1995

Elongational Rheometry of Coextruded Polymer Melts.

Ajit Vijay Pendse

Louisiana State University and Agricultural & Mechanical College

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_disstheses

Recommended Citation


This Dissertation is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Historical Dissertations and Theses by an authorized administrator of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.
INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.
ELONGATIONAL RHEOMETRY
OF COEXTRUDED POLYMER MELTS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in

The Department of Chemical Engineering

by

Ajit Vijay Pendse
B.S. & M.S., Indian Institute of Technology, Bombay, India, August, 1989
August, 1995
Acknowledgments

I would like to thank Dr. John Collier, my research advisor, for his guidance, cooperation and encouragement throughout the course of this work. At critical junctures during my research, he was always there to advise and support me; I gratefully acknowledge his help. I also thank Dr. Billie Collier for being such a great host for the many get-togethers that I have enjoyed at their home.

I thank the members of my committee, Dr. Armando Corripio and Dr. Frank Groves from the Department of Chemical Engineering, Dr. Paul Russo and Dr. William Daly from the Department of Chemistry, and Dr. Gary Byerly from the Department of Geology and Geophysics, for their cooperation and time.

Financial support from Polymer Laboratories, UK (now Rheometrics Inc. USA), and NSF (grant numbers DMC 8896Q30 and DMR 9202434) is gratefully acknowledged.

Dr. Hwan Chul Kim, my former colleague, helped me with my experiments and gave constructive suggestions in the early part of this work. Dr. Frank Baker (Rheometrics Inc.), Dr. Jay Janzen (Phillips Petroleum) and Dr. Roger Ross (DuPont Company) provided their critical suggestions from time to time and also supplied materials and information which has been used in this work. I thank them all for their help.
I thank Paul Rodriguez, and all the student workers in the Chemical Engineering Shop, Samson Martin, Kerry Jackson, Joe Bell and Pat Beard, who solved time and again my experimental and other puzzles. I am grateful to the Chemical Engineering staff for their help. I also thank Maryoud Elsunni, Douglas Krzystowczyk, Minqiu Lu and Ovidiu Romanoschi, my colleagues in our research group, for their support and many interesting discussions that we have had, academic or otherwise. I thank David Laura for helping me with the experimental work and Vibhas for his timely help with writing my dissertation. I thank Mahesh, Harish, Ramana and Amit, simply for being great friends.

Eleanor and John Earle filled the gap that I felt living away from my family. I deeply acknowledge their warm friendship that has enriched my stay at Baton Rouge.

My sister Abha, my brother-in-law Madhav, and my cousin Kumar have always been supportive. My uncle Baba and my aunt Aruna were an inspiration to me as a child. I acknowledge all their affection. Words fall short to express my gratitude towards my parents who have poured their love on me and have always been very patient; I dedicate this work to them.
Contents

Acknowledgments ................................................................. ii

List of Tables ................................................................. vii

List of Figures ................................................................. viii

Nomenclature ................................................................. xi

Abstract ................................................................................ xiii

1 INTRODUCTION .......................................................... 1
  1.1 Background ................................................................. 1
  1.2 Motivation ................................................................. 2
  1.3 Research objectives .................................................... 3
  1.4 Arrangement of this report ........................................... 4

2 LITERATURE REVIEW .................................................. 5
  PART I: Elongational flows ................................................ 5
      2.1 Definition of terms ................................................... 5
        2.1.1 Stress tensor: ....................................................... 5
        2.1.2 Deformation tensor: .............................................. 6
        2.1.3 Constitutive equations: ........................................ 6
      2.2 Classification of flows .............................................. 6
        2.2.1 Simple shear flow ................................................. 7
        2.2.2 Simple elongational flow ..................................... 8
        2.2.2.1 Planar ............................................................... 9
        2.2.2.2 Uniaxial ............................................................ 9
        2.2.2.3 Biaxial ............................................................. 10
        2.2.2.4 General ........................................................... 10
      2.3 Theoretical analysis .................................................. 10
        2.3.1 Constitutive equations .......................................... 10
        2.3.2 Shear viscosity .................................................... 13
        2.3.3 Elongational viscosity .......................................... 14
  PART II: Elongational rheometry ....................................... 17
      2.4 Measurement techniques .......................................... 17
        2.4.1 Indirect measurements ......................................... 18
        2.4.2 Stretching devices .............................................. 19
        2.4.3 Spin-line rheometers .......................................... 20
        2.4.4 Lubricated flow rheometers .................................. 21

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
3 METHODOLOGY

3.1 Introduction ........................................................................................................27
3.2 Coextrusion of polymeric melts: Basis for an elongational rheometer ............28
3.3 Planar geometry .....................................................................................................29
  3.3.1 Design of constant strain rate slit die .........................................................29
  3.3.2 Experimental verification ..............................................................................30
3.4 Commercial application: Uniaxial geometry ................................................................35
  3.4.1 Design of constant strain rate conical die ...................................................35
3.5 Theory ............................................................................................................37
  3.5.1 Assumptions .........................................................................................37
  3.5.2 Development .........................................................................................39
3.6 Stability of the rheometer .................................................................................43
  3.6.1 Transient nature of elongational flows ....................................................43
  3.6.2 Viscoelastic instabilities ..............................................................................46
3.7 Advantages and limitations ..............................................................................49

4 EXPERIMENTAL ....................................................................................................50

4.1 Apparatus ..........................................................................................................50
  4.1.1 Planar geometry: Coextrusion assembly ......................................................50
    4.1.1.1 Extruders ..................................................................................50
    4.1.1.2 Gear pumps ...............................................................................51
    4.1.1.3 Die ............................................................................................52
    4.1.1.4 Take-up device ...........................................................................56
  4.1.2 Uniaxial geometry: Advanced Capillary Extrusion Rheometer (ACER) .............56
    4.1.2.1 Drive section .............................................................................57
    4.1.2.2 Barrel ..........................................................................................58
    4.1.2.3 Dies ............................................................................................58
      4.1.2.3.1 Capillary die .........................................................................58
      4.1.2.3.2 Hyperbolic die .......................................................................58
    4.1.2.4 Procedure, data acquisition and control ..............................................59
4.2 Materials .............................................................................................................61
  4.2.1 Polyethylene ...............................................................................................61
  4.2.2 Polypropylene: ...........................................................................................61
  4.2.3 Nylon ........................................................................................................63
  4.2.4 Syndiotactic polystyrene: ..........................................................................63
4.3 Sample preparation ...............................................................................................63
  4.3.1 Planar geometry: Slit die ............................................................................63
  4.3.2 Uniaxial geometry: ACER die .....................................................................65
     4.3.2.1 Billet preparation: Pelletized sample ..............................................65
     4.3.2.2 Billet preparation: Powdered sample: ............................................66
5 RESULTS AND DISCUSSION ................................................................. 67
  5.1 Planar elongational viscosity ....................................................... 68
  5.2 Uniaxial elongational viscosity .................................................. 73
    5.2.1 Polypropylene ................................................................. 73
    5.2.1.1 HGX 030 .................................................................. 73
    5.2.1.2 Rheometrics ............................................................... 78
    5.2.2 Syndiotactic polystyrene (sPS) ......................................... 83
    5.2.3 Nylon-66 ....................................................................... 86
  5.3 Effect of molecular parameters ................................................. 89
  5.4 Summary .................................................................................. 91

6 CONCLUSIONS ....................................................................................... 93
  6.1 Scope for future work ............................................................... 94

References ................................................................................................. 96

Appendix A: Raw data ........................................................................... 101

Appendix B: Sample calculation .......................................................... 104

Appendix C: Pressure correction ......................................................... 105

Vita ........................................................................................................... 110
List of Tables

3.1 Hencky strain for planar and uniaxial geometry .............................................. 46
3.2 Weissenberg numbers for HGX 030 and LDPE in the barrel for the complete range of flow rates achieved in ACER ...................................................... 47
3.3 Deborah numbers for HGX 030 and LDPE in the die for the complete range of strain rates achieved in ACER ............................................................ 48
4.1 Viscosity of polyethylene melts ......................................................................... 62
4.2 Viscosity of polypropylene melts at 200 °C ...................................................... 62
5.1 Geometrical constants in the hyperbolic die ...................................................... 68
List of Figures

2.1 Classification of simple shear flow ....................................................... 8
2.2 Classification of simple elongational flow ............................................. 8
2.3 Indirect measurement of elongational viscosity ........................................ 18
2.4 Schematic diagram of the stretching method ............................................. 19
2.5 Spin-line rheometer ................................................................................. 21
2.6 Schematic of the orthogonal stagnation flow rheometer ......................... 24
3.1 Schematic of the flow pattern in the slit die used for determination of planar elongational viscosity ......................................................... 29
3.2 Experimental verification of the velocity profiles predicted by Kim (1993); the solid and dashed lines indicate the predicted values ............... 32
3.3 Tracer particle measured velocities as a function of volumetric flow rate and the centerline distance into a hyperbolic converging die .............. 33
3.4 Elongational strain rates calculated from tracer particle measured velocities as a function of volumetric flow rate in a hyperbolic converging die .............................................................. 34
3.5 Experimental evidence for interface stability in the slit die .................... 38
3.6 Force balance on the core across a converging die ................................... 40
4.1 Schematic of the coextrusion assembly ................................................... 51
4.2 Calibration chart for core gear pump ....................................................... 53
4.3 Calibration chart for skin gear pump ......................................................... 53
4.4 (a) Extrusion die showing the inserts (b) Hyperbolic insert for planar elongational rheometry ............................................................................... 54
4.5 Schematic of the hyperbolic slit die ......................................................... 55
4.6 Schematic of the Advanced Capillary Extrusion Rheometer (ACER) ... 57
4.7 Standard capillary die used in ACER for shear rheometry .............. 59
4.8 Hyperbolic conical die used in ACER for elongational rheometry .... 60
4.9 Two layered billet ............................................................................ 64
4.10 Schematic of the mold used for making two layered billets .......... 66
5.1 Planar elongational viscosity of HGX 030 and HGZ 200 at 200 °C as a function of elongational strain rate ............................... 69
5.2 Shear viscosity and planar Trouton ratio of HGX 030 at 200 °C at shear rates equivalent to applied elongational strain rates .......... 70
5.3 Shear viscosity and Trouton ratio of HGZ 200 at 200 °C at shear rates equivalent to applied elongational strain rates ............... 71
5.4 Uniaxial elongational viscosity of HGX 030 at 200 °C as a function of elongational strain rate ......................................................... 75
5.5 Shear viscosity and Trouton ratio of HGX 030 at 200 °C at shear rates equivalent to applied elongational strain rates ............... 76
5.6 Normalized planar and uniaxial viscosity of HGX 030 at 200 °C ......... 77
5.7 Uniaxial elongational viscosity of Rheometrics sample at 200 °C as a function of elongational strain rate .............................................. 79
5.8 Shear viscosity and Trouton ratio of Rheometrics sample at 200 °C at shear rates equivalent to applied elongational strain rates .......... 80
5.9 Comparison of elongational viscosity Rheometrics and HGX 030 at 200 °C .......................................................... 81
5.10 Comparison of the Trouton ratio of Rheometrics and HGX 030 at 200 °C ....................................................................................... 82
5.11 Uniaxial elongational viscosity of syndiotactic polystyrene melt at 280 °C and 300 °C as a function of elongational strain rate ......... 84

ix

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
5.12 Shear viscosity and Trouton ratio of syndiotactic polystyrene melt at 280 °C and 300 °C at shear rates equivalent to applied elongational strain rates ...................................................... 85

5.13 Uniaxial elongational viscosity of nylon-66 melt at 290 °C as a function of elongational strain rate ................................................................. 87

5.14 Shear viscosity and Trouton ratio of nylon-66 melt at 290 °C at shear rates equivalent to applied elongational strain rates .............................. 88

5.15 Correlation between the Trouton ratio and polydispersity index of polymer melts ................................................................. 90
Nomenclature

A Geometrical constants for the slit die, mm
a, b, c Constants used in the strain rate tensor, dimensionless
B Geometrical constants for the slit die, mm²
C Geometrical constants for the hyperbolic converging die, mm³
d Deformation tensor, s⁻¹
D Geometrical constants for the hyperbolic converging die, mm²
De Deborah number (Eq. 3.33)
e Eigenvalues of the velocity gradient tensor matrix, dimensionless
E Young’s Modulus, Pa
I First invariant of the stress tensor (Eq. 2.1)
II Second invariant of the stress tensor (Eq. 2.2)
III First invariant of the stress tensor (Eq. 2.3)
L Velocity gradient tensor, s⁻¹
m consistency of a power-law fluid, dimensions depend on n
Mₙ Number average molecular weight
Mₚ Weight average molecular weight
n Power-law index of a power-law fluid, dimensionless
Pᵢ Polydispersity index, Mₚ/Mₙ
p,p Isotropic or hydrostatic pressure, Pa
Q Volumetric flow rate, m³
S Cross sectional area, m²
Sₑ Equivalent Weissenberg number at wall for an equivalent Newtonian fluid
t Time, s
t’ Residence time, s
v Velocity, m/s
W Width of the slit die, m
We Weissenberg number (Eq. 3.37)
y Height of the slit die channel, m

Greek symbols

\( \dot{\gamma} \) Shear rate, s⁻¹
\( \Delta \) Gradient operator
\( \delta_{ii} \) Trace of velocity gradient tensor (Eq. 2.16)
\( \varepsilon \) Hencky strain, dimensionless
\( \dot{\varepsilon} \) Elongational strain rate, s⁻¹
\( \eta \) Viscosity, elongational or shear, as defined in the text, Pa.s
\( \lambda \) Characteristic relaxation time, s
\( \Lambda \)  Second viscosity coefficient
\( \sigma \)  Stress tensor, \( \text{Pa} \)
\( \tau \)  Pressure free stress tensor, \( \text{Pa} \)

Subscripts

1,2  Entrance and Exit positions in the die
E  Uniaxial
EP  Planar
EB  Equibiaxial
I  Interface
o  Initial
w  At the wall
Abstract

In most key polymer processing operations such as fiber spinning, blow molding and extrusion through a converging die, the dominant mode of flow is elongational. Rheological characterization of polymeric materials in elongational flow is critical for material quality control as well as for process modeling applications. Unlike shear flows, which have been studied extensively, elongational flows are not well understood, primarily due to the experimental difficulties involved in generating a pure and steady elongational flow field. There is a dearth of commercially available elongational rheometers in the present rheological literature; those that are commercially available, are useful only at elongational strain rates at least an order of magnitude lower than those encountered in typical industrial processes.

