Extrudate Swell of High Density Polyethylene in 

Capillary and Slit Dies

by

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Abstract

The analysis of extrudate swell in polymer melts is of great importance in many polymer processing operations and has been the subject of interest both experimentally and numerically. The main objectives of this research work are to obtain systematic and reliable extrudate swell data of a high molecular weight HDPE, to identify a suitable constitutive model that can precisely represent extrudate swell phenomena and to predict extrudate swell accurately under various processing and operating conditions.

A novel extrudate swell measuring system with an online data acquisition system is designed for the present work. This system allows one to measure extrudate swell profile under different conditions such as steady state or transient, gravity free, isothermal and non-isothermal conditions. Further, the set-up is suitable for both capillary and slit extrudates. A comprehensive analysis on the applicability and validity of various rheological (integral and differential/molecular) models in describing extrudate swell of a highly viscoelastic HDPE polymer over a broad range of shear rates (5 to 100s⁻¹) is carried out using FEM based ANSYS POLYFLOW®. The simulation results indicated that the integral constitutive equations of K-BKZ type can account for the significant memory effects of viscoelastic polymer melts such as HDPE. Overprediction of extrudate swell by the integral K-BKZ model invoked the importance of obtaining non-linear viscoelastic properties for a broader range of deformations/deformation rates. The newly available CPP fixture from AntonPaar is used to procure such non-linear viscoelastic data and thus to determine the accurate damping function. The simulation results of extrudate swell in capillary and slit dies are in good agreement with the experimental measurements using the newly determined damping function.

In addition, non-isothermal extrudate swell of the HDPE polymer is studied using the pseudo-time integral K-BKZ Wagner (i.e., the non-isothermal form) model with the differential Nakamura equation for the crystallization kinetics. The model is implemented in ANSYS POLYFLOW®. Extrudate swell measurements are obtained by extruding the polymer melt at 200°C through long capillary and slit dies to ambient air at 25°C and 110°C. The numerical results are found to be in very good agreement with the experimental observations.
Preface

This thesis entitled “Extrudate swell of high density polyethylene in capillary and slit dies” presents the research the author performed during his PhD study under the supervision of Professor Savvas G. Hatzikiriakos. The extrudate swell phenomenon of a high molecular weight high density polyethylene has been extensively studied both experimentally and numerically.

The results presented in Chapters 4, 5 and 6 are summarized in seven manuscripts published or to be submitted for publication:


The sixth paper has written mostly by Dr. Ehsan Behzadfar, and some of the experimental set-up details presented in this paper will be used in this thesis. All other manuscripts were written mostly by the author of this PhD, and revised by Prof. Savvas G. Hatzikiakos (research supervisor) and the other co-authors.
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- $2a$: entrance angle
- $b$: slip exponent of Navier’s slip law
- $a_T$: time-temperature shift factor
- $d$: diameter of the extrudate
- $t$: thickness of the extrudate from slit flow
- $h$: distance between parallel disks
- $h_T$: local heat transfer coefficient
- $g_i$: relaxation moduli
- $h(\gamma)$: damping function
- $\Delta H_f$: heat of fusion
- $k$: thermal conductivity
- $m$: Avrami index
- $n$: Wagner exponent
- $\hat{n}$: unit outward normal vector
- $p$: pressure
- $\Delta p$: applied pressure or pressure drop
- $q$: heat flow
- $q_n$: number of arms of pom-pom
- $t$: observer’s time
- $t_{1/2}$: half time of crystallization
- $(1/t_{1/2})_0$: intercept of Hoffman-Lauritzen fit
- $u$: velocity vector
- $A$: parameter of non-sphericity
- $B_D$: extrudate swell ratio in capillary die
- $B_T$: thickness swell ratio in slit die
- $C$: Hoffman-Lauritzen theory constant
- $C_P$: heat capacity
- $C_t$: Cauchy-Green tensor
- $C_t^{-1}$: Finger strain tensor
\( D \) diameter of the die
\( D_b \) diameter of the reservoir (barrel)
\( \mathbf{D} \) rate of deformation tensor
\( E_a \) activation energy
\( F \) normal force
\( \mathbf{F}_t \) deformation gradient tensor
\( G_i \) shear modulus in DCPP model
\( G^* \) complex modulus
\( G'(\omega) \) storage modulus
\( G''(\omega) \) loss modulus
\( G(t) \) relaxation modulus
\( H \) thickness of a slit die
\( \mathbf{I}_c \) first invariant of \( C_t \)
\( \mathbf{I}_c^{-1} \) first invariant of \( C_t^{-1} \)
\( \mathbf{I} \) unit tensor
\( K_{\max} \) kinetic parameter at the maximum crystal growth rate
\( K_N \) crystallization kinetic parameter
\( K_N(T) \) temperature dependent crystallization rate parameter
\( K_N(f_a) \) flow dependent crystallization rate parameter
\( L \) length of the die
\( L_{\text{ext}} \) extrudate length
\( \mathbf{L}_t \) velocity gradient tensor
\( M \) torque
\( M_W \) Weight average molecular weight
\( N \) number of relaxation modes
\( N_1 \ (\equiv \tau_{11}-\tau_{22}) \) first normal stress difference
\( N_2 \ (\equiv \tau_{22}-\tau_{33}) \) second normal stress difference
\( N_{1,w} \) first normal stress difference along the wall and free-surface
\( N_{1,\text{sym}} \) first normal stress difference along the axis of symmetry
\( P \) pressure
\( Q \) volumetric flow rate

\( R \) universal gas constant

\( \dot{R} \) quiescent crystallization rate

\( \alpha \) relative crystallinity fraction

\( \alpha_i \) material constant of Giesekus model for each mode

\( \alpha_p \) shear parameter of PSM damping function

\( \beta \) extensional parameter of Wagner or PSM damping function

\( \beta_{sl} \) slip coefficient of Navier’s slip law

\( \tau_{12} \) shear stress

\( \tau_w \) wall shear stress

\( \tau_{\gamma \delta} \) shear stress

\( \tau_a \) apparent or Newtonian shear stress

\( \tau_i \) individual contribution of extra stress tensor

\( \tau \) extra stress tensor

\( \gamma \) shear strain

\( \dot{\gamma} \) shear rate

\( \dot{\gamma}_A \) apparent shear rate

\( \varepsilon_H \) Hencky strain rate

\( \tilde{\zeta}_i \) non-dimensional shear material parameters of PTT model

\( \varepsilon_i \) non-dimensional elongational material parameters of PTT model

\( \zeta_i \) nonlinear material constants for each model in DCPP model

\( \lambda_i \) relaxation time

\( \bar{\lambda} \) mean relaxation time

\( \lambda_{si} \) relaxation time related to the stretching mechanism of DCPP model

\( \lambda_{ci} \) relaxation time of the crystallizing polymer melt

\( \eta_0 \) zero shear viscosity

\( \eta_i \) partial viscosity

\( \eta_{ci} \) partial viscosity of the crystallizing polymer melt

\( \eta_s^+ \) shear stress growth coefficient

\( \eta_s^- \) shear stress decay coefficient

xx
\( \eta_E^+ \)  
uniaxial stress growth coefficient

\( \eta_E^- \)  
uniaxial stress decay coefficient

\( \psi^+_1 \)  
first normal stress difference coefficient

\( \psi^-_1 \)  
first normal stress difference coefficient

\( \Lambda \)  
stretching scalar

\( \omega \)  
angular frequency

\( \rho \)  
density

\( \zeta \)  
elapsed time
### List of Abbreviations

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<tr>
<td>ALE</td>
<td>Arbitrary Lagrangian-Eulerian</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge Coupled Camera</td>
</tr>
<tr>
<td>CLIPS</td>
<td>C Language Integrated Programming System</td>
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<tr>
<td>HWNP</td>
<td>High Weissenberg Number Problem</td>
</tr>
<tr>
<td>K-BKZ</td>
<td>Kaye-Bernstein-Kearsley-Zapas</td>
</tr>
<tr>
<td>LLDPE</td>
<td>Linear Low-Density Polyethylene</td>
</tr>
<tr>
<td>LVE</td>
<td>Linear Viscoelastic Elasticity</td>
</tr>
<tr>
<td>LDPE</td>
<td>Low-Density Polyethylene</td>
</tr>
<tr>
<td>NGFS</td>
<td>Next Generation Fuel System</td>
</tr>
<tr>
<td>PSM</td>
<td>Papanastasiou-Scriven-Macosko</td>
</tr>
<tr>
<td>PP</td>
<td>Parallel Plate</td>
</tr>
<tr>
<td>PTT</td>
<td>Phan-Thien-Tanner</td>
</tr>
<tr>
<td>SER</td>
<td>Sentmanat Extensional Rheometer</td>
</tr>
<tr>
<td>STA</td>
<td>Simultaneous Thermal Analyzer</td>
</tr>
<tr>
<td>SAOS</td>
<td>Small Amplitude Oscillatory Shear</td>
</tr>
<tr>
<td>SFEM</td>
<td>Streamline Finite Element Method</td>
</tr>
<tr>
<td>SUPG</td>
<td>Streamline-Upwind/Petrov-Galerkin</td>
</tr>
<tr>
<td>TTS</td>
<td>Time-Temperature superposition</td>
</tr>
</tbody>
</table>
I would like take this opportunity to thank all the people who have supported me with this project over the past few years.

Firstly, I would like to express sincere gratitude and appreciation to my supervisor Prof. Savvas G. Hatzikiriakos for his advice, assistance and encouragement throughout my PhD research. His constant support and thoughtful insight helped me to address several challenges I faced during this research work. I would also like to thank Prof. Evan Mitsoulis for his constant support, valuable suggestions and comments throughout this project. I would also like to thank my colleagues Dr. Mahmoud Ansari, Dr. Ehsan Behzadfar and Ms. Marzieh Ebrahimi from Polymer Processing and Rheology Lab at UBC for giving me valuable experimental data at times and for having some thoughtful discussions on flow modeling and experimental analysis.

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To my parents
Chapter 1: Introduction

The relative increase in the dimensions of extrudate compared to those of the die due to the sudden release of stresses upon exiting the die is known as extrudate swell. This phenomenon plays a crucial role in several polymer processing operations (Mitsoulis 2010) such as blow molding, fiber spinning, film blowing, and profile extrusion. This project is related to the optimization of a novel manufacturing process referred to as Next Generation Fuel System (NGFS) developed by Kautex Textron GmbH & Co. One of the main steps of this process involves the sheet extrusion of two polymer sheets (refer FIGURE 1.1). Consequently, all the necessary fuel system components like pumps, valves and fuel gauges are held between these two sheets before the two sheets are welded together to form the fuel tank. With the help of the cavity tools on both sides of the sheets these parts are incorporated into the fuel tank in a simple step. Thus, the main challenge in this process is to control the thickness profile/distribution of the extruded sheets as it governs the thickness uniformity and thus the mechanical strength of the final product. In this thesis, the axisymmetric and flat sheet extrudate swell of a highly viscoelastic polymer melt such as High Density Polyethylene (HDPE) is studied in detail in order to devise a model that can be used for the optimization of NGFS process.

Extrudate swell in polymers occurs when long, entangled and coiled chains of molecules are forced to flow through a channel which converges from broad entrance to a narrow die, as usually happens in extrusion processes. Due to the “memory effect”, the polymer melt/fluid attempts to revert back to the original, un-oriented state as it exits the die. Such expansion of the extrudate is called extrudate swell. FIGURE 1.2 depicts the significant difference between extrudate swell observed for a viscoelastic fluid to that of Newtonian fluid. For capillary dies, the extrudate swell is defined as $B_D = d/D$, where $D$ is the die diameter and $d$ is the diameter of the extrudate. In slit dies, the thickness swell is defined as $B_T = t/H$, where $H$ is thickness of a slit die and $t$ is the thickness of the extrudate. This depends on the location of its measurement with a tendency of increasing in the downstream direction (Garcia-Rejon and Dealy 1982). In addition, extrudate swell in polymer melts depends on many parameters such as the past deformation history (memory effects), die design characteristics, viscoelastic properties of the material (extended) and process conditions (Tanner 1970, 1973, 2000, 2005; Koopmans 1988; Mitsoulis 2010).
FIGURE 1.1: Schematic representation of twin sheet extrusion process (first and key step in NGFS process) where the polymer sheets are extruded with a desired thickness profile in order to produce a fuel tank of uniform thickness when they are expanded to form the tank.

FIGURE 1.2: Extrudate swell observed in Newtonian fluid (water) (on the left) and Viscoelastic fluid (polystyrene standard) (on the right)
Early works on extrudate swell of polymer fluids in capillary and slit dies were presented in the 1970s (Tanner, 1970; Graessley et al., 1970; Vlachopoulos et al., 1972; Utracki et al., 1975; Han, 1973; Vlachopoulos, 1977; Huang and White, 1979), where the phenomenon was studied both experimentally and theoretically. The early numerical studies on the extrudate swell problem were mainly concerned with Newtonian fluids (Tanner 1973; Nickell et al. 1974). The advent of advanced numerical techniques and constitutive models made extrudate swell simulation possible for viscoelastic fluids, such as polymer melts and/or solutions (Crochet and Keunings 1982; Luo and Tanner 1986a, 1986b; Kiriakidis and Mitsoulis 1993). Although the extrudate swell mechanism has been studied extensively both experimentally and theoretically, it is not fully understood (Ansari et al. 2013; Ganvir et al. 2011; Kalyon et al. 1980; Béreaux et al. 2012; Konaganti et al. 2015). There are no studies to show quantitative agreement between experimental observations and flow model simulations. Such a model would be invaluable in optimization of this complex process. One of the main objectives of this work is to identify a constitutive model that can quantitatively predict the extrudate swell of the present HDPE resin over a wide range of parameters discussed above.

1.1 Literature review

As mentioned before, extrudate swell in polymer melts or solutions has been the subject of interest both experimentally and numerically for many researchers. Some of the important studies are reviewed below.

1.1.1 Experimental techniques for measuring swell

Although extrudate swell (which is significant under sufficiently high levels of stress) is usually considered as an instability for extrudates (Denn 2001; Georgiou 2003; Georgiou and Crochet 1994), it can be controlled to manufacture or produce products with desired dimensions and thus precise swell measurement is essential in polymer processing applications. However, accurate measurement of extrudate swell dimensions is a challenging task due to its sensitivity to processing, operating and measuring conditions.

One of the early methods of extrudate swell measurement in blow molding is the use of a pinch-off method combined with experimental photography where the extrusion rate, weight and
size of the solidified extrudate are very important for calculating the time-dependent swell. The inefficiency of this method is very apparent as it involves shrinkage of polymer extrudate upon direct extrusion to ambient air, thereby it does not consider the free relaxation and swelling of the extrudate (Kalyon et al. 1980; Dutta and Ryan 1982). Other methods include infrared transmission (Glascock 2007), filming method (Huang and Li 2006), charge coupled camera (CCD) (Maziers and Pestiaux 2009), and optical techniques (Swan et al. 1996; Béreaux et al. 2012), which also suffer from several setbacks including inability of detecting transparent objects (i.e., for many polymer melts), flat extrudates, transient measurements and complete determination of the extrudate profile. The effects of gravity (i.e., sagging) and ambient temperature also need to be controlled for accurate extrudate swell measurements. In addition, the measurement system should be noninvasive and capable of operating at high temperatures (i.e., in the range of polymer process temperatures).

1.1.2 Numerical studies on extrudate swell

Many researchers have attempted to predict the extrudate swell behavior in polymer melts or solutions using various constitutive equations including integral, differential, and molecular models and compared the results with experiments (Reddy and Tanner 1978; Luo and Tanner 1986a, 1986b, 1988; Goublomme et al. 1992; Housiadas and Tsamopoulos 2000; Béraudo 1998; Russo and Phillips 2010). The major difficulty in accurately assessing the extrudate swell in polymer melts is the choice of a constitutive equation that is appropriate for a wide range of deformations and deformation rates, both in shear and elongation.

1.1.2.1 Isothermal extrudate swell studies

There is a plethora of numerical studies reported on the simulation of extrudate swell of polymer melts or solutions. Interestingly, the majority of these studies focus on steady state isothermal swell/flow simulations and the numerical results are subsequently compared with experimental observations.

Most of the early computational works study the extrudate swell of highly viscoelastic polymer melts, such as linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE) and high-density polyethylene (HDPE) melts, using integral constitutive equations (Luo
and Tanner 1986a, 1986b; Luo and Mitsoulis 1989). Luo and Tanner (1986a, 1986b) have simulated the extrudate swell of a highly viscoelastic IUPAC-LDPE melt using the integral K-BKZ model for both long and short capillary dies using the streamline finite element method (SFEM). Luo and Mitsoulis (1990) have later modified this method to decouple the computation of the free surface shape and position from that of velocity and stress fields. This new finite element technique was successful in obtaining reliable numerical results for viscoelastic flow simulations with abrupt contraction that can simulate recirculating regions using integral constitutive equations.

Goublomme et al. (1992) and Barakos and Mitsoulis (1995) have further modified different characteristics of Luo and Mitsoulis’s method to address the numerical difficulties associated with SFEM and to account for the effects of upstream contraction and recirculation on extrudate swell at higher shear rates. In all the aforementioned studies, researchers have used integral K-BKZ model with a spectrum of relaxation times and a damping function either of the Wagner (Wagner 1976, 1979) or of the Papanastasiou (Papanastasiou et al. 1983) type. The swell predictions observed using memory integral constitutive equations are comparable with the experimental results for long dies. However, these models largely overpredict the swell in short dies with a length $L$ and a diameter $D$ ($0 \leq L/D \leq 5$), especially at high apparent shear rates (Kiriakidis and Mitsoulis 1993; Barakos and Mitsoulis 1995; Konaganti et al. 2015). Ansari et al. (2013) have also observed that the integral K-BKZ PSM model highly overestimates the extrudate swell of a HDPE polymer melt even after considering a non-zero second normal stress difference and significant amount of slip at the wall.

On the other hand, several authors have successfully demonstrated the use of differential constitutive equations such as the PTT, Giesekus and XPP models for the simulation of extrudate swell in polymer melts or solutions (Goublomme et al. 1992; Crochet and Keunings 1982; Crochet 1989; Rajagopalan et al. 1992; Guénette and Fortin 1995; Otsuki et al. 1999; Oishi et al. 2011). Most of the early efforts were focused on the well-known high Weissenberg number problem (HWNP). However, this problem was solved by using numerical schemes best suited for hyperbolic equations (Goublomme and Crochet 1993; Crochet 1989). Subsequently, Elastic-Viscous Stress Split (EVSS) (Rajagopalan et al. 1992) and/or Discontinuous Elastic-Viscous Stress Split (DEVSS) (Guénette and Fortin 1995) formulations on extra-stress tensor were
introduced to obtain convergent and numerically accurate solutions. In a recent study, Ganvir et al. (2009, 2011) have used an arbitrary Lagrangian-Eulerian (ALE) based finite element method and simulated transient extrudate swell of LLDPE and HDPE polymer melts. The numerical results showed good agreement with reported experimental results only corresponding to polymer melts of moderate elasticity (swell ratio of up to 1.4). Further, apparent shear rates as high as those used in practical applications could not be reached.

