{3 < \cos^2 \phi_j > -1}{2}. \tag{2.16}$$

Where $\phi_j$ is the angle between the crystal axis and the $j$-coordinate axis ($j = a$, $b$ or $c$), and $< \cos^2 \phi_j >$ represents the average value of the parameter $\cos^2 \phi_j$ evaluated for all the crystalline units present in the material.
The X-ray equipment used in this work consists of a BAS-1800 II IP scanner and a Micromax 2 X-ray generator (Osimic Inc.). This system uses a Microsource X-ray tube (Bede Scientific), coupled to a Microfocus Confocal Max-Flux Optic 2-D multilayer optics system, to generate a Cu Kα1 x-ray beam. A Mitsubishi RV-E2 robot with a CR-E116 robot controller is used to operate the Image Plate (IP) scanner. This X-ray equipment was designed by the CAEFF and is capable of simultaneous WAXD and Small Angle X-ray Scattering (SAXS) measurements. A full description and review of this system is presented in the work of Lopes (2005) and Lopes et al. (2006).
The film samples were cut to 2.54 cm by 2.54 cm and placed on a sample holder while making sure that the sample MD is positioned in a defined direction relative to the sample holder. This sample orientation aids in the interpretation of the data obtained. A sample to detector distance of 113 mm is used. The x-rays generated by the Micromax 2 generator have a wavelength of 0.1542 nm. The beam is focused on the sample with the aid of two video cameras showing the side and front view of the sample. The film samples were exposed to the x-rays for about 20 minutes in order to enhance the intensity of the images obtained. After exposure the image plates for the samples were scanned in the Fujifilm BAS-1800 II Image Plate scanner. The film structure and morphology can be determined by studying the intensity of the scattered x-rays as a function of diffraction angles (Sadeghi et al., 2007; Sakurai et al., 2005).

2.5 Hypothesis Testing

In this work the reported data are average values from a number of experimental runs. The reported data is then used to test a certain hypothesis about the effects of processing conditions on the film formation process in the air-gap. In order to verify that the observed trends in the results support the stated hypothesis, a statistical analysis of the data was conducted. The statistical analysis presented in this work involved determining if the reported mean value for a particular data point is less than or different from the mean value for another data point. For example, is the mean Heat of melting value at a draw ratio of 8.6 less than the mean Heat of melting value at a draw ratio of 12.8? If the answer to this question was yes then the hypothesis that increasing the draw ratio
increased the crystalline content of the film sample would be supported. The treatment presented here is based on the text by Ott and Longnecker (2001).

The procedure here is to designate the two mean values in question as \( \mu_1 \) and \( \mu_2 \). The two main cases tested in this work are;

Case I: is \( \mu_1 < \mu_2 \).

Case II: is \( \mu_1 \neq \mu_2 \).

For each case we create a null hypothesis \( H_0 \) and a research hypothesis \( H_a \). The research hypothesis is the statement that we intend to prove (Ott and Longnecker, 2001) while the null hypothesis is a negation of our research hypothesis.

For case I since we are trying to test the hypothesis that \( \mu_1 < \mu_2 \) the null and research hypothesis are then given as;

\[
H_0: \ \mu_1 - \mu_2 \geq 0 \\
H_a: \ \mu_1 - \mu_2 < 0
\]

In case II the hypothesis to be tested is that \( \mu_1 \neq \mu_2 \), therefore the null and research hypothesis are;

\[
H_0: \ \mu_1 - \mu_2 = 0 \\
H_a: \ \mu_1 - \mu_2 \neq 0
\]

Next we select a probability level, \( \alpha \), which we are willing to accept of making a type I error. A type I error arises from the wrongful rejection of the null hypothesis when it is indeed true (Ott and Longnecker, 2001). The value of \( \alpha \) is set to 0.05 in this work. This implies that we are willing to take a risk of wrongfully rejecting the null hypothesis 5 times out of 100.
In this work we assume that the calculated standard deviation for the reported mean values provides an accurate representation of the population standard deviation. For example in testing for the Heat of melting of the film samples we used 7 different samples for each batch. The test results are averaged and we determined a mean Heat of melting value and the standard deviation of the data. It is then assumed that the mean and standard deviation values give an accurate approximation for the mean and standard deviation for the population of all film samples from which the 7 test samples were selected.

In order to determine whether to reject or accept the null hypothesis we need to determine the critical t-value ($t_{\alpha}$) for the problem from the Student’s $t$ distribution table (Ott and Longnecker, 2001). We also need to calculate the test statistic ($t$) for the problem. For case I we reject the null hypothesis if $t \leq -t_{\alpha}$. For case II the null hypothesis is rejected if it is determined that $|t| \geq t_{\alpha/2}$.

In determining the critical t-value we need to calculate the degree of freedom ($df$) for our analysis. The critical t-value as read from the $t$ distribution table is the value at the intersection between the row corresponding to our calculated degree of freedom and the column that corresponds to the selected value of $\alpha$.

Calculation of the degree of freedom and the test statistic depend on if the standard deviations for the means being compared are the same or different i.e. whether $s_1 = s_2$ where $s_1$ and $s_2$ are the standard deviations for $\mu_1$ and $\mu_2$ respectively.
Method 1 ($s_1 = s_2$)

For method 1 we calculate the averaged standard deviation ($s_p$) for the two means as (Ott and Longnecker, 2001);

$$s_p = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}}. \quad (2.17)$$

Where $n_1$ and $n_2$ are the number of test samples used in obtaining $\mu_1$ and $\mu_2$ respectively. The degree of freedom is then calculated as;

$$df = n_1 + n_2 - 2. \quad (2.18)$$

The test statistic is given by;

$$t = \frac{\mu_1 - \mu_2}{s_p \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}}. \quad (2.19)$$

Method 2 ($s_1 \neq s_2$)

In method 2 the test statistic is denoted as $t'$. We do not use an averaged standard deviation. The degree of freedom for this method is calculated as;

$$df = \frac{(n_1 - 1)(n_2 - 1)}{(1-c)^2(n_1 - 1) + c^2(n_2 - 1)}. \quad (2.20)$$
Where $c$ is given by;

\[
    c = \frac{s_1^2 / n_1}{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}.
\]  

(2.21)

The test statistic is calculated using:

\[
    t' = \frac{\mu_1 - \mu_2}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}}. \tag{2.22}
\]

The results from the statistical analysis conducted (in order to test some of the research hypothesis encountered in this work) are presented in Chapters 3 and 4 and in Appendix B

**2.5 Summary**

In this chapter we present the experimental methods used in achieving some of the objectives set out for this research. We introduce methods for; the material characterization, the film casting experiments, and the study of the film properties help to elucidate the relationship between;

1. The polymer material properties;
2. The effect of processing conditions; and
3. The development of film structure and morphology as a direct response of the polymer material to the processing conditions utilized.
In Chapter 3 we present the results of the film casting experiments. Results of the film characterization experiments are presented in Chapter 4.
CHAPTER 3

EXPERIMENTAL INVESTIGATION OF FILM FORMATION

In film casting the film formation process in the air-gap (between the die and the chill roll) is a 3-dimensional, non-isothermal and extension-dominated flow process. In modeling flow processes, the objective is to apply knowledge of the material properties and the flow situation to predict variables of interest (Morrison, 2001). The flow process is analyzed in terms of the basic conservation and constitutive equations with the aid of the process/boundary conditions specified for that particular flow process (Pearson, 1985). A thorough understanding of the flow process is imperative if qualitatively reasonable and quantitatively accurate mathematical models are to be developed.

In developing mathematical models for the film casting process the main objective is to accurately predict the geometry (width and thickness profiles), kinematics (velocity field), stresses (resulting from flow deformations), molecular orientation (of the film) and thermodynamics (temperature field) for the process (Pearson, 1985). Thus, in this chapter the film casting process is studied from an experimental point of view by subjecting the molten polymer in the air-gap to systematic manipulations of the steady process/boundary conditions and measuring the steady state response of the film in the air-gap. We accomplish this by measuring the film width, the temperature and the velocity profiles as a function of machine and transverse direction position in the film web.
3.1 Effect of Draw Ratio on the Film Casting of Profax PH 835

Experiments were conducted using the Profax PH 835 sample in order to determine the effect of draw ratio on the film casting process. The draw ratio (DR), defined as the ratio of the velocity at the chill roll to the velocity at the die exit, can be varied in two ways. First, the DR can be varied by keeping the polymer throughput constant while changing the chill roll speed. Second, the DR can be varied by maintaining a constant chill roll speed while varying the polymer throughput. In this section, we present experimental results using both procedures. The specific experimental conditions for the experiments presented are shown in section 2.2, Table 2.1. In particular, experiments were conducted using an air-gap length of 8.8 cm and a die temperature of 220 °C. The draw ratios used are 6.5, 8.6, 10.7 and 12.8. The experiments were designed to study the effect of the draw ratio on the film width, the temperature profiles and the velocity profiles. The study of the width, temperature and velocity in the air-gap region provide information on the effect of the draw ratio on the film formation process in the air-gap.

3.1.1 Width Profiles

Figure 3.1 shows width profiles for experiments with an air gap distance of 8.8 cm and die temperature of 220 °C (test case I). The draw ratio is varied from 6.5 to 12.8 by varying the chill roll speed. Increasing the draw ratio increases neck-in due to conservation of mass. Since the draw ratio is varied by maintaining a constant throughput and varying the chill roll speed, increasing the draw ratio results from an increase in the chill roll velocity. The film dimensions at the chill roll are smaller than the film
dimensions at the die exit as a result of the extensional flow field in the region between the die exit and the chill roll (DR > 1). Therefore, due to the fact that mass has to be conserved, an increase in the draw ratio leads to an increase in the film neck-in. As with all the width profile data presented in this work the width profiles shown in Figure 3.1 are average values from at least 3 experimental runs. All the data points obtained show standard deviation values between 0.003 cm and 0.03 cm.

3.1.2 Temperature Profiles

In Figure 3.2, the centerline temperature profiles are shown for PP at four different draw ratios. The air gap length is 8.8 cm and the die temperature is maintained at 220 °C. The draw ratio is again varied from 6.5 to 12.8 (test case I) by manipulating the chill roll velocity. We observe that the film temperature at the chill roll decreases with increasing draw ratio. Thus, the film cools more rapidly in the gap as the draw ratio is increased. This result is consistent in that increasing the draw ratio for a given mass throughput causes increased neck-in, and resulted in a reduction in film thickness due to mass conservation. Conduction is then a significant contributor to the heat transfer process in the film. This argument is further supported in Figure 3.3 where for the same conditions as above the draw ratio is varied by maintaining a constant chill roll speed and changing the throughput (test case II). The film is still seen to cool faster at higher draw ratios. This effect of draw ratio on film temperature at the chill roll was also reported in the work by Acierno et al. (2000) for PET film casting. The centerline temperature profiles in Figure 3.2 and Figure 3.3 show three cooling zones. The first cooling zone ranges from x = 0 to approximately x = 5.1 cm (Δx₁). The second cooling zone ranges from x = 5.1 cm to
approximately x = 6.8 cm while the third cooling zone extends from x = 6.8 cm to the chill roll at x = 8.8 cm (∆x₃). These exact positions are specified for illustrative purposes only. In the second cooling zone the temperature profiles show a plateau region followed by a local maximum in temperature and then a decrease in temperature until the third cooling zone is encountered. In this third region the film temperature drops below the polymer melting point (T_m = 168 °C) - therefore the plateau region and local maximum in temperature may be due to a change in the film morphology (resulting from the coupling between the temperature drop and the flow field).

![Graph](image)

**Figure 3.1** PH 835 width profiles as a function of draw ratio (test case I).
Figure 3.2 Centerline temperature profile for PH 835 as a function of draw ratio (test case I).
Figure 3.3 Centerline temperature profile for PH 835 as a function of draw ratio (test case II).

In Table 3.1 the total temperature drop in the air-gap region ($\Delta T_{\text{total}}$), is reported as a function of the draw ratio for test case I. The total temperature drop is defined here as the difference in the temperature of the film at the die exit and the temperature of the film in the region close to the chill roll. Polymer films do not attain the temperature of the chill roll, at the initial point of contact, but continue to experience temperature drop along the circumference of the chill roll (Kanai and Campbell, 1999). Also reported are the
temperature gradients (with respect to draw direction distance, x) in zone 1 ($\Delta T_1/\Delta x_1$) and zone 3 ($\Delta T_3/\Delta x_3$). Table 3.2 reports the temperature drop and temperature gradients for the test case II. The temperature drop data in Tables 3.1 and 3.2 show that the temperature drop in the air-gap increases with an increase in the draw ratio. Comparing the temperature gradients for zones 1 and 3 shows that the film cools faster in zone 1. This is due to the change in film properties as the material transitions from a liquid to a solid state. The lower film temperatures in zone 3 also lead to an increase in film viscosity. This increase in film viscosity retards heat transfer from the film (Acierno et al., 2000).

Comparing the total temperature drops for case I and case II shows that at DR = 6.5 the $\Delta T_{\text{total}}$ for case I is greater than that for case II, while at DR = 10.7 and 12.8 the $\Delta T_{\text{total}}$ for case II is greater than that for case I. This may be due to the differences in the polymer throughput for cases I and II. At DR = 6.5 the throughput is higher for case II than for case I since the velocity at the chill roll is also higher for case II. This increase in polymer material flowing through the air-gap is responsible for the smaller temperature drop. For DR = 10.7 and 12.8 the throughput in case II is less than that for case I - therefore higher temperature drops are observed in case II.
Table 3.1 Temperature drop and thermal gradients for PH 835 case I experiments.

<table>
<thead>
<tr>
<th>DR</th>
<th>$\Delta T_{\text{total}}$ (°C)</th>
<th>$\Delta T_1$ (°C)</th>
<th>$\Delta T_2$ (°C)</th>
<th>$\Delta T_1/\Delta z_1$ (°C/cm)</th>
<th>$\Delta T_3/\Delta z_3$ (°C/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>70.64</td>
<td>56.46</td>
<td>6.93</td>
<td>11.15</td>
<td>3.46</td>
</tr>
<tr>
<td>8.6</td>
<td>75.26</td>
<td>58.8</td>
<td>10.50</td>
<td>11.53</td>
<td>5.25</td>
</tr>
<tr>
<td>10.7</td>
<td>82.82</td>
<td>63.92</td>
<td>9.24</td>
<td>12.53</td>
<td>4.62</td>
</tr>
<tr>
<td>12.8</td>
<td>87.02</td>
<td>65.81</td>
<td>13.23</td>
<td>12.90</td>
<td>6.62</td>
</tr>
</tbody>
</table>

Table 3.2 Temperature drop and thermal gradients for PH 835 case II experiments.

<table>
<thead>
<tr>
<th>DR</th>
<th>$\Delta T_{\text{total}}$ (°C)</th>
<th>$\Delta T_1$ (°C)</th>
<th>$\Delta T_2$ (°C)</th>
<th>$\Delta T_1/\Delta z_1$ (°C/cm)</th>
<th>$\Delta T_3/\Delta z_3$ (°C/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>65.18</td>
<td>51.74</td>
<td>7.35</td>
<td>10.15</td>
<td>3.68</td>
</tr>
<tr>
<td>8.6</td>
<td>75.26</td>
<td>58.8</td>
<td>10.5</td>
<td>11.53</td>
<td>5.25</td>
</tr>
<tr>
<td>10.7</td>
<td>86.6</td>
<td>64.13</td>
<td>15.12</td>
<td>12.57</td>
<td>7.56</td>
</tr>
<tr>
<td>12.8</td>
<td>89.6</td>
<td>71.06</td>
<td>12.45</td>
<td>13.93</td>
<td>6.30</td>
</tr>
</tbody>
</table>
Figure 3.4 shows representative transverse temperature profiles (as a function of distance from the die) for PH 835. The process conditions used are a draw ratio of 12.8, an air gap distance of 8.8 cm and a die temperature of 220 °C (test case I). It is seen that the temperature profiles start out flat at the die. As the chill roll is approached, there is a local minimum in temperature at the center of the film. The profile indicates that the central portion of the film cools at a faster rate than the film edges as the chill roll is approached. Sefzadeh et al. (2005), in their work on PET film casting, report that the temperature in the central portions of the film is higher than temperatures at the film edges. However, this occurs because of the film being thicker in the central region than at the edges due to the die design: the die used in their work has a non-uniform cross-section, with the central region being thicker than the edges. In some modeling work, the temperature in the web is sometimes assumed to vary only in the machine direction in order to simplify the simulations (see, for example, Alaie and Papanastasiou, 1991). The temperature profiles shown in Figure 3.4 indicate that temperature in the web also varies in the transverse direction by up to 10 °C, and this temperature difference can have a significant impact on the polymer rheology and hence the velocity profile. We observe that the variations in the temperature in the transverse direction become pronounced at about 3 cm from the die. The temperature profiles shown in Figure 3.4 are representative of the observed temperature profiles for all of the different processing conditions used for the Profax PH 835 sample.
3.1.3 Machine Direction Velocity Profiles ($v_x$)

Figure 3.5 shows a representative velocity map for Profax PH 835 film casting. Similar trends are observed for the other flow conditions. The experimental conditions include an air gap distance of 8.8 cm, a die temperature of 220 °C and a draw ratio of 8.6 (test case I). The draw direction component of the velocity ($v_x$) is shown as a function of both the transverse position in the web and the distance from the die. The results show that, for a particular distance from the die, lower velocities are obtained at the film edges than in the central portions of the film. In the central portions of the web, all of the polymer material is moving in the machine (or draw) direction. However, near the edge
of the film, the polymer is following a trajectory consistent with the neck in discussed above. In this region of the polymer web, the velocity vector of a fluid element contains both a draw direction velocity component (measured by the LDV system), and a component that acts perpendicular to the draw direction and towards the web centerline. Thus, the LDV system is measuring only a component of the velocity vector and the magnitude of this velocity component. We study the second, transverse direction component of the velocity \( v_y \) in a subsequent section of this chapter. At the chill roll, the film neck-in is complete and the film cross-section moves at the velocity of the chill roll. Thus, it is expected that close to the chill roll the draw direction velocity component will not vary as much as it does in the region close to the die. We are unable to obtain experimental velocity data in this region close to the chill roll (i.e. \( x = 7 \text{cm} \) to \( x = 8.8 \text{cm} \)).
Figure 3.5 Draw direction velocity map for PH 835 at DR = 8.6 (test case I).