Use of lubricated skin/core flow of polymer melts and a hyperbolic converging die is shown to result in essentially pure elongational flow at a constant elongational strain rate in the core. Experimental measurements on a laboratory scale coextrusion system in a planar slit die using tracer particles and an image analysis system confirm the predicted behavior and demonstrate the ability to achieve a constant elongational strain rate in the core layer. The technique is implemented on a commercial capillary rheometer by replacing the capillary die with a hyperbolic converging axisymmetric die to determine the uniaxial elongational viscosity of several polymer melts. A two layered billet for placement in the rheometer barrel is prepared by completely
encapsulating the core polymer with a polyethylene skin. Elongational viscosity at high extensional rates can be determined with this method; values in excess of 500 s\(^{-1}\) have already been achieved.

Agreement with the data available in the literature at equivalent elongational strain rates was found with polypropylene melts. Both polypropylene and syndiotactic polystyrene melts were observed to be strain softening in the range of strain rates studied. At low strain rates Nylon-66 melts showed a strain hardening behavior, followed by an apparent peak and a subsequent strain softening at higher strain rates.
Chapter 1

INTRODUCTION

1.1 Background

The term *Rheology*, coined in 1929 by Professor E.C. Bingham, is defined as the study of the deformation and flow of matter (Tanner, 1985). *Rheometry* is consequently defined as the science of the measurement techniques of the deformation of matter. Measurement of the deformation of matter can be viewed from two extremes: from the purely elastic response of a Hookean solid where the stress in the material is a function of the strain, to a purely Newtonian response where the stress in the body is a function of the rate of strain.

Major advances in rheology were made in the 1920's when there was a need to process and characterize important industrial materials such as rubber, plastics and paints. These materials show complex fluid-mechanical behavior which falls in-between the response of the Hookean (elastic) solids and the response of the Newtonian (viscous) fluids. This viscoelastic flow can be analyzed in terms of component flow fields such as simple shear flow or simple elongational flow. In order to standardize the measurements, a rheometer induces simple flow geometries on the samples. Material properties are measured in simple flows and rheometric...
functions such as viscosity are determined in a rheometer, and correlated with the observed behavior in industrial situations.

1.2 Motivation

Shear rheometry is very well developed and there are several commercial rheometers available (Walters, 1980; Dealy and Wissbrun, 1990). However, in the recent rheological literature, the importance of elongational rheometry has become apparent (Ferguson and Kemblowski, 1991). The motivation for the study of elongational flows is two fold: the realization that in several key industrial processes such as spinning, blow molding, injection molding, extrusion in converging dies etc, the dominant mode of flow is elongational, and that shear rheology alone is not sufficient to characterize materials such as polymer melts and solutions (Barnes et al., 1989). For instance, two polymer melts which show a similar shear thinning behavior where the shear viscosity decreases with increasing shear rate, may exhibit a completely different response in their elongational rheology. One melt (e.g. polypropylene) may show a decrease in the elongational viscosity (strain softening) whereas the other (e.g. polyethylene) may show an increasing viscosity (strain hardening) in the same range of strain rates (Barnes and Roberts, 1992). The differences in their resistances to elongational stretching directly reflect the different response of the two melts in industrial operations such as spinning. In such cases shear rheometry alone is inadequate to characterize the materials. Furthermore, elongational rheology, as a method of characterization of materials, is not limited to polymer melts. It has recently attracted the attention of researchers from diverse areas
such as rod like micelles (Prud’homme and Warr, 1994) and food processing of
doughs (Jansson, et al., 1994).

The difficulty of generating a steady and controlled elongational flow field has
severely restricted the development of commercial rheometers. The strain rate range
achieved in the currently available commercial extensiometers (the author is aware of
two, Rheometrics (1993) and Götffert GmbH, ref: Dealy and Wissbrun, 1990, p624)
is of the order of 10 s⁻¹, which is two orders of magnitude lower than that typically
generated in an industrial process such as melt spinning. Thus there exists a need for
developing an elongational rheometer that can generate higher strain rates, has a
simple design and is commercially viable.

1.3 Research objectives

The objectives of this work were the following:

1) To develop an elongational rheometer for polymer melts capable of generating
   high elongational rates; and

2) To characterize the elongational behavior of industrial grade polymers on the
   rheometer.

Using tracer particle measurements of the velocity profile in coextrusion, Kim
(1993) has shown that stable flow and nearly pure elongational flows can be obtained
using controlled conditions on coextrusion. In this research, the above concept was
first implemented on a laboratory-scale coextrusion assembly to develop a planar
elongational rheometer. The technique was then implemented on a conical geometry
as a uniaxial elongational rheometer on a commercial unit.
As the second objective, elongational viscosity of syndiotactic polystyrene, nylon-66 and three grades of polypropylene was determined on the rheometers developed in this work. Several grades of low viscous polyethylene were used as a skin layer for the purpose. The criteria for the selection of a suitable skin material are presented and stability parameters are determined.

1.4 Arrangement of this report

Literature review is presented in Chapter Two in two parts. Theoretical background on elongational flows is presented in Part I, and a review of available literature on elongational rheometers is presented in Part II. Chapter Three describes the methodology and the theory for the new elongational rheometer developed in this work. Experimental details, procedures and the materials used are described in Chapter Four. The elongational viscosity data obtained in this work are presented and compared with other data available in the literature in Chapter Five. Conclusions and scope for further study are discussed in Chapter Six.
Chapter 2

LITERATURE REVIEW

PART I: ELONGATIONAL FLOWS

2.1 Definition of terms

2.1.1 Stress tensor:

The stress tensor $\sigma$ can be defined as $\sigma_{ij}$ where each term is the magnitude of the stress in the direction $j$ acting on the area element whose normal vector points in the direction $i$.

Three invariant functions which are independent of the choice of the coordinate geometry) are defined as (Tanner, 1985):

$$ I = \sum \sigma_{ii} \quad (2.1) $$

$$ II = \frac{1}{2} \sum (\sigma_{ii} \sigma_{jj} - \sigma_{ij} \sigma_{ji}) \quad (2.2) $$

$$ III = |\sigma_{ij}| = \det \sigma \quad (2.3) $$

The first invariant is also called the trace of the stress tensor, denoted as $\text{tr}(\sigma)$. The rheological properties are expressed in terms of these invariants (Tanner, 1985) since a change of geometry should not affect the material properties.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
The stress tensor above contains the isotropic pressure term \(-pI\), therefore, deviatoric stress (extra or pressure free stress tensor) \(\tau\) is used:

\[ \tau = \sigma + pI \]  \hspace{1cm} (2.4)

2.1.2 Deformation tensor:

The deformation tensor \(d\) is defined as (Barnes et al., 1989):

\[ d = \frac{1}{2} (\nabla v + \nabla v^T) \]  \hspace{1cm} (2.5)

where superscript \(T\) stands for the transpose of the velocity field tensor \(v\); \(d\) is a symmetrical tensor.

2.1.3 Constitutive equations:

These equations relate a suitably defined stress tensor to the deformation variable such as strain tensor. The stress is expressed as a function of the invariants and the strain tensor:

\[ \sigma = f(d, I, II, III, \ldots) \]  \hspace{1cm} (2.6)

2.2 Classification of flows

Rheometers induce simple flow fields on the materials in order to facilitate the characterization of the material properties and to standardize measurement methods. Two classes of simple flows can be defined based on the relationship between the velocity gradients and the direction of the momentum flux: simple shear flow and simple extensional flow. In most practical situations the flow is a combination of the following basic types: simple shear flow and simple elongational flow.
2.2.1 Simple shear flow

The velocity field in simple shear flow (defined for discussion in a cartesian coordinate system) has only one component, e.g. $v_x$, which changes only in one direction, e.g. $y$:

$$v_x = v_x(y), \quad v_y = v_z = 0 \quad (2.7)$$

as shown in Figure 2.1(a). Such a flow can occur between two parallel plates or in the case of cylindrical geometry, in a tube (Poiseuille flow). The only non-zero term in the stress tensor has the form $\tau_{ij}$ (also $\tau_{ji}$ since the tensor is symmetrical) where $j$ is the velocity direction and $i$ is the velocity gradient direction. For the above coordinate system, the stress is equal to $\tau_{yx}$ ($=\tau_{xy}$ due to symmetry arguments). In matrix form:

$$\tau = \begin{pmatrix}
0 & \tau_{xy} & 0 \\
\tau_{yx} & 0 & 0 \\
0 & 0 & 0
\end{pmatrix} \quad (2.8)$$

In the Poiseuille (pipe or capillary) flow the non-zero component of the velocity is in $z$ direction and the velocity gradient is in the $r$ direction. The velocity and velocity gradients in Couette flow (Figure 2.1 (b)) are in the $\theta$ and the $r$ direction respectively. The stress tensor for all simple shear flows has the same form (in terms of zero and non-zero terms) as shown above when expressed in appropriate coordinate system.
2.2.2 Simple elongational flow

Figure 2.2 (a), (b) and (c) depict three classes of simple elongational flow: planar, uniaxial and biaxial (Barnes et al., 1989; Dealy and Wissbrun, 1990). These flows are classified according to the form of the velocity field.

Figure 2.2: Classification of simple elongational flow
2.2.2.1 Planar

In the cartesian coordinate system the velocity field for planar elongational flow is in the form:

\[ v_x = \dot{\varepsilon} x, \quad v_y = -\dot{\varepsilon} y, \quad v_z = 0 \]  \hspace{1cm} (2.9)

\( \dot{\varepsilon} \) is the constant elongational strain rate defined as

\[ \dot{\varepsilon} = \frac{\partial v_x}{\partial x} \]  \hspace{1cm} (2.10)

These type of flows are equivalent to stretching a thin flat sheet of material in one direction only. In this work the slit die (Chapter 5) is used to generate a planar elongational flow.

2.2.2.2 Uniaxial

The term uniaxial elongational flow is used in a velocity field of type:

\[ v_x = \dot{\varepsilon} x, \quad v_y = -\frac{\dot{\varepsilon}}{2} y, \quad v_z = -\frac{\dot{\varepsilon}}{2} z \]  \hspace{1cm} (2.11)

This type of flow is encountered in converging dies and spinning. Some workers (Petrie, 1979) consider spinning as a special class of flow, as strictly speaking, the extension in spinning is not uniform. Normal forces affect the dimensional uniformity and the velocity profile in the above equation is not followed. A major part of this work deals with uniaxial elongational flow in cylindrical geometry. Unless otherwise stated the term elongational viscosity in this work would refer to the uniaxial elongational viscosity.
2.2.2.3 Biaxial

This type of flow is encountered in film stretching operations such as blowing or when a circular free jet impinges on a flat plate. The extension of the material occurs in two directions. The velocity field for this flow is given as:

\[ v_x = \dot{\varepsilon} \, x, \quad v_y = \dot{\varepsilon} \, y, \quad v_z = -2 \dot{\varepsilon} \, z \]  
\[ (2.12) \]

2.2.2.4 General

In general, the tensor matrix for simple elongational flows is of the form:

\[
\tau = \begin{bmatrix}
\tau_{xx} & 0 & 0 \\
0 & \tau_{yy} & 0 \\
0 & 0 & \tau_{zz}
\end{bmatrix}
\]  
\[ (2.13) \]

where the diagonal terms are called the principal stress terms. The strain rate tensor for these flows is of the form:

\[
\dot{\gamma} = \begin{bmatrix}
a \dot{\varepsilon} & 0 & 0 \\
0 & b \dot{\varepsilon} & 0 \\
0 & 0 & c \dot{\varepsilon}
\end{bmatrix}
\]  
\[ (2.14) \]

where a, b and c are constants between -2 and 2.

2.3 Theoretical analysis

2.3.1 Constitutive equations

The constitutive equations model the fluid response to an imposed stress. Models of varying complexity have been developed (Bird et al., 1987; Vinogradov and Malkin, 1980) for purely viscous, viscoelastic and elastic behavior. In this research, the strain rate imposed is forced by the system geometry to be constant as long as the
volumetric flow rate is constant. Assuming that the deviatoric stress state is uniquely determined by the strain rate state, causes the deviatoric stress to also be constant for a constant volumetric flow rate. These conditions permit most constitutive equations to be used to model the flow. This enables but does not limit the application to the generalized Newtonian model or Reiner-Rivlin model (Bird et al., 1987). The complete generalized Newtonian constitutive equation is written as (Tanner, 1985):

\[ \tau_{ij} = \Lambda d_{kk} \delta_{ij} + 2 \eta d_{ij} \]  \hspace{1cm} (2.15)

where \( \Lambda \) is second viscosity coefficient generally independent of \( \eta \), and

\[ d_{kk} = \sum \frac{\partial v_k}{\partial x_k} \] \hspace{1cm} (2.16)

For incompressible fluids \( d_{kk} \) is zero so we get:

\[ \tau_{ij} = 2 \eta \dot{\gamma} \] \hspace{1cm} (2.17)

The implicit assumption in this model is that a steady state is achieved. Transient behavior is precluded in the model. This is consistent with the definition of viscosity as a material property at steady state. Petrie (1979) has pointed out the unsuitability of unsteady state data for elongational viscosity measurements. The property Stress Growth Coefficient (\( \eta_{E^+} \)) is used to differentiate the transient data from the steady state viscosity measurements. It has been shown (Tirtaatmadja and Sridhar, 1994) that the data on \( \eta_{E^+} \) obtained from transients with polymer melts show a straight line plot when plotted against strain up to the point it reaches a steady state.
It has been shown by Bird et al. (1987) that Reiner-Rivlin model for simple elongational flows can be expressed as the following:

\[\tau = -f_1(II,III)\dot{\gamma} - f_2(II,III)(\dot{\gamma} \cdot \dot{\gamma})\]  \hspace{1cm} (2.18)

where \(f_1\) and \(f_2\) are viscometric functions. The above model can be applied to flows that are steady, homogenous and irrotational.

For the sake of completeness, simple constitutive equations for elastic and viscoelastic behavior are also described. For a purely (linear) elastic body, Hooke’s law is the classical constitutive equation. Thus the stress and strain are related as:

\[\sigma = E \varepsilon\]  \hspace{1cm} (2.19)

where \(E\) is the Young’s modulus.