Limited studies exist on extrudate swell using both integral and differential rheological models on the same polymer melt of high elasticity, typically used in blow molding applications. Moreover, there is no systematic study of the extrudate swell of viscoelastic polymer melts where flow model predictions are compared with experimental results for various operating conditions (temperature and flow rate/apparent shear rate) relevant to polymer processing and for various geometrical characteristics such as length-to-diameter ratio, $L/D$ (in capillary dies), width-to-thickness ratio, $W/H$ (in slit dies), and the presence of the reservoir. The latter plays a significant role in the numerical predictions and their consistency with experimental results on extrudate swell as this thesis attempts to demonstrate.

1.1.2.2 Non-isothermal extrudate swell studies

The effects of temperature are very crucial in many polymer processing applications as the melts start crystallizing upon emergence from the die exits (Tanner 1985). These effects are more significant close to the phase change (transition from the melt to the solid state) where the temperature dependence is extremely high. Controlling the extrudate dimensions through the adjustment of local die temperature, melt temperature and cooling rates has been extensively employed in extrusion processes (Chang and Yang 1994). Given the significance of non-isothermal conditions in extrusion processes to control the dimensions and/or properties of the extrudate, understanding such processes has become the subject of interest both experimentally and numerically (Phuoc and Tanner 1980; Luo and Tanner 1985, 1987; Barakos and Mitsoulis 1996; Patel et al. 1991; Huynh 1998, 2000; Doufas and McHugh 2001; Ziabicki et al. 2004; Cherukupalli et al. 2005; Tanner and Qi 2005; Henrichsen and McHugh 2007; Kolarik and Zatloukal 2009; Wo et al. 2012; Doufas 2014).
Luo and Tanner have developed a temperature dependent integral constitutive equation of the K-BKZ type for simulating non-isothermal viscoelastic flows (Luo and Tanner 1987). Since then several researchers have used modified/improvised versions of this model to simulate non-isothermal viscoelastic flows such as capillary/slit extrusion (Barakos and Mitsoulis 1996; Marín and Rasmussen 2009), annular extrusion (Barakos and Mitsoulis 1996), and film blowing (Alaie and Papanastasiou 1993). On the other hand, several authors have also demonstrated the use of differential constitutive equations such Upper Convected Maxwell (UCM) (Cain and Denn 1988; Luo and Tanner 1985), PTT (Peters and Baaijens 1997; Muslet and Kamal 2004) and eXtended Pom-Pom (XPP) (Sarafrazi and Sharif 2008) models for non-isothermal polymer melt flow simulations. Moreover, these simulation studies were aimed mainly to account for the thermally induced extrudate swell and extrudate bending phenomena (Karagiannis et al. 1989; Phuoc and Tanner 1980; Barakos and Mitsoulis 1996; Chang and Yang 1994). However, the self-heating is not significant for the present HDPE extrusion experiments as the average velocity is very small due to the small radius or thickness of the dies used even at the highest shear rates studied. Similar behavior was observed for IUPAC extrusion measurements as reported by Luo and Tanner (1987). Moreover, many of these non-isothermal swell simulation studies lack accurate experimental validation and are limited only to fiber spinning and film blowing, where extrudate swell is relatively unimportant.

In addition, several researchers developed and used macroscopic continuum models that combine rheological constitutive equations with crystallization kinetics to simulate the non-isothermal extrusion processes like fiber spinning and film blowing. Most of these reported studies so far used simple shear thinning models (Patel et al. 1991; Ziabicki et al. 2004; Tanner 2003) or differential constitutive equations (Doufas and McHugh 2001; Doufas 2014) and the effects of crystallization on the fluid behavior are accounted by incorporating the Nakamura model (Nakamura et al. 1973) along with the Ziabicki (1976) or Hoffman-Lauritzen (Hoffman et al. 1976) equation. These studies have shown some successes in predicting the velocity and temperature distributions along the melt/film at least when advanced rheological models such as Giesekus, XPP and PTT are used in combination with appropriate crystallization kinetics.

However, it was found that the differential/molecular constitutive equations (such as Giesekus, PTT, and DCPP) cannot properly account for the memory effects associated with highly
viscoelastic polymer melts and fail to predict extrudate swell accurately (Béraudo et al. 1998; Konaganti et al. 2015, 2016a). This points that further work is needed for the development of a non-isothermal extrudate swell model with crystallization kinetics that can account for the memory effects associated with viscoelastic polymer melts accurately, while describing the ongoing crystallization across the extrudate.

1.2 Summary/concerns

Despite many efforts on the measurement and prediction of extrudate swell of viscoelastic polymer melts, the following gaps/concerns still remain:

- Limited experimental data are available on extrudate swell of viscoelastic polymer melts considering the effects of various parameters such as geometrical characteristics of the die, wall slip, and temperature (barrel and/or extrudate).
- Identification of a rheological model that can represent the extrudate swell behavior observed in highly viscoelastic polymer melts such as HDPE.
- There are very few systematic studies on the effect of temperature (of the barrel or extrudate environment) on extrudate swell experimentally and numerically.
- There are limited studies on the effects of rheological properties/parameters on the extrudate swell of polymer melts.

It is important to study the flow behavior of polymer melts and the associated swell phenomenon, considering parameters such as deformation history (i.e., memory effects), wall slip in the die, non-isothermal effects for the optimization of die design and process conditions and thus better prediction of extrudate swell.

1.3 Research objectives

The main objective of this research project is to obtain systematic and reliable extrudate swell data of a high molecular weight industrial grade HDPE and to accurately predict extrudate swell by identifying or developing suitable constitutive model. The particulars of the main objective are presented below:
1. To develop an efficient experimental technique with an on-line data acquisition system that can record reliable experimental data on extrudate swell. This was done by using a novel extrudate swell measurement system installed at the die exit. This system consists of a pair of movable optical micrometers to measure the extrudate dimensions and a pair of infrared heaters to maintain the ambient environment at a desired temperature. The new set-up is designed to eliminate the shortcomings of existing measuring techniques and can obtain gravity free and isothermal/non-isothermal swell readings.

2. To identify a suitable rheological/constitutive model that can accurately represent the extrudate swell phenomenon especially in a highly viscoelastic polymer melt such as HDPE. This was addressed by performing a detailed analysis on the applicability and validity of various rheological (integral and differential/molecular) models in describing extrudate swell of the studied HDPE melt in capillary dies at high shear rates (in the range of 5 to 100s$^{-1}$) (Konaganti et al. 2015). A series of extrudate swell experiments considering the effects of temperature, slip and die geometrical characteristics in capillary dies are carried out to gather the experimental data necessary for comparison with simulation results.

3. To study the non-linear viscoelastic flow properties of the polymer resin for a broad range of deformations/deformation rates in an attempt to determine the damping function of the material. The newly available CPP fixture mounted onto AntonPaar MCR 702 is used to procure such data. Obtaining the accurate damping function is found to be the most important in simulating extrudate swell in polymer melts (Konaganti et al. 2016a). The sensitivity analysis of extrudate swell predications to damping function is also examined in detail. The simulation results of extrudate swell in capillary and slit dies obtained using the newly determined damping function parameters are compared with their corresponding experimental observations (Konaganti 2016a, 2016b).

4. To develop a non-isothermal extrudate swell model that is appropriate for highly viscoelastic polymer melts while accounting for the ongoing crystallization throughout the extrudate volume. Non-isothermal extrudate swell measurements were carried out at a constant extrusion temperature inside the die and at different ambient air
temperatures (below the equilibrium melting point of the polymer) surrounding the extrudate. An integral constitutive model of K-BKZ type along with Nakamura crystallization kinetics is used to predict the non-isothermal extrudate swell measurements in capillary and slit dies.

1.4 Thesis organization

The organization of this dissertation is as follows. Details of the apparatuses used in this study, which include a rotational rheometer (AntonPaar MCR 502 or AntonPaar MCR 702) with parallel plate geometry, cone and plate (CP) geometry, cone partitioned plate fixture (CPP), Sentmanat Extensional Rheometer (SER) fixture, a capillary rheometer (Instron tester 4465), a novel extrudate swell measuring system (with a pair of optical micrometers (Keyence® LS-7030M) and a pair of infrared heaters), and Differential Scanning Calorimeter (DSC) (PerkinElmer STA 6000) and the methodology associated with these experimental techniques are described in Chapter 2 (Objective 1). The complete rheological characterization of the present resin using various integral, differential and molecular constitutive equations is presented in Chapter 3. Chapter 3 further includes the 2D FEM viscoelastic flow simulations in capillary dies using various constitutive models to identify an appropriate rheological model that can accurately represent the extrudate swell behavior of the present HDPE polymer. This allows a comprehensive comparison of the simulation results thus obtained using various models with the experimental observations (Objective 2). Chapter 4 reports the use of CPP fixture to obtain non-linear viscoelastic properties of the preset resin over a broad range of shear strains / shear rates. This was found to be very crucial for accurately determining the damping function parameters of the constitutive model and thus the predictions of extrudate swell. Furthermore, this chapter includes the sensitivity analysis of the damping function parameters on extrudate swell (Objective 3). A newly developed extrudate swell model that combines viscoelasticity using integral K-BKZ constitutive equation, crystallization kinetics using Nakamura model and thermal boundary conditions to simulate extrudate swell under non-isothermal conditions is presented in Chapter 5. Moreover, the comparison between the non-isothermal extrudate swell simulation results and experimental measurements are also presented in Chapter 5 (Objective 4). The conclusions summarizing the thesis and the recommendation for future research are presented in Chapter 6.
Chapter 2: Material and Experimental Methods

This chapter describes the apparatuses and the methodology associated with the experimental techniques used in this work. The apparatuses/instruments used in this study include a rotational rheometer (with parallel plate, CPP, and SER fixtures), a pressure driven capillary rheometer, a Simultaneous Thermal Analyzer (STA) to perform Differential Scanning Calorimetry experiments.

2.1 Material

A high molecular weight industrial grade HDPE (with weight average molecular weight, $M_w=206$ kg/mol, Polydispersity index, $PI = 10.8$) with MFI=5.72 g/10min was used in the present study.

2.2 Rotational rheometer

The polymer was rheologically characterized using a stress/strain controlled AntonPaar MCR501 rotational rheometer. The linear viscoelastic properties of the polymer used in this work were measured using small amplitude oscillatory shear (SAOS) or frequency sweep tests and the non-linear shear characteristics of the present resin were obtained by performing start-up of steady shear experiments. These experiments have been performed with the 25-mm parallel disk geometry and a gap of about 1 mm. The linear viscoelastic and non-linear shear properties can also be obtained using the cone and plate fixture. Further, the polymer was also characterized in uniaxial extension using the SER-2 universal testing platform fixture suitable for the AntonPaar MCR501 rheometer.

However, it is not possible to obtain reliable rheological data of viscoelastic polymer melts for higher strains and strain rates using the conventional parallel plate and cone and plate fixtures due to the well-known edge fracture instability (Dealy and Wissbrun 1996; Larson 1992). Thus the non-linear shear measurements were conducted for a broader range of deformation/deformation rates using the newly available cone-partitioned plate (CPP) geometry mounted onto AntonPaar MCR702 with TwinDrive® technology. All the experiments have been carried under Nitrogen gas to avoid any thermal degradation.
2.2.1 Parallel plate (PP) geometry

Parallel plate geometry is one of the most common rheological fixture to produce shear flows. As depicted in FIGURE 2.1, it has two parallel concentric disks where the upper disk rotates with respect to the lower, thus producing shear. This geometry is used primarily for the measurement of linear viscoelastic properties of polymer melts and is the preferred geometry for viscous melts for small strain material functions. Advantages of this rheometer is flow regularity and ease of sample preparation. On the other hand, non-homogeneous strain field and inability to reach high shear rates and strains due to edge fracture are its disadvantages (Macosko 1994).

![Parallel plate geometry diagram](image)

**FIGURE 2.1:** Schematic representation of parallel plate rheometer.

A series of frequency sweeps (SAOS tests) were performed at different temperatures ranging from 160-220°C with the 25-mm parallel disk geometry and a gap of about 1 mm. The time–temperature superposition (TTS) was used to generate the master curves at the reference temperature of 200°C at which the extrudate swell measurements were performed and the results are presented in Chapter 3.
2.2.2 Cone and plate (CP) geometry

Cone and plate geometry is one of the most popular rheometers for studying the viscoelastic properties of molten polymers due to its constant rate of shear and direct measurement of first normal stress difference, $N_1$. This geometry is based on the use of a circular disk and a small angle cone as shown in FIGURE 2.2. The sample is inserted between these two elements, and one is rotated while the other is held stationary. Unlike parallel plate geometry, cone and plate generates homogenous deformation, but it is also limited by elastic edge failure, and loss of sample at edges at high shear rates and strains.

A series of steady shear experiments have been performed using a cone and plate geometry of the rotational rheometer AntonPaar MCR 501 at a reference temperature of 200ºC at various shear rates ranging from 0.05 to 1 s$^{-1}$. The experimental results are given in Chapter 3.

FIGURE 2.2: Schematic representation of cone and plate rheometer.
2.2.3 Cone partitioned plate (CPP) geometry

This new CPP fixture mounted onto AntonPaar MCR 702 is used to complete the rheological characterization by conducting step-strain stress relaxation experiments for shear strains ranging from 0.1 to 7.5 and the start-up of steady shear experiments for shear rates in the range of 0.05 to 20 s\(^{-1}\). The rheological data thus obtained are discussed in detail in Chapter 4. FIGURE 2.3 illustrates the schematic of the setup, which consists of a cone geometry with a 4° angle at the bottom and a partitioned plate at the top. The effects of edge distortions can be avoided using a cone-partitioned-plate (CPP) fixture (Meissner et al. 1989; Snijkers and Vlassopoulos 2011). In this geometry, another partition has been added, only to shield off edge fracture. As depicted in FIGURE 2.3, the top geometry consists of a standard plate (center plate) attached to the transducer, surrounded by a coaxial stationary plate (outer stationary ring). Since the transducer takes into account only torque contributions from the center plate, the effects of the edge fracture will not be sensed immediately. Therefore, reliable shear flow data can be obtained even at high rates and strains. Small amount of sample, no trimming and uniform shear are other advantages of this fixture. With the help of CPP fixture, the well-known edge fracture instability (Dealy and Wissbrun 1996; Larson 1992) is postponed to the higher strains/strain rates. Snijkers and Vlassopoulos (2011) have validated the rheological measurements for polystyrene and polyisoprene for a similar fixture. It is worth noting that the present setup is specifically made for rheometers with two motors like the AntonPaar MCR702.
FIGURE 2.3: Schematic of cone and partitioned plate (CPP) fixture. The flow is generated by the lower part cone while the resulting torque is measured at the upper partitioned plate.

2.2.4 **SER (Sentmanat Extension Rheometer) universal testing platform**

Sentmanat Extensional Rheometer (SER) is a universal testing platform consisting of dual wind-up drums (referred to as master and slave drums) which can be used to generate uniaxial extensional data (Sentmanat 2004). Master drum rotates by the rotation of drive shaft, and the slave drum counter-rotates via intermeshing gears, that connect the two drums (see FIGURE 2.4). The sample is fixed between two drums by means of securing clips, and undergoes a uniform uniaxial stretching over an unsupported length, $L_0$. Using small amount of sample resulting in better controlling the temperature is one of the most important advantages of this fixture. For a constant drive shaft rotation rate, $\Omega$, the Hencky strain rate applied to the sample is defined as (Sentmanat, 2004): $\dot{\varepsilon}_H = 2\Omega R_w / L_0$, where $R_w$ is the radius of the wind-up drums, and $L_0$ is the fixed, unsupported length of the stretched sample which is equal to the centerline distance between two drums.
A series of uniaxial extensional rheology measurements were carried out for the present resin using the SER-2 Universal Testing Platform fixture suitable for the AntonPaar MCR501 for different Hencky strains in the range of 0.05 to 5 s⁻¹.

![SER testing platform diagram](image)

**FIGURE 2.4:** Schematic of SER (Sentmanat Extension Rheometer) testing platform.

### 2.3 Capillary rheometer

Capillary rheometer is the most commonly used instrument to measure the viscosity of the polymers. Compared to shear flow driven rheometers, the main advantage of a capillary rheometer includes its operation at high shear rates, closer to industrial processing conditions. The schematic representation of capillary rheometer is shown in **FIGURE 2.5**. The pressure drop and the velocity of the piston are the raw data obtained from this device and the following relations can be used to determine the apparent shear rate, $\dot{\gamma}_A$, and wall shear stress, $\tau_w$:

$$\dot{\gamma}_A = \frac{32Q}{\pi D^3}$$  \hspace{1cm} (2.1)
\[ \tau_w = \frac{D \Delta p}{4L} \]  

(2.2)

where \( Q, \Delta p, D \) and \( L \) are volumetric flow rate, applied pressure, die diameter and die length, respectively. Similarly, for a rectangular channel (slit) of height \( H \) and width \( W \) with \( W \gg H \), so that end effects can be neglected, the following expressions can be derived:

\[ \dot{\gamma}_A = \frac{6Q}{WH^2} \]  

(2.3)

\[ \tau_w = \frac{H \Delta p}{2L} \]  

(2.4)

In this project, a pressure-driven Instron (model #4465 equipped with a 9.52mm diameter reservoir) capillary rheometer of constant piston speed has been used to study the processing/slip behavior of the present polymer melt at 200ºC. It consists of four individual heating zones, which ensures precise temperature control along its length. Capillary extrusion experiments using dies of various length-to-diameter ratios (\( L/D = 5, 16, \) and 33, with \( D=0.79 \) mm) and diameters (such as \( D=0.43, 0.79, \) and 2.11 mm with \( L/D=16 \)) were carried out to apply all the necessary corrections such as Bagley and slip (Mooney analysis) to the raw data as presented in Appendix A. The polymer is extruded at a reference temperature of 200ºC for most of the swell measurements.
2.4 Extrudate swell measuring system

The experimental set-up for the extrudate swell measurements in capillary slit dies is shown in FIGURE 2.6. The experimental set-up consists of a pair of Keyence® LS-7030M optical micrometers. These micrometers are located near the die exit and can be moved both radially and axially to determine the complete extrudate swell profile. This set-up is useful for measuring the swell in both capillary and slit dies. In addition, the set-up includes a pair of heaters placed below the die exit on both sides of the extrudate. These heaters help to keep the ambient air at a desired temperature. Thus both isothermal and non-isothermal extrudate swell measurements (see FIGURE 2.6) can be performed. More specifics on the extrudate swell measuring system used in this study are given in Appendix B.
The extrudate swell measurements were performed using the following procedure: when the extrusion pressure reached steady-state, the extrudate was cut at the exit of the die and allowed to flow from the die exit in the downstream direction. The extrudate swell was recorded at the tip of the extrudate, when it reached micrometers’ location. This measurement is taken as the gravity-free extrudate swell value. The extrudate swell evolves with distance down the exit due to the continuous relaxation of the normal stresses (that represent memory of the polymer melt) and cannot be characterized by a single value (Huang and White 1980; Luo and Mitsoulis 1989; Behzadfar et al. 2015). This is true for both isothermal and non-isothermal measurements and is valid even for long extrudates. However, it is tedious to measure the complete extrudate swell profile for all the cases and most of our swell measurements were done only at a distance 20mm below the die exit, at which the extrudate swell reaches at least 90% of its final value. The measurements were repeated multiple times and only the average swell values are plotted in the figures reported in Chapters 3, 4, and 5. The reproducibility of swell readings is within ±5% for most of the readings. More details on the experimental set-up describing how to measure gravity-free and isothermal/non-isothermal swell measurements are presented elsewhere (Behzadfar et al. 2015).