Figure 3.6 shows draw direction velocity data, as a function of distance from the die and transverse position, for test case II at draw ratios of 6.5 and 12.8. The velocity values for DR = 6.5 at each location are seen to be higher than the velocity values for DR = 12.8. This occurs because the flow rate (and thus the velocity) at the die exit differs in the two experiments even though the velocity at the chill roll is the same for both draw ratios. Qualitatively, the velocity profiles show a similar trend to the velocity profiles in Figure 3.5 in that a maximum in the velocity occurs at the film centerline. A statistical
The analysis of the data (using $\alpha = 0.05$) shows that the velocity values for DR = 6.5 are higher than the velocity values for DR = 12.8 (see Appendix B).

**Figure 3.6** Draw direction velocity maps for PH 835 at DR = 6.5 and DR = 12.8 (test case II).

The draw direction velocity along the film centerline (i.e. $v_x$ as a function of $x$), is shown in Figure 3.7 as a function of draw ratio. Process conditions are a die temperature of 220 °C and air gap length of 8.8 cm. The draw ratio is varied from 6.5 to 12.8 (test case I). As expected, the velocity increases with increasing distance from the die due to the extensional flow in the web. The increased draw ratio also results in an increase in the velocity at the chill roll.
In Figure 3.8, we use the results from Figure 3.7 to calculate the centerline strain rate as a function of draw ratio and distance from the die. At low draw ratios (6.5 and 8.6), the strain rate increases only in the region close to the die. As the chill roll is approached, the strain rate goes through a maximum and then begins to decrease (although the velocity continues to increase). The decrease in strain rate along the centerline as the chill roll is approached may result from the cooling of the polymer film as the chill roll is approached. This reduction in temperature leads to an increased resistance to flow (which would be manifested as an increased viscosity). Thus, it should be more difficult to stretch the film in the region near the chill roll. However, this trend is not observed at higher draw ratios (DR = 10.7 and DR = 12.8). At higher draw ratios, the strain rate continues to increase with increasing distance from the die. Increasing the draw ratio (by increasing the chill roll speed) increases the tension applied to the film (Canning et al., 2001). We believe that the increased tension may overcome the increasing resistance to flow due to the film cooling (at high draw ratios). Thus, the strain rate continues to increase from the die to the chill roll. In the work by Canning et al. (2001) on film casting of a low-density polyethylene melt, the centerline velocity profile and tension in the film were measured while varying the draw ratio from 2.68 to 7.27. At DR = 2.68 the centerline velocity profile shows a decrease in the strain rate in the region near the chill roll. At DR = 7.27, the centerline strain rate was shown to increase with increasing distance from the die. The tension in the film (measured at a point on the film centerline) was also shown to increase with draw ratio.
Figure 3.7 Centerline velocity profiles for PH 835 as a function of draw ratio (test case I).
3.2 Impact of Material Properties and Process Conditions on PP Film Casting

In this section, we report results on film casting experiments performed using the X171 and X172 polypropylene samples. This study was intended to investigate the effect of material properties such as molecular weight (manifested via differences in the zero-shear viscosity) and process variables such as die temperature, draw ratio and air-gap length on the film formation process occurring in the air-gap region. As discussed in Chapter 2, the X171 sample has a higher zero shear viscosity (and molecular weight) than the X172 sample (as shown in Figure 2.4 and Figure 2.5). As in the previous section, we measure the width, temperature and velocity profiles in the film web while systematically varying the die temperature, draw ratio and air-gap length. The experimental set up and

**Figure 3.8** Centerline strain rates as a function of DR (test case I).
processing conditions are discussed and shown in section 2.2 and Table 2.2 respectively. The draw ratio was varied from 6.5 to 12.8 (by changing the take-up velocity), while the die temperature was set at 200 °C or 220 °C. The air-gap lengths employed in this study are 5 cm, 8 cm and 9 cm.

3.2.1 Width profiles

Figure 3.9 shows the width profiles for the X171 and X172 films at draw ratios of 6.5 and 12.8, and a die temperature of 220 °C. As before, the film neck-in is seen to increase with increasing draw ratio. The X172 film experiences a greater degree of neck-in as compared to the X171 film at a particular draw ratio. Figure 3.10 shows width profile as a function of die temperature, for the X171 sample at DR = 8.6. Increasing the die temperature increases the film neck-in. Taken together, Figures 3.9 and 3.10 demonstrate that changes in material properties or process conditions that lead to a reduction in polymer viscosity have the effect of increasing film neck-in. This result may be explained by the temperature dependence of the rheology of the polymer, and the interaction between edge-beads and neck-in (Smith and Stolle, 2000). In their work on non-isothermal film casting, Smith and Stolle (2000) state that edge-beads help restrict the amount of neck-in obtained in the region between the die and the chill roll. Increasing the viscosity of the film increases the ability of the edge beads to retard the film neck-in. Thus, it should be expected that either increasing the die temperature or reducing the polymer molecular weight will result in increased neck-in due to the reduced viscosity of the polymer.
Figure 3.9 Half-width profiles as functions of viscosity and draw ratio at die temperature of 220 °C.
Figure 3.10 Half-width profile as a function of temperature for X171 at DR = 8.6.

Table 3.3 summarizes the film half-width for the X171 and X172 films produced using a die temperature of 220 °C and DR = 6.5 and 12.8. The half-width for X171 films produced using a die temperature of 200 °C and DR = 6.5 and 12.8 is also presented in Table 3.3. Comparing half-width values shows that the neck-in is more significantly impacted by a change in material from X171 to X172 than by a change in the die temperature from 200 °C to 220 °C. For example, at DR = 12.8 there is a 10 % decrease in film half-width when comparing half-width values for the X171 and X172 samples while only a 5 % decrease in half-width is observed when comparing film width for the X171 films produced at die temperatures of 200 °C and 220 °C. This may be as a result of the greater decrease in zero-shear viscosity between the X171 and X172 samples at
220 °C as compared to the decrease in viscosity for the X171 sample at 200 °C and 220 °C. The zero-shear viscosity of the X171 sample decreases from 1170 Pa.s (at 200 °C) to 784 Pa.s (at 220 °C) while the X172 sample exhibits a zero-shear viscosity of 469 Pa.s at 220 °C. Thus, a greater change in viscosity results in greater film neck-in.

Table 3.3 Film half-width for the X171 and X172 samples (L = 9 cm).

<table>
<thead>
<tr>
<th>DR</th>
<th>X172, 220 °C (cm)</th>
<th>X171, 220 °C (cm)</th>
<th>X171, 200 °C (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>2.24</td>
<td>2.46</td>
<td>2.58</td>
</tr>
<tr>
<td>12.8</td>
<td>1.71</td>
<td>1.90</td>
<td>2.00</td>
</tr>
</tbody>
</table>

Figure 3.11 shows thickness profiles for the X171 and X172 films produced using a die temperature of 220 °C, L = 5 cm and DR = 8.6 and 12.8. Figure 3.12 shows the thickness profiles for the X172 films produced using die temperatures of 200 °C and 220 °C, L = 5 cm and DR = 8.6 and 12.8. In Figure 3.11 the X172 films are thicker than the X171 films. This is due to the greater width of the X171 films (resulting from the greater neck-in exhibited by the X172 sample). Since the throughput and density is the same for
the X171 and X172 samples, the cross-sectional area should be the same for both samples. Thus the greater width of the X171 film should result in the X172 films being thicker than the X171 films. In Figure 3.12 the X172 films produced using a die temperature of 220 °C are thicker than the X172 films produced using a die temperature of 200 °C. This is also as a result of the increased neck-in exhibited by the X172 sample upon increasing the die temperature from 200 °C to 220 °C. From Figure 3.11 and Figure 3.12 the edge-bead thickness is seen to increase with increase in die temperature or a decrease in polymer viscosity.

Figure 3.11 Thickness profile for X171 and X172 films at $T_{\text{die}} = 220$ °C.
Figure 3.12 Thickness profile for X172 films at $T_{\text{die}} = 200 \, ^{\circ}\text{C}$ and 220 °C.

Figure 3.13 compares the resulting width profiles for the X171 and X172 samples as a function of air-gap length at a draw ratio of 8.6. It is seen that increasing the air gap length increases the degree of neck-in at a constant draw ratio (Sakaki et al., 1996; Silagy et al., 1999; Acierno et al., 2000). This is due to the decrease in the Deborah number ($De$) as the air-gap length is increased. The Deborah number may be given as $De = \lambda(v_0/L)$, where; $\lambda$ is a relaxation time for the polymer, $v_0$ is the velocity at the die exit and $L$ is the air-gap length (Sollogoub et al., 2006). Increasing the Deborah number increases the viscoelastic response of the polymer in the air-gap region and reduces the amount of neck-in obtained (Sollogoub et al., 2006; Silagy et al., 1999). The film thickness was also observed to increase with an increase in the air-gap length. This observation is consistent
with the increase in neck-in as the air-gap length is increased. The 2-D model of Silagy et al. (1999) also predicts an increase in the film thickness and neck-in as the air-gap length is increased. Increasing the relaxation time also increases the Deborah number: thus, decreasing the die temperature or increasing the polymer molecular weight (increasing viscosity and thus increasing relaxation time) should lead to a decrease in neck-in.

Figure 3.13 Half-width profile as a function of air-gap for the X171 and X172 samples at a die temperature of 220 °C.
Table 3.4 shows the widths for film samples produced using the X171 and X172 PP samples at a die temperature of 220 °C. The films were produced while varying the draw ratio (DR) from 8.6 to 12.8 at air-gap lengths (L) of 5 cm and 8 cm. The X171 films are observed to be wider than the X172 films. This is due to the increase in neck-in experienced by the X172 sample, for the same set of processing conditions as were applied to the X171 sample.

### Table 3.4 Film widths for X171 and X172 samples produced at various DR and L.

<table>
<thead>
<tr>
<th>Air –gap length, L</th>
<th>X172 film width</th>
<th>X171 film width</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DR = 8.6</td>
<td>DR = 12.8</td>
</tr>
<tr>
<td>5cm</td>
<td>4.4 cm</td>
<td>4.05 cm</td>
</tr>
<tr>
<td>8cm</td>
<td>3.9 cm</td>
<td>3.3 cm</td>
</tr>
</tbody>
</table>

Figure 3.14 compares the thickness profile for X171 films produced using a die temperature of 220 °C and air-gap lengths of 5 cm and 8 cm. Again, due to the increased neck-in exhibited by the films produced using L = 8 cm, these films are thicker than the films produced using L = 5 cm. The film thickness profiles shown in Figures 3.11, 3.12 and 3.14 are averaged values from 5 test specimens. Figure 3.14 shows error bars plotted
using the standard deviation of the averaged values. A statistical analysis of the centerline thickness (using $\alpha = 0.05$) shows that the films produced using $L = 8$ cm are thicker than the films produced using $L = 5$ cm (see Appendix B).

![Graph showing thickness profiles](image)

**Figure 3.14** Thickness profile for X171 films at $T_{\text{die}} = 220$ °C.

### 3.2.2 Temperature profiles

Figure 3.15 shows temperature profiles, as a function of both transverse location and distance from the die, for the X171 and X172 samples at a draw ratio $DR = 8.6$, $L = 8$ cm and die temperature of 220 °C. The temperature profiles are flat near the die exit but show a local minimum as the chill roll is approached. The difference in temperature between the centerline and the film edges increases with increasing distance from the die.
exit. This is due to formation of edge beads. The temperature difference between the X171 and X172 samples, under identical process conditions, increases as the chill roll is approached. This may result from the increasing difference in thickness. The X171 films are thinner when compared to the X172 films, due to the increased neck-in of the X172 films. The temperature difference between the X171 and X172 samples shown in Figure 3.15 were found to be statistically significant (see Appendix B).

Figure 3.15 Temperature profile in web for the X171 and X172 samples at DR = 8.6 and die temperature of 220 °C.
Figure 3.16 compares centerline temperature profiles (as a function of distance from the die) for the X171 and X172 PP samples. The process conditions are draw ratios of 8.6, an air gap distance of 5 cm (X172) and 8 cm and a die temperature of 220 °C. It is seen that the X171 film cools more rapidly than the X172 film. The X171 sample has a higher viscosity and undergoes less film neck-in than the X172 sample (see Figure 3.9). Due to the physical constraint of mass conservation, reduced film neck-in should lead to increased draw down in film thickness. Hence, it should be easier to conduct heat away from the X171 film. The centerline temperature profiles for the X172 sample (at air gap distances of L = 5 cm and 8 cm) show that increasing the air-gap length also leads to an increase in the temperature drop obtained in the air-gap. This is due to the longer residence time of the film in the air-gap as a result of the increase in the air-gap length. The temperature difference between the X171 and X172 films near the chill roll is about 6 °C.
3.2.3 Machine direction velocity profiles ($v_x$)

The reported velocity values in this section are average velocities obtained from at least three separate runs for each condition. The standard deviation for the reported velocity data points are observed to range from 0.005 to 0.07 m/min. At least 95% of the data points (average values) obtained have standard deviation values that are less than 5% of the velocity value. Figure 3.17 and Figure 3.18 show centerline velocity profiles for X172 and X171 respectively at an air-gap length of 9 cm and die temperature of 220 °C. The velocity plots also show error bars obtained using the standard deviation (for each set
of data) about the mean value. The measured velocity increases from the die exit to the chill roll because the film is exposed to an extensional flow field. The velocity at the chill roll also increases with increasing draw ratio since the draw ratio is manipulated by maintaining a constant throughput while varying the chill roll velocity. The X172 centerline velocities are slightly higher than the X171 velocities. However, a statistical analysis of the data shows that the differences in velocity are not significant (see Appendix B). The statistical analysis was performed by using $\alpha = 0.05$.

In Figure 3.19 the centerline strain rates ($dv_x/dx$) are calculated for X171 and X172 using the velocity values shown in Figures 3.17 and 3.18. The strain rates increase near the die but at the lower draw ratio (8.6) the strain rates reach a maximum and then begin to decrease. At the higher draw ratio (12.8) the strain rate does not show a decrease. This is due to the fact that the film viscosity increases with increasing distance from the die exit (due to the decreasing temperature), resulting in an increased resistance to flow with distance from the die. At the higher draw ratio this effect is compensated for by the increased film tension as the draw ratio is increased (Canning et al., 2001). Thus, at the draw ratio of 12.8 the calculated strain rates show a continuous increase from die to chill roll.
Figure 3.17 Centerline velocity as functions of draw distance and draw ratio for X172 at a die temperature of 220 °C and L = 9 cm.
Figure 3.18 Centerline velocity as functions of draw distance and draw ratio for X171 at a die temperature of 220 °C and L = 9 cm.
Figure 3.19 Centerline strain rates for X171 and X172 at a die temperature of 220 °C and L = 9 cm.

In Figure 3.20 we report the draw direction velocity component ($v_x$) as a function of both transverse position and distance from the die in the air-gap region for the film casting experiments conducted using the X171 and X172 samples. Here, we use an air gap distance of 9 cm, a die temperature of 220 °C and DR = 8.6. As the fluid moves away from the die, the velocity increases due to the extensional flow field created by the difference in velocity at the die and the chill roll. At a given distance from the die, the maximum value is obtained in the central regions of the film. This trend was also observed for the PH 835 sample (Figure 3.5) and is primarily due to the technique used in
the velocity measurement. Based upon the primary orientation of the LDV equipment, the machine direction component of the velocity is generally measured. Streamlines in the central regions of the film are parallel to the x-direction. However, near the film edges, the path of fluid elements and the neck-in results in both machine direction and transverse direction velocity components. Comparing the velocity values for X171 to those of X172 shows only slight differences for measurements made at the same points in the web for both samples. Differences in the velocity values are expected since the streamlines for the samples differ (as a result of their different degrees of neck-in). Figure 3.20 also shows error bars plotted using the standard deviation values for the data points.

**Figure 3.20** Velocity map showing velocity as a function of transverse distance for X171 and X172 (DR = 8.6, L = 9 cm, $T_{\text{die}} = 220 \, ^{\circ}\text{C}$).
3.2.4 Transverse direction velocity profiles ($v_y$)

Due to the extensional flow field and neck-in experienced by the molten polymer in the region between the die exit and the chill roll, the velocity vector at each point in the flow will consist of both a machine direction ($v_x$) and a transverse direction ($v_y$) velocity component. In this section, we present results for experiments conducted in order to determine the transverse direction velocity component ($v_y$) as a function of position for the film in the air-gap region. A description of the experimental set-up used is given in section 2.2.3.

In calculating the values for $v_y$, we note that the direction of the velocity vector at any point in the flow, in relation to the measurement directions is as shown below in Figure 3.21.
Since $v_{60}$ and $v_x$ are projections of $v$ onto the $z_{60}$ and $x$ axes, respectively, the measured velocity values for the two components are given by

$$v_{60} = v \cdot \cos(\alpha) \text{ and } v_x = v \cdot \cos(\beta) \quad .$$  

(3.1)

The ratio ($J$) of $v_x$ to $v_{60}$ is

$$J = \cos(\beta)/\cos(\alpha) \quad .$$  

(3.2)

The equation for determining the transverse direction component of the velocity is then given as

$$v_y = v_x \cdot \tan(\beta) \quad .$$  

(3.3)
The value of $\beta$ is determined from the relationship between angles $\beta$ and $\alpha$ and the value of the parameter $J$. The derivation of equation 3.3 for both cases (I and II in Figure 3.21) is presented in Appendix A.

