<table>
<thead>
<tr>
<th>NAME (BLOCK LETTERS)</th>
<th>PERMANENT ADDRESS</th>
<th>DATE</th>
</tr>
</thead>
<tbody>
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</tbody>
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Name of author in full: MEERA RANGANATHAN

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The Transient Flow Rheology and Instabilities of Polyethylene Melts

By

Meera Ranganathan

Magdalene College
University of Cambridge

A dissertation submitted for the degree of Doctor of Philosophy
At the University of Cambridge

(August 1999)
Declaration

This dissertation is the result of my own work and includes nothing that is the outcome of work done by others, apart from the GPC measurement, TREF measurements and Gottfert capillary rheometer measurements provided by Dr. R.J. Koopmans from The Dow Chemical Company, Terneuzen, Netherlands, which is gratefully appreciated.

This thesis contains approximately 55100 words and precisely 102 figures and 12 tables.

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To Sopark, Rob and all the other inhabitants of the third floor lab who have made it a supporting and friendly "working" environment.

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iii
Summary

The assessment of polyester fabric is an important aspect in determining its quality and suitability for various applications, such as clothing, upholstery, and industrial uses. Polyester, also known as polyester or polyester fibers, is a versatile material that can be used in a wide range of products. The main characteristics of polyester include its durability, strength, and resistance to water and sunlight. However, its flammability is a concern in certain applications.

The aim of the research was to investigate the flammability of polyester fabric under specific conditions. The experiments were conducted using a standardized test method, which involved exposing the fabric to a controlled flame source and measuring the time it took for the fabric to ignite and the distance the flame traveled. The results showed that polyester fabric has good resistance to flame and does not spread easily.

The research findings indicated that polyester fabric is a suitable material for use in products where flammability is a concern. However, further research is needed to investigate the long-term effects of exposure to high temperatures and the potential for the release of toxic gases under fire conditions.
Summary

The extrusion of polymers such as polyethylenes can be inhibited by melt flow instabilities, which differ in nature from one type of polyethylene to the other. In this thesis, the rheology and flow of three polyethylenes, each having a distinct molecular structure is studied. These polyethylenes are High Density Polyethylene (HDPE), Polyolefin Elastomer (POE) and Linear Low Density Polyethylene (LLDPE). The objective of this thesis is to relate the rheological and processing behaviour of these polyethylenes and establish the type of flow instabilities exhibited by each of these polyethylenes. The main experimental work has been carried out using a newly developed two-piston capillary rheometer; Multipass Rheometer (MPR).

The parameters required to rheologically characterise the linear and non-linear behaviour (for lower shear rates) of these polyethylenes were determined from dynamic (oscillatory) experiments and step-strain experiments performed using the Rheometrics (RDS), parallel-plate rheometer. Similar measurements using a capillary geometry with the MPR were in close agreement with the data obtained using the RDS.

The flow of HDPE at higher shear rates is characterised by pressure oscillations of fixed amplitude, which occur when a critical shear stress is attained. These oscillations appear to be sustained by a periodic decompression-compression cycle in the capillary, which is governed by a stick-slip transition occurring at this critical shear stress. Depending on the shear rate, four different flow regimes, including a regime of pressure oscillations could be identified. This type of flow behaviour was mathematically modelled using melt compressibility rather than complex rheological or arbitrarily specified parameters. The predictions of this model were in good agreement with the experimental data. Flow birefringence experiments for HDPE also gave further insights into its unstable behaviour.

In comparison to HDPE, the transient flow of POE appeared to be strongly dependent on its shear history and this effect was named as the Delayed Pressure Build-up (DPB) effect. In DPB effect, the increase in apparent viscosity with apparent shear rate was delayed during the initial period of build-up of pressure across the capillary. Flow visualisation experiments for POE revealed the presence of layer near the walls of the capillary, associated with the development of the DPB effect. This layer appears to be a direct result of the flow of POE through the capillary and is independent of shear rate. LLDPE was found to exhibit flow characteristics observed for both POE and HDPE.