FIGURE 2.6: The Instron capillary rheometer along with the novel extrudate swell measurement set-up placed under the die exit (on the left) and a schematic (on the right) representing the ability of the present set-up to measure both isothermal and non-isothermal measurements.
2.5  Differential scanning calorimetry (DSC)

A PerkinElmer Simultaneous Thermal Analyzer (STA) 6000, which was calibrated with indium was used to study the thermal behavior of the present HDPE resin. All the measurements were carried out under N₂ at a flow rate of 20ml/min to avoid thermal degradation of the test samples. The melting and crystallization peaks of the HDPE resin were obtained by using multiple heating and cooling protocols applied on to 20 to 25mg of sample polymer in a ceramic pan. The sample was heated from a temperature of 50 to 200°C at the rate 20°C /min and was equilibrated for about 15 min to eliminate any thermal or flow histories. It was then cooled down to 50°C/min at the cooling rate of 20°C/min and reheated to 200°C at the same heating rate (i.e., 20°C/min) to determine the crystallization, T_c and melting, T_m peak temperatures, respectively. The values of crystallization, T_c and melting, T_m points determined are the averages of three different runs.

The isothermal crystallization was studied at different temperatures between the determined crystallization, T_c, and melting, T_m peak temperatures. In each test, the specimen was first melted at 200°C for 15 min to eliminate thermal history and then cooled to the desired crystallization temperature at the cooling rate of 10°C/min and the corresponding thermal behavior was recorded. The isothermal analysis is performed at four different temperatures 116, 118, 119, and 120°C. The relative crystallinity (α=X(t)/X_f) as a function of time t was defined to be the fractional area confined between the rate-time curve and the baseline (Kase and Matsuo 1965) and is calculated using Equation 2.5 (refer to schematic FIGURE 2.7):

\[
\frac{X(t)}{X_f} = \frac{\int_{t_0}^{t} \left( \frac{dH}{dt} \right) dt}{\int_{t_0}^{\alpha} \left( \frac{dH}{dt} \right) dt}
\]

(2.5)

where X_f is the total crystallinity at the end of primary crystallization process, H is the enthalpy, t_0 is time at the start of crystallization process.

The non-isothermal crystallization was studied at different cooling rates of 5, 10, 20, 30, and 40°C/min. The standard protocol of history elimination was used for all the non-isothermal
DSC experiments that is the sample was kept at 200°C for 15 min in each test. Similarly, the relative crystallinity developed during the cooling process is determined to be the fractional area confined between the rate-time curve and the baseline. At a given cooling rate, the relative crystallinity \((\alpha = X(T)/X_f)\) which is a function of temperature is calculated (Equation 2.6) by integrating the area under the crystallization peak of the DSC thermogram from the equilibrium melting temperature, \(T_m^0\) up to the desired temperature and can be given as follows (Patel and Spruiell 1991):

\[
\frac{X(T)}{X_f} = \frac{\int_{T_f}^{T} H(T')dT'}{\int_{T_f}^{T_f} H(T')dT'}
\]  

(2.6)

where \(T_f\) is the temperature corresponding to the intercept of the exotherm with the baseline in the glass transition temperature region.

FIGURE 2.7: Schematic representation of relative crystallinity fraction, \(\alpha\) computation.
Chapter 3: Extrudate Swell of HDPE: Modeling using Integral and Differential Constitutive Equations

The HDPE polymer used is rheologically characterized using the multimode integral (Kaye-Bernstein-Kearsley-Zapas referred to as the K-BKZ), the differential Phan-Thien-Tanner (referred to as the PTT), the Giesekus and the Double Convected POM-POM (referred to as the DCPP) models. The simulation results computed using ANSYS POLYFLOW® are compared with experimental swell measurements studying the effects of apparent shear rate ($\dot{\gamma}_A$), temperature, Length-to-Diameter ratio ($L/D$), and the presence of reservoir (contraction). A detailed analysis on the applicability and validity of the aforementioned rheological (integral and differential/molecular) models in describing extrudate swell of the studied HDPE melt in capillary dies at high shear rates (in the range of 5 to 100s$^{-1}$) is presented here. Such detailed analysis would help one to identify a suitable rheological/constitutive model that can accurately represent the extrudate swell phenomenon especially for a highly viscoelastic polymer melt such as the one used in the present study.

3.1 Mathematical modeling

3.1.1 Governing equations

The governing equations for the flow of incompressible fluids such as polymer melts under isothermal, creeping, gravity-free and steady flow conditions are given as:

$$\nabla \cdot \mathbf{u} = 0$$  \hspace{1cm} (3.1)

$$-\nabla p + \nabla \cdot \mathbf{\tau} = 0$$  \hspace{1cm} (3.2)

where $\mathbf{u}$ is the velocity vector, $p$ is the pressure, $\mathbf{\tau}$ is the extra stress tensor of the polymer melt. For viscoelastic fluids, such as polymer melts, constitutive equations that relate the stress tensor in terms of velocity gradients are required to complete the system of equations.
3.1.2 Constitutive equations

In this chapter, mainly the integral K-BKZ (with Wagner and Papanastasiou-Screen-Macosko (PSM) damping functions) (Papanastasiou et al. 1983; Wagner 1976) and the differential Phan-Than Tanner (PTT) (Phan-Thien and Tanner 1977) models were used for the extrudate swell simulations. In addition, the differential Giesekus (Giesekus 1982) and DCPP (Clemeur et al. 2003) models were also used for few computations to evaluate their ability in predicting extrudate swell in comparison with the K-BKZ and PTT constitutive equations. A detailed review comparing various constitutive equations for representing the rheological data of polymer melts has been reported by Larson (1987) which provides useful insights on selecting appropriate viscoelastic rheological models.

A version of K-BKZ model proposed by Papanastasiou et al. (1983) and later modified by Luo and Tanner (1988) used in the simulations, is given by:

\[
\tau = \frac{1}{1-\theta} \int_{-\infty}^{t} \sum_{n=1}^{N} \frac{g_i}{\lambda_i} e^{-(t-t')/\lambda_i} \left[ h(\mathbf{I}_{C}, \mathbf{I}_{C^{-1}}) \times [\mathbf{C}_{t}^{-1}(t') + \theta \mathbf{C}_{t}(t')] \right] dt'
\]

(3.3)

where \(\lambda_i\) and \(g_i\) are the relaxation times and relaxation moduli, respectively, \(N\) is the number of relaxation modes, \(I_C\) and \(I_{C^{-1}}\) are the first invariants of the Cauchy-Green tensor \(\mathbf{C}_t\), and its inverse Finger strain tensor \(\mathbf{C}_t^{-1}\), \(\theta\) is a material constant given by \(N_2/N_1 = \theta(1-\theta)\), \(N_1 (=\tau_{11}-\tau_{22})\) and \(N_2 (=\tau_{22}-\tau_{33})\) are first and second normal stress differences, respectively, with the value of \(\theta\) between \(-0.2\) to \(-0.1\) observed from experimental measurements.

The Cauchy-Green tensor \(\mathbf{C}_t\) is calculated by using the deformation gradient tensor \(\mathbf{F}_t\) as follows (Luo and Tanner 1986a):

\[
\mathbf{C}_t = \mathbf{F}_t^T \mathbf{F}_t
\]

(3.4)

The deformation gradient tensor \(\mathbf{F}_t\) is obtained from the following relation:
\[
\frac{DF(s)}{Ds} = -L_t(s)F_t(s)
\]  
(3.5)

\[
F_t(s) \big|_{t=0} = I
\]  
(3.6)

where \( L_t(s) \) is the velocity gradient tensor, \( s=t-t' \) is a dummy variable used to integrate along the path of the particle and \( I \) is the unit tensor. Further, the inverse Finger strain tensor \( C_t^{-1} \) is simply determined by inverting \( C_t \). More particulars on the determination of Cauchy-Green tensor \( C_t \) and Finger strain tensor \( C_t^{-1} \) are available in the literature (Luo and Tanner 1986a, 1988).

The function \( h \) is a strain-dependent memory (or damping) function. We have considered two damping functions, namely the Wagner and the PSM functions. The Wagner damping function is given by (Wagner 1976):

\[
h(I_{c_t}, I_{c_t'}) = \exp(-n(\beta I_{c_t'} + (1-\beta)I_{c_t} - 3)^{0.5})
\]  
(3.7)

where \( n \) and \( \beta \) are nonlinear model constants to be determined from shear and elongational flow data, respectively. The PSM (Papanastasiou et al. 1983) damping function is given by:

\[
h(I_{c_t}, I_{c_t'}) = \frac{\alpha_p}{(\alpha_p - 3) + \beta I_{c_t'} + (1-\beta)I_{c_t}}
\]  
(3.8)

where \( \alpha_p \) and \( \beta \) are model constants to be determined from shear and elongational flow data, respectively.

The PTT model has also extensively been used in the simulation of complex viscoelastic flows and was found to be one of the simplest differential models to represent both the shear and elongational properties of polymer solutions in entry flows (Quinzani et al. 1995). For a spectrum of \( N \) relaxation modes (six are used in the present simulation), the viscoelastic extra-stress tensor \( \tau \) is obtained as the sum of \( N \) individual contributions \( \tau_i \):

\[
\tau = \sum_{i=1}^{N} \tau_i,
\]  
(3.9)
Each individual contribution $\tau_i$ is described by the PTT constitutive equation (Phan-Thien and Tanner 1977; Phan-Thien 1978):

$$\exp \left[ \frac{\epsilon_i \lambda_i}{\eta_i} tr(\tau_i) \right] \tau_i + \lambda_i \left[ \left( 1 - \frac{\xi_i}{2} \right) \tau_i + \frac{\xi_i}{2} \Delta \tau_i \right] = 2\eta_i D$$  \hspace{1cm} (3.10)

The rate of deformation tensor $D$ is defined as: $D = (\nabla \mathbf{v} + (\nabla \mathbf{v})^T)/2$, where $\nabla \mathbf{v}$ is the velocity gradient tensor. The symbols $\nabla$ and $\Delta$ over the stress tensor $(\tau)$ represent the upper and lower convective time derivatives, while $\xi_i$ and $\epsilon_i$ are non-dimensional shear and elongational material parameters, respectively.

The Giesekus model is also one of the most realistic differential viscoelastic models and is best suited for shear flows, which can predict shear thinning viscosity and also normal stresses in all directions (Giesekus 1982). Like the PTT model, a multi-mode Giesekus model is used in the present work and the viscoelastic extra-stress tensor $\tau$ is obtained as the sum of $N$ individual contributions (Equation 3.9). The individual contribution of the extra stress tensor for the Giesekus model is defined by:

$$\left( I + \frac{\alpha_i \lambda_i}{\eta_i} \tau_i \right) + \lambda_i \nabla \tau_i = 2\eta_i D$$  \hspace{1cm} (3.11)

$\alpha_i$ is a material constant for each mode, which indicates the anisotropic mobility stimulated by flow characteristics.

The differential POM-POM model (based on a molecular theory) best suited for branched polymers, is also used in the present study for comparison. The original differential form of the POM-POM model was developed by McLeish and Larson (1998). The proposed model has undergone several modifications and changes to make it appropriate for numerical schemes/formulations and to represent viscoelastic flow under complex deformations. The formulation developed by Clemeur et al. (2003) referred to as Double Convected Pom-Pom (DCPP) model is used in the present paper. For a multi-mode DCPP model, the total extra stress tensor $\tau$ is defined as the sum of individual components and the extra stress tensor contribution by
each mode is given in terms of an orientation tensor $\mathbf{S}$, and a stretching scalar $\Lambda$ (state variables) as shown by the Equation below:

$$\mathbf{\tau}_i = \frac{G_i}{1 - \zeta_i} (3\Lambda^2 \mathbf{S} - \mathbf{I}) \quad (3.12)$$

where, $G_i$ and $\zeta_i$ are shear modulus and nonlinear material constants of each mode, respectively. The state variables, $\mathbf{S}$ (orientation tensor) and $\Lambda$ (stretch variable) are obtained from the following differential equations:

$$\lambda_i \left[ \left( 1 - \frac{\zeta_i}{2} \right) \mathbf{S} + \frac{\zeta_i}{2} \mathbf{v} \right] + \lambda_i (1 - \zeta) [2\mathbf{D} : \mathbf{S}] + \frac{1}{\Lambda^2} \left[ \mathbf{S} - \frac{\mathbf{I}}{3} \right] = 0 \quad (3.13)$$

$$\lambda_{si} \frac{D\Lambda}{Dt} - \lambda_{si} (\nabla \mathbf{v} : \mathbf{S})\Lambda + (\Lambda - 1) e^{\frac{2(\Lambda - 1)}{q_n}} = 0 \quad (3.14)$$

where $\lambda_i$ and $\lambda_{si}$ are the relaxation times related to the orientation and stretching mechanisms, respectively and $q_n$ represents the number of dangling arms at the ends of the pom-pom molecule.

### 3.1.3 Boundary conditions

The conservation equations (Equations 3.1 and 3.2) combined with the constitutive equation (either the integral or differential models) need to be solved along with suitable boundary conditions. The present problem is solved by applying well-known boundary conditions such as described in the literature (Béraudo et al. 1998; Barakos and Mitsoulis 1996; Mitsoulis 2010; Ansari et al. 2013). The boundary conditions for axisymmetric flows are discussed below. Similar boundary conditions will be applied for planar flows studied in the present work. Please refer to FIGURE 3.1 representing all the necessary boundary conditions to solve the extrudate swell problem of capillary extrusion.

(a) Along the domain entry, a fully developed velocity profile is imposed, which is in turn related to the volumetric flow rate.
(b) Along the center line (for example in the case of axisymmetric flows), and because of symmetry, the radial velocity component is set to zero, as well as the shear stresses.

(c) Along the solid walls (i.e., capillary and reservoir walls), usually the no-slip velocity boundary condition is imposed. If the polymer melt slips at the wall, which is the case for the HDPE studied here, a slip law that relates slip velocity \( V_s \) to the shear stress \( \tau_w \) of the form \( V_s = -\beta_{sl} \tau_w^b \) (with \( \beta_{sl} = 1565.7 \) mm/s/MPa\(^b\) and \( b = 3.4 \) corresponding to extrusion temperature 200ºC) is used. The slip law corresponding to extrusion temperatures other than the reference temperature of 200ºC are obtained by correcting the values of slip coefficient \( \beta_{sl} \) using the time-temperature shifting factor \( a_T \). The values of slip coefficient \( \beta_{sl} \) corresponding to extrusion temperatures 160ºC, 170ºC, and 180ºC are 793.6 mm/s/MPa\(^b\), 925.0 mm/s/MPa\(^b\), and 1131.5 mm/s/MPa\(^b\), respectively. The slip law exponent \( b \) remains same for all the extrusion temperatures.

The nonlinear slip law in extrudate swell simulation is a challenging problem. An auxiliary sweep method is used to address this issue. At first, an evolution scheme on flow rate (i.e., flow rate is increased gradually to the desired value) with full slip boundary condition. Then the solution is used as initial condition to solve the problem at desired slip with evolution on slip coefficient \( \beta_{sl} \) keeping the slip law exponent \( b \) constant. This method allowed solving the extrudate swell problem with nonlinear slip condition without any major convergence issues.

(d) Along the domain exit, usually zero surface tractions and zero transverse velocity (i.e., considering fully developed profile at the exit).

(e) At the free surface, zero surface tractions along with a kinematic boundary condition of no flow normal to the surface is applied, i.e., \( \mathbf{n} \cdot \mathbf{u} = 0 \), where \( \mathbf{n} \) is the unit outward normal vector to the free surface.

Similarly, a number of relevant boundary conditions need to be defined in the case of non-isothermal extrudate swell simulations, as will be discussed in Chapter 5.
FIGURE 3.1: Schematic representation of flow domain for a typical capillary extrudate swell simulation problem along with all the necessary boundary conditions.
3.1.4 Method of solution

The finite element method (FEM) for the flow simulations uses the \( u-v-p-h \) formulation \((\text{primitive variable approach})\) for the integral models, such as the K-BKZ Wagner/PSM as in viscous flows, and \( EVSS \) \((\text{mixed variable approach})\) (Rajagopalan et al. 1992) or \( DVSS \) formulation \((\text{enhanced mixed variable approach})\) (Guénette and Fortin 1995) for the differential models, such as the multi-mode PTT, Giesekus and DCPP models, combined with special streamline-upwind/Petrov-Galerkin (SUPG) formulation (Barakos and Mitsoulis 1995; Béraudo et al. 1998). The weak formulation of the problem is obtained using biquadratic approximation for the velocities, temperature, and free surface location and bilinear approximation for the pressures. The free surface location is determined in a coupled manner along with the solution of other primary variables. Despite the fact that the SUPG FEM formulation is found to be appropriate for solving stresses for the given velocity field, the method needs some improvements to solve highly convective and/or highly viscoelastic flows. To implement SUPG FEM formulation for such highly convective and/or viscoelastic flows, a special discretization scheme called non-consistent streamline upwind (SU) method is used. More particulars on this method can be found elsewhere (Marchal and Crochet 1987). The viscoelastic extra stress tensor is added as a body force \((\text{decoupled method})\) in the discretized momentum conservation equations. Further, the integral models include an appropriate numerical integration method \((\text{such as Gauss-Laguerre quadrature method})\) to determine the stress components along the streamlines (Luo and Tanner 1986). The above numerical schemes have been used in the numerical package ANSYS POLYFLOW®\(^\circ\), which has been licensed for use in the present work. Independent numerical results using the integral method outlined by Luo and Tanner (1986a, 1986b) and Luo and Mitsoulis (1989) have confirmed the numerical results obtained from ANSYS POLYFLOW®.

A typical FEM grid for a capillary die with length-to-diameter ratio of \( L/D = 16 \) is presented in FIGURE 3.2. The flow domain shows a 12:1 abrupt contraction with the diameter of the reservoir \((\text{barrel})\) \((D_b)\) being 9.52 mm and the diameter of the die being 0.79 mm \((D)\). The length-to-diameter ratio is 16, long enough to ensure fully developed flow conditions. The extrudate length \((L_{\text{ext}})\) considered in the simulations is 20 mm \((L_{\text{ext}}/D = 25)\), necessary to capture the memory effects associated with the viscoelastic flow simulations. The flow domain is meshed using a
mapped meshing technique and the arrangement of meshes/grids is such that the grids become denser towards the entry singularity, i.e. near the entrance of the die, and coarser grids are used away from the entry singularity. Similarly, a finer grid or more mesh elements are used towards the die exit to better capture the exit singularity. The mesh is chosen based on the experience from earlier studies (both viscous and viscoelastic) of our group (Ansari et al. 2013; Ansari and Mitsoulis 2013). The grid consists of 1900 elements and a mesh four times denser is also used by dividing each element into four sub-elements to check the mesh independency of the numerical results. The mesh independency is checked such that the differences between the overall pressures and swell ratios from both the meshes are <1%.