Since the stress response of a viscoelastic material is a function of both strain and strain rate, a characteristic time is involved in the model. The simplest model for viscoelastic behavior is given by the Maxwell model (Barnes et al., 1989):

\[\tau_{ij} + \lambda \frac{\partial}{\partial t} \tau_{ij} = 2 \eta_0 d_{ij}\]  \hspace{1cm} (2.20)

where \(\lambda\) is the characteristic relaxation time of the fluid. Maxwell’s equation has been used extensively to model transient shear behavior. Several variations of Maxwell’s equation have also been used to model elongational flows (Petrie, 1979). The Upper Convected Maxwell model yields the following equation (Petrie, 1979):

\[\eta_E = \frac{3\eta}{(1 + \lambda \dot{\gamma})(1 - 2\lambda \dot{\gamma})}\]  \hspace{1cm} (2.21)
This model predicts an unrealistic infinite rise in viscosity as the shear rate approaches a critical value (1/2λ) and therefore is limited in application. Nevertheless, as the data presented in this work (Chapter Five) indicate, the elongational viscosity of certain polymer melts like nylon or highly branched polyethylenes (Chohan, 1994; Barnes and Roberts, 1992) shows an increase with elongational strain rates in a certain range. Thus, Maxwell model captures the qualitative nature of elongational viscosity but fails to predict it quantitatively.

2.3.2 Shear viscosity

In simple shear flow, the apparent shear viscosity can be defined as the ratio of the shear stress and the shear rate:

\[ \eta_o = \frac{\tau_{xy}}{\dot{\gamma}} \]  \hspace{1cm} (2.22)

where this shear rate, \( \dot{\gamma} \), is defined as:

\[ \dot{\gamma} = \frac{\partial v_x}{\partial y} . \]  \hspace{1cm} (2.23)

Generally, for polymer melts, the shear viscosity is a strong function of shear rate at a given temperature. The power-law (Bird et al., 1960) models the shear viscosity and flow behavior over a large range:

\[ \eta = m \dot{\gamma}^{n-1} . \]  \hspace{1cm} (2.24)

\( m \) is the consistency and \( n \) is the power-law index. When \( n=1 \), the fluid is a Newtonian fluid.
2.3.3 Elongational viscosity

Application of the stated kinematic condition and the assumed stress state
determination to the planar elongational flow field gives the following stress
distribution (Barnes et al., 1989; Tanner, 1985):

\[ \tau_{xx} - \tau_{yy} = \dot{\varepsilon} \eta_{EP}(\dot{\varepsilon}) \]  \hspace{1cm} (2.25)

\[ \tau_{xy} = \tau_{yx} = \tau_{yz} = \tau_{zx} = 0 . \]  \hspace{1cm} (2.26)

The planar apparent elongational viscosity is defined as:

\[ \eta_{EP}(\dot{\varepsilon}) = \frac{\tau_{xx} - \tau_{yy}}{\dot{\varepsilon}} . \]  \hspace{1cm} (2.27)

The subscripts EP, EB and E are used to denote the planar, biaxial and uniaxial
elongational viscosity respectively. A similar treatment for uniaxial flow leads to:

\[ \tau_{xx} - \tau_{yy} = \dot{\varepsilon} \eta_{E}(\dot{\varepsilon}), \]  \hspace{1cm} (2.28)

\[ \tau_{xy} = \tau_{yx} = \tau_{yz} = \tau_{zx} = 0 . \]  \hspace{1cm} (2.29)

The uniaxial apparent elongational viscosity is defined as:

\[ \eta_{E}(\dot{\varepsilon}) = \frac{\tau_{xx} - \tau_{yy}}{\dot{\varepsilon}} \]  \hspace{1cm} (2.30)

in cartesian geometry. The analysis has been carried out in cylindrical geometry in
this work, where the elongational viscosity is defined as:

\[ \eta_{E}(\dot{\varepsilon}) = \frac{\tau_{rr} - \tau_{rr}}{\dot{\varepsilon}} . \]  \hspace{1cm} (2.31)
For biaxial flow:

\[
\tau_{xx} - \tau_{yy} = \tau_{zz} - \tau_{yy} = \dot{\varepsilon} \eta_{EB}(\dot{\varepsilon}) ,
\]

(2.32)

\[
\tau_{xy} = \tau_{xz} = \tau_{yz} = 0 .
\]

(2.33)

The biaxial apparent elongational viscosity is defined as:

\[
\eta_{EB}(\dot{\varepsilon}) = \frac{\tau_{xx} - \tau_{yy}}{\dot{\varepsilon}} .
\]

(2.34)

In case of planar elongational flow the deviatoric terms can be shown to be:

\[
d_{11} = \frac{\partial v_x}{\partial x} = \dot{\varepsilon}, \quad d_{22} = \frac{\partial v_y}{\partial y} = -\dot{\varepsilon} .
\]

(2.35)

For a Newtonian fluid, the generalized constitutive equation leads to the following:

\[
\tau_{11} = 2\eta \dot{\varepsilon}, \quad \tau_{22} = -2\eta \dot{\varepsilon} ,
\]

(2.36)

\[
\eta_{EP} = \frac{\tau_{xx} - \tau_{yy}}{\dot{\varepsilon}} = 4\eta
\]

(2.37)

A similar analysis of uniaxial flow gives us:

\[
\tau_{11} = 2\eta \dot{\varepsilon} \, , \quad \tau_{22} = -\eta \dot{\varepsilon} ,
\]

(2.38)

\[
\eta_{E} = \frac{\tau_{xx} - \tau_{yy}}{\dot{\varepsilon}} = 3\eta
\]

(2.39)

For biaxial flow the equations become:

\[
\tau_{11} = 2\eta \dot{\varepsilon} \, , \quad \tau_{22} = -4\eta \dot{\varepsilon} ,
\]

(2.40)
Comparing the above equations for elongational viscosity with the shear viscosity (equation 2.22) it can be concluded that the ratio of the elongational and shear viscosity at similar deformation rates is a scalar parameter. This ratio is called the Trouton ratio. This ratio is constant and independent of the strain rate for Newtonian fluids. As seen above, the Trouton ratio for uniaxial, planar and biaxial geometries for Newtonian fluids is equal to 3, 4 and 6 respectively. Some workers (Leal, 1992) have defined elongational viscosity in such a way that the Trouton ratio for all the three above geometries can be shown to be equal to 3. According to Leal (1992):

\[ \eta(\dot{\varepsilon}) = \frac{2\tau_{11} - (\tau_{22} + \tau_{33})}{2\dot{\varepsilon}}. \]  

(2.42)

In the present work this definition has not been used.

The Trouton ratio is one measure of the deviation of the fluid from Newtonian behavior. For polymer melts and solutions the value of Trouton ratio has been reported from 3 (at very low strain rates) to up to 200. As discussed in Chapter Five, the variation of Trouton ratio with strain rate can also be affected by the molecular parameters of the polymer. A review of the approaches to elongational rheometry and the data reported in the available literature is presented in the next part.
PART II: ELONGATIONAL RHEOMETRY

2.4 Measurement techniques

The simplest case for the measurement of elongational viscosity is presented by Newtonian fluids. As is shown in the previous section, the Trouton ratio \(\frac{\tau_{E}}{\eta}\) is constant for a given flow geometry; consequently, shear viscosity is adequate for complete rheological characterization of Newtonian fluids. On the other hand, non-Newtonian fluids, particularly polymer melts, due to the macromolecular structure, exhibit a complex dependency of elongational viscosity on the applied strain rate. As a result, it is necessary to use rheometers that can induce simple elongational flow fields.

The difficulties of generating pure and steady elongational flow-fields are two-fold. The first difficulty lies in the transient nature of the elongational flow of viscoelastic materials. Attaining steady state is necessary in order to obtain reliable data. The second difficulty lies in the experimental constraints of achieving pure elongational flow. It is difficult to generate shear free flow in case of confined geometry since the wall introduces shear stress components affecting the data. On the other hand, in free boundary flows the practical problem of achieving high extensional rates has to be overcome. There is therefore a "trade-off between high accuracy and the possibility of carrying out elongational tests as a matter of routine evaluation of polymer melts." (Petrie, 1979 p.74).

The techniques of elongational rheometry can be broadly classified in four categories: (1) Indirect measurements, where the data from shear rheology is
interpreted to obtain elongational parameters, (2) use of unconfined flow in stretching devices, (3) spinning, and (4) lubricated flow. A review of each approach is given in the following sections.

2.4.1 Indirect measurements

Cogswell (1981) proposed that the flow profile of a fluid through a constriction can be modeled as an elongational flow. The assumption was based on the observation that when a non-Newtonian fluid flows through a constriction, major component of the streamlines take a ‘wine glass’ shape (Figure 2.3). The flow along these streamlines was assumed to be purely elongational. The elongational viscosity was determined from the pressure drop and shear viscosity data:

\[
\eta_E = \frac{9}{32} \frac{(n+1)^2}{\eta} \left( \frac{P_o}{\dot{\gamma}} \right)^2
\]

(2.43)

where \( P_o \) is the pressure drop; \( n, \eta \) and \( \dot{\gamma} \) are respectively the power-law index, shear viscosity, and shear rate in fully developed flow at the same volume flow rate. The model however is a basic one and has restricted applications due to assumptions about the streamlines of the flow.

![Figure 2.3: Indirect measurement of elongational viscosity](image-url)
For conical converging devices, Cogswell (1972) suggested subtracting the shear induced pressure component from the total pressure drop and using the elongational component of the pressure drop to subsequently determine the elongational viscosity of the material. The drawback of this method was the unpredictable error involved in the determination of the shear component of the flow. For simple geometries and at low strain rates the data reported was found to be consistent with theory (Cogswell, 1972). In another approach, Binding and Walters (1988) used energy principles to determine the elongational viscosity of polymer solutions. The technique employed the measurement of exit pressure to determine the normal stress difference and the elongational viscosity. However, the theory was limited to application to shear thinning polymer solutions (Binding, 1988).

2.4.2 Stretching devices

In these rheometers, the sample was held between two clamps (Figure 2.4) and was stretched from the two ends (Ballman, 1965). In later approaches (Meissner, 1972; Ide and White, 1978; Rheometrics Data Sheet, 1993) the sample was kept in an oil bath or suspended on a hot inert gas from bottom and the clamps were replaced by rollers.

Figure 2.4: Schematic diagram of the stretching method
A major and unavoidable (due to the inherent design) disadvantage of this method was that in order to attain a constant extensional rate in the sample, the velocity of the movable block or the rotational speed of the rollers must vary exponentially with time. Even though this can be achieved with computer controlled motors, a constraint on the maximum strain rates is placed in this method (Barnes et al., 1989). Further, the suitability of this method lies in determining only very highly viscous materials as the sample holding becomes difficult with low viscosity materials. These types of test measurements are limited to deformations rates below 5 s\(^{-1}\) (Cheremisiniff, 1993).

The advantage of this method is that it is a direct and accurate technique of elongational viscosity measurement since the prescribed kinematics are closely followed (Mackay and Dajan, 1995). The method also captures the transient behavior of the elongational viscosity of the material and enables the measurement of viscosity growth coefficients (\(\eta_E\)).

2.4.3 Spin-line rheometers

In spin-line rheometers the data obtained from spinning experiments is used to determine the elongational viscosity of the fluids (Hudson, 1974). Controlling the elongation of the melt and maintaining the uniformity of the temperature are the major difficulties in this method and therefore result in inconsistent data (Petrie, 1979). Figure 2.5 shows a schematic of spinning flow.

Due to the normal stresses in the confined part of the flow, the fluid swells and reaches a maximum in the diameter prior to stretching introducing uncertainty in the
measurement of the extension. The advantage of this method is that high extensional strain rates can be achieved. The method is also more relevant in industrial practice as data about melt fracture and melt strength can be obtained. Petrie (1979) has reviewed large numbers of experimental data that are reported using this method, however, the process variables mentioned above make the interpretation of the data difficult.

2.4.4 Lubricated flow rheometers

The most important distinctive feature of the lubricated flow rheometers is that the flow takes place in a confined geometry. The technique has been more
extensively used in the determination of biaxial elongational viscosity. The basic method used in this approach is the introduction of a lubricant to reduce shear and the use of a controlled profile to regulate the strain rates.

Cogswell (1981) considered a single layered fluid flowing through converging dies. Some investigators (Shaw, 1975; Everage and Ballman, 1978; Winter et al., 1979) considered a single layered fluid with a thin coat of lubricating material like grease to lubricate the flow. Hsu et al. (1980) showed the impossibility of achieving simple extension in a single layered lubricated flow for several boundary conditions excluding, however, the slip condition. In this work the slip condition could be applicable for the core layer, the material of interest. However, the 100/1 core to skin viscosity ratio requirement is related to causing the core to be essentially in a pure elongational flow. That is, almost all of the shearing gradient is borne by the skin layer and the very low shearing gradient possible in the core without the interfacial slip is overwhelmed by the elongational flow.

Jones et al. (1987) measured elongational viscosity of polymer solutions using a stagnation lubricated converging flow rheometer and compared the results to data obtained by a commercial spin line rheometer. They reported Trouton ratios in the range 10-100 and found fair agreement between the two methods. Secor et al. (1987) analyzed a lubricated planar stagnation die by a numerical method, and reported agreement between the calculations and the available experimental results. Lubrication techniques, used to measure elongational viscosity in squeezing flow (Chatraei and Macosko, 1981) and converging flow (Jones et al., 1987; Zahorski, 1992), have
primarily concentrated on polymer solutions due to experimental restrictions. James and Chandler (1990) and James et al. (1990) used the lubricated converging flow for polymer solutions. Their analysis depended on the assumption that a high Reynolds number in the polymer solution causes the flow to be purely extensional. A detailed experimental verification was however not carried out. James (1990, 1991) discussed relaxing the high Reynolds number assumption to moderate values. Williams and Williams (1985) suggested a lubricant to sample viscosity ratio of between $10^2$ and $10^4$, and a lubricant to sample thickness ratio of between $10^2$ and $10^4$.

In the above methods, the lubricant was introduced as a thin layer and was not a part of the flow consideration. Kim et al. (1993) showed that by imposing certain conditions on the skin layer viscosity and the flow rate ratio, a nearly pure elongational flow in the core can be obtained. The conditions for eliminating shear from the core -- flow rate and viscosity ratio -- are theoretically predicted and experimentally verified. As will be described in greater detail in later chapters, this work utilizes the concept of coextrusion and controlled skin flow to develop planar and uniaxial rheometers.

Just as converging flow produces uniaxial elongation, diverging flow produces biaxial elongation (Winter et al., 1979). Several techniques have been used to determine the biaxial elongational viscosity of polymeric liquids. These include sheet inflation (Yang and Dealy, 1987; Denson and Hylton, 1980), lubricated squeezing flow (Chatraei and Macosko, 1981; Soskey and Winter, 1985), and diverging pressure flow (Winter et al., 1979). In the sheet inflation method, a circular molded sample
is clamped around its periphery, melted, and inflated by increasing the pressure in the fluid medium on one side. Yang and Dealy (1987) proposed that there is a universal relationship between displacement volume and strain near the center of the sample. In lubricated squeezing flow, a disk shaped sample is placed between two plates, melted, and subjected to a compressional depression (Chatraei and Macosko, 1981). If the surfaces are not lubricated, the flow is a complex one involving shearing and elongational components; whereas if a lubricant is provided, the deformation is purely elongational in nature.