The MPR was capable of providing an unique insight into the transient flow behaviour and instabilities for the three polyethylenes, because of its ability of repeatedly shear a given sample volume. In general, the flow of all three polyethylenes appears to be affected by polymer/wall interactions and/or polymer/polymer interactions near the wall.
Nomenclature

Conventional Symbols used for co-ordinate directions

Roman

$\alpha_1, \alpha_2, \beta_1, \beta_2$  Parameters determined from the flow curve of HDPE

- $\beta$  A Non-linear parameter in Wagner damping function
- $\chi$  Melt Compressibility
- $\chi$  Angle between analyser and polariser
- $\delta$  Loss angle
- $\Delta$  Level of birefringence
- $\delta_a$  Phase Difference between light beams
- $\Delta P$  Pressure difference across capillary or slit

$\Delta P_{\text{max}}$  Maximum Steady Pressure difference

- $\phi$  Isoclinic angle
- $\dot{\gamma}$  Linear Strain rate
- $\gamma$  Apparent shear rate
- $\dot{\gamma}_w$  Apparent Wall shear rate
- $\gamma$  Shear strain
- $\gamma_0$  Linear Magnitude of Strain
- $\gamma_i$  Non - Linear Magnitude of Strain
- $\gamma_w$  Wall shear strain
- $\eta$  Apparent viscosity

$\eta(\dot{\gamma})$  Apparent steady shear viscosity

$\eta^*(\omega)$  Complex viscosity

$\eta_0$  Zero-shear-rate steady flow viscosity

$\lambda$, $\lambda_i$  Relaxation time of polymer melt

$\rho$  Density of polymer melt

$\tau$  Shear stress

$\tau_w$  Wall shear stress

$\omega$  Angular Frequency
# Nomenclature

### English

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>B</td>
<td>Magnetic field</td>
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<tr>
<td>C</td>
<td>Cauchy strain tensor</td>
</tr>
<tr>
<td>C</td>
<td>Stress Optical Coefficient</td>
</tr>
<tr>
<td>C₁⁻¹</td>
<td>Finger strain tensor</td>
</tr>
<tr>
<td>D</td>
<td>Capillary Diameter, Slit Depth</td>
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<tr>
<td>E</td>
<td>Electric field</td>
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<tr>
<td>e</td>
<td>Extraordinary beam</td>
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<tr>
<td>G</td>
<td>Shear Modulus</td>
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<td>G(t)</td>
<td>Relaxation Modulus</td>
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<tr>
<td>G'</td>
<td>Elastic or Storage Modulus</td>
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<tr>
<td>G''</td>
<td>Viscous or Loss Modulus</td>
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<tr>
<td>g</td>
<td>Relaxation Strength</td>
</tr>
<tr>
<td>h</td>
<td>Gap Width between the RDS plates</td>
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<td>h</td>
<td>Thickness of Birefringent crystal</td>
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<td>h(l₁, l₂)</td>
<td>Wagner Damping Function</td>
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<tr>
<td>I</td>
<td>Intensity of light</td>
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<tr>
<td>I₁, I₂</td>
<td>First and Second Invariants of a tensor</td>
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<tr>
<td>Iᵣ</td>
<td>Intensity of light along X axis</td>
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<tr>
<td>Iᵧ</td>
<td>Intensity of light along Y axis</td>
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<tr>
<td>k</td>
<td>Damping Factor</td>
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<tr>
<td>L</td>
<td>Length of Capillary, Slit</td>
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<tr>
<td>m(t-t')</td>
<td>Memory function</td>
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<tr>
<td>N</td>
<td>Number of Maxwell elements</td>
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<tr>
<td>N₀</td>
<td>Order of fringes</td>
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<tr>
<td>nᵢᵧ</td>
<td>Birefringence tensor</td>
</tr>
<tr>
<td>o</td>
<td>Ordinary beam</td>
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<tr>
<td>P</td>
<td>Pressure in MPR barrels</td>
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<tr>
<td>P_b</td>
<td>Pressure in the bottom barrel</td>
</tr>
<tr>
<td>P_t</td>
<td>Pressure in the top barrel</td>
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<tr>
<td>Qᵢᵧ</td>
<td>Flow rate of melt through the capillary</td>
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<tr>
<td>Q_m</td>
<td>Rate of volume displacement in the barrels</td>
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<tr>
<td>r</td>
<td>Capillary radius - MPR</td>
</tr>
<tr>
<td>R</td>
<td>Barrel radius - MPR</td>
</tr>
<tr>
<td>Re</td>
<td>Reynolds number</td>
</tr>
<tr>
<td>Rᵣ</td>
<td>Radius of parallel plates - RDS</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
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</table>
\[ t, t \] time
\[ t' \] Past time
\[ V \] Volume occupied by sample in the MPR, Volume displaced by the piston movement in the MPR
\[ V_b \] Volume of melt in the bottom barrel
\[ V_{bi} \] Initial volume of melt in the bottom barrel
\[ V_{cap} \] Velocity of melt through the capillary
\[ v_p \] Velocity of pistons of the MPR
\[ V_t \] Volume of melt in the top barrel
\[ V_{ti} \] Initial volume of melt in the top barrel
\[ W \] Slit Width
\[ x_{max} \] Centre to Peak displacement of MPR pistons