FIGURE 3.2: A typical finite element grid for the simulation of the 12:1 abrupt circular contraction with \( L/D = 16, \) \( L_{ext}/D = 25, \) \( D=0.79 \) mm and \( 2a = 180^\circ. \)
The simulations were performed at various apparent shear rates, \( \dot{\gamma}_A \), ranging from 5 to 100 s\(^{-1}\) (experimental data are available over this range). The corresponding Weissenberg numbers (defined as mean relaxation time times the shear rate, \( \dot{\lambda}_A \dot{\gamma}_A \)) of the resin used in this study are in the range of 107.3 to 2146 with the mean relaxation time of 21.46 s (obtained using Equation 3.15). It should be noted that the simulations were performed considering the upstream contraction, and no convergence related problems were found within the range of Weissenberg numbers studied. FIGURE 3.3 shows the evolution of the global residual with the number of iterations at different flow rates for a typical 2D axisymmetric simulation of capillary swell \( L/D=16 \) (\( D=0.79 \text{mm} \)) using the integral K-BKZ Wagner model, indicating stable computations that reach convergence within the range of apparent shear rates/Weissenberg numbers studied.

FIGURE 3.3. Computational variable residual with the number of iterations at different apparent shear rates ranging from 5 to 100 s\(^{-1}\).
3.2 Results and discussion

3.2.1 Rheological characterization

The measurement of linear viscoelastic properties using a small-amplitude oscillatory shear (SAOS) test is well-established. The SAOS or frequency sweeps tests were carried using parallel plate geometry (refer to section 2.2.1 for more details). The master curves of the dynamic moduli $G'(\omega)$ and $G''(\omega)$ of the HDPE resin (with a Melt Flow Index, MFI=5.72g/10min) at the reference temperature of 200°C along with the Maxwell model predictions (using a six-mode relaxation spectrum) are shown in FIGURE 3.4. Constrained non-linear optimization technique is used to determine the discrete Maxwell relaxation spectrum parameters (Owens and Philips 2002). The fitted Maxwell parameters, relaxation times, $\lambda_i$, and the relaxation moduli, $g_i$, are listed in TABLE 3.1. Furthermore, the average relaxation time, $\lambda$, and the zero shear viscosity, $\eta_0$, can be calculated from:

$$\lambda = \frac{\sum_{k=1}^{N} g_k \lambda_k^2}{\sum_{k=1}^{N} g_k \lambda_k} \quad (3.15)$$

$$\eta_0 = \sum_{k=1}^{N} g_k \lambda_k \quad (3.16)$$

The values of these parameters are $\lambda = 21.46$ s, $\eta_0 = 215,196$ Pa·s, indicating a highly viscoelastic polymer melt.

The nonlinear model parameters $n$ and $\beta$ of the Wagner damping function, and the material parameters $\alpha_p$ and $\beta$ of the PSM damping function are obtained by fitting the shear and elongational rheological data such as the start-up of steady shear stress growth coefficient ($\eta_s^+$) and uniaxial stress growth coefficient ($\eta_E^+$). The corresponding model fittings along with the experimental rheological data are shown in FIGURE 3.5 and 3.6. As previously mentioned, the start-up of shear experiments were carried using cone and plate geometry (refer section 2.2.2 and 2.2.3 for more details) and the data could be collected only for shear rates up to $1s^{-1}$ due to the instabilities such
as edge fracture and sample ejection observed at higher strains/shear rates. However, it is found that obtaining such data at higher strains/shear rates is crucial for the accurate determination of damping function and thus extrudate swell, which would be discussed in greater detail in the next chapter. A value of $\theta = -0.15$ is used to study the effect of non-zero second normal stress difference on extrudate swell predictions and is found to decrease the swell only about 2 to 7% (depending on shear rate) and thus $\theta$ is not considered in the present simulations. This observation is in agreement with previous studies (Ansari and Mitsoulis 2013; Goublomme and Crochet 1993; Barakos and Mitsoulis 1996). The values of the relaxation spectrum and the material constants of the HDPE polymer melt at 200°C for both Wagner and PSM damping functions of the K-BKZ equations are listed in TABLE 3.1.

![Dynamic moduli, $G'$ and $G''$ (Pa) vs. Frequency, $\omega$ (rad/s)](image)

**FIGURE 3.4:** The master curves of storage ($G'$) and loss ($G''$) moduli and the corresponding fitting using a six-mode Maxwell spectrum at the reference temperature of $T_{ref} = 200^\circ$C (see TABLES 3.1, 3.2, 3.3 and 3.4).
TABLE 3.1: Relaxation spectrum at temperatures 160°C, 180°C, and 200°C for HDPE melt with K-BKZ model parameters (Wagner and PSM damping functions, $\theta=0$).

<table>
<thead>
<tr>
<th>Mode #</th>
<th>Relaxation spectrum</th>
<th>K-BKZ Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>160°C</td>
<td>180°C</td>
</tr>
<tr>
<td></td>
<td>$g_i$ (Pa)</td>
<td>$\lambda_i$ (s)</td>
</tr>
<tr>
<td>1</td>
<td>387808</td>
<td>0.0017</td>
</tr>
<tr>
<td>2</td>
<td>185307</td>
<td>0.015</td>
</tr>
<tr>
<td>3</td>
<td>93338</td>
<td>0.108</td>
</tr>
<tr>
<td>4</td>
<td>37766</td>
<td>0.796</td>
</tr>
<tr>
<td>5</td>
<td>12934</td>
<td>5.92</td>
</tr>
<tr>
<td>6</td>
<td>5025</td>
<td>60.76</td>
</tr>
</tbody>
</table>

TABLE 3.2: Relaxation spectrum at temperatures 160°C, 180°C, and 200°C for HDPE melt with PTT model parameters.

<table>
<thead>
<tr>
<th>Mode #</th>
<th>Relaxation spectrum</th>
<th>PTT Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>160°C</td>
<td>180°C</td>
</tr>
<tr>
<td></td>
<td>$\eta_i$ (Pa.s)</td>
<td>$\lambda_i$ (s)</td>
</tr>
<tr>
<td>1</td>
<td>658.26</td>
<td>0.0017</td>
</tr>
<tr>
<td>2</td>
<td>2736.25</td>
<td>0.015</td>
</tr>
<tr>
<td>3</td>
<td>10101.7</td>
<td>0.108</td>
</tr>
<tr>
<td>4</td>
<td>30052.3</td>
<td>0.796</td>
</tr>
<tr>
<td>5</td>
<td>76606.2</td>
<td>5.92</td>
</tr>
<tr>
<td>6</td>
<td>305387</td>
<td>60.76</td>
</tr>
</tbody>
</table>
FIGURE 3.5: Experimental data (symbols) and model fits (lines) of the shear stress growth coefficient $\eta^+_S$, using both integral (K-BKZ Wagner and K-BKZ PSM) and differential (PTT, Giesekus and DCPP) constitutive models.

FIGURE 3.6: Experimental data (symbols) and model fits (lines) of uniaxial stress growth coefficient $\eta^+_E$, using both integral (K-BKZ Wagner and K-BKZ PSM) and differential (PTT, Giesekus and DCPP) constitutive models.
The relaxation spectrum and the nonlinear material constants for the differential models (six-mode PTT, Giesekus and DCPP models) were obtained by fitting the corresponding constitutive equations simultaneously to the dynamic moduli, start-up of steady shear, and uniaxial elongation data. The detailed procedure for the fitting of PTT (Langouche and Debbaut 1990), Giesekus (Hulsen and Zanden 1991) and DCPP (Clemeur et al. 2003) model parameters are available in the literature and the calculated model parameters at 200°C are listed in TABLES 3.2, 3.3 and 3.4, respectively. The nonlinear materials parameters $\xi_i$ of the PTT model are set to zero as the effect of $N_2$ is not significant on extrudate swell and also to reduce the number of material parameters and thus the complexity of calculations associated with the model. The corresponding model fittings of differential models PTT, Giesekus and DCPP are also included in FIGURES 3.4, 3.5, and 3.6. It can be seen from FIGURES 3.4, 3.5, and 3.6, the rheological data (linear and nonlinear) are represented well by all constitutive equations.

TABLES 3.1 and 3.2 further include the relaxation spectrums at temperatures 160°C and 180°C that are necessary to study the effect of extrusion temperature on extrudate swell by using the integral K-BKZ and differential PTT models.

### TABLE 3.3: The relaxation spectrum along with Giesekus model parameters at 200°C.

<table>
<thead>
<tr>
<th>Mode #</th>
<th>$\eta_i$ (Pa.s)</th>
<th>$\lambda_i$ (s)</th>
<th>$\alpha_i$</th>
</tr>
</thead>
<tbody>
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<td>0.0009</td>
<td>0.01</td>
</tr>
<tr>
<td>2</td>
<td>1371.21</td>
<td>0.0075</td>
<td>0.39</td>
</tr>
<tr>
<td>3</td>
<td>5484.34</td>
<td>0.055</td>
<td>0.48</td>
</tr>
<tr>
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<td>15264.5</td>
<td>0.403</td>
<td>0.45</td>
</tr>
<tr>
<td>5</td>
<td>37988.7</td>
<td>2.99</td>
<td>0.35</td>
</tr>
<tr>
<td>6</td>
<td>154673</td>
<td>30.78</td>
<td>0.40</td>
</tr>
</tbody>
</table>

### TABLE 3.4: The relaxation spectrum along with DCPP model parameters at 200°C.

<table>
<thead>
<tr>
<th>Mode #</th>
<th>$G_i$ (Pa)</th>
<th>$\lambda_i$ (s)</th>
<th>$\lambda_{ni}$ (Pa)</th>
<th>$q_{ni}$</th>
<th>$\zeta_i$</th>
</tr>
</thead>
<tbody>
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<td>0.0009</td>
<td>0.0006</td>
<td>2</td>
<td>0.62</td>
</tr>
<tr>
<td>2</td>
<td>184712</td>
<td>0.0075</td>
<td>0.0055</td>
<td>2</td>
<td>0.02</td>
</tr>
<tr>
<td>3</td>
<td>93454</td>
<td>0.055</td>
<td>0.0372</td>
<td>7</td>
<td>0.04</td>
</tr>
<tr>
<td>4</td>
<td>37761</td>
<td>0.403</td>
<td>0.01</td>
<td>8</td>
<td>0.08</td>
</tr>
<tr>
<td>5</td>
<td>12862</td>
<td>2.98</td>
<td>0.113</td>
<td>11</td>
<td>0.02</td>
</tr>
<tr>
<td>6</td>
<td>5007</td>
<td>30.77</td>
<td>24.81</td>
<td>14</td>
<td>0.82</td>
</tr>
</tbody>
</table>
3.2.2 Flow pressure drop comparison

The pressure drop predictions obtained from the FEM flow simulations using all the constitutive equations, i.e., both integral and differential models, are compared with the experimental data of capillary extrusion in FIGURE 3.7. All the constitutive equations predict the total pressure drop of capillary extrusion reasonably well (within ± 10% error for most cases).

![Graph showing flow pressure drop comparison](image)

FIGURE 3.7: Experimental data (solid symbols) and model predictions of the total pressure drop for flow in a capillary having $L/D=16$ and $D=0.79$ mm, using the K-BKZ Wagner, K-BKZ PSM, PTT, Giesekus, DCPP models for the HDPE polymer melt at 200°C.

3.2.3 Extrudate swell simulations

Extrudate swell simulations were carried out to study its dependence on the capillary die geometric parameters, such as length-to-diameter ratio, $L/D$, presence of reservoir, and on the operating conditions, such as the apparent shear rate, $\dot{\gamma}_A$ and temperature.
3.2.3.1 Integral versus differential constitutive models

FIGURE 3.8 shows the variation of extrudate swell ratio, $B_D$ with apparent shear rate, simulated using the aforementioned constitutive equations, with reservoir, for the die with $L/D=16$ and $D=0.79$ mm. The values of the swell ratio, $B_D$, measured and the corresponding predicted values by the various models are those at a distance 20 mm ($L_{ext}/D=25$) from the die exit. At this distance the extrudate swell has been well developed and takes values close to about 90% of its ultimate value as can be seen below when the complete extrudate swell profiles are presented.

The swell ratio predicted using both integral (K-BKZ Wagner and K-BKZ PSM) and differential (PTT, Giesekus and DCPP) models increases with an increase of the apparent shear rate conforming to the general trend of experimental data. However, the integral K-BKZ model overpredicts the extrudate swell (~250% at high shear rates), while the differential models underpredict the results. In the case of the integral K-BKZ model, due to the memory effects, the melt attempts to attain its original shape in the reservoir as it exits the die (Barakos and Mitsoulis 1995, 1996; Ansari and Mitsoulis 2013). This is intriguing in a sense that while both integral and differential constitutive models represent the rheological data equally well, their predictions of extrudate swell are so distinctly different. This can be ascribed to the high elastic energy/memory effect associated with the integral K-BKZ model compared to that of differential models. On the other hand, all differential models used resulted into similar predictions. In an attempt to understand this problem, a more detailed analysis of the predictions of material functions by the two constitutive equations is performed (see Appendix C).
Figure 3.8: Experimental data (solid symbols) and model predictions of extrudate swell ratios predicted by using integral K-BKZ models with Wagner and PSM damping functions and differential PTT, Giesekus and DCPP models with reservoir.

FIGURE 3.9: Experimental data (solid symbols) and model predictions of extrudate swell ratios predicted by using K-BKZ models with Wagner and PSM damping functions and the PTT model with and without reservoir.
Extrudate swell simulations were carried without reservoir using the integral K-BKZ (Wagner and PSM) and differential PTT models and the results are presented in FIGURE 3.9. When the reservoir is excluded from the simulations, the predictions of the PTT, Giesekus and DCPP models only slightly change compared to those with the reservoir. On the other hand, for the K-BKZ case, excluding the reservoir causes significant decrease to the predictions. Therefore, memory effects are significant in flow simulations when integral models are used.

3.2.3.2 Swell profiles comparison

As discussed above, a single value of $B_D$ cannot characterize completely the extrudate behavior of the polymer as its profile is continuously been developed in the downstream direction once it is exiting the capillary die. The experimental extrudate swell profiles are compared with the simulated profiles using the K-BKZ PSM and PTT models at low and high apparent shear rates ($5 \text{ s}^{-1}$ and $100 \text{ s}^{-1}$), in FIGURES 3.10 (a) and (b), respectively. The predicted extrudate swell profiles using integral K-BKZ model keep developing along the length of the extrudate in a similar fashion with the corresponding experimental ones. It is also seen that the use of the integral K-BKZ PSM model without the presence of the reservoir results into good prediction of the whole extrudate profile. The swell predicted using the PTT model reaches its ultimate value very close to the die exit itself, indicating that the memory effects fade away fast (Guillet et al. 1996)

FIGURES 3.10: Comparison of experimental extrudate profiles with simulations for the capillary die having $L/D=16$ and $D=0.79 \text{ mm}$ at (a) a low shear rate, $5 \text{ s}^{-1}$ and (b) a high shear rate, $100 \text{ s}^{-1}$.
3.2.3.3 Pressure and stress profiles comparison

The model predictions of pressure $p$, shear stress $\tau_{12}$, and first normal stress difference $N_{1,w}$ along the wall and free-surface and first normal stress difference $N_{1,sym}$ along the axis of symmetry using K-BKZ (PSM) and PTT models, at an apparent shear rate of 26 s$^{-1}$, are depicted in FIGURES 3.11 (a) to (d), respectively. These profiles are in agreement with the general trends reported in earlier studies (Saramito and Piau 1994; Ahmed 1995; Béraudo et al. 1998; Ganvir et al. 2009).
As can be seen from FIGURES 3.11 (a) to (d), all these material function profiles along the flow domain predicted by integral K-BKZ PSM and differential PTT model are fairly similar. Some small differences exist near the die entry and exit singularities (especially for first normal stress difference along the symmetry axis) which cannot explain the significant differences in the extrudate swell predictions of the two models. Also, the first normal stress difference $N_{1,\text{sym}}$ along the axis of symmetry, predicted using the differential PTT model relaxes slightly faster than that predicted by integral K-BKZ model (FIGURE 3.11 (d)). These differences could be attributed to the variations in the numerical schemes/formulations associated with these two types of models.

### 3.2.3.4 The effect of die length

The effect of length-to-diameter ratio ($L/D$) on extrudate swell simulations using the K-BKZ PSM model is studied using three capillary dies of different $L/D$ ratios ($L/D= 5$, 16, and 33 all with diameter $D=0.79$ mm). The results are compared with experimental measurements in FIGURE 3.12 (a). The simulation results show that the swell ratio decreases with increasing the $L/D$ ratio, in qualitative agreement with the experimental observations. Flow in a longer die makes the memory effects fade away in the reservoir and causes a decrease in the extrudate swell.
Excluding the upstream reservoir eliminates the effect of die length on extrudate swell as can be seen in FIGURE 3.12 (b).

A similar trend was observed for extrudate swell simulations using the PTT model as well. The results are plotted in FIGURE 3.13. However, the effect of die length on swell is insignificant in comparison with integral model predictions and also with the actual measurements. It is worthy of mentioning that the simulation results using PTT model with and without reservoir are very similar. The comparison is consistent qualitatively, although there are significant quantitative differences. The decrease of the extrudate swell ratio with the length of the die (see also FIGURE 3.12(a) related to the fading memory of the viscoelastic polymers melt (Barakos and Mitsoulis 1995).

![Graphs showing extrudate swell simulations using the K-BKZ PSM model for three different dies with L/D=5, 16, and 33 and their comparison with experimental results (a) including the reservoir in the flow simulation (b) excluding the reservoir in the flow simulation.](image)
It would be very interesting to calculate the die length necessary for complete relaxation of memory effects associated with the integral K-BKZ model, when the reservoir is included in the flow simulations. For this purpose, the extrudate swell is calculated in capillary dies having various length-to-diameter ratios in the range of 5<L/D<500 (D=0.79 mm) at three different shear rates using the K-BKZ (PSM) model. The results are presented in FIGURE 3.14. An L/D ratio as high as 100 is needed for nearly complete relaxation of the memory effects. In this case, the swell ratio reaches the values obtained for the case ‘without reservoir’. The L/D value needed for complete relaxation becomes higher as the apparent shear rate is increased. These results show the strong memory effects associated with the use of integral constitutive equations such as the K-BKZ PSM model.
FIGURE 3.14: Variation of extrudate swell with length to diameter ratio, $L/D$, using the integral K-BKZ (PSM) model with reservoir at three different shear rates 11, 26, and 64 s$^{-1}$.