Figure 3.22 shows $v_x$ and $v_{60}$ velocity profiles for the X172 sample. The process conditions are $\text{DR} = 12.8$, $L = 8$ cm and a die temperature of 220 °C. The resulting calculated $v_y$ velocity profile is shown in Figure 3.23. In Figure 3.22 the $v_{60}$ velocity is greater than the $v_x$ velocity near the film edge; however, as the film centerline is approached the $v_x$ velocity is larger than the $v_{60}$ velocity. This is as a result of the stronger $y$-direction velocity components ($v_y$) that exist near the film edge due to neck-in. In the region near the film centerline the fluid particles move mainly in the $x$-direction - thus the $v_x$ velocity values are expected to be higher than the $v_{60}$ velocity values in the central regions of the film. This is due to the fact that the $y$-direction velocity component, $v_y$, decreases to a value of zero as the film centerline is approached. Figure 3.22 also shows error bars plotted using the standard deviation values for each data point.

In Figure 3.23 the $v_y$ velocity values are seen to decrease from the film edge to the film centerline. This is expected since the polymer moves primarily in the $x$-direction as the film centerline is approached, resulting in smaller values of the $y$-direction velocity components.
Figure 3.22 Plot of the magnitude of the $v_x$ and $v_{60}$ velocity components for X172 at $DR = 8.6$, $L = 8$ cm and a die temperature of $220^\circ$C.
The major source of error in the LDV method for measuring velocity arises from a misalignment of the laser head. A 1° misalignment angle will result in 0.015 % error in the measurements while a 4° misalignment angle will result in a 0.243 % error in the measured velocity values (Model LS50M Multiplexed LaserSpeed System Instruction Manual).

The accuracy of the method (used in this work) for determining the transverse direction component of the velocity is ascertained by calculating the velocity component, in the z60-direction, of the draw direction velocity at the centerline (i.e. y = 0). At the
centerline $v_{60}$ is the $v_x$ velocity component in a direction $30^\circ$ from the vertical. The calculated values are compared to the measured $v_{60}$ velocities, in Table 3.5. It is seen that in all cases the difference is less than 5 % of the calculated value.
Table 3.5 Comparison of measured velocity, $v_{60}$ to calculated $z_{60}$-direction velocity component.

| Table | X171, DR = 8.6 | | | |
|-------|----------------|----------------|----------------|
| x     | Vx  | V60   | Vx (cos 30) | Error (%) |
| 3 cm  | 0.862 | 0.726 | 0.7464 | 2.745 |
| 4 cm  | 1.127 | 0.956 | 0.9758 | 2.047 |
| 5 cm  | 1.363 | 1.179 | 1.180  | 0.1151 |

| Table | X171, DR = 12.8 | | | |
|-------|----------------|----------------|----------------|
| x     | Vx  | V60   | Vx (cos 30) | Error (%) |
| 3 cm  | 0.962 | 0.817 | 0.8332 | 1.932 |
| 4 cm  | 1.329 | 1.106 | 1.151  | 3.902 |
| 5 cm  | 1.645 | 1.429 | 1.425  | -0.3110 |

| Table | X172, DR = 8.6 | | | |
|-------|----------------|----------------|----------------|
| x     | Vx  | V60   | Vx (cos 30) | Error (%) |
| 3 cm  | 0.874 | 0.749 | 0.7569 | 1.042 |
| 4 cm  | 1.116 | 0.956 | 0.9665 | 1.082 |
| 5 cm  | 1.4   | 1.188 | 1.212  | 2.013 |

| Table | X172, DR = 12.8 | | | |
|-------|----------------|----------------|----------------|
| x     | Vx  | V60   | Vx (cos 30) | Error (%) |
| 3 cm  | 1.017 | 0.863 | 0.8807 | 2.012 |
| 4 cm  | 1.302 | 1.126 | 1.128  | 0.1359 |
| 5 cm  | 1.649 | 1.408 | 1.428  | 1.4023 |
Figure 3.24 presents a plot of the magnitude of the velocity vector as a function of position in the web for the X172 sample. The experiment was conducted using a die temperature of 220°C, air-gap length of 8cm and draw ratio of 8.6. The direction vectors for the velocity shown in Figure 3.24 are presented in Figure 3.25. The direction vectors in Figure 3.25 show that towards the film centerline the fluid particles tend to flow mainly in the draw (x) direction. The magnitude of the velocity is also seen to increase from the film edges to the film centerline as shown in Figure 3.24. In Chapter 5 numerical results from the FISIM model are compared to the experimentally determined results.
Figure 3.24 Calculated magnitude of the velocity vector as a function of position in the web for X172 at DR = 8.6, L = 8 cm and a die temperature of 220 °C.
Figure 3.25 Direction vectors for X172 at DR = 8.6, L = 8 cm and a die temperature of 220 °C.
3.3 Conclusions

Film casting experiments were conducted using polypropylene in order to investigate the film development in response to changes in the draw ratio, air-gap length and the die temperature. The draw and transverse direction velocity components, width and temperature profiles in the region between die and chill roll were measured as a function of position within the web. The effect of polymer viscosity on the film formation process was also investigated.

Increasing the die temperature or reducing the polymer molecular weight causes an increase in neck-in at a constant draw ratio. This is due to the differences in the viscosity, the temperature dependence of the rheology of the polymer, and the interaction between edge-beads and film neck-in. An increase in the air-gap length also increases the neck-in obtained in the air-gap since a change in the air-gap length changes the viscoelasticity of the flow (Deborah number) or the strain rate. This increase in neck-in also results in an increase in film thickness.

The centerline temperature profiles show that the film cools more rapidly in the machine direction as the draw ratio is increased (for a particular polymer sample) or as the polymer viscosity/molecular weight is increased (at a fixed draw ratio). This is due to the improved heat transfer from the web resulting from the decreasing film thickness. Increasing the draw ratio or increasing the polymer viscosity, increases the draw down in film thickness. The decrease in film thickness as a result of an increase in polymer viscosity is due to the reduction in film neck-in. Temperature profiles in the transverse direction indicate that the central portion of the film cools more rapidly than the film...
edges. This is also due to the film edges being thicker than the central portions of the film.

For the centerline velocity profile, increasing the draw ratio causes the strain rate in the web to increase in the region near the die exit. At low draw ratios, the centerline strain rate increases initially with increasing distance from the die, but goes through a maximum and starts to decrease as the chill roll is approached. This may result from the increase in viscosity (resulting in an increased resistance to flow) as the film cools with increasing distance from the die. At higher draw ratios, we find that the strain rate continues to increase from the die to the chill roll. We attribute this to the increase in film tension as the draw ratio is increased that overcomes the thermal effects. The draw direction component of the velocity (as a function of transverse position) has a larger magnitude in the central portions of the film than at the film edges. This is due to the no slip conditions at the die walls, and the neck-in of the film. The neck-in leads to a transverse direction velocity component perpendicular to the draw direction velocity. The transverse direction velocity component decreases in magnitude from the film edge to the film centerline. This is due to the polymer moving primarily in the draw direction as the film centerline is approached.
CHAPTER 4

INFLUENCE OF PROCESS CONDITIONS ON FILM PROPERTIES

The crystalline morphology and mechanical properties exhibited by polymer films, as a result of processing conditions, are significantly influenced by the polymer material properties. These material properties include molecular weight (MW), molecular weight distribution (MWD), tacticity and degree of stereo-regularity (Sakurai et al., 2005). During the film casting process, the amount of crystalline content developed in the polymer film, as a result of polymer orientation and flow-induced crystallization, affects the film mechanical strength (Alberty, 1983; Zhang and Ajji, 2005). An understanding of the relationships between processing conditions, film crystalline structure and film mechanical properties is essential for process optimization (Diez et al., 2005; Sakurai et al., 2005) and product design.

The end-use applications of polymer films are limited by the response of the film material to the thermal, chemical and mechanical environments that characterize a particular application.

Polymer films are usually produced in two stages in a typical film casting line. The first stage involves the extrusion of a polymer melt through a flat die and the subsequent
cooling of the film on a chill roll. The film obtained after the chill roll in this step is usually termed the “Primary film”. The second stage involves processing steps aimed at imparting desired end-use properties to the Primary film. An example of a major secondary processing step is uniaxial/biaxial stretching. We will refer to this class of films as “Processed film”. In this work the Primary film is subjected only to uniaxial stretching due to the limitations placed on the width of the Primary film by the CAEFF film casting equipment geometry (die width of 10.16 cm).

The Primary films employed in this chapter were produced using draw ratios of 8.6 and 12.8, die temperatures of 200 °C and 220 °C, and air-gap lengths of 5 cm, 8 cm and 9 cm. The processed film samples were obtained by stretching the primary film to 2X and 3X their initial length at 100 °C. The stretching rates used are 50 mm/s/s and 100 mm/s/s. In this chapter, only the X171 and X172 polypropylene samples are investigated. This allows for a direct study of the effect of material properties. The processing conditions used for producing the Processed films are summarized in Table 4.1.

In this chapter we study the relationship between polymer molecular weight, processing conditions, film morphology and film mechanical properties. We first study the effect of processing conditions on film orientation and crystallinity with the aid of wide angle x-ray diffraction (WAXD) and differential scanning calorimetry (DSC). Then, the relationship between the film morphology (orientation and crystallinity), developed during processing, and the film mechanical properties are studied using dynamic mechanical analysis (DMA) and tensile testing. The DMA and Tensile Testing results are usually calculated from Stress-Strain responses to deformation, thus, the effect of film thickness may be minimized.
Table 4.1 Processing conditions for Primary film samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Die Temperature</th>
<th>Draw ratio</th>
<th>Stretch ratio</th>
<th>Stretching rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>X171</td>
<td>220 °C</td>
<td>8.6</td>
<td>2X</td>
<td>100 mm/s/s</td>
</tr>
<tr>
<td>X171</td>
<td>220 °C</td>
<td>8.6</td>
<td>3X</td>
<td>100 mm/s/s</td>
</tr>
<tr>
<td>X171</td>
<td>220 °C</td>
<td>12.8</td>
<td>3X</td>
<td>100 mm/s/s</td>
</tr>
<tr>
<td>X172</td>
<td>220 °C</td>
<td>8.6</td>
<td>2X</td>
<td>100 mm/s/s</td>
</tr>
<tr>
<td>X172</td>
<td>220 °C</td>
<td>8.6</td>
<td>3X</td>
<td>100 mm/s/s</td>
</tr>
<tr>
<td>X172</td>
<td>220 °C</td>
<td>12.8</td>
<td>3X</td>
<td>100 mm/s/s</td>
</tr>
<tr>
<td>X172</td>
<td>200 °C</td>
<td>8.6</td>
<td>3X</td>
<td>50 mm/s/s</td>
</tr>
<tr>
<td>X172</td>
<td>200 °C</td>
<td>8.6</td>
<td>3X</td>
<td>100 mm/s/s</td>
</tr>
</tbody>
</table>
4.1 Wide Angle X-ray Diffraction

Isotactic polypropylene (i-PP) has been shown to crystallize in four forms; a monoclinic or α-form, a hexagonal or β-form, a γ-form and a mesomorphic form (Sperling, 2001; Diez et al., 2005; Choi and White, 2004). The γ-form is also referred to in literature as triclinic (Morrow and Newman, 1968; Diez et al., 2005) or orthorhombic (Bruckner and Meille, 1989; Alamo et al., 2005). This is due to Morrow and Newman (1968) assigning it a triclinic cell while Bruckner and Meille (1989) later showed that a triclinic cell would lead to some inconsistencies with the X-ray diffraction powder profile for this form of i-PP crystals. The mesomorphic form is obtained by quenching of molten i-PP. The α-form is the most stable form (Elias et al., 2000).

For i-PP, the different crystal forms are identified by reflections from the following planes at their corresponding angles (Agarwal et al., 2003, Bruckner et al., 1991);

**α-form**: (110) plane at $2\theta = 14.1^\circ$, (040) plane at $2\theta = 16.9^\circ$, (130) plane at $2\theta = 18.5^\circ$

(111) plane at $2\theta = 21.4^\circ$ and (-131) plane at $2\theta = 21.8^\circ$

**β-form**: (300) plane at $2\theta = 16.1^\circ$ and (301) plane at $2\theta = 21.4^\circ$

**γ-form**: (111) plane at $2\theta = 13.8^\circ$, (113) plane at $2\theta = 15.0^\circ$, (115) plane at $2\theta = 17.2^\circ$

(117) plane at $2\theta = 20.1^\circ$, (202) plane at $2\theta = 21.2^\circ$, (026) plane at $2\theta = 21.9^\circ$

The (300) plane is used as a marker for the β-form while the (117) is used as a marker for the γ-form. This is due to the uniqueness of their reflection angles when compared to those of the α-form.

**Mesomorphic form**: This form is identified by broad intense peaks at $2\theta = 14.8^\circ$ and $21.2^\circ$ and less intense peaks at $2\theta = 28.8^\circ$ and $42.6^\circ$ (Bruckner et al., 1991). The broad peaks imply that this crystalline form of i-PP is characterized by small and/or disordered
crystals. An interesting feature of this crystalline form is that when stretched or annealed the crystals reorganize themselves into the $\alpha$-form.

In this work, films for X-ray analysis were produced using the X171 and X172 polymer samples at draw ratios of 8.6 and 12.8. The air-gap length was 5 cm and die temperatures of both 200 °C and 220 °C were employed. Several of the primary film samples were then uniaxially stretched (at 100 °C) to 2X and 3X their initial gage length at rates of 50 mm/s/s and 100 mm/s/s.

During the film casting process an electrostatic pinning device was employed in order to maintain adequate contact between the polymer extrudate and the chill roll. This may be viewed as similar to quenching the molten film in a water bath and may have an impact on the film morphology. Several studies (Bruckner et al., 1991; Grubb and Yoon, 1986) have shown that quenching of polypropylene samples gives rise to the mesomorphic form of i-PP crystals.

Figure 4.1 shows X-ray diffraction images for an unstretched and a stretched sample. The unstretched sample was produced using $T_{\text{die}} = 220$ °C, DR = 8.6 and L = 5 cm. The stretched sample was obtained by uniaxial orientation of the unstretched sample to 3X the initial sample length. The images show broad concentric rings for the unstretched sample indicating a crystalline sample with little or no preferential orientation. The image for the stretched sample shows arcs which indicate a crystalline and oriented sample.
Figure 4.1 WAXD patterns for X171 film samples produced at $T_{\text{die}} = 220 ^\circ \text{C}$ and DR = 8.6. (a) unstretched sample (b) sample stretched to 3X the initial length.

Figure 4.2 shows the intensity profile as a function of $2\theta$ for a sample X172 film produced using a die temperature of 200 °C and DR = 8.6. In Figure 4.3, we show the intensity profile as a function of $2\theta$ for a film sample produced using $T_{\text{die}} = 200 ^\circ \text{C}$, DR = 8.6 and stretched to 3X its original length. In Figure 4.2 the peaks correspond to that for the mesomorphic form while the peaks in Figure 4.3 correspond to the $\alpha$-form while weak mesomorphic peaks can also be seen at $2\theta = 28^\circ$ and $43^\circ$. What this implies is that
the use of the pinning device and a chill roll during the film casting process leads to quenching of the polymer film thus leading to the development of the mesomorphic crystalline morphology (Grubb and Yoon, 1986; Bruckner et al., 1991; Elias et al., 2000). Since the mesomorphic form is characterized by small and/or disordered crystals the film modulus may be slightly lower than literature values for film produced using film casting with little or no quenching. This will be discussed later in the chapter. The intensity profile in Figure 4.3 shows that orienting the film samples leads to reorganization of the mesomorphic crystals into the $\alpha$-form of i-PP crystals. The weak peaks at $2\theta = 28^\circ$ and $43^\circ$ indicate that some of the mesomorphic crystals are excluded from the formation of $\alpha$-form crystals. The consequence of this finding is two-fold. First, there should be an increase in the modulus values reported for the oriented samples and secondly, double melting peaks may be exhibited in the DSC thermogram for the oriented samples. This double peak can be attributed to the smaller mesomorphic crystals melting at the lower temperature while the $\alpha$-form crystals melt at the higher temperature (Elias et al., 2000).

As stated in Chapter 2, the crystalline content of the film samples is calculated from the contributions of the crystalline and amorphous regions of the material, to the area under the diffractogram (equation 2.18).

$$CI = \frac{I_c}{I_c + I_a}.$$  \hspace{1cm} (2.18)

The crystalline and amorphous sections of the diffractogram are determined using the method suggested by Weidinger and Hermans (1961). The crystalline ($I_c$) and amorphous ($I_a$) areas were then calculated using the Grams 32 area calculation software. The values
obtained were also validated by counting the squares on a Microsoft Excel Graph of the diffractogram. Figure 4.4 shows the diffractogram for an X171 film sample stretched to 2X its initial length. The film was produced using a DR = 8.6 and T_{die} = 220 °C. This figure (4.4) shows the crystalline and amorphous contributions to the area under the diffractogram as determined using the Grams 32 software.

Figure 4.2 X172 film at T_{die} = 200 °C and DR = 8.6.
Figure 4.3 X172 film at $T_{\text{die}} = 200^\circ\text{C}$ and DR = 8.6. The film is stretch to 3X the initial length at 100 mm/s/s.
The percent crystallinities as determined from equation 2.18 (100*CI) are shown in Table 4.2 for the film samples with different processing histories. From Table 4.2 it is seen that the stretching increases the crystalline content for a particular film sample. Increasing the stretching distance from 2X to 3X the initial film length also increases the measured film crystallinity. This is due to the orientation imparted to the polymer molecules by stretching the film samples. Increasing the stretching distance increases the alignment of the polymer molecules in the draw direction thus increasing the formation of crystals.
Table 4.2 Relative areas for the crystalline peaks \( I_c \) (110, 040, 130, 111, and mesomorphic peak) and the amorphous region \( I_a \).