![Diagram of orthogonal stagnation flow rheometer](image)

**Figure 2.6: Schematic of the orthogonal stagnation flow rheometer**

The technique of orthogonal stagnation flow has been used for planar elongational viscosity measurement (Binding and Jones, 1989; Secor et al., 1987; Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Williams and Williams, 1985). In this method, the device that generates the orthogonal stagnation flow consists of four hyperbolic plates located symmetrically (Figure 2.6). It has two inlets and two outlets; the fluid diverges in the inlet and converges in the outlet. Lubricating fluid applied outside the testing fluid reduces the friction between the die and the sample. The elongational viscosity is calculated from the measurement of the exit pressure which can be obtained by extrapolating the pressures in the converging section.

Other techniques that cannot be included in any of the above categories are the opposed jet impingement technique and the bubble collapse technique. In the jet impingement technique of Mackay and Dajan (1995), a free boundary unconfined stagnation flow is generated by impinging two opposed jets. The model assumes that the flow between the two jets is purely elongational. The pressure drop required to pump the material through the jets is correlated to the stress using thermodynamic considerations. Uniaxial elongational viscosity is measured by this method. Strain rates of up to 500 s\(^{-1}\) have been reported.

In the bubble collapse technique (Macosko, 1994), a small bubble is blown at the end of the test fluid. Then at time t=0 the pressure inside the bubble is suddenly lowered or the pressure outside the bubble is suddenly increased. The decrease in the size of the bubble is recorded. If the deformation rate is reversed (i.e., the pressure in the bubble is suddenly increased), the growing bubble radius can be used to give the equibiaxial viscosity. The flow in this method is not stable and has not been studied as a rheometer.
2.5 Summary

From the review of the available literature it can be seen that there exists a compromise between the range of operation, the rigor of the underlying assumptions and the commercial applicability of the elongational rheometers. Available commercial rheometers are not able to generate strain rates that are industrially relevant. Although high strain rates have been achieved in rheometers for mobile systems like polymer solutions, such developments have not been done for polymer melts. Lubricated converging flow rheometers are most suitable for such systems, however, limiting assumptions in the lubricating layer have restricted their range of application.

The next chapter describes the methodology, design, advantages and limitations of the lubricated flow rheometer that was developed in this work.
Chapter 3

METHODOLOGY

3.1 Introduction

The desired characteristics of an elongational rheometer can be listed as follows: (1) pure elongational flow field should be imposed on the material to be characterized; (2) controllable and constant elongational strain rates should be imposed on the material to be characterized; (3) the imposed flow field should be stable and fully developed. In this research, an elongational rheometer was developed in the following stages. Kim et al. (1993) proposed the use of coextrusion and suggested process parameters that should be applied to meet condition (1) of the above. A die profile in slit geometry was designed to meet the condition (2). As a part of this dissertation the above parameters were experimentally confirmed on a pilot scale apparatus (described in Chapter Four). Theoretical analysis of the system was carried out to determine the planar elongational viscosity in the slit geometry. In the next stage of this dissertation, a commercial shearing flow rheometer was augmented to enable elongational flow measurements to be made using the basic components of it. This was accomplished by designing hyperbolic converging dies for uniaxial geometry and incorporating coextrusion principles on the commercial capillary shear rheometer.
The constant diameter capillary die was replaced by the above hyperbolic converging die. Theoretical analysis of the uniaxial geometry was carried out and stability criteria were investigated. In the following sections the stages are described in detail.

3.2 Coextrusion of polymeric melts: Basis for an elongational rheometer

In the previous works on lubricated flow elongational rheometers, grease or silicone oils were used to lubricate the material to be analyzed. However, a detailed analysis on the effect of the lubricant on the flow profile and on the stability of the resultant flow was not available. Furthermore, the lubricant was not considered as a part of the flow, thereby it was assumed that the material achieved true elongational flow. Collier et al. (1992), Kim et al. (1993) and Pendse et al. (1994) suggested the use of sheath-core (or skin-core) coextrusion as a means to essentially eliminate shear from the core material. The skin formed an essential part of the flow and the choice of an appropriate skin was found to be critical.

Kim (1993) numerically modelled the coextrusion system and determined the conditions for the viscosity ratio and the flow rate ratio between the skin and core that were necessary to essentially eliminate shear from the core. According to the conditions, the core to skin flow rate ratio should be between 7 to 10 and the core to skin viscosity ratio should be 100 or higher. A ratio of about 30 significantly eliminated the shear while a ratio of 100 or higher nearly completely pushed the shear to the skin layer. In addition to the above processing conditions, the skin and the core polymer melts had to be incompatible or immiscible to prevent changing the flow profile of the core.
3.3 Planar geometry

3.3.1 Design of constant strain rate slit die

After the conditions for generating a shear free flow in the core were obtained, the next stage was to design die profiles which could impose constant elongational strain rates in the core. For slit geometry, consider a die with width $W$ and a profile of height $y = f(x)$ (Figure 3.1).

If we assume a shear free flow (no gradient in the $y$ direction) then the flow rate $Q$ through the die is given as:

$$Q = 2 \ W \ y(x) \ v_x \quad (3.1)$$

where $v(x)$ is the velocity of the core. After rearranging the above equation, the elongational strain rate (as defined by equation 2.10) can be written as:
In the equation 3.2 if the profile \( y(x) \) takes the following form:

\[
y(x) = \frac{B}{x + A},
\]

where \( A \) and \( B \) are constants, then a constant elongational strain rate given by:

\[
\dot{\varepsilon} = \frac{Q}{2WB}
\]

is applied in the core throughout the converging section of the die.

It is to be noted that by virtue of this design, with a given geometry (by fixing \( A \) and \( B \)) the applied strain rate in the die can be varied linearly with the core flow rate. A pair of slit die inserts based on the above derived profile (equation 3.3) were designed and fitted in a window equipped die. A detailed description of the die and the inserts is given in Chapter Four. All the experiments for the planar elongational viscosity determinations were carried out using these inserts.

### 3.3.2 Experimental verification

In order to verify condition (1) as described in section 3.1, and also the strain rates predicted by equation 3.4, the velocity profile and the strain rates generated in the core were measured experimentally. Polypropylene melt was used in the core, and polyethylene was used as the skin material. The polypropylene used for the experiments was obtained from Phillips (Grade HGY 040). The melting point was found to be 164 °C and the zero shear viscosity at 200°C was 77382 Pa.s. The low
density polyethylene used was obtained from DOW (Type LLD-2) with a melting point 135 °C and zero shear viscosity of 63 Pa.s at 200 °C. The shear viscosity measurements of the polymer melts were carried out on a Bohlin VOR parallel plate rheometer.

Tracer particles (size 1mm x 1mm) were introduced with the feed in the core extruder to perform these measurements. The particles were visible through the glass window of the die (section 4.1.1.3). A video recording of the coextrusion was made on a VHS cassette. Digital imaging software, JAVA, manufactured by Jandel Scientific was used to measure the displacement of the tracer particles in the flow and transverse direction with time. From these data the velocity of the tracer particles at three different positions in the die was calculated. Strain rates were calculated from the velocity profile at these three positions.

A plot of the experimental observations (data points) is shown in Figure 3.2. The numerical results predicted by Kim (1993) are shown in solid and dashed lines. Close agreement between the experimental observations and the numerical predictions of the velocity profile is found.

In Figure 3.3 the tracer particle measured velocities as a function of volumetric flow rate and centerline distance into a hyperbolic converging die are shown. In Figure 3.4 the elongational strain rate predicted by equation 3.4 (solid line) and the experimentally observed values (dots) are plotted. The data follows the predicted straight line with $r^2=0.99$. 

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Figure 3.2: Experimental verification of the velocity profiles predicted by Kim (1993); the solid and dashed lines indicate the predicted values
Figure 3.3: Tracer particle measured velocities as a function of volumetric flow rate and the centerline distance into a hyperbolic converging die
Figure 3.4: Elongational strain rates calculated from tracer particle measured velocities as a function of volumetric flow rate in a hyperbolic converging die
3.4 Commercial application: Uniaxial geometry

The strain rate achieved on the coextrusion assembly in the planar geometry slit die was in the range from 0.02 to 0.5 s\(^{-1}\). The achievable range was limited by the maximum capacity of the gear pumps. Beyond this range, the gear pumps tended to slip and controlled flow rates were difficult to achieve. To overcome these limits and to generate strain rates closer to those observed in industrial operations, the lubricated converging flow adaptation technique was implemented using a commercial unit. The commercial unit used was the Advanced Capillary Extrusion Rheometer (ACER) which is a shear viscosity measurement device. The capillary rheometer consists of a barrel wherein the polymer pellets are packed and heated. In the standard operation, the melt is made to flow through a capillary die. The pressure drop and flow rate data are used to determine the shear rheology of the sample.

Implementation was carried out in two steps: (1) the standard cylindrical capillary die was replaced by a converging axially symmetric die and (2) since coextrusion was not possible within the system, a technique to charge two layered skin-core billets was developed. Detailed description of the ACER, the standard die and procedures for making billets is given in Chapter Four.

3.4.1 Design of constant strain rate conical die

By applying arguments similar to those used for slit geometry, the flow rate Q through an axially symmetrical (or uniaxial) converging die is given as:
\[ Q = \pi r^2(z) v_z \]  

(3.5)

where \( v(x) \) is the velocity of the core. The uniaxial elongational strain rate can be written as:

\[ \dot{\varepsilon} = \frac{\partial v_z}{\partial z} = \frac{Q}{\pi} \frac{\partial}{\partial z} \left( \frac{1}{r^2(z)} \right). \]  

(3.6)

If the profile \( r(z) \) takes the following form:

\[ r^2(z) = \frac{C}{z+D}, \]  

(3.7)

where \( C \) and \( D \) are constants, then a constant elongational strain rate is induced throughout the length of the die, given by:

\[ \dot{\varepsilon} = \frac{Q}{\pi C}. \]  

(3.8)

As it was in the case of the planar slit die, the elongational strain rate induced in the core material in the uniaxial geometry is a linear function of the core flow rate. With the above profile and the range of flow rates achieved on the ACER, theoretically, a strain rate range of 0.25 to 750 s\(^{-1}\) is possible in the die. The high core flow rates achieved in the ACER allow strain rates that are more than two orders of magnitude higher than those achieved in the slit die geometry. It must be noted that the strain rate induced in the core could be applicable provided the flow were stable under those conditions.

A description of the die and the mounting assembly of the ACER is given in Chapter Four. The same die was used in all the uniaxial elongational viscosity measurements in this research.
3.5 Theory

3.5.1 Assumptions

The following assumptions were made in order to analyze the elongational flow in the core. Since these assumptions are critical in defining the problem, each has been discussed in detail in this section.

(1) The flow is incompressible. This assumption is generally valid for rheological applications (Macosko, 1994) since compressibility effects are negligible as compared to the material effects.

(2) The core (the material to be analyzed) is assumed to be in pure elongational flow and the elongational strain rate is constant. This is the key assumption in this analysis. As shown in section 3.3.2, experimental evidence supports this assumption.

(3) The skin and core melts are completely immiscible. For the materials used in this work, experimental evidence (Figure 3.5) for polypropylene and polyethylene supports this assumption. The interface position could be seen through the glass windows during the coextrusion process when the core polymer was colored by a blue dye. A concentration of 0.02 weight percent of Disperse Blue 56 dye was mixed with the core polymer chips and fed into the core extruder. The total flow rate was fixed as 5 g/min, and the core/skin flow rate ratio was set as 9:1. After one hour, the colored core polymer could be seen through the glass window and the interface position could be clearly observed. For the other pairs of skin-core combinations, it has been assumed to be reasonably true based on the knowledge of the structure of the materials.
The flow is in a steady state. Experimental evidence for slit geometry suggests that the flow is steady in an Eulerian sense, i.e., the velocity at a fixed point in the coordinate system does not change with time. Unfortunately, due to the construction of the rheometer, it has not been possible to collect experimental evidence to prove or disprove the assumption in the case of uniaxial geometry. However, an instability for only polypropylene melts (Chapter Five) in a critical strain rate range (at about 1 s\(^{-1}\)) has been observed. This phenomenon has been observed by other workers as well (Janzen, 1994; Baker, 1993).

The flow is, however, not steady in a Lagrangian sense, i.e., after entering the elongational flow field a fluid element continues to deform for a finite length of time. Essentially, this phenomenon is the manifestation of the viscoelastic nature of the polymer melts. Tirtaatmadja and Sridhar (1994) have reported a dependence of the elongational viscosity of polymer melts on the applied strain and not strain rate up to a total strain of 3.5-4. This dependence was inferred from constant strain rate
measurements for which the viscosity was a function of time. Quantitative analysis on the stability of the coextrusion process in this research is carried out in section 3.6.

3.5.2 Development

Elongational viscosity for the planar and uniaxial geometries is defined in equations 2.27 and 2.31 respectively, in terms of the stress terms and the elongational strain rates. The strain rates in terms of the experimentally determined parameters (die design parameters and the process parameters) have been defined by equations 3.4 and 3.8 respectively.

Based on the above assumptions, as shown in Figure 3.6, the force balance in the flow direction (indicated by subscript 1) leads to:

\[ \tau_{11} \, dS = S \, dP \]  
(3.9)

\[ \tau_{11} \cdot \int_{\bar{S}_1}^{\bar{S}_2} \ln(S) \, dP = \int_{\bar{P}_1}^{\bar{P}_2} dP \]  
(3.10)

It is to be noted that the subscript 11 here is used as a generic principle flow directional stress component on a surface whose normal is in the same direction, irrespective of the geometry used. S is the cross-sectional area of the flow channel.

Two implicit assumptions have been made in going from equation 3.9 to equation 3.10. The first assumption is that the pressure P is the average pressure acting on the area normal to the flow axis. The pressure measurement was made at the die entry with a pressure transducer that was flush with the die surface. Using the momentum balance equations, it can be shown (Appendix C) that the numerical error
caused by this assumption is less than 0.01 percent of the range of the pressure transducer. The second assumption in the above step is that $\tau_{11}$ is constant. A constant strain rate $\dot{\varepsilon}$ is induced on the flow by the virtue of the die design, and by assuming that the stress state in the flow is uniquely determined by the strain rate state, it follows that $\tau_{11}$ should be constant along the flow.