3.2.3.5 The effect of temperature

The effect of extrusion temperature (isothermal case where the die and ambient temperature are the same) on extrudate swell is also studied by using both integral K-BKZ (PSM) (with no reservoir) and differential PTT models; for the capillary die with $L/D=16$, $D=0.79$ mm. The corresponding simulation results using K-BKZ PSM and PTT models along with experimental measurements are presented in FIGURE 3.15 (a) and (b), respectively. The simulation results show that the swell ratio decreases with the temperature of the polymer melt in qualitative agreement with the experimental observations. The elasticity or modulus of the polymer melt increases and the corresponding recoverable strains and the extrudate swell increases with decrease of temperature (Henderson and Rudin 1986). The decrease in swell with temperature could be further attributed to the change in velocity profile. The slip velocity increases with temperature of the polymer melt (Ansari et al. 2012), and thus reduces the extrudate swell to a certain degree.
3.3 Conclusions

The extrudate swell simulation of a high-molecular-weight HDPE was performed using 6-mode integral K-BKZ (Wagner and PSM damping functions) and differential PTT, Giesekus and DCPP models. The effects of apparent shear rate, temperature, presence of reservoir, and die geometrical parameters on extrudate swell were studied using these two different classes of constitutive models. The predictions were compared with available experimental observations. The results showed that the extrudate swell decreases with temperature and increases with apparent shear rate consistent with experimental observations. Similarly, the simulation results (of both integral K-BKZ and differential PTT models) obtained using dies of different lengths (i.e. different lengths with constant diameter in the present study) show that the extrudate swell decreases with increasing the L/D ratio, indicating the diminishing memory of the polymer melt with die length. It was found that the integral K-BKZ models (i.e., with Wagner and PSM damping functions) highly overpredict and the differential PTT, Giesekus and DCPP models underpredict the experimental measurements, indicating the significant elastic energy/memory effects associated with integral models. Nevertheless, it was found that only the integral K-BKZ model has the ability to predict evolving nature of swell in the downstream direction. Further, integral models have the ability to predict swell ratios as high as 2.0-2.5 (i.e., representing polymer with high elasticity),
which found not to be possible for differential models. Moreover, it is observed that appropriate rheological data are needed to obtain the damping function which is valid over a broader range of shear rates/strains. As demonstrated in the next chapter, a more complete rheological characterization leads to accurate prediction of extrudate swell in the case of integral models even when the reservoir is included in the simulations.
Chapter 4: Extrudate Swell – The Effect of Damping Function

As concluded in the previous chapter, integral models such as K-BKZ type are best suited for representing swell in highly viscoelastic polymers such as the present HDPE resin. The integral K-BKZ model can be used with several forms of strain dependent damping function available in the literature. The Wagner damping function is identified as one of the simplest forms and is found to be appropriate for swell simulations; in particular, it is found to describe well experimental data of sudden step strain and relaxation for the studied HDPE. Thus we used integral K-BKZ model with Wagner damping function for the simulations in this chapter. The mathematical model, boundary conditions and the corresponding method of solution of the problem are same as described in the previous chapter.

In this study, we first discuss the new rheological data obtained by using step strain and stress relaxation for a highly viscoelastic HDPE melt for a broader range of shear strains in the range from 0.1 to 7.5 and steady shear experiments at large shear rates up to 20s\(^{-1}\) to better determine the strain-dependent damping function. The development of the partitioned plate (from AntonPaar) acquired recently by our lab has allowed the determination of such rheological properties and thus the damping function. The corresponding numerical swell predictions are compared with the experimental results obtained using capillary dies of different aspect ratios \((L/D = 5, 16, \text{and} 33, D=0.79 \text{mm})\). The agreement is found to be remarkable accounting correctly for the memory effects when the upstream contraction is used. A detailed sensitivity analysis on the Wagner damping function (using Wagner exponent, \(n\), ranging from 0.15 to 0.5 and Wagner parameter, \(\beta\), ranging from 0.2 to 0.9) in predicting the extrudate swell of the present resin is carried out demonstrating that the extrudate swell is extremely sensitive to Wagner exponent, \(n\), of the damping function, implying that its determination is significant for free surface flows such as extrudate swell (Konaganti et al. 2016b).

Finally, the integral K-BKZ Wagner model with the newly obtained damping function parameters is used to simulate the extrudate swell observed in long slit dies \((L/H=40, W/H=18, H=1\text{mm} \text{and} L/H=40, W/H=36, H=0.5\text{mm})\) at different shear rates and the results are compared with the experimental measurements as presented at the end of this chapter.
4.1 Rheological characterization

4.1.1 Small-amplitude oscillatory shear (SAOS)

While rheological characterization was previously performed on this polymer, with the availability of the partitioned plate this was extended into the nonlinear range of wider deformations/deformation rates. The linear viscoelastic properties of the resin are obtained by performing a series of SAOS and frequency sweep tests. The master curves of the dynamic moduli $G'(\omega)$ and $G''(\omega)$ obtained at the reference temperature of 200°C along with the six-mode Maxwell model fits of the HDPE resin of this study are already given Chapter 3. The corresponding Maxwell parameters, relaxation times, $\lambda_i$, and the relaxation moduli, $g_i$, are listed in TABLE 4.1. Further, includes the relaxation spectra at temperatures 160, 170 and 180°C, necessary to study the effect of extrusion temperature.

4.1.2 Step-strain stress relaxation

As previously mentioned, determination of reliable data in the non-linear viscoelastic regime for a broad range of shear strains or strain rates is vital for accurate rheological modeling of the polymer melts particularly for shear free flows. These types of measurements for highly viscoelastic polymer melts are difficult due to complications and instabilities, such as wall slip and edge fracture observed at high shear strains or shear/strain rates (Larson 1992). However, some of these difficulties can be overcome with the use of the newly developed partitioned plate as discussed elsewhere (Snijkers and Vlassopoulos 2011). The data procured using CPP under low shear rates (0.01 to 1 s$^{-1}$) are further compared with the corresponding data obtained from conventional cone and plate fixture to ensure possible issues such as response time under high strains/strain rates, axial compliance of the upper plates, and alignment of gap in the CPP fixture didn’t affect the accuracy of the rheological measurements.

FIGURE 4.1 depicts the relaxation modulus ($G(t)$) data after a sudden imposition of different levels of step strains. Since the data are nearly parallel over a sufficiently long time, it is possible to vertically shift the data to linear viscoelastic data ($\gamma=10\%$) to obtain the “damping function”. This is shown in FIGURE 4.2. Several forms of damping functions such as Wagner,
PSM, and Osaki suitable for integral K-BKZ model are available in the literature (Huang and Li 2006). However, the Wagner damping function (Equation 3.7) fits the data better than the others. Please note that under simple shear as $I_C=I_C'=3+\gamma^2$, the Wagner parameter $\beta$ disappears and the Wagner damping function (Equation 3.7) reduces to a simple form, $h(\gamma)=\exp(-n\gamma)$. As it is shown in FIGURE 4.2, the experimental data is fit with $n=0.35$.

### TABLE 4.1: Relaxation spectrum at temperatures 160°C, 170°C, 180 °C, and 200°C for HDPE melt with K-BKZ Wagner model parameters ($n=0.35$ and $\beta=0.4$)

<table>
<thead>
<tr>
<th>Mode #</th>
<th>160°C</th>
<th>170°C</th>
<th>180°C</th>
<th>200°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$g_i$ (Pa)</td>
<td>$\dot{\lambda}_i$ (s)</td>
<td>$g_i$ (Pa)</td>
<td>$\dot{\lambda}_i$ (s)</td>
</tr>
<tr>
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<td>387808</td>
<td>0.00145</td>
</tr>
<tr>
<td>2</td>
<td>185307</td>
<td>0.015</td>
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</tr>
<tr>
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<td>0.108</td>
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</tr>
<tr>
<td>4</td>
<td>37766</td>
<td>0.796</td>
<td>37766</td>
<td>0.677</td>
</tr>
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</tr>
<tr>
<td>6</td>
<td>5025</td>
<td>60.76</td>
<td>5025</td>
<td>51.71</td>
</tr>
</tbody>
</table>

**FIGURE 4.1:** Step-strain relaxation data after imposition of sudden step strains of different levels for the HDPE melt at 200°C.
FIGURE 4.2: The resulting damping function obtained from step strain relaxation experiments plotted in FIGURE 4.1 (solid symbols) along with the Wagner model predictions using $n=0.35$ (best fit).

4.1.3 Steady shear

FIGURE 4.3 shows the shear stress growth coefficient data, $\eta^+_s$, at different shear rates ranging from 0.05 to 20 s$^{-1}$ along with the prediction of the K-BKZ Wagner model (Equation 3.3) using the Wagner damping function coefficient of $n=0.35$, which fits the data excellent. Although the value of $n$ obtained from fitting the damping function data is not the best fit value, the excellent agreement of Wagner model predictions to the start-up of steady shear data indicates that $n=0.35$ is the most appropriate value for the model. As described in section 3.2, the CPP setup allows to perform measurements at higher shear rates, while with a conventional cone-and-plate fixture, we could collect experimental data only up to the shear rate of 1 s$^{-1}$ (please refer to section 3.2.1).
FIGURE 4.3: Experimental data (symbols) and the K-BKZ Wagner model predictions (lines) of the shear stress growth coefficient, $\eta_S$.

FIGURE 4.4: The slip corrected flow curve of the HDPE at 200°C compared with the LVE data along with the steady-state values of start-up of shear experiments. Good agreement is shown, demonstrating the validity of the Cox-Merz rule. The plot also includes the K-BKZ Wagner model predictions for three different values of $n=0.2$, 0.35 and 0.5.
FIGURE 4.4 compares the predictions of the Wagner model with capillary data and steady shear data obtained from the partitioned plate (FIGURE 4.3). The small differences between the experimental data are due to small slip effects that are taken into account in the simulations (as described in the boundary conditions, refer section 3.2). The predictions of the K-BKZ model using various values of \( n \) show that the shear viscosity has a relatively weak sensitivity to \( n \). As will be seen later and contrary to shear viscosity (steady flow), extrudate swell is extremely sensitive to \( n \).

4.1.4 Uniaxial extension

In pure shear flow, the first invariants of the Cauchy–Green tensor \( C_t \), and its inverse Finger strain tensor \( C_t^{-1} \) are the same, and this is the reason why the parameter \( \beta \) is vanishing. However, for extensional flow the parameter \( \beta \) appears in the equations and it can be determined using extensional data. The same extensional data given in Chapter 3 are used here and plotted in FIGURE 4.5.

FIGURE 4.5: Experimental data (symbols) and the K-BKZ Wagner model predictions (lines) for three different values of \( \beta=0.2, 0.4 \) and 0.9 of the uniaxial stress growth coefficient, \( \eta_E^+ \). The value of 0.4 is the optimum value that describes the experimental data well.
In particular, FIGURE 4.5 plots the uniaxial stress growth coefficient data \( \eta_E^+ \) at different Hencky strain rates ranging from 0.05 to 5 \( s^{-1} \) along with the K-BKZ Wagner model predictions. The optimum value of the \( \beta \) that fits the data well is 0.4. The K-BKZ Wagner predictions for two additional \( \beta \) values of 0.2 and 0.9 are also included in FIGURE 4.5 to examine the sensitivity of the extrudate swell relative to the magnitude of the tensile stress growth coefficient.

### 4.2 Extrudate swell simulations

#### 4.2.1 Contour plots

FIGURE 4.6 describes the solution behavior of the simulation results for capillary extrudate swell, \( L/D=16, D=0.79 \) mm with reservoir at an apparent shear rate, \( \gamma_A=26s^{-1} \) using integral K-BKZ Wagner model \( (n=0.35 \) and \( \beta=0.4) \), for several variables such as the axial velocity \( (U_z) \), pressure \( (P) \), shear stress \( (\tau_{rz}) \), and first normal stress difference \( (N_f) \). All the contour plots are drawn with 11 equally spaced values within the respective minimum and maximum values. FIGURE 4.6 includes the axial velocity contours \( (U_z) \) and the pressure contours \( (P) \), they clearly show the transformation from a restrained flow inside the die to a shear free flow in the extrudate. Also, it is evident from the shear stress \( (\tau_{rz}) \) (FIGURE 4.6(c)) and first normal stress difference \( (N_f) \) (FIGURE 4.6(d)) contours that the flow is fully developed at distances equivalent to about one radius downstream from the die entry. These contour graphs of process/flow variables are in qualitative agreement with simulations for capillary, slit and annular dies reported in the literature (Barakos and Mitsoulis 1995; Mitsoulis and Hatzikiriakos 2012).
4.2.2 Damping function sensitivity analysis

4.2.2.1 Extrudate swell ratio dependence

In the previous chapter, the capillary swell measurements of the HDPE melt were compared with the simulation results using the integral K-BKZ Wagner model and the Wagner exponent $n=0.21$ was used due to the limited rheological data initially available. It was observed that the model largely overestimates the measured swell values using the integral K-BKZ Wagner model (with $n=0.21$) when the reservoir was included in the simulations.

To further study the effect of damping function on extrudate swell predictions, simulations were performed for different values of the Wagner exponent, $n$, ranging from 0.15 to 0.50, at different apparent shear rates ranging from 5 to 100 s$^{-1}$. The corresponding swell ratio results at a distance 20 mm from the die exit are presented in FIGURE 4.7. The integral K-BKZ model (Wagner damping function) predicts very large swell values for small exponent values (i.e., $n<0.28$ for the present polymer). For larger $n$ values the extrudate swell drops significantly. It is noted that the small values of $n$ correspond to a more elastic polymer that manifests itself with significant...
memory effects arising from the original shape of the polymer in the reservoir, which the melt attempts to recover upon exiting the die. While such small values of $n$ do not have a significant effect in steady shear flows, i.e. shear viscosity plotted in FIGURE 4.7, for free surface flows, such as extrudate swell, becomes significant. It is also noted that these effects are more dominant at high shear rates.

Apart from the exponent $n$, it is also important to understand the effect of the Wagner parameter, $\beta$, on the extrudate swell ratio. Simulations were performed for different values of the parameter, $\beta$, ranging from 0.2 to 0.9, at different apparent shear rates ranging from 5 to 100 s$^{-1}$, for a capillary die having an $L/D=16$ and $D=0.79\text{ mm}$. As can be clearly observed from FIGURES 4.7 and 4.8, the effect of $\beta$ on extrudate swell is not as significant as it is in the case of Wagner exponent $n$.

![FIGURE 4.7: The dependence of extrudate swell ratio predicted using the integral K-BKZ model (Wagner damping function) on the Wagner exponent $n$ at different apparent shear rates ranging from 5 to 100 s$^{-1}$ and using the optimum value of Wagner parameter, $\beta=0.4$.](image)
FIGURE 4.8. The dependence of extrudate swell ratio predicted using the integral K-BKZ model (Wagner damping function) on the Wagner parameter $\beta$ at different apparent shear rates ranging from 5 to 100 s$^{-1}$ and using the optimum value of Wagner exponent, $n=0.35$.

### 4.2.2.2 Extrudate swell profile variation

Similar conclusions can be drawn from the predictions of the whole extrudate profile. FIGURE 4.9 plots extrudate profiles using various values of the $n$ (0.15 to 0.5) of the Wagner damping function, using the K-BKZ Wagner model at an intermediate apparent shear rate, 26 s$^{-1}$. The predicted extrudate diameter swell profiles keep developing with axial length of the extrudate (i.e., distance from the die exit) in a similar fashion to the experimental profiles and as reported in the literature (Huang and White 1979; Luo and Mitsoulis 1989). This behavior emphasizes the capability of the integral K-BKZ model in predicting the evolving nature of extrudate swell. Furthermore, the extrudate swell profile shows significant dependence on the exponent value of $n$, similar to results plotted in FIGURE 4.7. Solid symbols represent the experimental data which are in agreement with the predictions for the optimum value of $n=0.35$. 
FIGURE 4.9: Comparison of simulated swell profiles for the capillary die having $L/D=16$ and $D=0.79$ mm at a moderate apparent shear rate of $26\text{s}^{-1}$ for the Wagner exponent $n$ ranging from 0.15 to 0.5 and using the optimum value of Wagner parameter, $\beta=0.4$. Solid symbols represent the experimental data in agreement with the predictions for the optimum value of $n=0.35$.

Similarly, FIGURE 4.10 shows the effect of Wagner parameter $\beta$ on the whole extrudate swell profile at an intermediate apparent shear rate of $26\text{s}^{-1}$ using different values of ‘$\beta$’ (0.2 to 0.9). This plot clearly demonstrates that the effect of Wagner parameter $\beta$ on extrudate swell profile is relatively insignificant compared to that of Wagner exponent $n$. Solid symbols represent the experimental data in agreement with the predictions for the optimum value of $\beta=0.4$. It is worthy of mentioning that the value of ‘$\beta$’ is determined with certainty from uniaxial extensional data using the SER fixture. It is determined easier than $n$ which requires stress relaxation experiments at high strains which suffer from edge fracture. Therefore, it is crucial to determine the Wagner exponent $n$ value properly in order to predict extrudate swell accurately, in particular when using a highly viscoelastic polymer melt such as the present resin. This is possible with the newly available CPP fixture presented above (Snijkers and Vlassopoulos 2011).
FIGURE 4.10 Comparison of simulated swell profiles for the capillary die having $L/D=16$ and $D=0.79$ mm at a moderate apparent shear rate of $26\text{s}^{-1}$ for the Wagner parameter $\beta$ ranging from 0.2 to 0.9 and using the optimum value of Wagner exponent, $n=0.35$. Solid symbols represent the experimental data in agreement with the predictions for the optimum value $\beta=0.4$.

4.2.2.3 Stress profiles comparison

FIGURE 4.11 shows the predictions of pressure $p$, shear stress $\tau_{12}$, and first normal stress difference $N_{1,w}$ along the wall and free-surface and first normal stress difference $N_{1,\text{sym}}$, along the axis of symmetry obtained from flow simulations using the integral K-BKZ Wagner constitutive equation, at an apparent shear rate of $26\text{s}^{-1}$, respectively. The significant differences between these profiles corresponding to the three different values of the Wagner exponent $n=0.2$, 0.35, and 0.5, clearly indicate that any deviations in the non-linear viscoelastic parameters of a polymer melt will be reflected in the computations of field/process parameters (such as pressure, shear stress, and first normal stress difference) and thus on the respective swell predictions, when the integral constitutive equation is used. This plot emphasizes the importance of characterizing and using the correct material parameters (particularly those related to the damping function) to precisely simulate the viscoelastic flows.
In particular, the differences between the normal stress difference profiles along the wall and the symmetry axis (refer FIGURES 4.11(c) and (d)) corresponding to the three different Wagner exponents considered here could explain the extreme sensitivity of swell computations to low values of Wagner exponent, $n$. As can be noticed in FIGURE 4.11(c), the difference between the first normal stress difference at the wall using $n=0.2$ and $0.35$ is much higher than that of $n=0.35$ and $n=0.5$. Also, FIGURE 4.11 (d) depicts that the relaxation of first normal stress difference within the die land pertaining to $n=0.2$ is considerably slower than that of $n=0.35$ and $0.5$.