<table>
<thead>
<tr>
<th>Materials and conditions</th>
<th>( I_c ) (110)</th>
<th>( I_c ) (040)</th>
<th>( I_c ) (130)</th>
<th>( I_c ) (111)</th>
<th>( I_c ) (meso)</th>
<th>( I_a )</th>
<th>100CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>X171, 8.6, 220C 2X, 100R</td>
<td>13</td>
<td>6.3</td>
<td>4.1</td>
<td>10</td>
<td>1.6</td>
<td>37</td>
<td>49</td>
</tr>
<tr>
<td>X171, 8.6, 220C 3X, 100R</td>
<td>17</td>
<td>5.1</td>
<td>3.2</td>
<td>9.5</td>
<td>1.6</td>
<td>36</td>
<td>50</td>
</tr>
<tr>
<td>X171, 12.8, 220C 3X, 100R</td>
<td>6.3</td>
<td>3.7</td>
<td>2.8</td>
<td>10</td>
<td>1.6</td>
<td>22</td>
<td>53</td>
</tr>
<tr>
<td>X172, 8.6, 220C 2X, 100R</td>
<td>15</td>
<td>7.0</td>
<td>2.9</td>
<td>10</td>
<td>1.3</td>
<td>36</td>
<td>50</td>
</tr>
<tr>
<td>X172, 8.6, 220C 3X, 100R</td>
<td>16</td>
<td>7.9</td>
<td>4.8</td>
<td>13</td>
<td>1.1</td>
<td>39</td>
<td>52</td>
</tr>
<tr>
<td>X172, 12.8, 220C 3X, 100R</td>
<td>8.6</td>
<td>4.3</td>
<td>2.1</td>
<td>5.7</td>
<td>0.56</td>
<td>17</td>
<td>56</td>
</tr>
<tr>
<td>X172, 8.6, 200C 3X, 50R</td>
<td>7.4</td>
<td>4.1</td>
<td>3.3</td>
<td>13</td>
<td>1.8</td>
<td>20</td>
<td>60</td>
</tr>
<tr>
<td>X172, 8.6, 200C 3X, 100R</td>
<td>3.0</td>
<td>2.1</td>
<td>2.1</td>
<td>9.6</td>
<td>1.4</td>
<td>12</td>
<td>60</td>
</tr>
</tbody>
</table>

In Table 4.3 we present data on the Hermans orientation factors for the a, b, and c crystallographic axes. The orientation factor with respect to a crystallographic axis \( j \) is calculated using equation 2.19

\[
f_j = \frac{3 \langle \cos^2 \phi_j \rangle - 1}{2}.
\]  

The orientation factor \( f_b \) is calculated using reflections from the (040) planes since the normal to this plane is parallel to the b-axis as shown in Figure 4.5 (Sadeghi et al., 2007). There are no reflections associated with planes that are perpendicular to the c-axis thus...
the c-axis orientation factor $f_c$ is calculated using diffraction intensities from the (110) and (040) planes (Zhang and Ajji, 2005). The quantity $<\cos^2 \phi_j>$ is first calculated for the c-axis by using the equation (Zhang and Ajji, 2005);

$$<\cos^2 \phi_c> = 1 - 1.099 <\cos^2 \phi_{110}> - 0.901 <\cos^2 \phi_{040}> .$$

(4.1)

The orientation factor $f_c$ is then calculated using equation 2.19. The a-axis orientation factor $f_a$ is calculated from the orientation factors $f_b$ and $f_c$ using equation 4.2 given as (Zhang and Ajji, 2005, Sadeghi et al., 2007)

$$f_a + f_b + f_c = 0 .$$

(4.2)

A Hermans orientation factor value of 0 indicates no preferential orientation, a value of -0.5 indicates that molecules are oriented perpendicular to the crystallographic axis (i.e. $\phi_j = 90^\circ$), and a value of 1 indicates that the chains are oriented parallel to the crystallographic axis (i.e. $\phi_j = 0^\circ$). Thus, from Table 4.3, we surmise from the values for $f_a$, $f_b$ and $f_c$ that the polymer molecules are preferentially oriented along the c-axis. (c-axis orientation from the table is close to 1 indicating molecules are parallel to this axis while the a and b-axis orientation are both close to -0.5 indicating perpendicular orientation to those axes). High orientation factor values also indicate that the films are highly oriented and that further stretching may not yield much improvement to the film properties. The orientation factor is also seen to increase with increasing strain. Increasing the strain from 2X to 3X increases the level of orientation thus we see the increase in $f_c$ (e.g. 0.952 to 0.984 for the X172 sample produced using DR = 8.6). The unstretched samples show
little or no orientation as can be seen from their WAXD images. Previously, orientation factor values ranging from 0.7 to 0.93 have been reported for polypropylene samples (Sadeghi et al, 2007; Choi and White, 2004). The high orientation factor values along the c-axis may also be due to the unconstrained nature of the uniaxial stretching used in this work.

**Table 4.3** Crystalline axis Hermans orientation factors.

<table>
<thead>
<tr>
<th>Material and conditions</th>
<th>$f_a$</th>
<th>$f_b$</th>
<th>$f_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>X171, 8.6, 220C, 2X, 100R</td>
<td>-0.48</td>
<td>-0.48</td>
<td>0.96</td>
</tr>
<tr>
<td>X171, 8.6, 220C, 3X, 100R</td>
<td>-0.48</td>
<td>-0.49</td>
<td>0.97</td>
</tr>
<tr>
<td>X171, 12.8, 220C, 3X, 100R</td>
<td>-0.49</td>
<td>-0.49</td>
<td>0.98</td>
</tr>
<tr>
<td>X172, 8.6, 220C, 2X, 100R</td>
<td>-0.47</td>
<td>-0.48</td>
<td>0.95</td>
</tr>
<tr>
<td>X172, 8.6, 220C, 3X, 100R</td>
<td>-0.49</td>
<td>-0.49</td>
<td>0.98</td>
</tr>
<tr>
<td>X172, 12.8, 220C, 3X, 100R</td>
<td>-0.49</td>
<td>-0.49</td>
<td>0.99</td>
</tr>
<tr>
<td>X172, 8.6, 200C, 3X, 50R</td>
<td>-0.49</td>
<td>-0.49</td>
<td>0.98</td>
</tr>
<tr>
<td>X172, 8.6, 200C, 3X, 100R</td>
<td>-0.49</td>
<td>-0.49</td>
<td>0.99</td>
</tr>
</tbody>
</table>
Figure 4.5 The 040 and 110 crystal planes with respect to the a, b, and c crystallographic axes.

4.2 Differential Scanning Calorimetry

In this section, results on the thermal characterization of the primary and processed films using Differential Scanning Calorimetry (DSC) are presented. The experiments study the effect of processing conditions on the film crystallinity. The percent crystallinity calculated using the DSC method is also compared to the percent crystallinity calculated from the WAXD method. From DSC measurements, the percent crystallinity, as stated in section 2.4.1, is calculated from equation 2.16.
\[ X_c = \frac{\Delta H_m}{\Delta H_m^0}. \]  

In equation 2.16 \( \Delta H_m \) is the heat of melting in J/g for the semi-crystalline sample, \( \Delta H_m^0 \) is the heat of melting for a 100 % crystalline sample in J/g and \( X_c \) is the degree of crystallinity. In this work a value of \( \Delta H_m^0 = 209 \text{ J/g} \) for a fully crystalline polypropylene sample (Chen et al, 2006) is employed. The heat of melting for each film sample is calculated from the area under the melting peak of the DSC thermogram.

Figure 4.6 shows heating curves/thermograms for X172 films produced at a die temperature of 200 °C, air-gap length of 5 cm and DR = 8.6 and 12.8. In this work, the melting endotherm shows up as a peak since the differential heat flow is calculated by subtracting the reference heat flow from the sample heat flow. Both films show melting peaks at about 145 °C. The heating curves for Primary films stretched to 2X and 3X their initial length, at 100 mm/s/s are presented in Figure 4.7. The films were produced using a die temperature of 220 °C, DR = 8.6 and L = 5 cm. Note the difference in the nature of the melting peaks in Figure 4.7 when compared to the melting peaks in Figure 4.6 (i.e. two melting peaks versus a single melting peak).
Figure 4.6 Heating curve for X172 films with $T_{\text{die}} = 200$ °C and $L = 5$ cm.

Figure 4.7 Heating curve for processed X171 films with $T_{\text{die}} = 220$ °C and $L = 5$ cm and $\text{DR} = 8.6$. Stretcher acceleration used is 100 mm/s/s.
The heating curves in Figure 4.7 show two melting peaks, indicating the presence of two crystalline forms in the processed film (Ferrer-Balas et al., 2001; Elias et al., 2000). As shown by the X-ray diffractograms presented in section 4.1, the Primary film samples crystallize mainly in the mesomorphic form due to the quenching action of the chill roll. Thus the heating curves in Figure 4.6 exhibit single melting peaks. Upon stretching of the Primary film, the orientation of the polymer molecules in the draw direction enables the reorganization of the small and/or disordered mesomorphic crystals into the monoclinic \( \alpha \)-form (Bruckner et al., 1991; Grubb and Yoon, 1986). This is indicated by the peak intensities detected in the X-ray diffractograms of the stretched samples. These diffractograms also contain weak peaks that are indicative of the mesomorphic form thus indicating that some of the mesomorphic crystals are excluded from the formation of the \( \alpha \)-form crystals.

The heating curves for the Primary and Processed film samples (examples are shown in Figures 4.6 and 4.7) are used in calculating the amount of crystalline material present in a film. Pyris 1 software is used in specifying the temperature program for the DSC experiments and also in calculating the heat of melting (\( \Delta H_m \)) for a particular film sample.

Table 4.4 shows percent crystallinity values and peak temperature (\( T_p \)) for X171 films produced at \( T_{\text{die}} = 220 \, ^\circ\text{C}, \, L = 5 \, \text{cm} \) and \( \text{DR} = 6.5, \, 8.6 \) and 12.8. The reported values are averages from tests conducted on 7 samples per batch. The standard deviation about the mean is reported in square brackets. Table 4.4 also presents percent crystallinity values for X171 films stretched to 2X and 3X their initial length at an acceleration of 100 mm/s/s. A statistical analysis of the data in Table 4.4 (using \( \alpha = 0.05 \)) shows that the
difference in heat of melting for films produced at DR = 6.5 and films produced at DR = 8.6 is not significant. The difference in heat of melting for the remaining entries is found to be statistically significant (see Appendix B). The results indicate that the film crystallinity is increased slightly by increasing the draw ratio from 8.6 to 12.8. This is a result of the increased temperature drop obtained in the film as the draw ratio is increased. The driving force for the formation of mesomorphic crystals is the temperature difference between the PP melt and the quench temperature. An increase in this temperature difference results in a decrease in the crystalline content of the PP sample (Grubb and Yoon, 1986; Kanai and Campbell, 1999). The increase in the crystallinity of the Processed film as the stretch ratio is increased is due to the effect of draw induced crystallization resulting from the increased molecular orientation obtained by increasing the stretch ratio. The differences that exist between the values of percent crystallinity calculated using the DSC and WAXD techniques may be attributed to the sample crystalline structure. The WAXD technique is sensitive to crystal size and regularity while the DSC technique may have contributions to the heat of melting from imperfect crystals (personal correspondence with Prof. Mike Ellison).
Table 4.4 Degree of crystallinity and peak temperatures for X171 (Primary and Processed) films.

<table>
<thead>
<tr>
<th>X171, T_{die} = 220 °C, L = 5cm</th>
<th>ΔH_{m} (J/g) [S.D.]</th>
<th>T_{p} (°C)</th>
<th>100X_c (%)</th>
<th>100CI(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DR(6.5)</td>
<td>76.74 [2.33]</td>
<td>145.70</td>
<td>36.72</td>
<td></td>
</tr>
<tr>
<td>DR(8.6)</td>
<td>77.39 [2.66]</td>
<td>146.10</td>
<td>37.03</td>
<td></td>
</tr>
<tr>
<td>DR(12.8)</td>
<td>80.44 [2.00]</td>
<td>145.50</td>
<td>38.49</td>
<td></td>
</tr>
<tr>
<td>DR(8.6), 2X, 100R</td>
<td>87.30 [0.13]</td>
<td>148.30</td>
<td>41.77</td>
<td>48.10</td>
</tr>
<tr>
<td>DR(8.6), 3X, 100R</td>
<td>91.00 [0.09]</td>
<td>150.90</td>
<td>43.54</td>
<td>49.98</td>
</tr>
<tr>
<td>DR(12.8), 3X, 100R</td>
<td>94.14 [0.34]</td>
<td>148.60</td>
<td>45.04</td>
<td>53.28</td>
</tr>
</tbody>
</table>

Table 4.5 presents percent crystallinity and peak temperature for Primary and Processed X172 films. The Primary film is produced using T_{die} = 200 °C, L = 5 cm and DR = 8.6 and 12.8. A statistical analysis of the data shows that the differences in the reported heat of melting values are significant except for when comparing films produced using a stretching rate of 50 mm/s/s to films produced using a stretching rate of 100 mm/s/s (see Appendix B). Thus, the increase in stretching rate does not improve the film crystallinity.

Table 4.6 shows percent crystallinity and peak temperature for X172 (Primary and Processed) films. The primary films are produced using T_{die} = 220 °C, L = 5 cm and DR = 8.6 and 12.8. The differences in the heat of melting values reported in Table 4.6 were determined to be statistically significant (see Appendix B). In Table 4.5, we see the same trend of Table 4.4 in which increasing the draw ratio results in increased film crystallinity. Comparing X_c for films stretched to 3X their initial length at an acceleration
of 50 mm/s/s to $X_c$ for films stretched to 3X their initial length but at an acceleration of 100 mm/s/s shows no significant differences in degree of crystallinity. Film stretching is usually done at fast enough stretch rates so as to minimize polymer chain relaxation during stretching (Fried, 2002; Kanai and Campbell, 1999), and thus it appears that a stretch acceleration of 50 mm/s/s is high enough to achieve optimal crystallinity. Comparing results for X172 films in Table 4.6 to results for the X171 films in Table 4.4 it is seen that the X172 Processed films show a higher degree of crystallinity than the X171 Processed films (as determined from a statistical analysis of the data). This may be as a result of the higher degree of molecular orientation present in the X172 Processed films (see orientation factor $f_c$ in Table 4.3). The differences in the Heat of melting values for the X171 and X172 Primary films were determined not to be significant (see Appendix B).

Table 4.5 Degree of crystallinity and peak temperatures for X172 (primary and processed) films. The primary films are produced at $T_{\text{die}} = 200^\circ\text{C}$.

<table>
<thead>
<tr>
<th>X172, $T_{\text{die}} = 200^\circ\text{C}$</th>
<th>$\Delta H_m$ (J/g) [S.D.]</th>
<th>$T_p$ ($^\circ\text{C}$)</th>
<th>100$X_c$ (%)</th>
<th>100CI (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DR(8.6)</td>
<td>79.08 [0.69]</td>
<td>145.40</td>
<td>37.84</td>
<td></td>
</tr>
<tr>
<td>DR(12.8)</td>
<td>81.06 [0.53]</td>
<td>145.40</td>
<td>38.78</td>
<td></td>
</tr>
<tr>
<td>DR(8.6), 3X, 50R</td>
<td>91.90 [0.02]</td>
<td>148.90</td>
<td>43.97</td>
<td>59.37</td>
</tr>
<tr>
<td>DR(8.6), 3X, 100R</td>
<td>91.40 [0.39]</td>
<td>148.60</td>
<td>43.73</td>
<td>59.89</td>
</tr>
</tbody>
</table>
Table 4.6 Degree of crystallinity and peak temperatures for X172 (primary and processed) films. The primary films are produced at $T_{\text{die}} = 220 \, ^\circ\text{C}$.

<table>
<thead>
<tr>
<th>X172, $T_{\text{die}} = 220 , ^\circ\text{C}$</th>
<th>$L = 5\text{cm}$</th>
<th>$\Delta H_m , (\text{J/g}) , [\text{S.D}]$</th>
<th>$T_p , (^\circ\text{C})$</th>
<th>$100X_c , (%)$</th>
<th>$100CI , (%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DR(8.6)</td>
<td></td>
<td>77.37 [0.23]</td>
<td>145.6</td>
<td>35.14354</td>
<td></td>
</tr>
<tr>
<td>DR(12.8)</td>
<td></td>
<td>78.94 [0.10]</td>
<td>145.1</td>
<td>36.17703</td>
<td></td>
</tr>
<tr>
<td>DR(8.6), 2X, 100R</td>
<td></td>
<td>91.2 [0.39]</td>
<td>148.7</td>
<td>43.63636</td>
<td>50.40</td>
</tr>
<tr>
<td>DR(8.6), 3X, 100R</td>
<td></td>
<td>95.9 [1.17]</td>
<td>148.9</td>
<td>45.88517</td>
<td>52.64</td>
</tr>
<tr>
<td>DR(12.8), 3X, 100R</td>
<td></td>
<td>98.4 [0.42]</td>
<td>149.1</td>
<td>47.08134</td>
<td>55.93</td>
</tr>
</tbody>
</table>

The range of percent crystallinity values exhibited by the X171 and X172 films, as determined by the DSC method are comparable to that presented in literature. The crystalline content for quenched i-PP samples have been reported to range from 30-40 % (Farrow, 1965; McAllister et al., 1978; Diez et al., 2005). In their work, Grubb and Yoon (1986), report the crystalline content to be increased from 37 % (for the quenched sample) to 40-55 % upon stretching at 100 °C.
4.3 Dynamic Mechanical Analysis

In this section we present results on the study of the polypropylene film mechanical properties using Dynamic Mechanical Analysis (DMA). The film samples were subjected to temperature ramp tests in order to determine the dependence of the storage modulus $E'$ on temperature. Before conducting the temperature ramp tests a strain sweep test was conducted in order to determine the linear viscoelastic limit for the samples. Figure 4.8 shows $\sigma$ and $E'$ as functions of % strain, at a frequency of 6.283 rad/s and a temperature of 30 °C, for an (unstretched) X172 film sample. The region where the stress shows a linear dependence on the strain is the linear viscoelastic region for the material. For this study the film samples are cut to about 5 mm in width and 38 mm in length. The film thickness is registered at the onset of the test and is used in calculation of the film cross-sectional area and thus the stress applied to the sample during testing. An initial test gage length of 23 mm is used. The DMA temperature ramp tests are conducted at a strain of 0.5 %, frequency of 6.283 rad/s and a heating rate of 5 °C/min. The initial and final temperatures used are 30 °C and 130 °C respectively. The strain of 0.5 % was chosen because it was in the LVE Limit. The frequency of 1 Hz is routinely used in many DMA tests and the heating rate of 5 °C/min was selected in order to allow for temperature uniformity throughout the test samples.
Figure 4.8 Stress and modulus as functions of percent strain for X172 film produced using $T_{\text{die}} = 200$ °C, DR = 12.8 and L = 5 cm.