For slit geometry, integrating between the limits, with the area of the slit die going from $S_1(=2W_y_1)$ to $S_2(=2W_y_2)$ and pressure going from $P_1$ to $P_2$, we get:

$$
\tau_{xx} = \frac{\Delta P}{\ln(y_1/y_2)}.
$$

(3.11)

![Figure 3.6: Force balance on the core across a converging die](image)

For uniaxial geometry, integrating between the limits, with the area of the circular die going from $S_1(=\pi d_1^2/4)$ to $S_2(=\pi d_2^2/4)$ and pressure going from $P_1$ to $P_2$, we get:
The incompressibility assumption states (Bird et al., 1987):

\[ \nabla \cdot \mathbf{v} = 0 \]  
(3.13)

\[ - d_{xx} + d_{yy} + d_{zz} = 0 \]  
(3.14)

where \( d_{ij} \) is the principal component of the deformation tensor defined in equation 2.5.

(1) For planar geometry in the flow field defined in cartesian coordinates, this implies:

\[ \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} = 0 \]  
(3.15)

\[ d_{xx} = \frac{\partial v_x}{\partial x} = \dot{\varepsilon} \]  
(3.16)

\[ d_{yy} = \frac{\partial v_y}{\partial y} = -\dot{\varepsilon} \]  
(3.17)

\[ d_{zz} = \frac{\partial v_z}{\partial z} = 0 \]  
(3.18)

Therefore the transverse direction deformation rate is equal to the negative of the flow direction deformation rate and the same relationship between stress components also occurs when the assumption that the stress state is uniquely determined by the strain rate state is made. Consequently,
The planar elongational viscosity as defined in equation 2.27 can then be calculated for the core material using the equation above and the expression for the elongational strain rate (equations 3.4):

\[
\eta_{el} \propto \frac{2WB}{\ln(y_1/y_2)} \frac{\Delta P}{Q}
\]  

(3.22)

(2) For cylindrical coordinates:

\[d_{\pi} + d_{\theta\theta} + d_{zz} = 0\]  

(3.23)

\[d_{\pi} = \frac{\partial v_r}{\partial r} = -\frac{\dot{\varepsilon}}{2}\]  

(3.24)

\[d_{\theta\theta} = \left(\frac{1}{r} \frac{\partial v_{\theta}}{\partial \theta} + \frac{v_r}{r}\right) = \frac{v_r}{r} = -\frac{\dot{\varepsilon}}{2}\]  

(3.25)

\[d_{zz} = \frac{\partial v_z}{\partial z} = \dot{\varepsilon}\]  

(3.26)

Therefore the transverse direction deformation rate is equal to hoop direction deformation rate, and they are both equal to the negative of half the flow direction deformation rate. The same relationship between stress components also occurs if the
assumption similar to the one made in the planar case, that the stress state is uniquely determined by the strain rate state, is made. Therefore:

\[ d_{\theta\theta} = d_{rr} = -\frac{\dot{\varepsilon}}{2} = -\frac{1}{2} d_{zz} \quad (3.27) \]

\[ \Rightarrow \tau_{\theta\theta} = \tau_{rr} = -\frac{1}{2} \tau_{zz} \quad (3.28) \]

The uniaxial elongational viscosity as defined in equation 2.31 can be calculated for the core from the equation above and from the elongational strain rates (equation 3.8).

\[ \eta_E = \frac{3\pi}{4} \frac{C \Delta P}{\ln(r_1/r_2) Q} \quad (3.29) \]

In both cases, the elongational viscosity is obtained as a product of two terms: one term containing the geometrical or the die design parameters, and the other term containing the process parameters to be measured in the experiment, namely, pressure drop across the die and the flow rate of the core.

3.6 Stability of the rheometer

The stability of the lubricated flow converging rheometer can be examined from two approaches. In the first, the transient nature of the elongational flow of the core is considered. In the second, the interaction of the elastic and viscous effects on the stability of the core and the interface of the skin and core is considered.

3.6.1 Transient nature of elongational flows

Elongational flows are considered to be strong flows (Tanner, 1985), i.e., the net effect of the flow field on a fluid element is that of stretching. Mathematically,
in a homogenous elongational flow, the relative position vector \( r \) between two material particles separates at a rate:

\[
\dot{r} = \mathbf{L} \cdot r ,
\]

(3.30)

where \( \mathbf{L} \) is the velocity gradient tensor defined as:

\[
L_{ij} = \frac{\partial v_i}{\partial x_j} .
\]

(3.31)

The solution for the position vector for \( \mathbf{L} \) independent of time is (Petrie, 1979):

\[
r = r_0 \exp(\mathbf{Lt}) .
\]

(3.32)

The nature of the solution can be determined by the scalar eigenvalues \( e \) of the \( \mathbf{L} \) matrix which can be determined by solving the following equation:

\[
\det(\mathbf{L}) - e \cdot \mathbf{I} = 0 ,
\]

(3.33)

where \( \mathbf{I} \) is a unit tensor. The solution grows exponentially with time if the real part of any eigenvalue in the velocity gradient tensor matrix is positive. For incompressible flows, \( \text{tr}(\mathbf{L}) \) is zero, so the sum of the eigenvalues of \( \mathbf{L} \) is zero and hence the flow will be strong if at least one of the eigenvalues has a positive real part. It has been shown by Petrie (1979) that in case of elongational flows, the real part of at least one of the eigenvalues is positive. Elongational flows are, therefore, strong flows. On the other hand, the real parts of the eigenvalues in viscometric flows (eg. simple shear flow) are zero or negative as a result the net effect on a material particle is rotation or translation. These flows are classified as weak flows.
Since polymer melts are essentially macromolecules, the time scales of the stretching effect are longer. A quantitative estimate of the degree of stretching in the induced elongational flow field is given by defining a Hencky strain $\epsilon$ (Ferguson and Kemblowski, 1991):

$$\epsilon = \ln \left( \frac{S_1}{S_2} \right). \quad (3.34)$$

The subscripts 1 and 2 denote the entry and exit positions respectively. For slit geometry the Hencky strain becomes:

$$\epsilon = \ln \left( \frac{y_1}{y_2} \right), \quad (3.35)$$

and for uniaxial geometry:

$$\epsilon = 2 \ln \left( \frac{r_1}{r_2} \right). \quad (3.36)$$

Recent data on elongational viscosity data on polymer melts (Hingman and Marczinke, 1994; Tirtaatmadja and Sridhar (1994)) indicate a wide spread (a range of 4-7) in the Hencky strain range required to attain a steady state in the flow. It should be noted that the extent to which the sample should be stretched increases exponentially with the Hencky strain.

The Hencky strain for the two geometries used in this work can be calculated from the respective die dimensions (Table 3.1). The numbers in the table indicate that a steady flow is achieved in the uniaxial rheometer; on the other hand, the flow in the planar rheometer only marginally attains a steady flow.
3.6.2 Viscoelastic instabilities

Extensive literature is available on the instabilities in extrusion (Petrie and Denn, 1976; Langlado et al., 1985) and in coextrusion (Chen, 1991; Hinch et al., 1992) of polymeric flows. However, the stability analysis in the literature has been carried out on simple shear flow geometries, not on elongational flows. Also, the constitutive equations that are used in the stability analysis are not adequate for describing elongational flows over a large strain rate range. Consequently these results are not directly applicable to homogenous elongational flows.

However, the feed section (barrel) of the uniaxial rheometer conforms to a simple shear flow geometry and even though the flow through it plays no part in the measurement of elongational viscosity, it can provide useful insight about the stability of the fluid at the entry in the elongational flow field. A similar analysis at the die exit, although rigorously inapplicable for the geometry, has also been carried out.

Two critical stability parameters (Petrie, 1979) are defined as, Weissenberg number:

\[ \text{We} = \lambda \dot{\gamma}, \tag{3.37} \]

and, Deborah number:
\[ \text{De} = \frac{\lambda}{t'} \quad \text{(3.38)} \]

The characteristic time of the process, \( t' \), can be defined for the rheometer system as the time required for the melt to flow through the geometry in consideration. For the arrangement in ACER, \( t' \) corresponds to the residence time of the polymer melt in the barrel. It has been calculated by dividing the ram speed by the barrel length. Table 3.2 lists the Weissenberg numbers and Table 3.3 lists the Deborah numbers calculated from the dimensions of ACER and the die (Chapter Four). Relaxation times (\( \lambda \)) of 0.38 s for HGX 030 (Janzen, 1994) and 0.005 s (Larson, 1988) for polyethylene were used for these calculations. The highest speed achievable in the ACER (3000 mm/min = 0.05 m/s) was used in all the calculations to obtain the most conservative stability parameter estimation.

Table 3.2: Weissenberg numbers for HGX 030 and LDPE in the barrel for the complete range of flow rates achieved in ACER

<table>
<thead>
<tr>
<th>Material</th>
<th>We</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>1.4074</td>
</tr>
<tr>
<td>PE</td>
<td>0.0769</td>
</tr>
</tbody>
</table>

According to Tanner (1985), at the critical value of \( SR = \lambda \tau_w/\eta \), extrusion flow instability is observed. \( SR \) is equivalent to the Weissenberg number at the wall for an equivalent Newtonian fluid. The critical value is reported to lie between 1 and 10.
The critical strain rate range can then be calculated ($\dot{\gamma} = SR/\lambda$) as 2.63 - 26.3 $s^{-1}$. An instability in this range has been observed in this work (Chapter Five) and has also been reported by Janzen (1994) and Baker (1993). Only at the instability, the extrudate showed a stick-slip behavior with oscillating pressure. Both below and beyond the critical flow rates, a stable extrudate was observed. Below the critical stress, a no-slip condition could be prevailing in the fluid; beyond the critical value a stable slip between skin and core could occur. At the critical value the flow profile could be unstable, flipping between the two regimes.

Table 3.3: Deborah numbers for HGX 030 and LDPE in the die for the complete range of strain rates achieved in ACER

<table>
<thead>
<tr>
<th>Material</th>
<th>De</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>50.89</td>
</tr>
<tr>
<td>PE</td>
<td>0.6696</td>
</tr>
</tbody>
</table>

Petrie (1979) has indicated that for $De < 1$ the elastic effects become unimportant. There is no general agreement in the available literature over the critical $De$ to cause instability (Tanner, 1985) in the flow. The above calculations indicate that even at high flow rates (i.e., at high strain rates) the elastic effects in polyethylene will not be dominant; however, these effects will become dominant in polypropylene and may cause an instability in the flow.
3.7 Advantages and limitations

Key features of the lubricated converging flow rheometer described above are:

1. It allows the measurement of the extensional viscosity of polymer melts at strain rates up to two orders of magnitude higher than those reported in the literature.

2. No separate assembly is required to construct the system. The application can be an auxiliary unit to an existing capillary melt rheometer without the need of elaborate additional apparatus.

3. The system is flexible and a broad range of constant strain rates can be achieved with relative ease by using appropriate insert profiles in the die with controlled volumetric flow rate and the available ram speeds.

4. It is possible to analyze very small samples as they can be sandwiched in the core between other samples encapsulated by a common skin layer. This is particularly useful for materials that are available in only small quantities.

The limitations of the rheometer developed in this work are:

1. The choice of a suitable skin material is critical. The skin polymer should meet the conditions discussed in this chapter in order to ensure that the core undergoes a pure extensional flow.

2. A drawback that is inherent in the method is that the transient data is lost due to the averaging of the stresses along the flow axis.
Chapter 4

EXPERIMENTAL

4.1 Apparatus

4.1.1 Planar geometry: Coextrusion assembly

Figure 4.1 shows the schematic assembly which was used for the determination of planar elongational viscosity. The assembly consisted of two extruders and gear pumps, a slit die, image analysis device and a take-up device.

4.1.1.1 Extruders

The extruder for the core layer was a twin screw co-rotating intermeshing laboratory extruder model ZE 25 manufactured by Berstorff Corporation. The extruder had two 25 mm diameter screws which were 745 mm long and the center-to-center distance between them was 21.5 mm. The power of the motor supplied with the extruder was 10.5 KW, and the maximum speed was 500 rpm. There were six zones, each equipped with a 2.1 KW heater and a Eurotherm Corporation digital controller (model 808 or 847) connected to the control panel. A temperature profile along the extruder zones could be maintained by setting the desired temperature on the controller. A dedicated personal computer PC 386 could be used to run the extruder in a closed loop control to maintain constant pressure if desired.
Figure 4.1: Schematic of the coextrusion assembly

The skin extruder was a 19 mm single screw extruder manufactured by Brabender Instrument Incorporated. The extruder had a length-to-diameter ratio of 20:1 and a compression ratio of 4:1. It included a 1.12 KW 220 volt model PL-V 150 motor with a maximum speed of 2400 rpm, and a gear reduction box with a reduction ratio of 20:1. The speed controller for the motor was a Fincor model 2400 MK II DC motor controller manufactured by Fincor Incom International Incorporated. There were two heating zones with the heaters supplied by Brabender Instruments Company.

4.1.1.2 Gear pumps

A high pressure Zenith gear pump with a rated flow capacity of 1.752 cc/rev was used for the core. The pump was driven by a 0.37 KW DC motor manufactured by Pacific Scientific with the maximum rpm of 1800. Two different sets of reducing boxes (10:1 and 80:1) were used to generate the desired flow rates. A 1 KW box-type
heater, custom designed by Parker Hannifin Corporation, was used to heat the core gear pump.

The gear pump for the skin polymer was a high pressure Zenith gear pump with a rated capacity of 0.297 cc/rev. The capacity of the skin gear pump was lower than that of the core gear pump to allow for a lower (about 1/10) flow rate at attainable rpm. A 110 volt, 0.19 KW DC drive with a maximum rotation of 1,725 rpm manufactured by General Electric Corporation was used with a 5:1 reducer box. A pair of 500 Watt cartridge heaters was used to heat the gear pump.

The gear pumps were calibrated to measure the melt flow rates. The calibration was performed by running the extruders till they reached steady state and then measuring the weight of the extrudate for one minute. A plot of the rpm settings of the controller and the corresponding flow rate is given for the core (Figure 4.2) and for the skin (Figure 4.3).