FIGURE 4.11 Comparison of (a) Pressure $p$ (b) Shear stress $\tau_{12}$ (c) First normal stress differences $N_{1,W}$ along the wall and free-surface and (d) First normal stress differences $N_{1,sym}$, along the axis of symmetry, using the integral K-BKZ model with three different Wagner exponents $n = 0.2$, 0.35 and 0.5 and using Wagner parameter $\beta=0.4$, at an apparent shear rate of $\dot{\gamma}_A = 26s^{-1}$. 
4.2.3 Comparison with experimental measurements – Capillary dies

4.2.3.1 Effect of die length (length/diameter ratio)

Apart from rheological properties or material functions, an ideal constitutive equation should be able to capture the memory effects accurately. A check to validate this is to see if the swell predictions using the new Wagner exponent \( n=0.35 \) would be able to predict the effect of die length on extrudate swell with the presence of the reservoir. FIGURE 4.12 depicts the variation of predicted extrudate swell of the present resin with apparent shear rate for three capillary dies of different \( L/D \) ratios \( (L/D= 5, 16, \text{ and } 33 \text{ with diameter } D=0.79 \text{ mm}) \) compared with experimental measurements, to study the effect of die length on extrudate swell. The simulation results show that the swell ratio decreases with increasing the \( L/D \) ratio confirming the general trend observed by many researchers (Luo and Mitsoulis 1989; Barakos and Mitsoulis 1995; Konaganti et al. 2015). The memory effects fade out with die length due to the longer residence times in longer dies and thus the extrudate swell also decreases with die length. As can been seen, there is slight overprediction of simulation results to the experimental observations for the short die \( L/D=5 \), especially at large shear rates. This can be attributed to experimental error (less than 10%) since at small \( L/D \) the magnitude of the swell is high and its development occurs fast upon the emergence of the melt from the die. Overall, the numerically predicted swell ratios are in good agreement with the experimental observations. This asserts the importance of obtaining reliable non-linear viscoelastic data for a broad range of deformations/strains and deformation rates/shear rates to accurately characterize viscoelastic polymer melts and in turn to predict the extrudate swell behavior, especially at high deformations/deformation rates observed in practical applications.
4.2.3.2 Extrudate swell profiles

As mentioned earlier, an important aspect of extrudate swell in polymer melts is that it continuously evolves as it exits the die in the downstream direction, i.e., the direction of extrusion. This is related to the continuous relaxation of normal stresses with distance in the downstream direction from the exit (Huang and Lu 2006; Mitsoulis and Hatzikiriakos 2012). FIGURE 4.13 shows the comparison of experimental profiles with the simulated ones using the K-BKZ Wagner model at apparent shear rates of 5 s\(^{-1}\), 26 s\(^{-1}\), and 100 s\(^{-1}\) for the capillary die with L/D=16 and D=0.79mm. As can be seen, the Wagner model swell profile predictions with n=0.35 are in excellent agreement with the experimental results.
4.2.3.3 Effect of extrusion temperature

The effect of extrusion temperature (isothermal case) on extrudate swell is examined using integral K-BKZ Wagner model with the new damping function parameters including the reservoir for the capillary die with \(L/D=16\), \(D=0.79\) mm. As can be seen from FIGURE 4.14, the simulation results are in good agreement with the experimental observations. The simulation results show that the swell ratio decreases with increasing temperature of the polymer melt, consistent with experimental observations and is ascribed to decrease in the elasticity or modulus of the polymer melt and thus the corresponding recoverable strains and extrudate swell (Henderson and Rudin 1986).
FIGURE 4.14: Variation of extrudate swell with temperature: simulation results using integral K-BKZ Wagner model (lines) compared with experimental measurements (solid symbols) for a capillary die having $L/D=16$ and $D=0.79$ mm at shear rates, 11 s$^{-1}$, 26 s$^{-1}$ and 64 s$^{-1}$.

4.2.4 Comparison with experimental measurements – Slit dies

The integral K-BKZ Wagner model using the newly determined damping function parameters is further used to simulate the swell observed in long slit dies. The problem becomes two dimensional and planar symmetric as the memory is not significant in long dies and thus reservoir is not included in the flow domain. The details of the mesh used, some of the contour plots, and stress profiles across the flow domain are presented in Appendix D.

4.2.4.1 Effect of width to die gap (W/H)

FIGURE 4.15 depicts the effect of die width to thickness ratio on the thickness swell measurements in long slit dies in comparison with simulation results using integral K-BKZ Wagner model. As shown, the thickness swell is decreased with increasing the width to thickness (die gap) ratio, $W/H$. This behavior is well captured by the simulation results, and the predictions
match the experimental results reasonably well. This is analogous to the effect of die gap on thickness swell in annular dies (Tanoue and Iemoto 1999).

![Graph showing extrudate swell simulations and experimental results](image)

**FIGURE 4.15:** Extrudate swell simulations (lines) using the K-BKZ Wagner model with $n = 0.35$ and $\beta=0.4$, for two different dies with $W/H=18$ and 36 ($L/H=40$, $W=18\text{mm}$) and their comparison with experimental results (solid symbols).

### 4.2.4.2 Extrudate swell profiles

**FIGURE 4.16** presents the comparison of thickness swell profiles of the present HDPE measured under isothermal conditions with simulation results of thickness swell obtained using the integral K-BKZ Wagner model at low and high shear rates, 5 and $100\text{s}^{-1}$, respectively. As can be seen, the simulation results are in good agreement with the experimental observations. The simulation results further emphasize the capability of integral constitutive equations, such as the K-BKZ Wagner model, in predicting the evolving nature of extrudate swell in the downstream direction (Konaganti et al. 2015, 2016a).
4.3 Conclusions

The non-linear shear flow properties of the polymer melt were investigated by the use of cone-and-partitioned plate (CPP) fixture of Anton Paar MCR702, which allowed us to characterize the polymer by procuring reliable rheological data for a broader range of shear strains and shear rates. It was found that the swell ratios computed using the 2D FEM based axisymmetric extrudate swell simulations including the reservoir using the new damping function parameters match the experimental measurements well. In addition, the extreme sensitivity of the swell predictions to the Wagner exponent value, $n$, in comparison to that of the Wagner parameter, $\beta$, of the damping function was also studied in this chapter. Furthermore, swell simulations were carried out for three capillary dies with different aspect ratios, $L/D=5$, 16 and 33. The simulation results showed that the swell decreases with die length and are in good agreement with the experimental observations. This confirms that the simulations now account for the associated memory correctly, using the newly determined Wagner damping function. The extrudate swell measured at different extrusion temperatures ranging from 160 to 200°C in capillary showed that swell increases with decreasing the extrusion temperature. The simulation results using integral K-BKZ model with reservoir
demonstrated the same trend and are in good agreement with the experimental results. In addition, the extrudate swell ratios measured in two long slit dies are also predicted very well using the integral K-BKZ Wagner model with the new damping function parameters. The simulation results in slit dies further confirmed the general trend of decreasing swell with width to die gap ($W/H$) ratio. The study demonstrates the importance of damping function in accurately predicting the behavior of a polymer melt in free surface flow simulations such as extrudate swell.
Chapter 5: Non-Isothermal Extrudate Swell of HDPE Melt including Crystallization Kinetics

In this chapter, the non-isothermal extrudate swell of the HDPE in long capillary and slit dies is studied using integral K-BKZ Wagner constitutive model including crystallization kinetics. A two dimensional finite element based approach is used to simulate non-isothermal extrudate swell in the presence of crystallization. The crystallization of the HDPE extrudate is considered in the mathematical formulation using the differential form of the Nakamura model. This non-isothermal extrudate swell phenomenon is simulated using the pseudo-time integral K-BKZ model with the Wagner damping function (i.e., the non-isothermal form K-BKZ Wagner model) along with the differential form of the Nakamura model to account for the crystallization of extrudate. The above formulation was implemented in ANSYS POLYFLOW®. In addition, the non-isothermal extrudate swell experimental data in long capillary and slit dies are measured at different ambient temperatures, to be compared with the numerical results. This study demonstrates the use of viscoelasticity and thermal boundary conditions accompanied by crystallization kinetics to predict the non-isothermal extrudate swell in long capillary and slit dies.

5.1 Mathematical modeling

5.1.1 Crystallization kinetics

Assuming isokinetic condition, the Nakamura formulation (Nakamura et al. 1973; Tanner 2002, 2003; Tanner and Qi 2005) to compute the relative crystallinity fraction ($\alpha$) under quiescent variable temperature conditions is given by the following equation.

$$\alpha = \frac{X(t)}{X_f} = 1 - \exp \left[ - \left( \int_0^t K_N dt \right)^m \right]$$  \hspace{1cm} (5.1)

where $m$ is the Avrami index to be determined from isothermal crystallization experiments and $K_N$ is the crystallization kinetic parameter related to the quiescent crystallization rate and is a function
of temperature and flow conditions. For process modeling the differential form of the Nakamura relation is more useful and it reads as follows:

\[
\frac{D\alpha}{Dt} = \dot{R} = m(1-\alpha)[-\ln(1-\alpha)]^{(m-1)/m} K_N
\]  

(5.2)

In addition to the thermal conditions, polymer crystallization is also sensitive to the molecular orientation caused by the flow conditions (Tanner 2002). For flows dominated by shear (such as extrusion) the crystallization kinetic parameter can be given as follows:

\[
K_N(T, f_a) = K_N(T)K_N(f_a)
\]  

(5.3)

where \(K_N(T)\) and \(K_N(f_a)\) represent the temperature and flow dependent crystallization rate parameters, respectively. There are several forms (Eder and Janeschitz-Kriegl 1998; Keller and Kolnaar 1998; Doufas et al. 2000; Zuidema et al. 2001; Janeschitz-Kriegl 2003; Zheng and Kennedy 2004; Ziabicki et al. 2004) that relate the flow dependent crystallization rate parameter, \(K_N(f_a)\) to the flow variables (such as shear rate, first normal stress difference, shear strain, recoverable shear strain, and stress) and are summarized in detail in an excellent review by Tanner and Qi (2005). In the present work, all the extrusion experiments were carried out at the reference temperature of 200°C way above the equilibrium melting point (i.e., 142°C) of the studied HDPE resin. The ambient environment/air surrounding the extrudate is kept at different temperatures below the equilibrium melting point in order to examine several cases of non-isothermal extrudate swell and the capability of the model to capture these. Therefore, the effect of flow induced crystallization inside the die is not accounted in the present simulations. The polymer melt undergoes transition from a constrained flow (shear dominated flow for extrusion using long dies) to a shear free flow and flow dependent crystallization rate parameter, \(K_N(f_a)=1\) is used under very low or negligible shear rates as reported by Wassner and Maier (2004). Thus for the present scenario, the crystallization kinetic parameter depends only on temperature, in particular for fast crystallization polymers such as HDPE.

The thermal crystallization kinetic parameter or the temperature dependent crystallization rate parameter \(K_N(T)\), is given by a Gaussian-like temperature dependence proposed by Ziabicki (1976) and is used to study the quiescent crystallization observed in many polymer processing
operations (Patel et al. 1991; Doufas et al. 1999; Doufas and McHugh 2001; Ziabicki 2004; Patel et al. 2008; Doufas 2014):

\[ K_N(T) = K_{max} \exp \left[ -4(\ln 2) \frac{(T - T_{max})^2}{D^2} \right] \]  

(5.4)

where \( K_{max} \) is a kinetic parameter at the maximum crystal growth rate at a temperature \( T_{max} \) under quiescent crystallization conditions, and \( D \) is the half-width of the Gaussian crystallization rate curve. The material-specific parameters \( K_{max}, T_{max} \) and \( D \) of the Ziabicki model can be determined by fitting the crystallinity data from isothermal crystallization experiments. The parameters are further validated by using the same parameters to fit the relative crystallinity data obtained from non-isothermal crystallization experiments. The detailed procedure to determine these parameters is presented in detail later in this chapter.

### 5.1.2 Governing equations

The general set of governing equations for the flow simulation of incompressible fluids such as polymer melts under creeping and steady flow conditions include continuity, momentum and energy balance equations as given below (Luo and Tanner 1987; Alaie and Papanastasiou 1993; Barakos and Mitsoulis 1996; Peters and Baaijens 1997; Beaulne and Mitsoulis 2007):

\[ \nabla \cdot \mathbf{u} = 0 \]  

(5.5)

\[ -\nabla p + \nabla \cdot \mathbf{\tau} = 0 \]  

(5.6)

\[ \rho C_p \nabla T = \nabla q + \nabla \cdot \mathbf{\tau} + \rho \Delta H_f \frac{D\alpha}{Dt} \]  

(5.7)

where \( \mathbf{u} \) is the velocity vector, \( p \) is the scalar pressure, \( \mathbf{\tau} \) is the extra stress tensor of the polymer melt, \( \rho \) is the density, \( T \) is the temperature \( C_p \) is the heat capacity, \( q \) is heat flow, \( \Delta H_f \) is the heat of fusion, and \( \alpha \) is relative crystallinity fraction.
The same integral K-BKZ constitutive model with Wagner damping function is used for the present simulations; where the extra stress tensor, \( \tau \) is related to the deformation history (Papanastasiou et al. 1983; Luo and Tanner 1986) is as follows:

\[
\tau = \frac{1}{1-\theta} \int_{-\infty}^{t} \sum_{i=1}^{N} \frac{\eta_i}{\lambda_i^2} e^{-(t-t')/\lambda_i} h(I_{C^{-1}, I_C}) \times [C^{-1}(t') + \theta C(t')] dt' \tag{5.8}
\]

where \( \eta_i \) and \( \lambda_i \) are the partial viscosities and relaxation times, respectively, \( N \) is the number of relaxation modes, \( I_C \) and \( I_{C^{-1}} \) are the first invariants of the Cauchy–Green tensor \( C_t \), and its inverse Finger strain tensor \( C_t^{-1} \). \( \theta \) is given by \( N_2/N_1 = \theta/(1-\theta) \), \( N_1 \equiv \tau_{11} \) and \( N_2 \equiv (\tau_{22} - \tau_{33}) \) are the first and second normal stress differences, respectively. The material constant, \( \theta \), is not considered in the these simulations as well. The Wagner damping function is (Wagner 1976 and 1979):

\[
h(I_{C^{-1}, I_C}) = \exp \left( -n \left( \beta I_{C^{-1}} + (1-\beta)I_C - 3 \right)^{0.5} \right) \tag{5.9}
\]

where \( n \) and \( \beta \) are non-linear material constants obtained from shear and extensional rheological data, respectively.

The required constitutive equation for the non-isothermal modeling is derived from the isothermal one (Equation 5.8) and is obtained by applying the time-temperature shifting concept as described by Luo and Tanner (1987). The complete details on deriving the non-isothermal integral K-BKZ model can be found in the literature (Luo and Tanner 1987; Peters and Baaijens 1997; Beaulne and Mitsoulis 2007). According to the differential form of Moorland-Lee hypothesis (1960), the equation that relates particle’s elapsed time, \( \xi \) with observer’s time, \( t \) is given as follows:

\[
d\xi = \frac{dt}{a_T(T)} \tag{5.10}
\]

where \( a_T(T) \) is time-temperature shifting factor defined by the Arrhenius equation (Dealy and Wissbrun 2012) found to be appropriate for the present polymer melt and is given by:
\[
a_i(T) = \exp \left[ - \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right]
\]  
(5.11)

where \(E_a\) is activation energy and \(R\) is the universal gas constant. The activation energy constant of the polymer melt studied in this paper is determined from the application of the time-temperature superposition (TTS) of LVE data at different temperatures and is included in TABLE 5.2. The differential form of Morland-Lee hypothesis (Equation 5.10) in its integral form becomes:

\[
\xi = \int_0^t a_i \left[ T(t') \right] dt'
\]  
(5.12)

The non-isothermal form of the integral K-BKZ model is obtained by replacing the observer's time \(t\) in Equation 5.8 with the particle's time, \(\xi\) using Equation 5.12. The resulting non-isothermal version of the constitutive equation is:

\[
\tau = \frac{1}{1-\theta} \int_{-\infty}^{\xi(t)} \sum_{i=1}^{N} \frac{\eta_{ci} e^{-(\xi-\xi')(\|\lambda\|)}}{\lambda_i^2} h(I_{ci},I_{ci}) \times [C^{-1}(t'(\xi')) + \Theta C(t'(\xi'))] d\xi'
\]  
(5.13)

Similar to the relationships reported in the literature, the effect of crystallinity on the partial viscosities of the crystallizing melt is related to relative crystallinity fraction or volumetric crystalline fraction, \(\alpha\) (Metzner 1985; Kitano et al. 1981; Tanner 2002; Tanner 2003):

\[
\frac{\eta_{ci}}{\eta_i} = \left(1 - \frac{\alpha}{A}\right)^2
\]  
(5.14)

where \(\eta_{ci}\) is the viscosity of the crystallizing melt, \(\alpha\) is the relative crystallinity fraction, \(A\) is a constant that represents non-sphericity and variable crystal size and its value is usually between 0.44 and 0.6. In this work, it is chosen be 0.54 to be consistent with the many studies reported in the literature (Tanner 2002; Tanner 2003; Tanner and Qi 2005).

The relaxation time behavior of the crystallizing polymer melt can be given as follows as determined experimentally by Boutahar et al. (1998):
\[ \lambda_{ci} = \lambda_i (1 - \alpha)^{1/2} \]  \hspace{1cm} (5.15)

The viscoelastic stresses computed using the above non-isothermal integral K-BKZ model (Equation 5.13) enter the energy equation (Equation 5.7) as a contribution to the viscous dissipation term.

As described above, the mathematical model forms a set of mass, momentum, energy balance equations along with the relationships of quiescent crystallization kinetics appropriate for extrusion. The resulting equations need to be solved simultaneously with appropriate boundary conditions to simulate the non-isothermal extrudate swell behavior that includes crystallization kinetics.

### 5.1.3 Boundary conditions

The following are the general set of boundary conditions used for the simulation of non-isothermal extrudate swell in viscoelastic polymer melts (Luo and Tanner 1987, Patel et al. 1991, Chang and Yang 1994; Barakos and Mitsoulis 1996; Coppola et al. 2004; Sarafrazi and Sharif 2008; Sun et al, Doufas 2014).

A fully developed velocity profile \( u_z(r) \) (corresponding to the constant flow rate) at the inlet, a nonlinear slip condition where the slip velocity \( V_s \) is related to the wall shear stress \( \tau_w \) using \( V_s \) (mm/s) = -1565.7\( \tau_w \) (MPa)\(^{3.4} \) (details can be found in Ref. 25) at the wall, and zero surface traction and transverse velocity at the domain exit, zero tractions and the kinematic boundary condition of no flow \( n.u = 0 \) on the extrudate/free-surface, zero transverse velocity \( u_r \) and shear stress \( \tau_{rz} \) along the axis of symmetry are the common boundary conditions used as described in the previous chapters. For the thermal boundary conditions, we have a constant temperature at the die inlet and wall \( T_w = T_0 \), a convective boundary condition of the form \( q = h_T(T - T_a) \) on the free surface, \( h_T \) is the local heat transfer coefficient (Vlachopoulos and Strutt 2002) and \( T_a \) is the ambient temperature, zero heat flux at the domain exit and the axis of symmetry. Regarding the boundary conditions for the crystallinity, we considered zero crystallinity fraction at the die inlet, insulated boundary (i.e., \( \frac{\partial \alpha}{\partial t} = 0 \)) for all the remaining boundaries (Sun et al. 2000).
All the relevant boundary conditions used for the present simulations are compiled in a schematic shown in FIGURE 5.1.