Figure 4.9 shows $E'$ as a function of temperature for X172 primary films produced at DR = 8.6 and 12.8. Also shown is the modulus data for the X172 film produced at a draw ratio of 8.6 and stretched to 3X the initial length. It is seen that increasing the draw ratio increases the magnitude of the storage modulus. Subsequent uniaxial stretching of the film samples also results in an increase in the modulus. This is due to the increase in percent crystallinity obtained by increasing the draw ratio (for the Primary film) and by an increase in molecular orientation and crystallinity upon stretching of the primary film. Figure 4.9 also compares the modulus for films tested in the TD to the modulus for films tested in the MD at a draw ratio of 12.8. The results show no appreciable difference in the
modulus values. This implies that the Primary films do not exhibit any substantial preferential orientation as was observed from the WAXD image shown in Figure 4.1.

Figure 4.10 reports the modulus as a function of temperature for X171 films that are stretched to 2X and 3X the initial length. Again, the results indicate that increasing the stretching ratio increases the film modulus. This is also as a result of the increased orientation and crystallinity obtained by increasing the stretching ratio for the processed films. The crystallinity data in Tables 4.4, 4.5, and 4.6 corroborate this assertion. The stretched samples exhibit the typical curve behavior observed for highly crystalline samples (Sperling, 2001). The storage modulus curves for the Primary film samples show a plateau modulus as the temperature is increased. The modulus also decreases from this plateau value as the polymer melting point (148 °C) is approached due to the phase transition from solid to liquid.
Figure 4.9 Modulus as a function of temperature for X172 films. The processing conditions for the primary film are $T_{\text{die}} = 200$ °C and $L = 5$ cm.
In Figure 4.11 we compare modulus values for X172 processed film with different stretch rates. As reported above for the crystallinity data (Table 4.5), increasing the stretching rate does not show any marked improvement in film modulus. This is as a result of the acceleration of 50 mm/s/s being high enough to impart high levels of orientation and crystallinity to the film samples (Tables 4.2 and 4.5). The damping coefficient (tan δ) for the stretched samples shows a peak at about 80 °C which may be
due to the onset of a plateau in the storage modulus as temperature is increased. The plateau modulus region is due to the development of molecular entanglements by the polymer chains. The DMA modulus values reported by Elias et al. (2000), for Primary and Processed polypropylene films, are in the same range as the values reported in this work (i.e. $10^8$-$10^{10}$ Pa).

![Graph](image)

**Figure 4.11** Modulus as a function of temperature for X172 processed films. The film samples are stretched at two different rates. The processing conditions for the primary film are $T_{die} = 200$ °C, DR = 8.6 and L = 5 cm while the films were stretched to 3X the initial length.
4.4 Tensile Testing

The effect of processing conditions on the film mechanical properties is studied in this section. The Tensile Testing method is used to determine the effect of the film morphology (developed as a result of processing) on the film tensile properties. The film samples were tested in tensile mode using an Instron Tensile Testing machine (Model #) and the mechanical properties such as Tensile Modulus and Yield Stress were determined from the resulting stress-strain curve.

The results for the tensile properties of the unstretched samples are compared in Tables 4.7 and 4.8. From the results presented the samples made at DR = 12.8 show higher moduli (Young’s Modulus and E-Modulus) than the samples made at DR = 8.6. This is due to the higher degree of crystallinity imparted to the film sample through the use of a higher draw ratio. The values for yield stress do not seem to show any material dependence. The yield stress values reported in Tables 4.7 and 4.8 also do not show any significant dependence on air-gap length or draw ratio as determined from a statistical analysis of the data (using $\alpha = 0.05$. See Appendix B). The modulus values reported in this work are of the same magnitude as literature values (Ferrer-Balas et al., 2001).
**Table 4.7** Tensile properties for unstretched samples at $L = 5$ cm and $T_{\text{die}} = 220$ °C. The value in ( ) is the standard deviation. All other values are average values.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus of Elasticity (MPa)</th>
<th>E-modulus (MPa)</th>
<th>Yield Stress (MPa)</th>
<th>Yield Elongation (%)</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X171, DR = 8.6</td>
<td>870 (25.5)</td>
<td>707.0 (34.2)</td>
<td>30 (8.7)</td>
<td>7.5 (0.4)</td>
<td>0.222</td>
</tr>
<tr>
<td>X172, DR = 8.6</td>
<td>890 (21.5)</td>
<td>720.0 (21.6)</td>
<td>27.0 (4.4)</td>
<td>7.6 (0.3)</td>
<td>0.227</td>
</tr>
<tr>
<td>X171, DR = 12.8</td>
<td>952 (25.5)</td>
<td>777.4 (23.2)</td>
<td>21.7 (0.3)</td>
<td>6.3 (0.5)</td>
<td>0.180</td>
</tr>
<tr>
<td>X172, DR = 12.8</td>
<td>1006 (19.3)</td>
<td>789.4 (63.1)</td>
<td>23.4 (0.6)</td>
<td>6.6 (0.8)</td>
<td>0.170</td>
</tr>
</tbody>
</table>

**Table 4.8** Tensile properties for unstretched samples at $L = 8$ cm and $T_{\text{die}} = 220$ °C. The value in ( ) is the standard deviation. All other values are average values.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus of Elasticity (MPa)</th>
<th>E-modulus (MPa)</th>
<th>Yield Stress (MPa)</th>
<th>Yield Elongation (%)</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X171, DR = 8.6</td>
<td>890 (9.8)</td>
<td>653.8 (30)</td>
<td>26.1 (5.5)</td>
<td>7.7 (0.2)</td>
<td>0.246</td>
</tr>
<tr>
<td>X172, DR = 8.6</td>
<td>822 (11.8)</td>
<td>652.8 (44.2)</td>
<td>27 (4.4)</td>
<td>7.9 (0.1)</td>
<td>0.258</td>
</tr>
<tr>
<td>X171, DR = 12.8</td>
<td>981 (13.9)</td>
<td>759.2 (22.9)</td>
<td>28.6 (8.4)</td>
<td>6.9 (0.5)</td>
<td>0.194</td>
</tr>
<tr>
<td>X172, DR = 12.8</td>
<td>871 (13.8)</td>
<td>647.4 (21)</td>
<td>27 (7.8)</td>
<td>7.5 (1.1)</td>
<td>0.210</td>
</tr>
</tbody>
</table>
The tensile properties for the stretched films are reported in Tables 4.9 and 4.10. Table 4.9 compares tensile properties for the films stretched to 3X and 2X their original gage length. The samples that were stretched 3X show higher modulus, yield stress and tensile strength than the samples that were stretched 2X. This is as a result of the greater degree of orientation and crystallinity obtained by stretching the samples to 3X rather than 2X. The X172 samples also seem to show higher values of modulus, tensile strength and yield stress than the X171 samples. The stretched samples made from film produced at DR = 12.8 also show higher values for these tensile properties than the stretched samples made from films produced at a DR = 8.6. As seen from the crystallinity data obtained using the DSC and WAXD methods, this maybe attributed to the higher degree of crystallinity present in films produced at a higher draw ratio.

Comparing results in Table 4.7 to the results in Table 4.9, the stretched samples show higher values for modulus and yield stress. The stretched samples also show higher elongation at the yield point. These trends are again due to the increased orientation and degree of crystallinity obtained by uniaxially stretching the films (Sperling, 2001; Fried, 2002).

Table 4.10 compares tensile properties for film samples stretched to 3X the initial gage length but at 2 different stretch rates. The samples are X172 films made using a die temperature of 200 °C, an air-gap length of 5 cm and DR = 8.6. The sample stretched at the slower rate exhibits higher modulus (Young’s Modulus and E-Modulus) but the difference in modulus is shown to be statistically insignificant (see Appendix B). The yield stress and the tensile strength for both samples do not differ significantly. Slow stretch rates result in low orientation and crystallinity. This occurs because the polymer
molecules tend to relax as they are being stretched. At high stretch rates the polymer chains do not relax as easily thus the stress generated at these high rates is enough to cause greater degrees of orientation. The tensile properties reported here do not differ much since the stretching rates are high and inhibit significant polymer chain relaxations. Thus stretching the films at a higher speed of 100 mm/s/s may not offer any marked improvement in the film strength. This finding was earlier corroborated by the DSC, DMA data.

Table 4.9 Tensile properties for stretched samples with L = 5 cm and T\textsubscript{die} = 220 °C. The value in ( ) is the standard deviation. All other values are average values.

<table>
<thead>
<tr>
<th>Sample, DR, Strain, acceleration (mm/s/s)</th>
<th>Modulus of Elasticity (MPa)</th>
<th>E-modulus (MPa)</th>
<th>Yield Stress (MPa)</th>
<th>Yield Elongation (%)</th>
<th>Tensile Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X171, 8.6, 3X, 100</td>
<td>990 (48.7)</td>
<td>918.7 (51.8)</td>
<td>217 (3.8)</td>
<td>31.3 (1.2)</td>
<td>216.9 (3.8)</td>
</tr>
<tr>
<td>X172, 8.6, 3X, 100</td>
<td>1004 (48.4)</td>
<td>948.5 (51)</td>
<td>228.8 (16.6)</td>
<td>34 (1.9)</td>
<td>228.8 (16.6)</td>
</tr>
<tr>
<td>X171, 8.6, 2X, 100</td>
<td>664 (35.6)</td>
<td>664.9 (44.6)</td>
<td>163.8 (13.7)</td>
<td>33.6 (35)</td>
<td>163.8 (13.7)</td>
</tr>
<tr>
<td>X172, 8.6, 2X, 100</td>
<td>786 (66)</td>
<td>765.1 (54)</td>
<td>176.5 (10.4)</td>
<td>31.1 (3.5)</td>
<td>176.5 (10.4)</td>
</tr>
<tr>
<td>X171, 12.8, 3X, 100</td>
<td>1043 (86.5)</td>
<td>1019.1 (84.9)</td>
<td>228.1 (32.3)</td>
<td>32.3 (1.8)</td>
<td>228.1 (19.4)</td>
</tr>
<tr>
<td>X172, 12.8, 3X, 100</td>
<td>1202 (67.5)</td>
<td>1188.8 (55.3)</td>
<td>251.6 (20.7)</td>
<td>32 (7.2)</td>
<td>251.6 (20.7)</td>
</tr>
</tbody>
</table>
Table 4.10 Tensile properties for stretched samples with $L = 5$ cm and $T_{\text{die}} = 200$ °C. The value in ( ) is the standard deviation. All other values are average values.

<table>
<thead>
<tr>
<th>Sample, DR, Strain, acceleration (mm/s/s)</th>
<th>Modulus of Elasticity (MPa)</th>
<th>E-modulus (MPa)</th>
<th>Yield Stress (MPa)</th>
<th>Yield Elongation (%)</th>
<th>Tensile Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X172, 8.6, 3X, 100R</td>
<td>938 (44)</td>
<td>901.3 (37.2)</td>
<td>224.3 (14.9)</td>
<td>34.8 (2.6)</td>
<td>224.3 (14.9)</td>
</tr>
<tr>
<td>X172, 8.6, 3X, 50R</td>
<td>1007 (74.3)</td>
<td>963.9 (71.3)</td>
<td>220.1 (12.4)</td>
<td>34.3 (4.3)</td>
<td>226.5 (14.9)</td>
</tr>
</tbody>
</table>

4.5 Conclusions

In this chapter we studied the effect of processing conditions on the primary and the processed film. It is found that increasing the draw ratio during film casting increases the film crystallinity. The film samples produced during film casting are seen to develop mesomorphic crystals due to the quenching action of the chill roll. These small crystals reorganize into the larger monoclinic crystals during uniaxial stretching of the primary film. Increasing the stretching ratio from 2X to 3X is seen to increase the film orientation and crystallinity.

The processing conditions are seen to have an effect on the film morphology. The developed film morphology is in turn seen to affect the film mechanical properties. The studies using DMA and Tensile Testing show that increasing the draw ratio during film
casting increases the film modulus. This is due to the increase in crystalline content. An increase in the stretching ratio, during uniaxial stretching, is seen to increase the film strength. This is due to the increased orientation and film crystallinity obtained via uniaxial stretching.
CHAPTER 5

MODEL VERIFICATION

The Center for Advanced Engineering Fibers and Films (CAEFF) is providing industry with fiber and film design methods based on computer-aided simulations supported by experimental characterization and on-line process measurements. To support this effort, in this chapter we present work on the verification of the film casting simulation model (developed by CAEFF) with the aid of the experimental results accumulated during the course of this study. We begin by presenting a summary of the 2D non-isothermal model and the constitutive equation used in relating stress to deformation. Next we present work on the calculation of material parameters used in the simulation process. Finally, simulation results are compared to experimental data.

5.1 Model Overview

The labeling for the coordinate system used in developing the 2D film casting model is shown in Figure 5.1. This labeling is similar to that for the coordinate systems used in the theoretical works on film casting that are of relevance to this study (Cox and von Oehsen, 2007; Rajagopalan, 1999; Sollogoub et al., 2006).
In Figure 5.1 $L$ is the air-gap length, $W_L$ is the film half-width (at the chill roll) and $h$ is the film thickness. The film thickness varies with position in the web. The film casting model being developed at CAEFF is a 2D, non-isothermal, viscoelastic model. The numerical and dimensional complexity of the complete problem is simplified by using the membrane or thin film approximation (since the film thickness is considered to be very small when compared to the width and draw distance) to reduce the 3D film casting problem to a 2D problem (Pearson, 1985; Sollogoub et al., 2006; Cox and von Oehsen, 2007). This reduces the velocities, stresses and temperatures to the in-plane components i.e. $v = v(x, y, 0)$, $\sigma = \sigma(x, y, 0)$, and $T = T(x, y, 0)$ respectively, where $x$ is the draw
direction, $y$ is the transverse direction and $z$ is the thickness direction. The velocities, stresses and temperature are then considered constant throughout the film thickness. Using this formulation $v = v(x, y)$, $\sigma = \sigma(x, y)$, $T = T(x, y)$ are then average properties and the stress tensor is reduced to a plane stress tensor with only 4 non-zero components. The momentum and mass balances are integrated throughout the film thickness and with the assumptions of negligible inertia, surface tension and gravity they can be written as

\begin{equation}
\nabla \cdot (hv) = 0 \quad (5.1)
\end{equation}

\begin{equation}
\nabla \cdot (h\sigma) = 0 \quad . \quad (5.2)
\end{equation}

The total stress tensor $\sigma$ is made up of the extra stress tensor $\tau$ and an isotropic pressure $p$ and can be written as

\begin{equation}
\sigma = pI + \tau \quad . \quad (5.3)
\end{equation}

In equation 5.3 $I$ is the identity tensor. Due to the thin film approximation used here, the $z$-component of the momentum balance reduces to

\begin{equation}
p = -\tau_{zz} \quad (5.4)
\end{equation}

and the stress tensor $\sigma$ is given as
\[
\sigma = \begin{pmatrix}
\tau_{xx} - \tau_{zz} & \tau_{xy} & 0 \\
\tau_{xy} & \tau_{yy} - \tau_{zz} & 0 \\
0 & 0 & 0
\end{pmatrix}.
\]  

(5.5)

In order to solve the momentum equation we must provide a constitutive equation relating the stress tensor to the deformation. In this study the Giesekus equation is used as the constitutive model in order to account for the viscoelastic nature of the polymer materials. The Giesekus equation is written as (Giesekus, 1982; Bird et al., 1987; Morrison, 2001; Larson, 1988)

\[
\tau = \tau_s + \tau_p
\]

\[
\tau_s = -\eta_s \dot{\gamma}
\]

(5.6)

\[
\tau_p + \lambda I \tau_{p(l)} = \alpha \frac{\lambda}{\eta_p} \left\{ \tau_p \cdot \nabla \tau_p \right\} = -\eta_p \dot{\gamma}
\]

In equation 5.6, the extra stress tensor is made up of contributions from the solvent (\(\tau_s\)) and the polymer (\(\tau_p\)). The model parameters in the Giesekus equation are; the relaxation time \(\lambda\), the mobility factor \(\alpha\) and the solvent (\(\eta_s\)) and polymer (\(\eta_p\)) contributions to the zero-shear rate viscosity (\(\eta_0\)). The quantity \(\tau_{p(l)}\) represents the upper convected time derivative of \(\tau_p\) and is written as

\[
\tau_{p(l)} = \frac{\partial \tau_p}{\partial t} + v \cdot \nabla \tau_p - \nabla v^T \cdot \tau_p - \tau_p \cdot \nabla v
\]

(5.7)

By substituting for \(\tau_p\) (using \(\tau + \eta_s \dot{\gamma}\)) equations 5.6 can be written as a single constitutive equation (Bird et al., 1987)
\[ \tau + \lambda_1 \tau_{(1)} - a \frac{\lambda_1}{\eta_0} \{ \gamma \cdot \tau \} - a \lambda_2 \{ \gamma \cdot \tau + \dot{\gamma} \} = -\eta_0 \left[ \dot{\gamma} + \lambda_2 \gamma_{(2)} - a \frac{\lambda_2^2}{\lambda_1} \{ \gamma \cdot \dot{\gamma} \} \right]. \quad (5.8) \]

In equation 5.8, \( \eta_0 \) is the zero-shear rate viscosity, \( \lambda_2 \) is the retardation time, and \( a \) is the modified mobility parameter. These three parameters are written in terms of \( \alpha, \eta_s, \eta_p \) as

\[
\eta_0 = \eta_s + \eta_p : \lambda_2 = \frac{\lambda_2}{\eta_p} = \frac{\alpha}{1 - (\lambda_2 / \lambda_1)}. \quad (5.9)
\]

Since the film casting process is non-isothermal, a non-isothermal form of the Giesekus equation is used in the model development (Joo et al., 2002)

\[
\tau_p + \text{Def} \frac{T_0}{T} \left\{ \tau_{p(1)} - \frac{1}{T} (v \cdot \nabla T) \tau_p \right\} - a \frac{\text{Def} T_0}{1 - \beta} \frac{T}{T} \{ \tau_p \cdot \tau_p \} = -(1 - \beta) f \left\{ \nabla v + \nabla v^T \right\} \quad (5.10)
\]

where \( \beta \) is the ratio of the solvent viscosity to the zero-shear rate viscosity (i.e. \( \eta_s / \eta_0 \)), and \( f \) is an Arrhenius form of the temperature dependence of the zero-shear rate viscosity given as (Joo et al., 2002)

\[
f(T, \theta) = \exp \left\{ -\frac{\Delta H}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) + 4\theta^2 \right\} \quad . \quad (5.11)
\]

In equation 5.11, \( \theta \) is the degree of crystallinity and accounts for the effect of crystallization on the zero-shear rate viscosity. Equation 5.11 also represents the temperature dependence of the relaxation time and the activation energy \( \Delta H \) is assumed
to be equal for both the zero-shear rate viscosity and the relaxation time (Sollogoub et al., 2006). The Deborah number (in equation 5.10) for film casting can be written as (Sollogoub et al., 2006)

$$De = \lambda \frac{v_0}{L} \quad (5.12)$$

where $v_0$ is the velocity at the die exit and $L$ is the air-gap length.