4.1.1.3 Die

A die designed by Lakshminarayan (1984) was used in the experiment. Figure 4.4 (a) shows the close up of one half of the die. The die was equipped with glass windows to allow imaging of the tracer particles which were used in determining the velocity profile of the flow. The glass windows were made from a high pressure Macbeth gage glass manufactured by Corning Glass Works. The die was assembled by bolting together two symmetrical halves with the glass window and the insert, shown in Figure 4.4 (b), inside the die.
Figure 4.2: Calibration chart for core gear pump

Figure 4.3: Calibration chart for skin gear pump
Figure 4.4: (a) Extrusion die showing the inserts (b) Hyperbolic insert for planar elongational rheometry
The design of the die permitted a choice of the die profile. In this work however, only a constant width hyperbolic converging shape was used. Figure 4.4 (b) shows the hyperbolic die used in the experiment. Figure 4.5 shows the dimensions of this hyperbolic slit die insert. The insert was made of 316 stainless steel.

The die was heated by two 1,600 watt plate heaters manufactured by Industrial Heaters Company. A Dynisco Model TPT 432 A-10M-6/18 transducer was used to measure the pressure and the temperature of the polymer inside the die. The pressure transducer had a range of 0-70 MPa.

\[
\text{Curve Profile: } y = \frac{B}{x + A}
\]

\[
A = 4.3942 \text{ mm} \\
B = 43.096 \text{ mm}^3
\]

Figure 4.5: Schematic of the hyperbolic slit die
4.1.1.4 Take-up device

The discharged polymer ribbon was rolled through a take-up device which was used in all the runs primarily to prevent the melt from accumulating around the die exit. The gap between the die exit and the take-up device varied from 4-8 inches and was adjusted according to the processing conditions. The take-up device consisted of two sets of rollers, each with a 3 inch wide natural rubber belt. The rollers were driven by a 0.19 KW 110 volt motor with a maximum speed of 1725 rpm and a 5:1 gear reduction box. The two belts supported the extruded polymer ribbons; the space between the two belts could be adjusted by rotating a handle located at the bottom of the device. The device was fabricated at the machine shop in the Chemical Engineering Department, Louisiana State University.

4.1.2 Uniaxial geometry: Advanced Capillary Extrusion Rheometer (ACER)

The determination of uniaxial elongational viscosity was done by adapting the computer controlled capillary rheometer ACER manufactured by Polymer Laboratories Ltd., UK (now a part of Rheometrics Inc., USA). A schematic of the ACER is shown in Figure 4.6. The polymer was packed in the cylindrical barrel, and a capillary die was fitted at the end of it. The barrel was heated with band heaters. A drive section at the top moved the ram through the length of the barrel pushing the polymer melt through the die at the programmed volumetric flow rate. A pressure transducer attached flush with the wall of the barrel 5 mm above the die was used to measure the pressure drop across the die. The following sections describe the components of the ACER in greater detail:
4.1.2.1 Drive section

A Compumotor 4.47 KW stepper motor provided the movement of the holder and the attached ram down the length of the barrel. The ram could be detached from the holder to allow packing of the material in the barrel. The maximum possible ram travel length was 300 mm. The range of the ram speed was 0.5-3000 mm/min. At the end of the ram that was in contact with the melt, a brass or a Teflon sealing could be screwed on to prevent the melt from slipping above the ram. The ram and the holder were made of stainless steel.
4.1.2.2 Barrel

The inside diameter of the barrel was 20 mm. A Terwin Instruments Ltd. pressure transducer (Model 1076-D6) was attached flush with the barrel wall through a sealing arrangement 5 mm above the die. Two transducers of range 70 MPa and 200 MPa were used in the experiments. The choice of the transducer depended on the range of the pressure that was required for the given sample. The die was placed in a die holder and this was then screwed in at the bottom of the barrel. The barrel was equipped with band heaters which maintained the barrel and the die at the set temperatures. Using the controller in the ACER, temperature from ambient to up to 350 °C could be maintained within ±1 °C.

4.1.2.3 Dies

4.1.2.3.1 Capillary die

The standard die used for shear viscosity measurement is shown in Figure 5.7. The bottom (discharge) end was undercut to achieve an L/D ratio of 20. This arrangement, by controlled depth of undercutting, allowed a range of L/D ratios while keeping the same external length to fit in the die holder. For the die used in the experiments, the range of apparent shear rates achieved was $5.33 \times 10^1$-$1.6 \times 10^5$ s$^{-1}$. Tungsten Carbide was used as the material of construction for the capillary dies. The capillary dies manufactured by Polymer Laboratories were provided with the ACER.

4.1.2.3.2 Hyperbolic die

Figure 4.8 shows the hyperbolic die designed for the experiment. The dies were manufactured by Scientific Fabrication Service Inc., Plaquemine, LA. Electro-
Discharge Machining technique was used by the manufacturer to shape the inner die profile to the required design equation. The material used was Type D-2 Tool-steel. In this case the complete length of the die was used to minimize entrance losses and end-corrections. Corresponding to the available ram speeds, the range of elongational strain rates achieved was $2.665 \times 10^{-1} - 7.5 \times 10^2 \text{ s}^{-1}$. The profile of the die was designed according to the following equation:

$$r^2 = \frac{6.2531}{z + 6.2657 \times 10^{-2}}. \quad (4.1)$$

![Diagram of die profile](image)

Figure 4.7: Standard capillary die used in ACER for shear rheometry

4.1.2.4 Procedure, data acquisition and control

The data acquisition and control software provided by Polymer Laboratories with the ACER was installed on an IBM 386 33 MHz PC. The experiment could be set by the operator from the computer screen and keyboard. Input parameters for the experiment included the temperature of the polymer melt, the ram speeds, the diameter
and the length of the die, and the range of the pressure transducer. Since a minimum number of points at steady state was required, a maximum of 8 ram speeds could be set in one experiment. The procedure described below was followed for both shear and elongational viscosity measurement. Any departure from the procedure is noted in Chapter Five.

The barrel was preheated to the required temperature and packed with the sample. These samples were in the form of polymer pellets in case of shear rheology, and two layered billets for elongational rheology, prepared as described in section 4.3.2. A heat soak for 30 minutes was allowed for the sample to reach a thermal steady state prior to the start of the experiment. The range of shear (or elongational) strain rates were applied in steps of ram speeds, each speed corresponding to a fixed
strain rate. The pressure drop across the die and the temperature of the melt were then recorded. Statistical analysis to compute standard deviation of the raw data for pressure drop was carried out. The pressure and the corresponding speeds were then smoothed and plotted. The elongational viscosity parameters were determined separately on a spreadsheet (Quattro Pro). In the case of shear viscosity measurements, the rheological plots were obtained using the ACER software.

4.2 Materials

The core materials used for the elongational rheology were: commercial grades of polypropylenes, syndiotactic polystyrene and nylon-66. Commercial grades of polyethylene were used as the skin material for all the grades of the core polymers.

4.2.1 Polyethylene

Table 4.1 shows the summary of the different grades of polyethylene used in the work. In addition, the grade DOW LLD-2 was used in the tracer particle measurement in the planar die. The zero shear viscosity of this grade was 63 Pa.s at 200 °C.

4.2.2 Polypropylene:

Table 4.2 shows the summary of the different grades of polypropylenes provided by Phillips 66. The details of the material supplied by Rheometrics Inc. were not available from the supplier. In addition to those listed in the table, grade HGY 040 was used in the planar rheometer to perform the tracer particle measurement. The zero shear viscosity of the sample was 77382 Pa.s at 200 °C. The molecular weight of HGX 030 was 300,000 and the polydispersity index ($M_w/M_n$) was between 4 and 6 (Janzen, 1994).
Table 4.1: Viscosity of polyethylene melts

<table>
<thead>
<tr>
<th>Strain rate</th>
<th>PE (log Pa.s)</th>
<th>DOW 2503 (290°C)</th>
<th>DOW LDPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>log((\gamma))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.13</td>
<td>-</td>
<td>-</td>
<td>1.95</td>
</tr>
<tr>
<td>1.43</td>
<td>1.69</td>
<td>1.49</td>
<td>1.90</td>
</tr>
<tr>
<td>1.73</td>
<td>1.35</td>
<td>1.89</td>
<td></td>
</tr>
<tr>
<td>2.03</td>
<td>1.24</td>
<td>1.84</td>
<td></td>
</tr>
<tr>
<td>2.43</td>
<td>1.12</td>
<td>1.83</td>
<td></td>
</tr>
<tr>
<td>2.73</td>
<td>2.20</td>
<td>1.77</td>
<td></td>
</tr>
<tr>
<td>3.12</td>
<td>-</td>
<td>1.67</td>
<td></td>
</tr>
<tr>
<td>3.43</td>
<td>-</td>
<td>1.58</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2: Viscosity of polypropylene melts at 200 °C

<table>
<thead>
<tr>
<th>Strain rate</th>
<th>PP (log Pa.s)</th>
<th>HGX 030</th>
<th>HGZ200</th>
</tr>
</thead>
<tbody>
<tr>
<td>log((\gamma))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.13</td>
<td>3.51</td>
<td>3.18</td>
<td></td>
</tr>
<tr>
<td>1.43</td>
<td>3.37</td>
<td>2.92</td>
<td></td>
</tr>
<tr>
<td>1.73</td>
<td>3.17</td>
<td>2.81</td>
<td></td>
</tr>
<tr>
<td>2.03</td>
<td>2.97</td>
<td>2.71</td>
<td></td>
</tr>
<tr>
<td>2.43</td>
<td>2.70</td>
<td>2.46</td>
<td></td>
</tr>
<tr>
<td>2.73</td>
<td>2.49</td>
<td>2.25</td>
<td></td>
</tr>
<tr>
<td>3.12</td>
<td>2.20</td>
<td>1.97</td>
<td></td>
</tr>
<tr>
<td>3.43</td>
<td>1.98</td>
<td>1.78</td>
<td></td>
</tr>
</tbody>
</table>

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
4.2.3 Nylon

Nylon-66 was supplied by DuPont. The melting point of the sample was 280 °C and the material was available in a powdered form. The operating temperature was 290 °C. Prior to analysis the sample was dried for four hours at 60 °C under nitrogen to remove moisture. This procedure is essential to prevent degradation of nylon at elevated temperature. The polydispersity index of this sample was reported to be 2 (Ross, 1995).

4.2.4 Syndiotactic polystyrene:

Syndiotactic Polystyrene was supplied by DOW Chemical. The melting point of the material was 280 °C. The analysis of the material was done at two operating temperatures, 290 °C and 300 °C. The molecular weight of the sample was 4.5×10^5 with the polydispersity index of 2.5.

4.3 Sample preparation

4.3.1 Planar geometry: Slit die

The coextrusion assembly for the determination of elongational viscosity in planar geometry enabled the direct charge of the polymer melts into the die from the two extruders. The melt temperature in the die was maintained at 200 °C. The six temperature zones of the twin-screw core extruder were maintained at the temperatures 170 °C, 180 °C, 190 °C, 200 °C, 200°C and 200 °C respectively. The two zones of the skin extruder were maintained at 135 °C and 200 °C respectively. All the intermediate junctions and lines were maintained at 200 °C. The charge was allowed to reach thermal steady state for two hours. The skin extruder and skin gear pump were started...
first, then after 15 minutes of discharge the core extruder and the core gear pump were started. The above procedure was used to enable the skin layer to uniformly coat the core layer.

The minimum pressure requirements across the gear pumps were 500 psi and 100 psi for the core and the skin respectively. Polypropylene melts tend to create an extrudate with bubbles and cavities. By careful pressure and temperature combinations the above occurrence can be minimized (Hingman and Marczinke, 1994). For this system the best combination was found to be the temperature setting of 200 °C and the extruder exit pressure between 600-800 psi.

The flow was allowed to reach a steady state for 15 minutes after the start of the coextrusion. The take-up speed was adjusted such that the ribbon was supported without being pulled from the die exit. The melt flow rates of the skin and core melt were determined from the calibration charts and the pressure was recorded from the transducer on the die.

Figure 4.9: Two layered billet
4.3.2 Uniaxial geometry: ACER die

A two layered billet (Figure 4.9) was inserted in the barrel to introduce a steady flow of two polymers in skin-core form through the hyperbolic die of the ACER. The material to be analyzed was packed in the core layer, and the skin layer consisted of the lubricant material. The core material was available in two forms: pellets or powder. The sample preparation method depended on the form of the core.

4.3.2.1 Billet preparation: Pelletized sample

A mold for the billet was made from a copper tube of size 7/8 inch BWG 18 (ID 0.777 inch). The above size of the tube was chosen as it resulted in a billet that fit closely in the barrel of the ACER. A flange was welded on one end of the tube and the other end was kept free. The flange (Figure 4.10) was fitted in place of the slit die on the coextrusion assembly. The tube was sprayed with a mold release agent from inside and the extrudate was charged in from the two extruders. The gear pump rpms were adjusted to maintain the required flow rate ratio. The tube was insulated, the flanges were clamped and the coextrusion was started. When the tube was filled with the polymer, the extrusion was stopped, the tube was detached and quenched in ice-water. The billet was then removed and cut to sample lengths (4-8 inches).

It was possible to pull the inner solid cylinder of the core polymer out of the surrounding shell since the skin and core polymer melts were incompatible. The resulting shell and core were observed for irregularities and only smooth and regular samples were accepted for runs.
Figure 4.10: Schematic of the mold used for making two layered billets

4.3.2.2 Billet preparation: Powdered sample:

A billet was first made using only the skin material following the above procedure. A hole of 13.5 mm diameter was drilled on one end of the billet using a lathe until 10 mm length of material remained at the other end, resulting in a hollow cylinder with one end closed for sealing. The powdered core material was then compacted in the shell. The shell was sealed on the open end using the skin material to prevent spilling or contamination of the core polymer.

The data obtained from the experimental set-ups described in this chapter is presented in the next chapter; elongational rheology in two geometries and the shear rheology of the polymer samples described in section 4.2 are presented and discussed.
Chapter 5

RESULTS AND DISCUSSION

Commercial grade polyolefins (polyethylene and polypropylene), syndiotactic polystyrene, and nylon-66 were chosen to be analyzed for elongational and shear viscosity determination on the lubricated converging flow rheometer developed in this work. Polypropylene melts were analyzed in planar and uniaxial geometries. Syndiotactic polystyrene and nylon-66 were analyzed in uniaxial geometry. Polyethylene was used as the skin layer for all the measurements. Several grades of polyethylene were used as a skin layer; the choice of a particular grade depended on the shear viscosity ratio of the polyethylene melt and the core material used. For polypropylene melts the DOW LLD-2 and DOW LDPE grades were used. More than one grade was used for the same material and no difference was observed in the results. DOW LDPE grade of polyethylene was used for the syndiotactic polystyrene melt and DOW 2503 was used for the nylon-66 melt.