FIGURE 5.1: Relevant boundary conditions of non-isothermal extrusion flow through a long capillary die.

5.1.4 Method of solution

Initially, the system of equations described for the non-isothermal flow simulation are solved without considering the crystallization kinetics using the primitive variable approach in terms of velocities, pressure, temperature, and free surface, i.e., \(u-v-p-T-h\) formulation (for 2D non-isothermal case) along with the SUPG FEM formulation. The weak formulation of the problem is obtained using biquadratic approximation for the velocities, temperature, and free surface location and bilinear approximation for the pressures. The SUPG FEM formulation is found to be appropriate for solving stresses for the given velocity field. The method is further improved to solve highly convective and/or highly viscoelastic flows by incorporating a special discretization scheme called non-consistent streamline upwind (SU) method (Marchal and Crochet 1987). The viscoelastic extra stress tensor is added as a body force (decoupled method) in the discretized momentum conservation equations. The computation of the stress tensor components uses an appropriate numerical integration technique, such as the Gauss-Laguerre quadrature method (Luo and Tanner 1986). This well-known numerical scheme has been made available in the numerical package ANSYS POLYFLOW®.
As mentioned before, partial viscosities and relaxation times of the crystallizing polymer melt (i.e., extrudate under non-isothermal conditions in this work) depend on the relative crystallinity fraction ($\alpha$). Also, the enthalpy of fusion acts as a heat source in the energy balance equation (refer Equation 5.7). The relative crystallinity fraction ($\alpha$) is evaluated with the help of transport equation (Equation 5.2) and is solved simultaneously along with all the necessary governing equations. The simulation results of steady-state non-isothermal swell without crystallization are used as initial guesses/solutions for these simulations. The Nakamura form of crystallization kinetics and the transport equation of relative crystallinity are implemented in the ANSYS POLYFLOW® formulation using a user defined function written in CLIPS (C Language Integrated Programming System) language.

A typical two dimensional FEM grid for a long capillary die with length-to-diameter ratio of $L/D=33$, $D=0.79\,\text{mm}$, extrudate of length ($L_{\text{ext}}$) 20 mm (i.e., $L_{\text{ext}}/D=25$) is considered for the capillary simulations. The length of the extrudate 20 mm for the simulations reported in this paper is chosen upon performing simulations using different extrudate lengths and also based on the experience from our previous studies. As mentioned earlier, it was observed that the swell is at least 90% recovered at this distance down the exit. The mesh over the flow domain is generated by using a typical mapped-mesh technique. A mapped-mesh of 2240 elements and 9177 nodes is used for the present capillary swell simulations. Finer elements are used close to the die exit and the wall to take care of any singularities. The mesh independency of the numerical results is studied by using a denser mesh created by subdivision of each element into four sub-elements. By refining the mesh, we have more elements concentrated near the die exit and wall where the solution is expected to be most sensitive. The mesh independency is validated such that the differences between the overall pressures, solution vector of the velocity and swell ratios from both meshes are <1%. More details on the procedure followed for mesh refinement analysis can be found elsewhere (Luo and Mitsoulis 1990). Similar mesh has been used for non-isothermal swell simulations in long slit dies. Both capillary and slit die simulations were performed over a broad range of apparent shear rates from 5 to 100s$^{-1}$, no convergence related problems were observed within the range of Weissenberg numbers, i.e., mean relaxations times apparent shear rate, (107.3 to 2146) studied.
5.2 Results and discussion

5.2.1 Rheological characterization

The present resin has been well characterized rheologically as described in detail in chapters 3 and 4. The rheological or material parameters corresponding to the reference temperature of 200ºC (see TABLE 4.1) are used for the simulations reported in this chapter.

5.2.2 Crystallization kinetics

FIGURE 5.3 depicts the typical DSC thermograph of the present HDPE measured at a rate of 20ºC/min. The melting and the crystallization peak temperatures are observed at 132.3ºC and 113.5ºC, respectively and the onset of crystallization at 118.6 ºC (see FIGURE 5.3).

![DSC Thermogram](image)

**FIGURE 5.2:** The DSC thermograph of the HDPE polymer of present study. The melting and cooling peaks were observed at 132.3ºC and 113.5ºC, respectively. The onset of crystallization temperature, $T_{onset}=118.6$ºC is also marked in the plot.
The relative crystallinity data for the present HDPE obtained from isothermal crystallization experiments at four different temperatures, namely, 116, 118, 119, and 120°C are depicted in FIGURE 5.3. As can be observed from the data, with crystallization temperature the probability of obtaining stable nuclei becomes lower and thus longer time periods are required for the crystallization. Further, the data clearly shows that the time taken for half of the crystallization to occur (i.e., half time, \( t_{1/2} \), a measure of crystallization rate) strongly depends on the crystallization temperature (refer TABLE 5.1).

The isothermal Avrami relation (Equation 5.1) is used to model the isothermal/quiescent crystallization obtained from DSC. As the Avrami equation does not account for the secondary crystallization process and thus is valid only within in the primary growth region corresponding to the relative crystallinity of 20 to 80% (Mandelkern 2002; Patki et al 2007; Derakhshandeh 2014). FIGURE 5.4 shows the Avrami analysis of the present data within this crystallinity range. The half times and the Avrami indices at each crystallization temperature studied are listed in TABLE 5.1. The Avrami indices thus calculated are around 2. The fractional number is generally ascribed to several factors including volume changes on crystallization, incomplete crystallization, annealing and various mechanisms involved during crystallization (Shan and Lickfield 2007). The Avrami index obtained here is lower than the theoretical value and can be attributed to the nucleation effect observed in commercial polyethylene resins (Janimak and Stevens 2000).
FIGURE 5.3: Isothermal crystallization data for HDPE used in this study at different crystallization temperatures.

FIGURE 5.4: Avrami analysis of HDE’s isothermal crystallinity data.
An empirical model proposed by Ziabicki that relates crystallization half-times to temperature is given by:

\[
\left( \frac{1}{t_{1/2}} \right) = \left( \frac{1}{t_{1/2}} \right)_{\text{max}} \exp \left[ -4 \ln(2) \left( \frac{T - T_{\text{max}}}{D} \right)^2 \right]
\]  

(5.15)

The parameters \( (1/t_{1/2})_{\text{max}} \), \( T_{\text{max}} \), and \( D \) can be obtained using a non-linear regression method. It is noted that the parameter \( K_{\text{max}} \) in Equation 5.4 is nothing but \( (\ln 2)^{1/n} \left( \frac{1}{t_{1/2}} \right)_{\text{max}} \). However, performing non-linear regression analysis on limited experimental data over a narrow temperature range can lead to inaccurate values. Since the isothermal crystallization experiments can only be carried over a narrow temperature range (in particular for HDPE) at low undercoolings, such data need to be extrapolated to lower temperatures (i.e., high super-coolings) in order to make the data appropriate to study the crystallization observed in polymer processing (Patel et al. 1991; Doufas 2014).

Therefore, the data has been extrapolated to lower temperatures using the well-known Hoffman-Lauritzen theory (Hoffman et al. 1976):

\[
\left( \frac{1}{t_{1/2}} \right) = \left( \frac{1}{t_{1/2}} \right)_{0} \exp \left[ -\frac{U^*}{R_{0}(T - T_{\infty})} \right] \exp \left[ -\frac{C}{T \Delta Tf} \right]
\]  

(5.16)

where \( U^* \) is the activation energy for segmental jump rate in polymers, \( T_{\infty} - 30^\circ \text{C} \), \( f (=2T/(T+T_{\infty}^0)) \) is the correction factor to account the drop in latent heat of fusion (\( \Delta H_f \)) as the temperature is decreased. FIGURE 5.5 shows the Haffman-Lauritzen fit (using Equation 5.16) of the experimental data and the constants \( (1/t_{1/2})_0 \) and \( C \) are found to be \( 58s^{-1} \) and \( 4.974\times10^4 \left( ^\circ \text{K} \right)^2 \), respectively. Using these constants, the half times of crystallization can now be extrapolated to lower temperatures as shown in FIGURE 5.6. The Ziabicki model parameters are determined by fitting Equation 5.15 to the extrapolated data and are included in TABLE 5.2. All the physical and thermal properties of the present HDPE resin required for non-isothermal viscoelastic flow simulations are also given in TABLE 5.2.
TABLE 5.1: Half-times and Avrami indices at the four different crystallization temperatures for the studied HDPE resin.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Half-time, t1/2 (s)</th>
<th>Avrami index, n</th>
</tr>
</thead>
<tbody>
<tr>
<td>116</td>
<td>80</td>
<td>2.03</td>
</tr>
<tr>
<td>118</td>
<td>123</td>
<td>2.13</td>
</tr>
<tr>
<td>119</td>
<td>156</td>
<td>2.02</td>
</tr>
<tr>
<td>120</td>
<td>208</td>
<td>1.89</td>
</tr>
</tbody>
</table>

TABLE 5.2: The necessary physical and thermal properties of the present HDPE resin. Also, includes Ziabicki model parameters.

<table>
<thead>
<tr>
<th><strong>Ziabicki model parameters</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{max}$ (s$^{-1}$)</td>
</tr>
<tr>
<td>$T_{max}$ (°C)</td>
</tr>
<tr>
<td>$D$ (°C)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Physical and thermal properties of the studied HDPE</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium melt point, $T_m^0$ (°C) (McHugh et al. 1993)</td>
</tr>
<tr>
<td>Glass transition temperature, $T_g$ (°C) (Chen et al. 2011)</td>
</tr>
<tr>
<td>Activation energy of segmental jump, $U^*$ (kJ/mol) (Hoffman &amp; Weeks 1962)</td>
</tr>
<tr>
<td>Melting peak temperature, $T_m$ (°C)</td>
</tr>
<tr>
<td>Crystallization peak temperature, $T_c$ (°C)</td>
</tr>
<tr>
<td>Reference temperature, $T_0$ (°C)</td>
</tr>
<tr>
<td>Onset of crystallization temperature, $T_{onset}$ (°C)</td>
</tr>
<tr>
<td>Activation energy, $E_a$ (kJ/mol)</td>
</tr>
<tr>
<td>Universal gas constant, $R$ (J/mol°C)</td>
</tr>
<tr>
<td>Density, $\rho$ (kg/m$^3$)</td>
</tr>
<tr>
<td>Heat capacity, $C_p$ (kJ/kg°C) (Martienssen &amp; Warlimont 2005)</td>
</tr>
<tr>
<td>Enthalpy of fusion, $\Delta H_f$ (J/kg) (McHugh et al. 1993)</td>
</tr>
<tr>
<td>Thermal conductivity, $k$ (W/m°C) (Martienssen &amp; Warlimont 2005)</td>
</tr>
<tr>
<td>Heat transfer coefficient, $h_f$ (W/m$^2$°C) (Vlachopoulos &amp; Strutt 2002)</td>
</tr>
</tbody>
</table>
\[ \ln\left(\frac{1}{t_{1/2}}\right) + \frac{U^*}{R(T-T_0)} \]

FIGURE 5.5: Haffman-Lauritzen fit of isothermal crystallization data.

FIGURE 5.6: Inverse half time data extrapolated using Haffman-Lauritzen theory along and the corresponding Ziabicki model fit.
A series of non-isothermal crystallization experiments were performed on the present polymer at different cooling rates, namely 5, 10, 20, 30, and 40 ºC/min and the corresponding data are given in FIGURE 5.7. The differential form of the Nakamura model (Equation 5.2) along with the Ziabicki model for the Avrami crystallization parameter (Equation 5.4) is considered to be one of the most appropriate ways of predicting such non-isothermal crystallization data and is used in this study as well. An infinitely small value of relative crystallinity at each cooling rate is used as initial condition and the same Ziabicki model parameters obtained from fitting the isothermal crystallization data (listed in TABLE 5.2) are used to predict the relative crystallinity profiles (refer to FIGURE 5.7 where the solid lines are the model predictions) using the differential form of the Nakamura model. As can be seen, the model predictions are in good agreement with the experimental data validating the use of Ziabicki model parameters obtained from the isothermal crystallization data (Patel and Spruiell 1991, Derakhshandeh et al. 2014).

FIGURE 5.7: Non-isothermal crystallization data obtained at various cooling rates and the corresponding model fittings using the differential form of Nakamura model.
5.2.3 Extrudate swell simulations

A series of isothermal (die and ambient environment are kept at the same temperature, i.e., 200ºC) and non-isothermal (die is kept at an extrusion temperature of 200ºC and ambient air at 25ºC or 110ºC) extrudate swell measurements are carried out using long capillary and slit dies. The simulations were performed using the aforementioned mathematical model to predict the experimental extrudate swell data and the results are presented in this section.

5.2.3.1 Contour plots

The solution behavior of the present non-isothermal swell simulation results is described by the contour plots of capillary extrudate swell, \( L/D = 33, D = 0.79 \) at an apparent shear rate, \( \dot{\gamma}_A = 26 \) s\(^{-1}\) using the K-BKZ Wagner model with Nakamura crystallization kinetics as shown in FIGURE 5.8. The results shown are for the case of polymer melt at 200ºC extruded to ambient air at 70ºC. FIGURE 5.8 includes the contour plots for several process/flow variables such as the axial velocity \( U_z \), pressure \( P \), shear stress \( \tau_{rz} \), first normal stress difference \( N_1 \), temperature \( T \), and relative crystallinity \( \alpha \). All the contour plots are drawn with 11 equally spaced values between the corresponding minimum and maximum values. The axial velocity contours \( U_z \) (FIGURE 5.8(a)) and the pressure \( P \) (FIGURE 5.8(b)) contours clearly demonstrate the transition of polymer melt from a well constrained flow inside the die to a shear free flow in the extrudate. In addition, the contours of shear stress \( \tau_{rz} \) (FIGURE 5.8(c)), and first normal stress difference \( N_1 \) (FIGURE 5.8(d)) indicate that the flow is fully developed until very close to the die exit and most of the flow rearrangement happens at the proximity of die exit. Most importantly, the contour plots of temperature \( T \) and relative crystallinity \( \alpha \) are also included in FIGURE 5.8. It is evident from FIGURE 5.8(e) that the temperature of the extrudate drops gradually with distance down the die due to convective heat transfer to the surrounding environment and in a similar fashion the relative crystallinity fraction \( \alpha \) (shown in FIGURE 5.8(f)) increases steadily with extrudate length. The contour graphs of process/flow variables reported here are in qualitative agreement with the simulation results for capillary, slit and annular dies in the literature (Kiriakidis and Mitsoulis 1993; Barakos and Mitsoulis 1996; Sun et al. 2000; Doufas 2014).
5.2.3.2 **Effect of shear rate on quiescent crystallization**

As mentioned before, since the extrusion temperature (200°C) is well above the equilibrium melting point (142°C) it is rational to consider that there is no or limited FIC crystallization inside the die. This behavior was observed in the capillary flow several HDPEs or polypropylenes reported in the literature where the extrusion temperatures are well above their corresponding equilibrium melt points (Titomanlio 1990; Lino 2008; Derakhshandeh et al. 2015). FIGURE 5.9 shows the flow curves of the present HDPE at different extrusion temperatures shifted by applying the time-temperature superposition using the shift factors determined from LVE measurements (at
the reference temperature, \( T_0 = 200^\circ C \). Good superposition of the data indicates that there is no crystallization inside the capillary, at least within the extrusion temperature range 160 to 200ºC.

Moreover, as the polymer melt is extruded to ambient temperatures below the equilibrium melting point and the flow becomes shear free (i.e., very low or negligible shear rates). The effect of shear rate or flow variables on FIC would be insignificant as reported elsewhere (Wassner and Maier 2000; Tanner 2002). Thus, the apparent shear rate (which in turn controls the crystallization time of the extrudate at a particular ambient temperature) only influences quiescent crystallization.

To elucidate the effect of apparent shear rate on non-isothermal viscoelastic flow simulations with crystallization kinetics, the contour plots of temperature (isotherms) near the die exit region of capillary die \((L/D=33, D=0.79\text{mm})\) at three different apparent shear rates \((5, 26, \text{and } 100\text{s}^{-1})\) when the polymer melt at 200ºC is extruded to ambient air at 70ºC are presented in

![Flow Curve](image)

**FIGURE 5.9:** The flow curves of the present HDPE polymer at different temperatures shifted by using TTS using the shift factors determined from LVE measurements \((T_0=200^\circ C)\). The solid line represents the flow curve corresponding to LVE measurements.
FIGURE 5.10. The ambient temperature 70°C is chosen for these simulations as the present polymer has the highest crystallization rates around this temperature (refer FIGURE 5.6). FIGURE 5.10 clearly shows that the temperature drop is higher at low apparent shear rate compared to high apparent shear rates in consistent with previous works (Barakos and Mitsoulis 1996, Luo and Tanner 1987). The relative crystallinity fraction profiles computed on the free surface at these three different apparent shear rates given in FIGURE 5.11 clearly indicate the degree of quiescent crystallization is predominant when the temperature drop is high and the extrudate surface temperature is close to the maximum crystallization rate temperature, $K_{\text{max}}=74^\circ\text{C}$ (refer TABLE 5.2). Similar results were obtained using a long slit die (L/H=40, W/H=18, H=1mm), not presented here.

FIGURE 5.10: Contour plots of temperature in non-isothermal extrudate swell simulations at three apparent shear rates 5, 26, and 100 s$^{-1}$ where the polymer melt at 200°C is extruded through a long capillary die to ambient air at 70°C.
5.2.3.3 Effect of ambient temperature on quiescent crystallization

In order to examine the effect of ambient environment/air temperature on quiescent crystallization, a series of non-isothermal swell simulations are performed keeping the polymer melt inside the die at a constant temperature of 200°C but the ambient air at various temperatures from 40 to 100°C. The corresponding contour plots of relative crystallinity fraction in the extrudate region are given below in FIGURE 5.12. As can be clearly observed from the contour plots, the amount of crystallization in the extrudate shows a maximum with ambient air temperature (within the ambient air temperature range of 40 to 100°C) and the maximum crystallization seems to occur when the ambient air is kept at the temperature of 70°C. This is due to the fact the extrudate temperature is close to the maximum rate crystallization temperature $K_{max}=74^\circ$C (refer TABLE 5.2) and thus leads to very high crystallization rates in comparison with other ambient air temperatures.
FIGURE 5.12: The contour plots of relative crystallinity fraction ($\alpha$) over the extrudate at different ambient temperatures from 40-100°C obtained at an apparent shear rate of 26s$^{-1}$ using a long capillary die of $L/D=33$, $D=0.79$mm.