In addition to the fluid mechanics equations, because the film casting process is non-isothermal an energy balance is written for the system and is given as;

$$\rho C_p h \left( v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y} \right) + 2 h_{tot} (T - T_{air}) = 0 \quad . \quad (5.13)$$

In equation 5.13 $h_{tot}$ is the heat transfer coefficient and is calculated using the method of Lamberti et al. (2001). The quantities $\rho, C_p, \text{ and } T_{air}$ are the density, heat capacity and ambient air temperature respectively while $h$ represents the film thickness. This form of the energy balance (equation 5.13) neglects viscous dissipation (Sollogoub et al., 2006).

For film casting processes employing large air-gap lengths ($L$), flow induced crystallization may become a factor. Flow induced crystallization is accounted for in the CAEFF film model by modifying equation 5.13 using the method of Nakamura et al. (1973) and Lamberti et al. (2001). The modified equation can be written as;

$$\rho C_p h \nabla y \cdot \nabla T + 2 h_{tot} (T - T_{air}) = \rho h \Delta H_c y \cdot \nabla X_c \quad (5.14)$$
where \( \Delta H_c \) is the heat of crystallization for the polymer and \( X_c \) is the degree of crystallinity. The degree of crystallinity is dependent on the crystallization rate (Ziabicki, 1976, Lamberti et al., 2001). Due to the non-isothermal and extensional nature of the film casting process the CAEFF model makes use of a form of the crystallization rate that is a function of temperature and molecular orientation. The non-isothermal crystallization rate \( K(T, f_a) \) is given as (Ziabicki, 1976; Joo et al., 2002);

\[
K(T, f_a) = K_{\text{max}} \exp \left\{ -4 \ln 2 \left( \frac{T - T_{\text{max}}}{D_c + T_0} \right) + Cf_a^2 \right\}
\] (5.15)

where \( K_{\text{max}} \) is the maximum crystallization rate, \( T_{\text{max}} \) is the temperature at which the maximum crystallization rate occurs, \( D_c \) is the crystallization half-width and \( T_0 \) is a reference temperature. The procedure for the determination of \( K_{\text{max}}, T_{\text{max}}, \) and \( D_c \) from experimental DSC data is presented in the following section. The method for calculating the stress induced crystallization coefficient, \( C \) and the molecular orientation factor, \( f_a \) is outlined in Ziabicki (1976) and Joo et al. (2002).

### 5.2 Calculation of Model Parameters

In order to verify the accuracy and usefulness of the 2D film model described in the previous section, it is imperative to determine certain model parameters. These calculated parameters are usually determined from experimental, material characterization data. These parameters can then be employed in the film casting model and in turn used to study the accuracy of the film casting model in predicting experimentally observed width,
temperature, velocity and stress profiles for a given material. In this section we begin by presenting the method used to obtain the parameters in the Giesekus equation through the use of shear rheology data. We then present the calculations of the crystallization parameters from the DSC data.

5.2.1 Giesekus Constitutive Parameters

The Giesekus constitutive model can be solved analytically for steady simple shear flows. The equations obtained can then be fit to experimental data for the particular flow type. For our studies we have accumulated data on steady state shear viscosities, as well as the dynamic rheological properties, as a function of shear rate (frequency) and temperature. For the Giesekus model the expressions for shear viscosity $\eta$ is given as (Bird et al., 1987);

$$\frac{\eta}{\eta_0} = \frac{\lambda_2}{\lambda_1} + \left(1 - \frac{\lambda_2}{\lambda_1}\right) \frac{(1 - f_g)^2}{1 + (1 - 2\alpha)f_g}$$  \hspace{1cm} (5.16)

where

$$f_g = \frac{1 - \chi}{1 + (1 - 2\alpha)\chi}; \hspace{0.5cm} \chi^2 = \frac{(1 + 16\alpha(1 - \alpha)(\lambda_1\dot{\gamma})^2)^{1/2} - 1}{8\alpha(1 - \alpha)(\lambda_1\dot{\gamma})^2}. \hspace{1cm} (5.17)$$

In equations 5.17 $\dot{\gamma}$ is the shear rate and all the other parameters are as earlier stated in section 5.1. The Giesekus model expressions for the storage ($G'$) and loss ($G''$) moduli are given as (Bird et al., 1987);
\[ G'' = \eta_0 \omega \frac{l + \lambda_1 \lambda_2 \sigma^2}{l + \lambda_1^2 \sigma^2} \]  

(5.18)

and

\[ G' = \eta_0 \omega \frac{(\lambda_1 - \lambda_2)}{l + \lambda_1^2 \sigma^2} \]  

(5.19)

Using equations 5.16, 5.18 and 5.19 we can determine \( \eta_0, \lambda_1, \alpha \) and \( \lambda_2 \). The non-isothermal form of the Giesekus equation used in this model (equation 5.10) requires the input parameters \( \eta_0, \lambda_1, \alpha \) and \( \beta \). The parameter \( \beta \) is calculated by substituting for \( \eta_0 \) and \( \eta_s \) in terms of \( \eta_p \) using equations 5.9. That is;

\[
\begin{align*}
\eta_s &= \eta_p \left( \frac{\lambda_2}{\lambda_1} \right) \\
\eta_0 &= \eta_p \left( 1 + \left( \frac{\lambda_2}{\lambda_1} \right) \right) \\
\beta &= \frac{\eta_s}{\eta_0} = \frac{\lambda_2 / \lambda_1}{1 + \left( \frac{\lambda_2}{\lambda_1} \right)}
\end{align*}
\]  

(5.20)

The first step in determining the Giesekus model parameters that are specific to the polymer material is to determine the zero-shear rate viscosity at various temperatures (in this work 180 °C, 200 °C and 220 °C) and subsequently the temperature dependence of the zero-shear rate viscosity. The shear viscosity data are fitted to the Carreau model given as:
\[ \eta_{\text{cal}}(T) = \eta_0(T) \left[ 1 + (\lambda_c \dot{\gamma})^2 \right]^\frac{n-1}{2}. \]  

Equation 5.21 is fitted to the complex viscosity data by using a least squares regression scheme. In this method we write a MATLAB program to minimize the function;

\[ \sum_{i=1}^{k} \left[ \ln(\eta_{\text{data}}) - \ln(\eta_{\text{cal}}) \right]^2. \]  

In equations 5.21 and 5.22, \( \eta_{\text{data}} \) is the experimental shear viscosity data, \( \eta_{\text{cal}}(T) \) is the calculated viscosity from equation 5.21, \( \eta_0 \) is the calculated zero-shear rate viscosity, \( \lambda_c \) is a relaxation time and \( n \) is a power law exponent. The summation in equation 5.22 is over the set of data points \( \left( \dot{\gamma}, \eta_{\text{data}} \right) \) and \( k \) is the total number of data points employed in the fitting routine.

After the zero-shear rate viscosities are determined for \( T = 180 \, ^\circ \text{C}, 200 \, ^\circ \text{C} \) and \( 220 \, ^\circ \text{C} \), an Arrhenius type equation is then used to determine the temperature dependence of the zero-shear rate viscosity;

\[ \eta_0 = Ae^{\frac{B}{T}} \]  

where \( A \) and \( B \) are Arrhenius constants. We could use two solution schemes for calculating \( A \) and \( B \). The first scheme would be to take a log of both sides of equation 5.23 giving;

\[ \ln(\eta_0) = \ln(A) + (B / T) \]  

(5.24)
So that a plot of $\ln(\eta_0)$ vs. $(1/T)$ should give a slope of $B$ and a y-axis intercept of $\ln(A)$.

The second scheme would involve using a regression scheme to minimize the function;

$$
\sum_{i=1}^{3} \left[ \ln(\eta_0) - \ln(A \exp(B / T)) \right]^2.
$$

(5.25)

where for this case $k = 3$ since we have experimental data available at 3 different temperatures. In this study the complex viscosity data for the polymer samples (X171 and X172) is used to substitute for the shear viscosity data since the samples seem to obey the Cox-Merz rule (Morrison, 2001). Figure 5.2 shows a comparison of the shear and complex viscosity data for the X171 sample at 200 °C. The plots are made assuming an equivalency between the frequency, $\omega$ (for the complex viscosity data) and the shear rate, $\gamma$ (for the shear viscosity data). The drop off in the shear viscosity is due to the instability of the cone-and-plate apparatus at shear-rate that are close to 10 s$^{-1}$. 
**Figure 5.2** Shear and complex viscosity for X171 at 200 °C.
Table 5.1 presents the results of the Carreau model parameters for the X171 and X172 samples. In Table 5.2 we present results for the Arrhenius constants for the X171 and X172 samples. Figure 5.3 shows a comparison of the experimental and calculated shear viscosity as a function of shear rate for the X171 sample.

Table 5.1 Carreau model parameters for the X171 and X172 samples.

<table>
<thead>
<tr>
<th></th>
<th>X171</th>
<th>X172</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>η₀</td>
<td>λ</td>
</tr>
<tr>
<td>180C</td>
<td>1700.1</td>
<td>0.086012</td>
</tr>
<tr>
<td>200C</td>
<td>1125.3</td>
<td>0.059738</td>
</tr>
<tr>
<td>220C</td>
<td>759.58</td>
<td>0.047585</td>
</tr>
</tbody>
</table>

Table 5.2 Arrhenius constants.

<table>
<thead>
<tr>
<th></th>
<th>X171</th>
<th>X172</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.0832</td>
<td>0.0432</td>
</tr>
<tr>
<td>B</td>
<td>4497.2</td>
<td>4565.3</td>
</tr>
</tbody>
</table>
Figure 5.3 Carreau model predictions for the X171 sample complex viscosity.

After using the Carreau model to determine the values for \( \eta_0 \) we can use equations 5.18 and 5.19 to calculate the relaxation time \( \lambda_1 \) and the retardation time \( \lambda_2 \) for the Giesekus model. Here again we use a regression scheme and minimize the function;

\[
\sum_{i=1}^{k} \left[ \ln(G'_{\text{data}}) - \ln(G'_{\text{cal}}) \right]^2 + \left[ \ln(G''_{\text{data}}) - \ln(G''_{\text{cal}}) \right]^2 \right]. \tag{5.26}
\]

The calculated values for \( \lambda_1 \) and \( \lambda_2 \) can then be used to fit equations 5.16 and 5.17 to the data for the complex viscosity in order to determine the mobility factor (\( \alpha \)). Using a
sum of least squares regression scheme we write a MATLAB routine to minimize the function;

\[ \sum_{i=1}^{k} \left[ \ln(\eta^k_{data}) - \ln(\eta^k_{cal}) \right]. \tag{5.27} \]

The calculated values for \( \alpha, \lambda_1, \lambda_2 \) and \( \beta \) (for the X171 and X172 samples) are shown in Table 5.3. The comparison of the predicted \( \eta, G', \) and \( G'' \) to experimental data is shown in Figures 5.4, 5.5 and 5.6.

**Table 5.3** Giesekus model parameters for the X171 and X172 samples.

<table>
<thead>
<tr>
<th></th>
<th>X171</th>
<th>X172</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda_1 )</td>
<td>0.0604</td>
<td>0.0437</td>
</tr>
<tr>
<td>( \lambda_2 )</td>
<td>0.0069</td>
<td>0.0062</td>
</tr>
<tr>
<td>( \beta )</td>
<td>0.1022</td>
<td>0.1238</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.2333</td>
<td>0.2155</td>
</tr>
<tr>
<td>( \lambda_1 )</td>
<td>0.0069</td>
<td>0.0062</td>
</tr>
<tr>
<td>( \lambda_2 )</td>
<td>0.1022</td>
<td>0.1238</td>
</tr>
<tr>
<td>( \beta )</td>
<td>0.2333</td>
<td>0.2155</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.2333</td>
<td>0.2155</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>X171</th>
<th>X172</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda_1 )</td>
<td>0.0458</td>
<td>0.0352</td>
</tr>
<tr>
<td>( \lambda_2 )</td>
<td>0.0061</td>
<td>0.0060</td>
</tr>
<tr>
<td>( \beta )</td>
<td>0.1175</td>
<td>0.1447</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.2460</td>
<td>0.1786</td>
</tr>
<tr>
<td>( \lambda_1 )</td>
<td>0.0369</td>
<td>0.0231</td>
</tr>
<tr>
<td>( \lambda_2 )</td>
<td>0.1386</td>
<td>0.045</td>
</tr>
<tr>
<td>( \beta )</td>
<td>0.1973</td>
<td>0.1623</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.2323</td>
<td>0.2323</td>
</tr>
</tbody>
</table>
Figure 5.4 Giesekus model predictions for the X171 sample storage and loss moduli at 200 °C.
Figure 5.5 Giesekus model predictions for the X172 sample storage and loss moduli at 200 °C.
5.2.2 Crystallization Kinetic Parameters

The CAEFF model incorporates the effects of flow induced crystallization. The calculation of the crystallization kinetic parameters is presented in this section.

The experimental procedure used here is to first study the non-isothermal cooling curves (at various cooling rates) for the polymer samples as shown in Figures 5.7 and 5.8. Figure 5.7 shows the cooling curves for the X171 samples. The curves correspond to cooling rates of 5 °C/min, 10 °C/min, and 20 °C/min. At each cooling rate the polymer
sample crystallizes over a temperature range due to the large size of polymer molecules. The crystallization peaks are also seen to shift towards lower temperatures as the cooling rate is increased. This is also due to the large size of polymer molecules (Chen et al., 2006). At low cooling rates polymers have sufficient time to activate nucleation sites (Chen et al., 2006), and allow for the migration of the polymer molecules to the nucleation sites. Thus, crystallization can occur at higher temperatures. As the cooling rate is increased the sluggish polymer molecules still diffuse slowly to nucleation sites, and folding of the polymer molecules occurs at a slower pace relative to the cooling rate (Chen et al., 2006). Therefore, increasing the cooling rate shifts the crystallization peaks to lower temperatures. Figure 5.8 also shows the same trend for the X172 sample (i.e. melting peaks shifted to lower temperatures as the cooling rate is increased).
Figure 5.7 DSC cooling curves for the X171 sample at cooling rates of 5 °C/min, 10 °C/min and 20 °C/min.
Due to the broad nature of the crystallization exotherm (at each cooling rate) and the shift in the crystallization peak (to lower temperatures) as the cooling rate is increased a broad temperature range was selected/used for the isothermal crystallization experiments. The temperature range used is from 115 °C to about 60 °C at intervals of 5 °C. At each temperature an isothermal crystallization experiment was conducted by initially heating the sample at 40 °C/min from 30 °C to 200 °C. Next the sample was held at 200 °C for 5 minutes in order to eliminate the sample thermal history. The sample is then cooled rapidly at 400 °C/min to the selected crystallization temperature and maintained at this

Figure 5.8 DSC cooling curves for the X172 sample at cooling rates of 5 °C/min, 10 °C/min and 20 °C/min.
temperature for about 10 minutes. This isothermal crystallization experiment is repeated at each selected temperature within the chosen temperature range.

The isothermal crystallization experiments were conducted in order to determine the parameters $D$, $K_{\text{max}}$ and $T_{\text{max}}$ to be used in the energy balance for film casting model. These parameters fit into the equation used for determining the temperature dependence of the crystallization rate. The equation is a modified form of equation 5.15 and is given as

$$k(T) = K_{\text{max}} \exp \left[ -4 \ln 2 \left( \frac{(T - T_{\text{max}})^2}{D^2} \right) \right] . \quad (5.27)$$

In equation 1 $K_{\text{max}}$ is the maximum rate constant (in sec$^{-1}$), $T_{\text{max}}$ is the temperature at which the maximum rate constant occurs and $D$ is the Full Width at Half Maximum (FWHM) of the curve obtained by plotting the reciprocal crystallization half-time ($t_{1/2}$) as a function of temperature. This plot is usually of the form shown in Figure 5.9 below (Ziabicki, 1976; Wood and Bekkedahl, 1946).
The crystallization rate is proportional to the inverse of the crystallization half-time (Ziabicki, 1976; Zhang et al., 2003). The crystallization half time is the time required to reach 50% crystallization. From Figure 5.9 it is seen that the crystallization rate increases with temperature, reaches a maximum and then decreases as the temperature is increased further. This trend is due to two competing processes as the temperature is increased (Ziabicki, 1976; Sperling, 2001). These two processes are the molecular transport in the melt and the rate of nucleation (Sperling, 2001). The rate of nucleation decreases with increasing temperature while the molecular transport in the melt increases with increasing temperature. The molecular transport dominates at lower temperatures while the nucleation rate is the controlling factor at high temperature. At the temperature of the
maximum crystallization rate these two competing processes are approximately equal, hence the maximum in the rate constant.

Figure 5.10 shows the DSC crystallization curves for the X171 sample at various temperatures. The indicated heat flow is per gram of sample.