Planar elongational viscosity was computed using equation 3.22 and the uniaxial elongational viscosity was computed using equation 3.29. Table 5.1 lists the geometrical parameters used for the two die geometries. The raw data collected for the runs is tabulated in Appendix A. A sample calculation for obtaining the
elongational viscosity from raw data is presented in Appendix B. Statistical analysis of the raw data was carried out on ACER, all the calculations and plotting of the final data was carried out on Quattro Pro. A log-log scale has been used in all the plots for two reasons: (1) a large range of strain rates and viscosities are covered, and, (2) the exponential dependence of the viscosity on strain rates (well documented in the literature in the case of shear rheology and expected in the case of elongational rheology) is well depicted by the choice of the log-log scale.

Table 5.1: Geometrical constants in the hyperbolic die

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planar</td>
<td>A = 4.3942 mm</td>
</tr>
<tr>
<td></td>
<td>B = 43.096 mm²</td>
</tr>
<tr>
<td>Uniaxial</td>
<td>C = 6.2531 mm³</td>
</tr>
<tr>
<td></td>
<td>D = 6.2657 \times 10^{-2} mm</td>
</tr>
</tbody>
</table>

5.1 Planar elongational viscosity

Two commercial grades of polypropylene (HGX 030 and HGZ 200) were used for planar elongational viscosity determination in the slit rheometer. Figure 5.1 shows the elongational viscosity of the two polymer melts measured at 200 °C. The pressure drop data obtained was very stable; the standard deviation obtained for the data was
Figure 5.1: Planar elongational viscosity of HGX 030 and HGZ 200 at 200 °C as a function of elongational strain rate.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Figure 5.2: Shear viscosity and planar Trouton ratio of HGX 030 at 200 °C at shear rates equivalent to applied elongational strain rates.
Figure 5.3: Shear viscosity and Trouton ratio of HGZ 200 at 200 °C at shear rates equivalent to applied elongational strain rates
smaller than the size of the data points. Figure 5.2 and figure 5.3 show the shear viscosity and Trouton ratio of HGX 030 and HGZ 200 respectively. The following observations can be made about the results obtained for the planar elongational viscosity of the above melts:

1. The planar elongational viscosity of polypropylene melts in the given extensional rate range decreases with increasing strain rate. Recent work on polypropylene melts at lower or comparable strain rates (Barnes and Roberts, 1992; Hingman and Marczinke, 1994) has indicated that except at very small strain rates \(10^{-3} \text{ s}^{-1}\) polypropylene melts show a strain thinning behavior as indicated in this work. As the data presented in the later sections, the above trend has been also observed at higher strain rates.

2. The observed Trouton ratios are higher by 2-3 orders of magnitude than the theoretically predicted value of 4 for Newtonian fluids. According to Leal (1992, p59) the "ratio of the normal stress difference...to the strain rate is observed in some viscoelastic fluids to exceed the shear viscosity (that is, the ratio of shear stress to shear rate) by many orders of magnitude." At very small strain rates \(10^{-3} \text{ s}^{-1}\), which could not be induced in the rheometer developed in this work) the theoretical limit for a Newtonian fluid has been observed for polymer melts (Mackay and Dajan, 1994).

3. The two grades of melts behave differently in the extent of their strain thinning property. This observation has been the prime motivation for the study of the elongational properties. Thus, shear rheology alone is not adequate to
completely characterize polymeric materials. As described in later sections, a peak observed in the elongational viscosity for nylon-66 further strengthens the argument.

(4) On a log-log scale the shear and elongational viscosity curves tend to become parallel (Trouton ratio reaches a constant) at increasing strain rates. The above observation, suggested by Barnes and Roberts (1992), has not been confirmed in the literature primarily because elongational viscosity at high strain rates (>100 s⁻¹) has not been well documented. As shown in the next section, the above holds true for polypropylene melts over the strain rate range achieved in this work (533 s⁻¹).

5.2 Uniaxial elongational viscosity

5.2.1 Polypropylene

Two commercial grades of polypropylene were analyzed in the uniaxial geometry rheometer, HGX 030 and an unidentified sample sent for analysis by Rheometrics Inc.

5.2.1.1 HGX 030

These samples were available as pellets. The billets for the material were made according to the procedure described in section 4.3.2.1.

The uniaxial elongational viscosity of HGX 030 at 200 °C as a function of the elongational strain rate is presented in Figure 5.4. The shear viscosity and the Trouton ratio as a function of the strain rate at 200 °C are presented in figure 5.5.
(1) As observed for the planar case, a strain thinning behavior in the sample is also observed in uniaxial geometry. At equivalent strain rates (<50 s\(^{-1}\)), the data agree within the order of magnitude with that presented in the literature (Barnes and Roberts, 1992; Hingman and Marczinke, 1994). At higher strain rates (>100 s\(^{-1}\)) data was not available in the literature to compare.

(2) An anomaly in the data appeared at the strain rate of 1 s\(^{-1}\). The anomaly is in the form of an instability in the pressure drop which resulted in a deviation from the trend. Several researchers in industry (Baker, 1993; Janzen, 1994) have reported a similar instability in shear mode occurring at the corresponding stress level (0.1 to 1 MPa). In the literature, the phenomenon has been reported but is not well understood (Macosko, 1994). A possible explanation could be the existence of an instability island (Chen, 1991) in the phase plane plot of the flow (a plot of viscosity ratio vs. flow rate ratio at different elasticity ratio of the two fluids).

(3) The Trouton ratio of HGX 030 in the uniaxial geometry (figure 5.5) is higher than the theoretical limit of 3. The ratio reaches a near constant value at strain rates higher than 50 s\(^{-1}\).

(4) In order to compare the two geometries the elongational viscosity data for the planar and the uniaxial case were normalized. The planar viscosity data were divided by the theoretical value (for Newtonian flow) of 4 and the uniaxial data were divided by the equivalent value of 3. Thus, for the same strain rate...
Figure 5.4: Uniaxial elongational viscosity of HGX 030 at 200 °C as a function of elongational strain rate
Figure 5.5: Shear viscosity and Trouton ratio of HGX 030 at 200 °C at shear rates equivalent to applied elongational strain rates.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Elongational Viscosity (Pa.s)

1E7
1E6
1E5
1E4
1E3

Strain Rate (1/s)
1E-2 1E-1 1E0 1E1 1E2 1E3

- HGX030 (Capillary)  - HGX030(Slit)  - HGZ200(Slit)

Figure 5.6: Normalized planar and uniaxial viscosity of HGX 030 at 200 °C

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
range, it was expected that the two sets of data should coincide. The resulting data are plotted on figure 5.6. Qualitatively, the trends agree but the normalized planar elongational viscosity is higher than normalized uniaxial elongational viscosity. The possible source of error could be the fact that the Hencky strain in the planar case was 3.08, and as discussed in section 3.6, the flow could still be in the transient phase. Other possible source could be in the difference in the geometry of the feeding section and the die flow channel and the placement of the pressure transducer. A circular pipe feeds the melt into the rectangular slit geometry, and this change in the flow profile could be affecting the data. It should be noted that these effects are minimized in the conical geometry by designing the entry diameter of the hyperbolic conical die to be the same as the diameter of the feeding barrel.

5.2.1.2 Rheometrics

The Rheometrics sample was available in powdered form. The billets for this material were prepared using the procedure described in 4.3.2.2.

The elongational viscosity of the Rheometrics sample at 200 °C is presented in figure 5.7. The Trouton ratio and the shear viscosity are presented in figure 5.8.

(1) As was expected for polypropylene melts this sample also showed strain thinning behavior. Beyond the strain rate of 50 s\(^{-1}\) the viscosity showed a decrease in the strain thinning. Since this was at the higher limit of the strain rates that could be achieved on this rheometer, the strain hardening trend that the data suggest, could not be established.
Figure 5.7: Uniaxial elongational viscosity of Rheometrics sample at 200 °C as a function of elongational strain rate
Figure 5.8: Shear viscosity and Trouton ratio of Rheometrics sample at 200 °C at shear rates equivalent to applied elongational strain rates.
Figure 5.9: Comparison of elongational viscosity Rheometrics and HGX 030 at 200 °C.
Figure 5.10: Comparison of the Trouton ratio of Rheometrics and HGX 030 at 200 °C
(2) The anomaly in the data similar to that described earlier for HGX 030 at the same strain rate range (0.1-1 s\(^{-1}\)) is observed.

(2) The Trouton ratio did not vary significantly with the strain rate. As observed for HGX 030, the elongational viscosity curve became nearly parallel to the shear viscosity curve. The increase in the Trouton ratio occurred at the higher limits of the rheometer and as mentioned above in the case of elongational viscosity, the trend is suggested but not established.

(3) In order to compare the data with HGX 030 both viscosities are plotted on the same plot (Figure 5.9). The elongational viscosity of Rheometrics sample was lower than that of HGX 030 at lower strain rates but at higher strain rates the two sets of data came closer. Trouton ratios (Figure 5.10) of the two melts do not change significantly with strain rates in the observed range.

5.2.2 Syndiotactic polystyrene (sPS)

The procedure described in section 4.3.2.2 was used to prepare billets for this material as it was available in powdered form. The material was analyzed at two operating temperatures: 280 °C and 300 °C. Since the material was prone to thermal degradation at elevated temperature the thermal history described in section 4.1.2.4 was not suitable. The following procedure was followed for all the sPS samples. The material was first heated to 200 °C (where it was stable) for 15 minutes and then heated to the operating temperature and maintained there for 15 minutes prior to starting the experiment.
Figure 5.11: Uniaxial elongational viscosity of syndiotactic polystyrene melt at 280 °C and 300 °C as a function of elongational strain rate
Figure 5.12: Shear viscosity and Trouton ratio of syndiotactic polystyrene melt at 280 °C and 300°C at shear rates equivalent to applied elongational strain rates.
The elongational viscosity of the sample at the two operating temperatures is plotted in Figure 5.11. The Trouton ratio and the shear viscosity is shown in figure 5.12. Stable results for strain rates higher than 10 s\(^{-1}\) were not obtained for sPS melt.

1) In the observed range, the elongational viscosity of sPS samples decreases with the strain rate. The decrease is sharper than that observed for polypropylene melts. No data on the elongational viscosity of sPS was available for comparison.

2) As expected, the elongational viscosity of sPS decreased with an increase in the temperature (Figure 5.11). The strain thinning was steeper at 300 °C than that at 280 °C.

3) The Trouton ratios were smaller than those observed for polypropylene melts. The Trouton ratio seems to decrease slightly with increasing strain rate in the observed range.

5.2.3 Nylon-66

Nylon-66 was available in powdered form. The sample was pre-treated as described in section 4.2.3 prior to making the billets (section 4.3.2.2). The extrudates were sent to DuPont Company for thermal analysis to detect any possible thermal degradation. The analytical results were not received to date, however, a visual inspection (Ross, 1995) indicated no degradation.

The operating temperature for this sample was 290 °C. Figure 5.13 presents the elongational viscosity data obtained for the sample. Trouton ratio and the shear viscosity are plotted in Figure 5.14.
Figure 5.13: Uniaxial elongational viscosity of nylon-66 melt 290 °C as a function of elongational strain rate

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Figure 5.14: Shear viscosity and Trouton ratio of nylon-66 melt 290 °C at shear rates equivalent to applied elongational strain rates

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
(1) An apparent slight initial increase in the elongational viscosity with increasing strain rate is observed followed by an apparent peak at strain rate of 2-5 s\(^{-1}\). The increase is significantly higher than the standard deviation of the data. At higher strain rate the viscosity drops showing a strain thinning behavior. In the available literature, there was no elongational rheology data on this material at the strain rates generated in this work. However, the slight increase and then drop at 1 s\(^{-1}\) is consistent with observed behavior in industry for spinning nylon-66 (Ross, 1995). The result is a dramatic deviation from the shear rheology of the material where the shear viscosity remains nearly constant at shear rates 1-10 s\(^{-1}\) and then slightly drops with increasing shear rate for shear rates greater than 100 s\(^{-1}\) (figure 5.14).

(2) The Trouton ratio of the sample was two orders of magnitude higher than the theoretical limit of 3 for a Newtonian fluid. The Trouton ratio as a function of strain rate nearly follows the elongational viscosity curve, primarily because at the induced strain rate range the shear viscosity is found to be nearly constant.

5.3 Effect of molecular parameters

Figure 5.15 shows a plot of the Trouton ratios of HGX 030, Nylon-66 and syndiotactic polystyrene. The polydispersity index of each melt is indicated in the legend. The data indicate that the spread of the molecular weight may affect the dependence of the Trouton ratio on the elongational strain rates. The Trouton ratio decreases with increasing strain rate for a narrow distribution (PI=2-2.5) of molecular
Figure 5.15: Correlation between the Trouton ratio and polydispersity index of polymer melts

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
weight; for nylon-66 and syndiotactic polystyrene melts in this case. For a broader molecular spread polymer (PI=4-6), e.g. polypropylene, the Trouton ratio seems to be relatively insensitive to the strain rate. A sharper shear thinning behavior of narrow molecular weight distribution polymers as compared to a more diffused shear thinning behavior of broad molecular weight distribution polymers is well known in shear viscosity (Macosko, 1994; Cogswell, 1981), but a similar study in elongational behavior is not available. A recent study on the effect of branching on polyethylenes (Chohan, 1994) concluded that the elongational viscosity is dependent on the degree of branching present in the molecule structure. The present data indicate a correlation between the elongational rheology and the molecular weight distribution of the polymer melt. More detailed study is desirable in this area.

5.4 Summary

Elongational viscosity data, presented for several polymer melts indicate that the shear rheology alone cannot describe the response of all polymer melts to the applied deformation. As indicated by the above data, the response of the polymer melts to induced elongational flow field could vary from a strain softening one to a strain insensitive to a strain hardening one. Molecular weight and molecular weight distribution of the polymers further affect the elongational rheology. For processing operations such as melt spinning and film blowing, the data could be critical, both in designing and in quality control. For melts such as nylon-66, a peak in the viscosity could necessitate a narrow but a well-defined window of operation.
It should be noted that the data determined in this work is presented in a raw form. An empirical fit for each material can be essentially computed, but will have little physical meaning. As discussed in the literature review, a general theoretical treatment for elongational flows which can fit all the available data is missing. Further, the elongational rheological data, particularly steady state data at high strain rates is not readily available. The present work is an effort in this area of the field. Empirical constitutive equations to relate all data by one general equation have been developed (Barnes and Roberts, 1992) but the assumptions made in the derivation restrict the application, and more work is needed in that area.
Chapter 6

CONCLUSIONS

The following conclusions can be drawn from the study:

(1) It is possible to generate nearly shear free elongational flow in a core polymer melt using skin-core coextrusion process by imposing conditions on the skin to core viscosity ratio and flow rate ratio. Experimental observations confirm theoretical predictions made in prior research.