5.2.3.4 Comparison with experiments

We found that the apparent shear rate (or flow rate) only has a moderate effect on isothermal extrudate swell of the present polymer, i.e., isothermal extrudate swell ratio increases slightly with apparent shear rate as observed by both experiments and simulations (Behzadfar et al. 2015, Konaganti et al. 2016a, 2016b) and similar behavior was observed by many researchers as published elsewhere (Anand and Bhardwaj 1980; Garcia-Rejon 1980; Barakos and Mitsoulis 1996). In this work, to understand the effect of apparent shear rate on non-isothermal extrudate swell, swell measurements are carried out at various shear rates keeping the ambient environment
well below the extrusion temperature, say 110°C or 25°C. The non-isothermal and isothermal swell measurements and the corresponding simulation results of long capillary die are compared in FIGURE 5.13(a). As can be seen, apparent shear rate has a considerable effect on extrudate swell compared to that of isothermal conditions. Similar results are obtained when a long slit die (\(L/H=40\), \(W/H=18\), \(H=1\)mm) is used to describe non-isothermal extrudate swell at different apparent shear rates as shown in FIGURE 5.13(b).

Further, FIGURES 5.13(a) and (b) also demonstrate the effect of ambient temperature or the degree of cooling (i.e., temperature drop) on non-isothermal extrudate swell. As depicted, extrudate swell ratio decreases with decreasing the ambient air temperature. This can be attributed to the “hot layer effect” due to the significant cooling (temperature drop) of extrudate surface. The substantial heat loss on the free-surface leads to temperature at the exit plane lower than the wall temperature forming an effective hot layer near the die wall. The hot layer formed causes decrease in swell, according to the inelastic swelling mechanism. This behavior is explained in greater detail in a pioneering work by Luo and Tanner (1987).

FIGURE 5.13: The extrudate swell as a function of apparent shear rate when the polymer melt at 200°C is extruded to two different ambient temperatures 25°C & 110°C using (a) a long capillary die of \(L/D=33\), \(D=0.79\)mm and (b) a slit die long slit die of \(L/H=40\), \(W/H=18\), \(H=1\)mm. Solid symbols represent the experimental data and solid lines are corresponding simulation predictions.
As described in Chapters 3 and 4, extrudate swell evolves in the downstream direction upon exiting the die. To further validate this, the non-isothermal extrudate swell profiles (obtained by measuring swell ratios at different distances down the exit at an apparent shear rate of $26s^{-1}$) are compared with the simulated swell profiles for both capillary and slit dies in FIGURES 5.14(a) and (b), respectively. The simulation results are found to be in very good agreement with the experimental measurements.

![Graph](image)

**FIGURE 5.14:** Non-isothermal extrudate swell profile data compared with simulation results using the integral K-BKZ (Wagner) model with Nakamura crystallization kinetics at an apparent shear rate of $26s^{-1}$ in long (a) Capillary and (b) Slit dies.

### 5.3 Conclusions

The effect of non-isothermal conditions (i.e., in particular ambient temperature) on the extrudate swell of a high molecular weight HDPE is examined both experimentally and numerically. A pseudo-time based non-isothermal integral K-BKZ model including crystallization kinetics described by the Nakamura model is implemented in ANSYS POLYFLOW® to simulate non-isothermal extrudate swell. The simulation results further indicated that at a fixed shear rate, the amount/rate of crystallization on the extrudate shows a maximum with ambient temperature, similar to the crystallization kinetics described by Ziabicki model. Also, the non-isothermal extrudate swell measurements in long capillary and slit dies were obtained at two different ambient...
temperatures 110°C and 25°C and are validated using the simulation results. The described mathematical model demonstrated the importance considering the effects of viscoelasticity and thermal boundary conditions accompanied by crystallization kinetics to predict the non-isothermal extrudate swell in viscoelastic polymer melts.
Chapter 6: Conclusions and Recommendations

This chapter summarizes the important results and observations obtained from the modeling and experiments reported in the thesis. Recommendations for further research are also provided.

6.1 Conclusions

Key conclusions and contributions to the knowledge are described below.

- A novel, reliable and efficient extrudate swell measuring set-up with an on-line data acquisition system is designed and used in the present work. This system allows one to measure extrudate swell under different conditions (steady state or transient), gravity free, isothermal and non-isothermal conditions. The system can also measure the complete extrudate profile by moving the micrometers to different locations in the downstream direction. Moreover, the measuring system is suitable for both capillary and slit extrudates.

- A comprehensive analysis on the applicability and validity of various rheological (integral and differential/molecular) models in describing extrudate swell of a high molecular weight viscoelastic HDPE polymer over a broad range of shear rates (5 to 100s⁻¹) is performed. It was found that only integral constitutive model such as K-BKZ type can account for the significant memory effects associated with such polymer melts. Further, integral models can also predict the evolving nature of the swell.

- Overestimation of experimental extrudate swell by the K-BKZ model invoked the importance of procuring non-linear viscoelastic flow properties of such highly viscoelastic polymer resins for a broader range of deformations/deformation rates in an attempt to determine the accurate damping function of the material.

- The Cone Partitioned Plate (CPP) fixture from AntonPaar was used to procure non-linear rheological data of the studied HDPE resin for shear strains as high as 7.5 and shear rates as high as 20s⁻¹ which was not possible using conventional fixtures (like parallel plate and cone and plate). Thus, a more complete rheological characterization was performed.
A new damping function that is appropriate for a wide range of deformations / deformation rates was determined using the data obtained from CPP fixture. This has proven to be extremely important in simulating free surface flows such as extrudate swell in highly viscoelastic polymer melts. The simulation results of extrudate swell in capillary and slit dies obtained using the newly determined damping function parameters explained the overprediction of the extrudate swell when the contraction was included in the simulations.

A detailed sensitivity analysis of extrudate swell predictions with Wagner damping function parameters revealed that extrudate swell is extremely sensitive to Wagner exponent, \( n \), in comparison with the parameter, \( \beta \) to be relatively less important.

A non-isothermal extrudate swell model that is appropriate for highly viscoelastic polymer melts was developed and implemented to address the ongoing crystallization over the extrudate. The model combines the integral K-BKZ Wagner model with the differential form of the Nakamura crystallization kinetics to predict non-isothermal extrudate swell measurements in capillary and slit dies.

### 6.2 Recommendations for future work

Several important aspects of extrudate swell in viscoelastic polymer melts are yet to be studied. Some of the recommendations are summarized below, as possible objectives for future work.

- In order to completely explore the capability of the integral constitutive models in representing viscoelastic phenomena such as extrudate swell, the present work should be extended to three dimensional free surface flows, possibly using FEM formulation such as 3D Lagrangian integral method (3D-LIM) (Rasmussen 2000). This would allow one to study the effects of complex die head designs (as found in industry) on extrudate swell of polymer melts.

- So far, the flow simulation of viscoelastic polymer melts in co-extrusion (or multi-layer extrusion) with free-surface and interface predictions using integral constitutive models has gained no or very little attention. A systematic study on such systems would be of great interest for both academia and industry.
- Even though the rheology and constitutive modeling of complex thermoplastic polymer systems such as block copolymers, polymer blends (miscible or multiphase), polymer composites have been studied to some extent (Osaki et al. 1979; Rolón-Garrido and Wagner 2009; Jaishankar and McKinley 2014). The extrudate swell behavior of such complex systems has not been investigated both experimentally and numerically. A detailed study on extrudate swell of such polymer blends/composites would be very useful to understand their implications in their processing techniques.
Bibliography


Huynh BP (2000) XIIIth International Congress on Rheology. Cambridge, UK


Appendices

Appendix A: Bagley and slip (Mooney analysis) of the capillary data

The Bagley correction that relates the extra pressure needed by the melt to flow into the capillary die can be calculated by plotting the pressure versus die aspect ratios (L/R) at fixed apparent shear rates. By extrapolating the straight lines to zero L/R, the excess pressure (Bagley correction) can be calculated. The total pressure drop in a capillary is considered as the sum of pressure drop across the capillary ($\Delta p_{cap}$) and pressure drop due to ends ($\Delta p_{ends}$):

$$\Delta p = \Delta p_{cap} + \Delta p_{ends} = \frac{2\tau_w L}{R} + \Delta p_{ends}$$  \hspace{1cm} (A.1)

$$\tau_w = \frac{\Delta p - \Delta p_{ends}}{2L/R},$$  \hspace{1cm} (A.2)

where $\Delta p_{ends}$ is the ends pressure. Figure A.1 shows the Bagley plot of HDPE used in this study.

![Bagley plot of the HDPE capillary data at 200°C.](image)

FIGURE A.1: Bagley plot of the HDPE capillary data at 200°C.
When it occurs, wall slip reduces the shear rate near the wall and complicates the analysis of experimental data. Several studies and methods have been proposed to account for slip effects (Mooney, 1931; Ramamurthy, 1986; Hatzikiriakos and Dealy 1992; Rosenbaum and Hatzikiriakos 1997). The Mooney analysis method is a well-established method which can be used to calculate the true apparent shear rate corrected for the effect of slip, $\dot{\gamma}_{A,s}$ (Mooney 1931).

The Bagley-corrected flow curves of the HDPE polymer melt at 200°C, using capillary dies of three different diameters $D=0.43, 0.79$ and 2.11 mm (all having the same $L/D=16$) along with LVE data are presented in FIGURE A.2. The diameter dependence of the flow curve and the significant deviation of the capillary data from the LVE curve (no-slip) indicate the presence of slip for the present polymer melt. The data in FIGURE A.2 can be used to determine the slip velocity of this polymer as a function of wall shear stress using the well-established Mooney analysis (1931). The calculated slip velocity from the Mooney analysis is plotted as a function of the wall shear stress in FIGURE A.3. The slip data is fitted with a nonlinear slip law, $V_s = -\beta_{sl} \tau_w^b$, with $\beta_{sl} = 1565.7$ mm/s/MPa and $b=3.4$, indicating considerable slip for the present polymer melt.

![FIGURE A.2: The Bagley-corrected flow curves using three different capillary dies of diameters $D=0.43, 0.79$, and 2.11 mm (with $L/D=16$) along with the LVE plotted as a flow curve (no-slip). The diameter dependence of the flow curves implies the presence of slip, and the Mooney method can be used to determine slip as a function of the wall shear stress.](image-url)
FIGURE A.3: The slip velocity ($V_s$) as a function of wall shear stress ($\tau_w$) for the HDPE melt at 200$^o$C. The continuous line is a fit to the experimental data indicating a slope of 3.4.
Appendix B: More details on extrudate swell measuring system

The dimensions of extrudate swell are measured using a pair of Keyence® LS-7030M optical micrometers, shown in Figure B.1. In these micrometers, a uniform beam of parallel light is emitted from the transmitter and it is received and monitored by the receiver on the other side. If there is an object in between, based on the shadow and using image analysis, it is possible to calculate the dimensions of the object. Having ±0.15μm repeatability and ±2μm measurement accuracy, this setup ensures reliable measurements. It is worth to note that this setup has an option to correct the swell measurement in case of object tilts (Figure B.2).

FIGURE B.1: Keyence® LS-7030M optical micrometers used for extrudate swell measurements

To use these micrometers for in-line extrudate swell process, it is necessary to have a setup imbedded next to the die exit which can host the micrometers. Such a setup has been developed in our lab, which is depicted in Figure B.3. This setup enables one to rotate the micrometers to have them aligned to the extrudate face (in case of extrusion with slit dies), shifting the micrometers up and down to do the measurements at specific extrudate lengths and moving the micrometers back and forth to adjust the image resolution in order to perform more reliable measurements.
FIGURE B.2: Monitor image depicting tilt correction using Keyence® LS-7030M optical micrometer.

FIGURE B.3. Set-up to hold and move optical micrometers for reliable extrudate swell data.
Appendix C : Evaluation of material functions

As mentioned in Chapter 3, to explain the significant differences between the extrudate swell predictions of the integral K-BKZ (Wagner or PSM) and those of the PTT model, several material functions were calculated and presented, particularly those not measured experimentally. The material functions in steady shear, such as the shear viscosity ($\eta$), and the first normal stress difference coefficient ($\Psi_1 = N_1 / \dot{\gamma}^2$) are presented in FIGURES C.1(a) and (b), respectively. All the three constitutive equations, namely the K-BKZ with Wagner, K-BKZ with PSM, and PTT models, represent the variation of shear viscosity and first normal stress difference coefficient with shear rate nearly the same.

In addition, the start-up and relaxation/decay material functions are also calculated using the three constitutive equations. The transient material functions calculated and plotted in FIGURES C.2 (a)-(d) are the shear stress growth coefficient $\eta_S^+$, and the shear stress decay coefficient $\eta_S^-$, the first normal stress difference coefficient $\psi_1^+$, and first normal stress difference coefficient $\psi_1^-$.

FIGURE C.1: Variation of (a) shear viscosity ($\eta$) and (b) first normal stress difference coefficient ($\psi_1$) with shear rate predicted by using the K-BKZ constitutive model with Wagner and PSM damping functions and the PTT constitutive model.
decay coefficient $\psi_1$. As clearly shown in FIGURES C.2 (a)-(d), the three constitutive equations predict similar results, and thus their distinctly different behavior in extrudate swell prediction cannot be explained.

FIGURES C.2: Predictions of several material functions of the HDPE polyethylene melt at 200°C using the K-BKZ models with Wagner and PSM damping functions and the multi-mode PTT model (a) shear stress growth coefficient ($\eta^+$) (b) shear stress decay coefficient ($\eta^-$) (c) first normal stress difference coefficient ($\psi_1^+$), and (d) first normal stress difference decay coefficient ($\psi_1^-$).
The elastic recoil/recoverable strain predictions (in both shear and elongation) are of great importance in polymer processing phenomena, such as extrudate swell in extrusion and spinning, distortion in injection molding, and shrinkage in film blowing. The recovery is also closely associated with memory effects and thus it seems appropriate to compare the predictions from the two models in an attempt to understand the discrepancy between the swell predictions of integral and differential rheological models. The steady recoverable strains during shear and elongation, using the integral K-BKZ model with a simple exponential Wagner damping function, allows simple analytical expressions as described by Laun (1986). However, when the PSM damping function is used, the material functions cannot be expressed in simple analytical forms and thus the steady recoverable deformations (both shear and elongational) were determined numerically by using a MATLAB program. The recoverable shear and elongational strains using the PTT model can also be determined by the methods described in Tanner and Nasseri (2003) and Tanner et al. (2005).

The steady recoverable shear and elongational strains using the three constitutive equations calculated (K-BKZ Wagner, K-BKZ PSM and multi-mode PTT models) are depicted in FIGURES C.3 (a) and (b), respectively. All three constitutive equations predict similar steady elastic strains/recoverable deformations. Elastic recovery (and stress relaxation) upon a change in flow kinetics, considered to be strongly related to extrudate swell, also showed no dependence on the rheological model/constitutive equation, at least under simple deformations such as steady shear and elongation. As shown in FIGURES C.1, C.2, and C.3, it was observed that all the material functions during steady shear (dynamic), start-up flow (transient), relaxation and recovery were represented quite well using the three constitutive equations (described in this paper), leaving the significant difference between swell predictions made by integral K-BKZ and differential PTT models as an intriguing problem to explain.
FIGURE C.3: Predictions of (a) steady recoverable shear strain ($\gamma_{r,s}$) and (b) steady recoverable elongational strain ($\varepsilon_{r,s}$) using the K-BKZ model with Wagner and PSM damping functions and the multi-mode PTT model.
Appendix D : Contour plots and stress profiles in long slit dies

The mathematical model, boundary conditions, and the method of solution used for swell simulation is slit dies is the same as described in Chapter 3. A typical two-dimensional flow domain with die length, \( L \) (40 mm is a typical length) and thickness, \( H \) (0.5 mm is a typical thickness) is discretized using a mapped-mesh technique and is used for the thickness swell simulations of this study. A mapped-mesh grid of 980 elements is used for the simulations and the mesh independency of the numerical results is studied by using a denser mesh obtained by dividing each element into four sub-elements. The mesh independency is validated such that the differences between the overall pressures and swell ratios from both meshes are < 1%. The simulations were performed at various apparent shear rates ranging from 5 to 100s\(^{-1}\). The Weissenberg numbers (defined as the ratio of mean relaxation time times the shear rate) for the present polymer are in the range of 105 to 2100 considering mean relaxation time of 21s. No convergence related issues were observed within the range of Weissenberg numbers studied.

FIGURE D.1 depicts the contour plots of several variables in thickness simulation, such as the stream function \((STF)\), axial velocity \((U_y)\), pressure \((P)\), shear stress \((T_{yz})\), and first normal stress difference \((N_1)\) predicted by the integral K-BKZ Wagner model near the exit of the die at an apparent shear rate of 5s\(^{-1}\). All the contour plots are presented in an equally spaced 11 intervals between the corresponding minimum and maximum values. FIGURE D.1(a) shows the contours of stream function \((STF)\) obtained by integrating the velocity field. It should be noted that the maximum value of stream function corresponds to the flow rate. The axial velocity contours \((U_y)\) in FIGURE D.1(b) and the pressure contours in FIGURE D.1(c) clearly show the change from a confined flow inside the die to a shear free flow in the extrudate. It is noticed from the shear stress (FIGURE D.1(d)) and first normal stress (FIGURE D.1(e)) contours that the flow is fully developed at distances relatively close to the die exit. Most of the flow rearrangement occurs near the die exit at distances equivalent to about one die gap. These contour plots are in qualitative agreement with that of capillary, slit and annular dies reported in the literature (Luo and Mitsoulis, 1989; Kiriakidis and Mitsoulis, 1993; Barakos and Mitsoulis, 1995).
The effect of shear rate on the K-BKZ Wagner model predictions of extrudate thickness swell, pressure, shear stress and first normal stress difference profiles at the wall and free surface with axial distance, at shear rates, 5 s\(^{-1}\), 26 s\(^{-1}\) and 100 s\(^{-1}\), are presented in FIGURE D.2. These profiles are in qualitative agreement with the general trends reported in the literature (Ahn and Ryan 1992, Mitsoulis and Hatzikiriakos 2012, Al-Muslimawi et al., 2013). From FIGURE D.2(a), it can be further observed that swell ratio increases with apparent shear rate at any point down the die exit. The differences in swell ratios at different apparent shear rates can be further explained by the considerable differences in shear stress (FIGURE D.2(c)) and first normal stress (FIGURE D.2(d)) profiles as shown below. Another interesting aspect to be noticed is that the relaxation of first normal stress difference (refer FIGURE D.2(d)) occurs very close to the die exit for the lowest shear rate 5 s\(^{-1}\) in comparison with shear rates 26 s\(^{-1}\) and 100 s\(^{-1}\), which further confirms the general trend of increasing the swell ratio with the apparent shear rate.
FIGURE D.2: Comparison of (a) Thickness swell $B_T$ (b) Pressure $P$ (c) shear stress $\tau_{yz}$ (d) First normal stress differences $N_1$ profiles, along the wall and free-surface predicted using integral K-BKZ (Wagner) model at three different apparent shear rates 5, 26 and 100s$^{-1}$. 