![DSC cooling curves for the crystallization of the X171 sample at various temperatures.](image)

**Figure 5.10** DSC cooling curves for the crystallization of the X171 sample at various temperatures.

From Figure 5.10 it is seen that decreasing the temperature from 115 °C to 95 °C reduces the time required for the isothermal crystallization to proceed to completion. In this range of temperatures the crystallization rate increases as the temperature is decreased. Also notice that only the curve for the isothermal crystallization at 115 °C
exhibits complete crystallization. The curves for the other temperatures (in Figure 5.10) do not begin at the zero heat flow line. This is due to the fact that the sample crystallization began before the set crystallization temperature was attained in the DSC equipment (Hernandez-Sanchez et al., 2004). The curves shown in Figure 5.10 are then used to determine the degree of crystallinity as a function of time. This is done by integrating the area under the crystallization curve as (Zhang and Xin, 2006; Zhang et al., 2003)

\[
X(t) = \frac{\int_{0}^{t} (dH / dt) dt}{\int_{0}^{\infty} (dH / dt) dt}.
\]  

(5.28)

In equation 5.28 the degree of crystallinity is calculated relative to the total amount of crystalline material obtained during the crystallization process. Previous calculations of the degree of crystallinity in this work (Chapter 4) were based on a 100 % crystalline material. For the temperatures at which the full DSC crystallization curve was not obtained, the curves are extrapolated to the zero heat flow line as shown in Figure 5.11. The new curve is then used in the calculation of the degree of crystallinity.
Figure 5.11 DSC Thermogram for the X171 sample at 95 °C. The crystallization curve is extrapolated to the zero heat flow line.

Figure 5.12 shows the degree of crystallinity as a function of time, for some of the temperatures used in this study. From Figure 12 the half-time at the various crystallization temperatures can be determined. The integrals shown in equation 5.28 were determined by using the Trapezoidal rule (Kreyzig, 1983) to calculate the area under the crystallization exotherms.
Figure 5.12 Degree of crystallinity as a function of time, for the X171 sample at various temperatures.
Due to the limitations inherent in the Clemson thermal equipment, only 4 data points could be obtained for this procedure. The data was fit to equation 5.27, and from this limited data the isothermal crystallization rate curve was determined. Figure 5.13 shows a fit of the crystallization data (for the X172 sample) to the equation 5.27.

**Figure 5.13** Plot of reciprocal half-time vs. Temperature for X172. This plot is used for determining model parameters for the energy equation.

From this plot we determined the relevant crystallization parameters to be used in the energy equation for the FISIM 2-D film casting model. The results for the X171 and
X172 samples are shown in Table 5.4. In the next section we present results from comparisons between the model predictions and experimental results.

**Table 5.4** Crystallization parameters.

<table>
<thead>
<tr>
<th>Parameter (°C)</th>
<th>X171</th>
<th>X172</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kmax (s⁻¹)</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Tmax (°C)</td>
<td>80</td>
<td>78</td>
</tr>
<tr>
<td>D (°C)</td>
<td>30</td>
<td>34</td>
</tr>
</tbody>
</table>

**5.3 Model predictions vs. Experimental Data**

In this section the model predictions using the FISIM software developed by the CAEFF is compared to some experimental film casting results. As discussed above, material parameters used in the calculations are obtained from rheology and DSC curves. Process parameters used in the calculations are identical to those employed experimentally.
In Figure 5.14 we present a comparison between the model prediction and the experimentally determined half-width profile for the X172 sample. The experimental conditions used here are \( T_{\text{die}} = 220 \, ^{\circ}\text{C} \), \( L = 9 \, \text{cm} \) and \( DR = 8.6 \).

![Graph showing comparison between model prediction and experimental results.](image)

**Figure 5.14** Model verification of the prediction for the width profile.

From Figure 5.14 it is seen that the model does a reasonable job of predicting the experimental results. The model under-predicts the degree of neck-in exhibited by the X172 sample at the given process conditions. This may be due to the thin film
approximation. The thin film approximation does not hold at the film edges due to the formation of edge-beads. See Pearson (1986) for a good discussion on applicable boundary conditions (on the film edges) that could be used in conjunction with the thin film approximation. The thin film approximation would still apply in the central region of the film.

Figure 5.15 compares the experimental centerline temperature profile to the model prediction for the X172 sample and the same process conditions as in Figure 5.14. We find that the model slightly under-predicts the temperature drop observed experimentally in the air-gap. Better accuracy of the simulation may be obtained by using different methods for calculating the heat transfer coefficient, and a fully 3-D energy equation.

In Figure 5.16 the centerline velocity profile is shown for the X172 sample under identical process conditions to those presented above (Figures 5.14 and 5.15). The model shows very good agreement with the experimental results. This may result from the fact that the thin film approximation holds best at the film centerline and that the 2-D model adequately captures the kinematics of the flow at the centerline.
Figure 5.15 Model verification of the prediction for the temperature profile.
Figure 5.16 Model verification of the prediction for the velocity profile.

Figure 5.17 presents a comparison of the centerline velocity profile for the PH 835 sample at DR = 8.6, L = 8.8 cm and die temperature of 220 °C. The model is again seen to accurately predict the centerline velocity profile. Comparing the centerline velocity profile for the PH 835 sample (Figure 5.17) to the centerline velocity profile for the X172 sample (Figure 5.16), it is seen that the decrease in strain rate (near the chill roll) is slightly more pronounced for the PH 835 sample. As reported in Chapter 3, the PH 835 sample cools to below its melting point temperature, in the air-gap, while the X172
sample does not cool to below its melting point temperature before the chill roll is approached. Therefore a greater resistance to flow (near the chill roll) is expected for the PH 835 sample. The model is clearly seen to capture this coupling between the flow kinematics and temperature dependence of the polymer viscosity (earlier presented in Chapter 3).

Figure 5.18 shows model predicted width profiles for the X172 sample at air-gap lengths of 5 cm and 8 cm. Qualitatively, when compared to the experimental results the model is seen to capture the increase in neck-in as the air-gap length is increased. Figure 5.19 shows the model predictions for the X172 centerline temperature profiles for air-gap lengths of 5 cm and 8 cm. Again, the model adequately captures the qualitative features of the air-gap dependence in the temperature profile. These features are due to the longer residence time (for the material in the air-gap) as the air-gap length is increased. Figure 5.20 presents model predicted centerline velocity profiles for the X172 sample at air-gap lengths of 5 cm and 8 cm (along with experimental results at an air-gap of 8 cm). The velocity values (at particular distances from the die) are higher for L = 5 cm due to the shorter air-gap length and the subsequent greater values of the strain rate.
Figure 5.17 Model prediction vs. experiment for PH 835 at $T_{\text{die}} = 220$ °C, DR = 8.6, and $L = 8.8$ cm for the velocity profile.
Figure 5.18 Model prediction for X172 width profiles at L = 5 cm and 8 cm. Here $T_{\text{die}} = 220 \, ^\circ\text{C}$, DR = 8.6, and L = 8 cm.
Figure 5.19 Model prediction for X172 centerline temperature profiles at \( L = 5 \) cm and \( 8 \) cm. Here \( T_{\text{die}} = 220 \) °C, \( \text{DR} = 8.6 \), and \( L = 8 \) cm.
Figure 5.20 Model prediction for X172 centerline temperature profiles at \( L = 5 \) cm and 8 cm. Here \( T_{\text{die}} = 220 \) °C, DR = 8.6, and \( L = 8 \) cm.
5.4 Conclusions

In this chapter we presented a development for the CAEFF FISIM 2-D film casting model. The model predictions were then compared to some of the experimental data. To perform these comparisons, constitutive equation parameters were fit directly from the polymer rheology and thermal characterization data. In addition, process parameters were identical to those employed in the experiments. The model is found to provide reasonable predictions for the film neck-in and temperature drop in the air-gap. The model gives very good predictions for the centerline velocity profile. The model is seen to capture the coupling between the flow kinematics and temperature dependence of the material viscosity. The model also predicts the increase in film neck-in and temperature drop in the air-gap as the air-gap length is increased.
CHAPTER 6

CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

Film casting is an important industrial process for the production of polymeric films. In this research work, a thorough experimental and numerical investigation of the cast film process was undertaken using a unified approach. Thermal and mechanical properties of the polymers employed was performed both for material characterization and to determine simulation parameters. The film casting process was investigated, and the films produced were evaluated. Using identical parameters to those employed experimentally, numerical simulations were performed using CAEFF FISIM software, and the predictions were compared to the experimental results. In this chapter we summarize the key findings of this work. In particular, we report on the effect of material properties and process conditions on the film formation process in the air-gap and on the resultant film thermal/mechanical properties. To fully investigate the film formation, measurements were made throughout the polymer film in the air-gap region.

The film formation process in the air-gap depends on process conditions such as the draw ratio and the die temperature. Increasing the draw ratio increases the film neck-in in the air-gap due to the physical constraint of mass conservation. The die temperature impacts the film geometry by virtue of the temperature dependence of the polymer viscosity. A reduction in the die temperature results in a decrease in the film neck-in. The
polymer viscosity increases with decreasing temperature, and increasing the polymer viscosity increases the ability of the edge-beads to restrict film neck-in. An increase in the air-gap length was also found to increase the film neck-in. This is due to the decrease in the strain rate as the air-gap is increased. The polymer material properties also affect the geometry obtained in the film formation process. Reducing the polymer molecular weight increases the film neck-in at a constant draw ratio. This is due to the decrease in viscosity as the polymer molecular weight is decreased, and as noted above, decreasing the polymer viscosity decreases the ability of the edge-beads to restrain the amount of neck-in obtained in the air-gap. The increase in neck-in was also seen to result in an increase in film thickness.

The experimentally measured temperature profiles demonstrate that the temperature drop in the air-gap increases with increasing draw ratio due to the improved heat transfer from the web with a decreasing film thickness. Temperature profiles in the transverse direction indicate that the central portion of the film cools more rapidly than the film edges because the film edges are thicker than the central portions of the film.

The flow process kinematics is coupled to the temperature dependence of the viscosity. The centerline strain rate was found to depend on the interaction between the tension applied to the film (as a result of the draw ratio) and the increasing resistance to flow (due to the decreasing temperature) as the chill roll is approached. The draw direction component of the velocity (as a function of transverse position) was found to decrease from the film centerline to the film edges. The polymer film moves primarily in the draw direction as the film centerline is approached.
A unique feature of this work was measurement of the transverse direction velocity component \(v_y\) in the air-gap. To the best of our knowledge, this is the first experimental work that reports this velocity component for the film casting process. The transverse direction velocity component was seen to decrease from the edges of the film towards the film centerline. This is due to the strong transverse direction velocity components that exist near the film edges as a result of the film neck-in. The molten polymer in the air-gap moves primarily in the draw direction near the film center; therefore the transverse direction velocity component vanishes at the film centerline.

The film morphology developed in the air-gap is dependent on the process conditions. The film mechanical properties were also shown to depend on the developed film morphology and the processing history. The Primary film crystallized in the mesomorphic crystalline form of i-PP. This is attributed to the quenching action of the chill roll. The Processed film samples exhibited the monoclinic crystalline form for i-PP. This was due to the mesomorphic crystals (present in the Primary film) being re-organized into the monoclinic crystalline form during uniaxial stretching of the Primary film samples. An increase in the stretching ratio, during uniaxial stretching, is seen to increase the film strength. This is due to the increased orientation and film crystallinity obtained from the secondary processing (uniaxial stretching) of the Primary film.

The 2-D membrane model developed by the CAEFF was verified using the experimental data accumulated during the course of this work. The model predictions were compared to some of the experimental data. The model predictions show good agreement with the reported experimental results. The predicted temperature drop was found to be typically within 5% of the experimentally determined values, while the
centerline velocity predictions are typically within 2% of the measured values. Predicted values of the film width at the chill roll are approximately 10% higher than those measured experimentally.

6.2 Recommendations for Future Work

This work reports an experimental and numerical study of the film casting process. The integrated approach between experiment and modeling developed in this work can be used in advancing research into developing computer-aided simulation methods for the design and optimization of industrial scale film casting processes. Based on our findings, there are various aspects of this work that present opportunities for further advances in understanding the film casting process. Some recommendations for future research efforts are briefly discussed in this section.

Edge-bead formation is an undesirable aspect of film casting since an important goal in film production is thickness uniformity in the Primary films. Edge-beads are usually trimmed before secondary processing of the Primary film (Pearson, 1985). In this work, the uniform thickness die was seen to produce films with non-uniform thickness - the film edges were thicker than the central regions of the film. This edge-bead formation could be combated through the use of a variable thickness (bowed) die. The die design would allow for the die thickness to decrease from the centerline towards the die edges. A second method for combating the formation of edge-beads may be the use a uniform thickness die with non-uniform polymer throughput across the die lip. The die design would allow for more material to flow through the central regions of the die than through the end-regions of the die lip. This could be achieved by the use of a modified coat-
hanger die design. A third method for controlling edge-bead formation may be the use of localized cooling jets in the air-gap.

An experimental study into methods for reducing edge-bead would be greatly enhanced by the development of a fully 3-D viscoelastic film casting model and simulation package. The process simulations using a 3-D model would help pinpoint the most effective die designs (or areas in the web for cooling jet application) that results in film thickness uniformity.

The film formation process in the air-gap can also be studied by making either on-line birefringence or Raman measurements. Birefringence may arise in the polymer film due to molecular orientation in the air-gap. The on-line birefringence measurements would provide an insight into the evolution of the film morphology from the die exit to the chill roll.

The effect of uniaxial stretching conditions on the Processed film properties was studied in this work. A further study would be on the effect of biaxial stretching conditions. For example, the effect of using sequential biaxial stretching versus simultaneous biaxial stretching on the film properties could be investigated. This study should employ a die with width of at least 6 inches to allow for production of primary film samples that are wide enough to be stretched using the CAEFF biaxial stretcher. The secondary processing steps (uniaxial and biaxial stretching) also provide opportunities for the development of process models with the capacity to predict film properties that may result from a particular set of processing conditions. This model should rely upon inputs from the CAEFF FISIM film casting model or from experimentally determined Primary film properties.
Other areas that require further investigation include the model being developed at the CAEFF. As shown in Chapter 5, the 2-D Giesekus model does a reasonable job in predicting experimental results, but still leaves room for improvement. This model can be improved by using a full 3-D model in terms of the continuity, momentum and energy equations. The predictions of the model could also be improved by the use of a multimode Giesekus constitutive model since this will provide a better fit to the rheological data accumulated during the course of this work. The model employed in this work makes use of the thin film approximation, which was also assumed to hold at the film edges. The films produced using film casting exhibit edge-beads therefore the thin film approximation will not hold at the film edges. The development of a fully 3-D model would help tackle this obstacle.
Appendix A

Derivation of Calculation Method for the Transverse Velocity Component

To facilitate the derivation we again present Figure 3.21, showing the direction of the velocity in relation to the measurement directions.

\[ V_{60} \]
\[ V \]
\[ V_x \]
\[ z_{60} \]
\[ x \]
\[ 30^\circ \]

**Figure 3.21** Relative velocity vector directions for the experiments set-up used in the determination of \( v_y \).

Since \( v_{60} \) and \( v_x \) are projections of \( v \) onto the \( z_{60} \) and \( x \) axes, respectively, the measured velocity values for the two components are given by
\[ v_{60} = v \cdot \cos(\alpha) \text{ and } v_x = v \cdot \cos(\beta) \] \hspace{1cm} (3.1)

The ratio \( J \) of \( v_x \) to \( v_{60} \) is

\[ J = \frac{\cos(\beta)}{\cos(\alpha)} \] \hspace{1cm} (3.2)

At the point where \( v \) is parallel to \( z_{60} \)

\[ \alpha = 0^\circ, \beta = 30^\circ \text{ and } J = 0.866 \] \hspace{1cm} (3.3)

At the point where \( v \) is parallel to \( x \)

\[ \alpha = 30^\circ, \beta = 0^\circ \text{ and } J = 1.155 \] \hspace{1cm} (3.4)

These values are important since they aid in determining which equations to use when solving for \( v_y \) using values for \( v_{60} \) and \( v_x \). A trigonometrical analysis of the problem gives the result that for both case I and case II

\[ v_y = v_x \cdot \tan(\beta) \] \hspace{1cm} (3.5)

where for case I,

\[ \beta = 30^\circ + \alpha \] \hspace{1cm} (3.6)

\[ \frac{v_{60}}{\cos(\alpha)} = \frac{v_x}{\cos(30^\circ + \alpha)} \] \hspace{1cm} (3.7)
and

\[ J \cos (\alpha) = \cos (30^\circ + \alpha) \]  

(3.8)

Expanding the RHS of equation 3.8 gives

\[ J \cos (\alpha) = \cos(30^\circ)\cos(\alpha) - \sin(30^\circ)\sin(\alpha) = 0.866\cos (\alpha) - 0.5\sin (\alpha). \]

Therefore

\[ \frac{\sin (\alpha)}{\cos (\alpha)} = \frac{(0.866 - J)}{0.5} \]

(3.9)

\[ \tan (\alpha) = \frac{(0.866 - J)}{0.5} \]

Since J is known, α and β can both be determined.

Also,

\[ v_x = v \cos (\beta) \]

So

\[ v_y = v \cos (90^\circ - \beta) = v \sin (\beta) = (v_x/\cos (\beta)) \sin (\beta) \]
and

\[ v_y = v_x \tan(\beta) \quad . \quad (3.5) \]

For case II,

\[ \beta = 30^\circ - \alpha \quad (3.10) \]

\[ \frac{v_{60}}{\cos(\alpha)} = \frac{v_y}{\cos(30^\circ - \alpha)} \quad (3.11) \]

and

\[ J \cos(\alpha) = \cos(30^\circ - \alpha) \quad . \quad (3.12) \]

Expanding the RHS gives

\[ J \cos(\alpha) = \cos(30^\circ) \cos(\alpha) + \sin(30^\circ) \sin(\alpha) \]

\[ = 0.866 \cos(\alpha) + 0.5 \sin(\alpha) \]

Therefore

\[ \frac{\sin(\alpha)}{\cos(\alpha)} = \frac{J - 0.866}{0.5} \]

\[ \tan(\alpha) = \frac{(J - 0.866)}{0.5} \quad (3.13) \]
J is known, therefore $\alpha$ and $\beta$ can both be determined as;

\[ v_x = v \times \cos (\beta) \]

\[ v_y = v \times \cos (90^\circ - \beta) \]

\[ = v \times \sin (\beta) \]

\[ = (v_x / \cos (\beta)) \times \sin (\beta) \]

and

\[ v_y = v_x \times \tan (\beta) \]  \hspace{1cm} \text{(3.5)}
Appendix B

Results of Research Hypothesis Testing

The results from the statistical analysis conducted in order to test some of the research hypothesis encountered in this work are presented in this Appendix.