(2) Converging die profiles can be designed such that the elongational strain rate induced in the core is constant and only a function of the flow rate of the core through the die. Experimentally observed strain rates agree closely with the predicted values and the dependence on flow rates is found to be linear.

(3) A laboratory scale planar rheometer to study the elongational rheology of polymer melts was developed by coupling the above two concepts. Implementation of the process on a commercial capillary rheometer (ACER) was carried out by replacing the standard capillary die by a conical hyperbolic converging die. A patent has been issued on the process (Collier, 1994).

(4) Stable flows are observed in the planar elongational rheometer. The stability of flow in the uniaxial geometry was not able to be confirmed experimentally.
due to the inability of visual observation of the melt. Stability parameters calculated for the entry flow to the uniaxial elongational rheometer indicate a stable flow prior to the die entry. It was experimentally observed that in a critical range of strain rates (0.5-3 s⁻¹), the coextruded flow can become unstable, however, the flow was found to be stable above and below the critical limits. The range of the observed instability agrees with the literature and industrial observations. The instability could be due to interfacial slippage; however, more work is needed in this area to correlate the theoretical analysis with the observed behavior.

(5) It was possible to generate strain rates up to 533 s⁻¹ in the uniaxial rheometer. Commercial grades of polypropylene, syndiotactic polystyrene and nylon-66 melts were analyzed. Polyethylene was used as a skin layer in all the experiments. General agreement with the available literature for equivalent strain rates was found. It can be concluded from the data obtained that the elongational rheometer developed in this work can detect significant rheological response of polymer melts to induced stress that cannot be characterized by shear rheology alone.

(6) The design of the rheometer does not allow measurement of the transient behavior of polymer melts.

(7) Analysis of the core polymer melt requires a choice of appropriate lubricant or skin to be made. The conditions necessary to develop pure elongational
flow in the core are that the flow rate ratio of core to skin should be about 10 and the viscosity ratio should be at least $10^2$.

### 6.1 Scope for future work

1. Explore the possibility of developing a constitutive equation that can account for strain hardening and strain softening behavior in elongational rheology as well as non-Newtonian behavior in shear rheology.

2. Generate extensive data for a large range of strain rates to develop general empirical or semi-empirical models for elongational rheology.

3. Investigate instabilities occurring in elongational flows in coextrusion.

4. Explore the possibility of end-correction in the lubricated flow rheometer; study the effect of Hencky strain on the elongational viscosity of polymer melts.

5. Develop flow systems that can be used to study the transient elongational behavior at high elongational strain rates.

6. Investigate a possible relationship between the molecular parameters such as molecular weight, polydispersity index and the extent of branching in the polymer, and the elongational viscosity and Trouton ratio behavior of the polymer melt.
References


## Appendix A

### RAW DATA

<table>
<thead>
<tr>
<th>Sample</th>
<th>Speed (mm/min)</th>
<th>Diameter (mm)</th>
<th>Sigma T 3 (os)</th>
<th>Pressure (KPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>13.6</td>
<td>41</td>
<td>1795000</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>13.6</td>
<td>49</td>
<td>2620000</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>13.6</td>
<td>55</td>
<td>3241000</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>13.6</td>
<td>45</td>
<td>3999000</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>13.6</td>
<td>86</td>
<td>4137000</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>13.6</td>
<td>70</td>
<td>1795000</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>13.6</td>
<td>54</td>
<td>2620000</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>13.6</td>
<td>108</td>
<td>3241000</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>13.6</td>
<td>13</td>
<td>3999000</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>13.6</td>
<td>41</td>
<td>4137000</td>
</tr>
</tbody>
</table>

- **HGZ020**
  - Pressure (KPa): 200°C
  - Speed (mm/min): 5, 10, 15, 20, 25, 30, 35, 40, 45, 50
  - Diameter (mm): 13.6

- **Rheometric Pressure (KPa)**
  - Pressure (KPa): 200°C
  - Speed (mm/min): 5, 10, 15, 20, 25, 30, 35, 40, 45, 50
  - Diameter (mm): 13.6

- **S-PS**
  - Pressure (KPa): 280°C
  - Speed (mm/min): 5, 10, 15, 20, 25, 30, 35, 40, 45, 50
  - Diameter (mm): 13.6

- **S-PS**
  - Pressure (KPa): 300°C
  - Speed (mm/min): 5, 10, 15, 20, 25, 30, 35, 40, 45, 50
  - Diameter (mm): 13.6

- **HGZ030**
  - Pressure (KPa): 200°C
  - Speed (mm/min): 5, 10, 15, 20, 25, 30, 35, 40, 45, 50
  - Diameter (mm): 13.6

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Speed (mm/min)</th>
<th>Diameter (mm)</th>
<th>HGX030 Pressure (KPa) 200°C</th>
<th>Rheometric Pressure (KPa) 200°C</th>
<th>HGZ200 Pressure (KPa) 300°C</th>
<th>S-PS Pressure (KPa) 280°C</th>
<th>Nylon-66 Pressure (KPa) 290°C</th>
<th>Sigma</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>32</td>
<td>13.35</td>
<td>8850</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>14</td>
<td>129</td>
<td>15.4</td>
<td>14850</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>34.47</td>
</tr>
<tr>
<td>14</td>
<td>257.4</td>
<td>15.4</td>
<td>18320</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>120.9</td>
</tr>
<tr>
<td>15</td>
<td>254</td>
<td>13.3</td>
<td>17190</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>55.83</td>
</tr>
<tr>
<td>15</td>
<td>128</td>
<td>13.3</td>
<td>14000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>149</td>
</tr>
<tr>
<td>16</td>
<td>16</td>
<td>13.5</td>
<td>6960</td>
<td></td>
<td>19930</td>
<td>1210</td>
<td>882.8</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>8</td>
<td>13.5</td>
<td>5032</td>
<td></td>
<td>14930</td>
<td>11670</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>0.05</td>
<td>13.5</td>
<td>359</td>
<td></td>
<td>33740</td>
<td>19930</td>
<td>1210</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>32</td>
<td>13.5</td>
<td>10620</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>128</td>
<td>13.5</td>
<td>14860</td>
<td></td>
<td>14930</td>
<td>11670</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>64</td>
<td>13.5</td>
<td>11000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>13.5</td>
<td>862.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>2</td>
<td>13.5</td>
<td>1110</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>4</td>
<td>13.5</td>
<td>2665</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>128</td>
<td>13.5</td>
<td>14930</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>64</td>
<td>13.5</td>
<td>11670</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>512</td>
<td>13.3</td>
<td>22542</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1020</td>
<td>13.3</td>
<td>33740</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>512</td>
<td>13.3</td>
<td>19930</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>1020</td>
<td>13.3</td>
<td>38830</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1019</td>
<td>13.85</td>
<td>57150</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample</td>
<td>Speed (mm/min)</td>
<td>Diameter (mm)</td>
<td>HGX030 Pressure (KPa) 200 C</td>
<td>Rheometric Pressure (KPa) 200 C</td>
<td>HGZ200 Pressure (KPa) 200 C</td>
<td>S-PS Pressure (KPa) 300 C</td>
<td>S-PS Pressure (KPa) 280 C</td>
<td>Nylon-66 Pressure (KPa) 290 C</td>
</tr>
<tr>
<td>--------</td>
<td>----------------</td>
<td>--------------</td>
<td>----------------------------</td>
<td>-------------------------------</td>
<td>----------------------------</td>
<td>--------------------------</td>
<td>--------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>31</td>
<td>1996</td>
<td>12.95</td>
<td>67670</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>1993</td>
<td>13.5</td>
<td>64910</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>1024</td>
<td>13.5</td>
<td>54790</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td>4437</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2405</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2811</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2932</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2613</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>8</td>
<td>13.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>4</td>
<td>13.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>16</td>
<td>13.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>32</td>
<td>13.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>64</td>
<td>13.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>128</td>
<td>13.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>512</td>
<td>13.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>256</td>
<td>13.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>128</td>
<td>13.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sigma values correspond to the pressure values in the table.
Appendix B

SAMPLE CALCULATION

The data from the sample ID 51 in Appendix A is chosen for demonstration. The flow rate of the melt is calculated from the speed of the ram in the barrel and the area of flow of the core. For the data:

\[ Q = \frac{\pi (13.5 \times 10^{-3})^2}{4} \cdot \frac{16 \times 10^{-3}}{60} = 3.817 \times 10^{-8} \text{ m}^3/\text{s} \]  

(B.1)

The strain rate is calculated by using equation 3.8:

\[ \dot{\varepsilon} = \frac{3.817 \times 10^{-8}}{\pi \times 6.2531 \times 10^{-5} \times \left(\frac{20^2}{13.5^2}\right)} = 4.26 \text{ s}^{-1} \]  

(B.2)

The last term is the correction factor for the diameter of the core to account for skin thickness.

The elongational viscosity is calculated by using equation 3.14:

\[ \eta_B = -\frac{3\pi}{4} \cdot \frac{6.2531 \times 10^{-5} \times \frac{20^2}{13.5^2}}{\ln(20 \times 10^{-3}/1 \times 10^{-3})} \cdot \frac{5238 \times 10^3}{3.817 \times 10^{-8}} = 2.05 \times 10^5 \text{ Pa.s} \]  

(B.3)
Appendix C

PRESSURE CORRECTION

Planar geometry

The shear free flow in the core assumption causes all the terms other than those in the principle diagonals of the stress and the strain tensors to be zero. The components of the momentum balance equation can be solved yielding the two non-zero component equations as follows:

\[
\rho \frac{\partial v_x}{\partial x} = -\frac{\partial P}{\partial x} + \frac{\partial \tau_{xx}}{\partial x} \quad \text{(C.1)}
\]

\[
\rho \frac{\partial v_y}{\partial y} = -\frac{\partial P}{\partial y} + \frac{\partial \tau_{yy}}{\partial y} \quad \text{(C.2)}
\]

However, for the hyperbolic die surface and stream line shapes, and assumed behavior, the gradients of the deviatoric stress tensor are zero; therefore the momentum balance equations are simplified further.

\[
\frac{\partial \tau_{xx}}{\partial x} = -\frac{\partial \tau_{yy}}{\partial y} = 0 \quad \text{(C.3)}
\]

\[
\rho \frac{\partial v_x}{\partial x} = -\frac{\partial P}{\partial x} \quad \text{(C.4)}
\]
\[ \rho v_y \frac{\partial v_y}{\partial y} = -\frac{\partial P}{\partial y} \]  

(C.4)

By integration and combination of the two expressions for pressure gradients, an expression for pressure can be obtained.

\[ P = -\rho \varepsilon^2 \left( \frac{x^2}{2} \right) - \rho \varepsilon^2 \left( \frac{y^2}{2} \right) + C_1 \]  

(C.5)

Define \( P = P_{0,0} \) at \( x = 0, y = 0 \) \( \Rightarrow \) \( C_1 = P_{0,0} \)

Define \( P = P_{1,0} \) at \( x = 0, y = y_{1,0} \). Then

\[ C_1 = P_{1,0} + \rho \varepsilon^2 \left( \frac{y_{1,0}^2}{2} \right) \]  

(C.7)

Therefore two equivalent expressions for pressure in terms of either measuring the pressure on the center plane or at the interface are:

\[ P = -\rho \varepsilon^2 \left( \frac{x^2}{2} \right) - \rho \varepsilon^2 \left( \frac{y^2}{2} \right) + P_{0,0} \]  

(C.8)

Also

\[ P = -\rho \varepsilon^2 \left( \frac{x^2}{2} \right) - \frac{\rho \varepsilon^2}{2} (y^2 - y_{1,0}^2) + P_{1,0} \]  

(C.9)

\[ P_{0,0} = P_{1,0} + \frac{\rho \varepsilon^2 y_{1,0}^2}{2} \]  

(C.10)

The definition of the pressure (at some flow direction coordinate \( x \)) averaged over the half flow channel from the center line to the skin/core interface is:
From the equation for pressure as a function of position, the pressure at the skin/core interface as a function of the flow direction is

\[ P_i(x) = -\rho \dot{\varepsilon}^2 \left(\frac{x^2}{2}\right) - \frac{\rho \dot{\varepsilon}^2 y_1^2}{6} + P_{0,0} \]  

(C.13)

Therefore the average pressure can also be expressed as

\[ P_{ave}(x) = P_i(x) + \frac{\rho \dot{\varepsilon}^2 y_1^2}{3} \]  

(C.14)

The error \( e_P \) in using the interface pressure in place of the average pressure in the planar geometry is:

\[ e_P = P_{ave}(x) - P_i(x) = \frac{\rho \dot{\varepsilon}^2 y_1^2}{3} \]  

(C.15)

**Uniaxial geometry**

As was done in the planar flow, the non-zero components of the momentum balance equation are solved. Then using the fact that the stress components are forced to be constant due to the die geometry, expressions for pressure and average pressure are derived.
The error $e_v$ in using the interface pressure in place of the average pressure in the uniaxial geometry is:

$$e_v = P_v - P_{0,0}$$

To get the maximum error possible, the errors $e_p$ and $e_v$ are evaluated at the maximum strain rates possible in the respective geometries. The data used for the calculations are:

$$\rho = 10^3 \text{ Kg/m}^3$$

$$y_1 = 9.8 \times 10^{-3} \text{ m}$$
\[ r_1 = 1 \times 10^{-2} \text{ m} \]
\[ \dot{e}_p = 0.5 \text{ s}^{-1} \]
\[ \dot{e}_u = 750 \text{ s}^{-1} \]

The errors calculated from equations C.15 and C.22 are:

\[ e_p = 8.00 \times 10^3 \text{ Pa} (= 1.14 \times 10^{-8} \% \text{ range of the pressure transducer}) \]
\[ e_u = 4.68 \times 10^3 \text{ Pa} (= 6.69 \times 10^{-3} \% \text{ range of the pressure transducer}) \]
Vita

The author was born in Navgaon, India, on December 29, 1965. He received his Five Year Integrated Masters degree in Chemical Engineering from Indian Institute of Technology, Bombay, India. In August 1989, he entered the graduate program in the Department of Chemical Engineering, Louisiana State University, Baton Rouge, for his doctoral studies.
Candidate: Ajit Vijay Pendse

Major Field: Chemical Engineering

Title of Dissertation: Elongational Rheometry of Coextruded Polymer Melts

Approved:

[Signature]
Major Professor and Chairman

[Signature]
Dean of the Graduate School

EXAMINING COMMITTEE:

[Signature]

Date of Examination:

April 17, 1995