Table B-1 presents the results on the statistical analysis of the difference in the reported velocity (at the centerline) for the Profax PH835 sample at DR = 6.5 and 12.8 respectively. Here $\mu_1$ and $\mu_2$ represent the velocity at a given distance $x$, from the die exit, for DR = 12.8 and DR = 6.5 respectively. We test the hypothesis that the magnitude of the velocities for DR = 6.5 are higher than the corresponding values for DR = 12.8. This is due to the draw ratio being changed by manipulating the polymer throughput while maintaining a constant chill roll speed. Therefore the testing format for case I (i.e. $\mu_1 < \mu_2$) is used. It is seen that the null hypothesis is rejected for all the data points. Therefore we conclude that the velocity at DR = 6.5 is higher than the velocity at DR = 12.8. Since three runs were used for determining the average velocity the value of $df = 4$ for method 1 (i.e. $s_1 = s_2$). The $df$ values for method 2 are presented in Table B-1.
Table B-1 Comparing centerline velocities for the Profax PH-835 sample.

<table>
<thead>
<tr>
<th>x (cm)</th>
<th>DR = 12.8</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th>Critical t values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Velocity (m/min)</td>
<td>s₂</td>
<td>Velocity (m/min)</td>
<td>s₁</td>
<td>df</td>
<td>t'</td>
</tr>
<tr>
<td>2</td>
<td>0.497</td>
<td>0.006</td>
<td>0.658</td>
<td>0.013</td>
<td>2.815</td>
<td>-19.48</td>
</tr>
<tr>
<td>3</td>
<td>0.725</td>
<td>0.014</td>
<td>0.907</td>
<td>0.014</td>
<td>4.000</td>
<td>-15.92</td>
</tr>
<tr>
<td>4</td>
<td>0.958</td>
<td>0.018</td>
<td>1.142</td>
<td>0.020</td>
<td>3.956</td>
<td>-11.84</td>
</tr>
<tr>
<td>5</td>
<td>1.185</td>
<td>0.022</td>
<td>1.371</td>
<td>0.018</td>
<td>3.849</td>
<td>-11.33</td>
</tr>
<tr>
<td>6</td>
<td>1.414</td>
<td>0.031</td>
<td>1.561</td>
<td>0.028</td>
<td>3.959</td>
<td>-6.095</td>
</tr>
</tbody>
</table>

The results for the analysis on the effect of air-gap length on the film thickness are presented in Table B-2. Here μ₁ and μ₂ represent the average thickness (at the film centerline) for L = 5 cm and L = 8 cm respectively. The reported data are for the X172 sample at T_die = 220 °C. We test the hypothesis that the film thickness at L = 8 cm is greater than the film thickness at L = 5 cm due to the increased degree of neck-in exhibited at L = 8 cm. Thus the testing format for case I (i.e. μ₁ < μ₂) is used. The null hypothesis is rejected for the draw ratios studied. Therefore we conclude that the increase in air-gap length from 5 cm to 8 cm leads to an increase in film thickness. Since 5 test specimens were used for determining the average thickness the value of df = 8 for method 1 (i.e. s₁ = s₂). The df values for method 2 are presented in Table B-2.
Table B-2 Comparing effect of air-gap length on the thickness profile for the X172 sample.

<table>
<thead>
<tr>
<th>DR</th>
<th>Thickness (mm)</th>
<th>s₁</th>
<th>s₂</th>
<th>df</th>
<th>t'</th>
<th>t</th>
<th>t ≤ -tα</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.6</td>
<td>0.216</td>
<td>0.006</td>
<td>0.248</td>
<td>0.002</td>
<td>5.097</td>
<td>-12.16</td>
<td>-12.17</td>
</tr>
<tr>
<td>12.8</td>
<td>0.154</td>
<td>0.006</td>
<td>0.212</td>
<td>0.004</td>
<td>6.604</td>
<td>-19.41</td>
<td>-19.43</td>
</tr>
</tbody>
</table>

In Table B-3 we present the results on the statistical analysis of the difference in the reported centerline temperatures for the X171 and X172 samples. Here μ₁ and μ₂ represent the temperature at a given distance x, from the die exit, for the X171 and X172 samples respectively. We test the hypothesis that the centerline temperatures of the X172 sample, are higher than the corresponding values for the X171 sample. Thus the testing format for case I (i.e. μ₁ < μ₂) is used. The null hypothesis is rejected for the data sets presented. Therefore we can conclude that the X172 sample exhibits higher centerline temperatures than the X171 sample due to the smaller thickness of the X171 sample. Since three runs were used for determining the average temperature the value of df = 4 for method 1 (i.e. s₁ = s₂). The df values for method 2 are presented in Table B-3.
**Table B-3** Comparing Temperature Profiles for X171 and X172.

| x (cm) | X171 T (°C) | s₁ | X172 T (°C) | s₂ | df | t' | t | t ≤ -tₐ |
|-------|-------------|----|-------------|----|----|----|----|-----|---------|
| 4     | 178.3       | 0.315 | 180.4       | 0.524 | 3.279 | -5.949 | -5.953 | yes |
| 6     | 166.7       | 0.234 | 169.7       | 0.556 | 2.687 | -8.614 | -8.619 | yes |
| 8     | 146.3       | 0.321 | 152.4       | 0.294 | 3.970 | -24.15 | -24.17 | yes |

In Tables B-4 and B-5 are presented the results on the statistical analysis of the difference in the reported centerline velocities at DR = 8.6 and 10.7 respectively. Here μ₁ and μ₂ represent the velocity at a given distance x, from the die exit, for the X171 and X172 samples respectively. We test the hypothesis that the magnitude of the velocities for the X172 sample, are higher than the corresponding values for the X171 sample. Thus the testing format for case I (i.e. μ₁ < μ₂) is used. It is seen that the null hypothesis could not be rejected for some of the data points. Therefore we cannot conclude that the X172 sample exhibits higher velocity magnitude than the X171 sample due to the higher viscosity of the X171 sample. Since three runs were used for determining the average velocity the value of df = 4 for method 1 (i.e. s₁ = s₂). The df values for method 2 are presented in Tables B-4 and B-5.
Table B-4 Centerline velocity comparison for draw ratio of 8.6.

<table>
<thead>
<tr>
<th>X171</th>
<th>X172</th>
<th>Critical t-values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>velocity (m/min)</td>
<td>s₁</td>
</tr>
<tr>
<td>0.500</td>
<td>0.012</td>
<td>0.520</td>
</tr>
<tr>
<td>0.700</td>
<td>0.020</td>
<td>0.780</td>
</tr>
<tr>
<td>0.950</td>
<td>0.031</td>
<td>0.980</td>
</tr>
<tr>
<td>1.120</td>
<td>0.010</td>
<td>1.220</td>
</tr>
<tr>
<td>1.320</td>
<td>0.017</td>
<td>1.370</td>
</tr>
</tbody>
</table>

Table B-5 Centerline velocity comparison for draw ratio of 10.7.

<table>
<thead>
<tr>
<th>X171</th>
<th>X172</th>
<th>Critical t values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>velocity (m/min)</td>
<td>s₁</td>
</tr>
<tr>
<td>0.510</td>
<td>0.010</td>
<td>0.470</td>
</tr>
<tr>
<td>0.760</td>
<td>0.035</td>
<td>0.790</td>
</tr>
<tr>
<td>1.020</td>
<td>0.015</td>
<td>1.110</td>
</tr>
<tr>
<td>1.270</td>
<td>0.015</td>
<td>1.360</td>
</tr>
<tr>
<td>1.530</td>
<td>0.020</td>
<td>1.560</td>
</tr>
</tbody>
</table>
The results for tests on the Heat of melting values of the X171 Primary and Processed films are presented in Table B-6. Here we test the hypothesis that increasing the draw ratio increases the crystalline content of the films. We also test the hypothesis that uniaxial stretching also increases the film crystallinity. To test the stated hypothesis we use case I. In Table B-6 $\mu_1$ refers to the heat of melting value at a given process condition and $\mu_2$ refers to the heat of melting value for the process condition given directly below. For instance if $\mu_1$ refers to DR = 6.5 then $\mu_2$ refers to DR = 8.6. From Table B-6 we see that the difference in the heat of melting for the films produced using DR = 6.5 and DR = 8.6 is not significant. But the differences are significant for the other entries. Therefore the increasing the draw ratio from 8.6 to 12.8 does increase the crystalline content of the films. The increase in the stretching ratio from 2X to 3X is also seen to increase the film crystallinity. For calculations using method 1 $df = 12$ since we tested 7 samples for each film batch. The $df$ values for method 2 are also reported in Table B-6.
Table B-6 Heat of melting for the X171 sample films.

<table>
<thead>
<tr>
<th>Draw Ratio</th>
<th>Heat of melting</th>
<th>s</th>
<th>t</th>
<th>t'</th>
<th>df</th>
<th>t ≤ -tα</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>76.74</td>
<td>2.330</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.6</td>
<td>77.39</td>
<td>2.660</td>
<td>-0.486</td>
<td>-0.486</td>
<td>11.79</td>
<td>no</td>
</tr>
<tr>
<td>12.8</td>
<td>80.44</td>
<td>2.000</td>
<td>-2.427</td>
<td>-2.425</td>
<td>11.14</td>
<td>yes</td>
</tr>
<tr>
<td>8.6, 2X</td>
<td>87.30</td>
<td>0.130</td>
<td>-9.065</td>
<td>-9.056</td>
<td>6.051</td>
<td>yes</td>
</tr>
<tr>
<td>8.6, 3X</td>
<td>91.00</td>
<td>0.090</td>
<td>-61.97</td>
<td>-61.91</td>
<td>10.68</td>
<td>yes</td>
</tr>
<tr>
<td>12.8, 3X</td>
<td>94.14</td>
<td>0.340</td>
<td>-23.64</td>
<td>-23.62</td>
<td>6.837</td>
<td>yes</td>
</tr>
</tbody>
</table>

In Table B-7 we present results from the statistical tests on the X172 film samples produced using $T_{\text{die}} = 200 \, ^{\circ}\text{C}$. The tests were conducted using the same methods and hypothesis as presented for the data in Table B-6. We see that increasing the draw ratio from 8.6 to 12.8 increases the crystalline content of the films. Uniaxial stretching also increases the degree of crystallinity of the films. Comparing the heat of melting values for the films stretched at 50 mm/s/s and 100 mm/s/s shows that there is no significant difference in the heat of melting values. Therefore the increase in stretching rate did not improve the crystalline content of the films.
Table B-7 Heat of melting for X172 films produced using $T_{\text{die}} = 200$ °C.

<table>
<thead>
<tr>
<th>Draw Ratio</th>
<th>Heat of Melting (J/g)</th>
<th>s</th>
<th>t</th>
<th>t'</th>
<th>df</th>
<th>$t \leq -t_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.6</td>
<td>79.08</td>
<td>0.690</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.8</td>
<td>81.06</td>
<td>0.53</td>
<td>-6.02686</td>
<td>-6.02097</td>
<td>11.25184</td>
<td>yes</td>
</tr>
<tr>
<td>8.6,3X,50R</td>
<td>91.90</td>
<td>0.02</td>
<td>-54.1275</td>
<td>-54.0746</td>
<td>6.017088</td>
<td>yes</td>
</tr>
<tr>
<td>8.6,3X,100R</td>
<td>91.40</td>
<td>0.39</td>
<td>3.390852</td>
<td>3.387537</td>
<td>6.031558</td>
<td>no</td>
</tr>
</tbody>
</table>

Table B-8 presents results from the analysis of the heat of melting data for the X172 films produced with a die temperature of 220 °C. As for the case of the X171 films the hypothesis holds true that increasing the draw ratio increases the film crystallinity. The uniaxial stretching is also seen to increase the crystallinity of the films. Increasing the stretch ratio increases film crystallinity.
Table B-8 Heat of melting for X172 films produced using $T_{\text{die}} = 220 \, ^{\circ}\text{C}$.

<table>
<thead>
<tr>
<th>Draw Ratio</th>
<th>Heat of Melting (J/g)</th>
<th>s</th>
<th>t</th>
<th>t'</th>
<th>df</th>
<th>$t \leq -t_{\alpha}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.6</td>
<td>77.37</td>
<td>0.230</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.8</td>
<td>78.94</td>
<td>0.100</td>
<td>-16.58</td>
<td>-16.56</td>
<td>8.190</td>
<td>yes</td>
</tr>
<tr>
<td>8.6 2X</td>
<td>91.20</td>
<td>0.390</td>
<td>-80.64</td>
<td>-80.57</td>
<td>6.786</td>
<td>yes</td>
</tr>
<tr>
<td>8.6 3X</td>
<td>95.90</td>
<td>1.170</td>
<td>-10.09</td>
<td>-10.08</td>
<td>7.317</td>
<td>yes</td>
</tr>
<tr>
<td>12.8 3X</td>
<td>98.40</td>
<td>0.420</td>
<td>-5.326</td>
<td>-5.321</td>
<td>7.521</td>
<td>yes</td>
</tr>
</tbody>
</table>

In Table B-9 results from the tests on the differences in the heat of melting for the X171 and X172 sample films are presented. The analysis shows that there are no significant differences in the heat of melting for the X171 and X172 Primary films. The X172 Processed films exhibit higher heat of melting values than their X171 counterparts. This may be attributed to the greater molecular orientation of the X172 samples as indicated by the Herman’s orientation factor.
Table B-9 Comparing Heat of melting for X171 and X172 at $T_{\text{die}} = 220 \, ^\circ\text{C}$.

<table>
<thead>
<tr>
<th>Draw Ratio</th>
<th>X171</th>
<th>X172</th>
<th>Critical t-values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Heat of Melting (J/g)</td>
<td>s₁</td>
<td>Heat of Melting (J/g)</td>
</tr>
<tr>
<td>8.6</td>
<td>77.39</td>
<td>2.660</td>
<td>77.37</td>
</tr>
<tr>
<td>12.8</td>
<td>80.44</td>
<td>2.00</td>
<td>78.94</td>
</tr>
<tr>
<td>8.6, 2X</td>
<td>87.30</td>
<td>0.130</td>
<td>91.2</td>
</tr>
<tr>
<td>8.6, 3X</td>
<td>91.00</td>
<td>0.090</td>
<td>95.9</td>
</tr>
<tr>
<td>12.8, 3X</td>
<td>94.14</td>
<td>0.340</td>
<td>98.4</td>
</tr>
</tbody>
</table>

Using Table B-10 we test if the use of different stretch rates improves the film tensile properties. We see that there are no statistically significant differences in the Tensile properties for Processed films produced using stretching accelerations of 50 mm/s/s and 100 mm/s/s. Here the hypothesis testing was performed using case II (i.e. testing that $\mu_1 \neq \mu_2$). We could not reject the null hypothesis, therefore it is concluded that using the stretching rate of 100 mm/s/s does not offer any marked improvement to the film properties. During the tensile testing experiments, 5 samples were tested for each batch therefore for method 1 $df = 8$. As in previous table the $df$ for method 2 is presented in Table B-10.
Table B-10 Comparing Tensile properties for different stretch rates.

<table>
<thead>
<tr>
<th></th>
<th>X172 100R</th>
<th>X172 50R</th>
<th>Critical t-values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µ₁</td>
<td>s₁</td>
<td>µ₂</td>
</tr>
<tr>
<td>modulus</td>
<td>938.0</td>
<td>44.00</td>
<td>1007</td>
</tr>
<tr>
<td>e-mod</td>
<td>901.3</td>
<td>37.20</td>
<td>963.9</td>
</tr>
<tr>
<td>yield</td>
<td>224.3</td>
<td>14.90</td>
<td>220.1</td>
</tr>
</tbody>
</table>

Tables B-11 and B-12 present statistical analysis on differences in the Yield stress as a function of draw ratio and air-gap length. The first row shows the decision arrived at when comparing the yield stress for draw ratio of 12.8 at air-gap lengths of 5 cm and 8 cm. The second row presents decision on comparing the effect of draw ratio on the yield stress for DR = 8.6 and DR = 12.8. The results show that the Yield stress shows no significant dependence on the draw ratio or the air-gap length.
Table B-11 Comparing Yield stress as function of DR and L for X171.

<table>
<thead>
<tr>
<th>DR, L</th>
<th>Yield stress</th>
<th>s</th>
<th>t</th>
<th>t'</th>
<th>df</th>
<th>t ≤ -tα</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.8, 5cm</td>
<td>21.70</td>
<td>0.300</td>
<td>-1.837</td>
<td>-1.836</td>
<td>4.010</td>
<td>no</td>
</tr>
<tr>
<td>8.6, 8cm</td>
<td>26.10</td>
<td>5.500</td>
<td>-0.557</td>
<td>-0.557</td>
<td>6.897</td>
<td>no</td>
</tr>
<tr>
<td>12.8, 8cm</td>
<td>28.60</td>
<td>8.400</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table B-12 Comparing Yield stress as function of DR and L for X172.

<table>
<thead>
<tr>
<th>DR, L</th>
<th>Yield stress</th>
<th>s</th>
<th>t</th>
<th>t'</th>
<th>df</th>
<th>t ≤ -tα</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.8, 5cm</td>
<td>23.40</td>
<td>0.600</td>
<td>-1.030</td>
<td>-1.029</td>
<td>4.047</td>
<td>no</td>
</tr>
<tr>
<td>8.6, 8cm</td>
<td>27.00</td>
<td>4.400</td>
<td>-0.557</td>
<td>-0.557</td>
<td>6.897</td>
<td>no</td>
</tr>
<tr>
<td>12.8, 8cm</td>
<td>27.00</td>
<td>7.800</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


BETA LaserMike LS205 Guage Instruction Handbook.


<www.polymerohio.org> (March 18th 2007)

<www.prnewswire.com> (March 18th 2007)