**Abbreviations**

- **CGCT** Constrained Geometry Catalyst Technology
- **DPB effect** Delayed Pressure Build-up effect
- **FE** Fluoroelastomer
- **GPC** Gel Permeation Chromatography
- **HDPE** High Density PolyEthylene
- **K-BKZ** Kaye - Bernstein, Kearsley and Zapas
- **LCB** Long Chain Branching
- **LDPE** Low Density PolyEthylene
- **LLDPE** Linear Low Density PolyEthylene
- **Mc** Critical Molecular Mass
- **Mn** Number Average Molecular Mass
- **Mw** Weight Average Molecular Mass
- **MI** Melt Index
- **MPR** Multipass Rheometer
- **MW** Molecular Weight
- **MWD** Molecular Weight Distribution
- **PI** Polydispersity index
- **POE** PolyOlefin Elastomer
- **PSD** Principal Stress Difference
- **RDS** Rheometrics Dynamics Spectrometer
- **SCB** Short Chain Branching
- **SSSD** Small-Scale Surface Distortion
- **TREF** Temperature Rising elution Fractionation
# Table of Contents

**TITLE PAGE** ........................................................................................................................................ i

**DEDICATION** .................................................................................................................................... ii

**DECLARATION & ACKNOWLEDGEMENTS** ......................................................................................... iii

**SUMMARY** ........................................................................................................................................ iv

**NOMENCLATURE** ............................................................................................................................... v

1. **INTRODUCTION** .............................................................................................................................. 1
   1.1 Background to the Thesis .................................................................................................................. 1
   1.1.1 Classification of Polyethylenes .................................................................................................. 2
   1.1.2 Polyethylene Processing and Melt Flow Instabilities ................................................................ 3
   1.2 Polyethylene Samples and Experimental Apparatus ....................................................................... 5
   1.2.1 High Density Polyethylene (HDPE) .......................................................................................... 6
   1.2.2 Polyolefin Elastomer (POE) ....................................................................................................... 6
   1.2.3 Linear Low Density Polyethylene (LLDPE) ............................................................................... 7
   1.2.4 The Multipass Rheometer ......................................................................................................... 8
   1.3 Objectives and Structure of the Thesis ............................................................................................ 8

2. **BACKGROUND TO RHEOLOGY AND EXPERIMENTAL TECHNIQUES** ............................ 11
   2.1 Rheological Characterisation of Polymers ....................................................................................... 11
   2.1.1 Linear Viscoelasticity ................................................................................................................. 12
   2.1.2 Non-linear Viscoelasticity .......................................................................................................... 17
   2.2 Experimental Apparatus and Techniques ....................................................................................... 20
   2.2.1 The Rheometrics Dynamic Spectrometer (RDS) ..................................................................... 20
   2.2.2 The Multipass Rheometer (MPR) ............................................................................................. 22
   2.3 Background to Flow Birefringence Technique ............................................................................. 28
   2.3.1 Interpretation of Flow Birefringence Patterns ........................................................................ 29
   2.3.2 Flow Birefringence in the MPR ............................................................................................... 30
   2.4 Summary and Conclusions ........................................................................................................... 31

3. **STRUCTURAL AND RHEOLOGICAL CHARACTERISATION OF HDPE, POE**
   AND LLDPE ..................................................................................................................................... 33
   3.1 Introduction to Characterisation of Polyethylene Samples ............................................................ 33
   3.1.1 Characterisation of Molecular Structure .................................................................................... 33
   3.2 Rheological Characterisation of Polyethylene samples ................................................................. 38
   3.2.1 Determination of the linear Viscoelastic Region ........................................................................ 38
   3.2.2 Determination of the Relaxation Spectrum ............................................................................... 40
   3.2.3 Determination of the Damping Factor, k .................................................................................. 44
   3.2.4 Steady Shear Rate Response .................................................................................................. 46
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2.5 Determination of Zero-Shear-Rate Steady Flow Viscosity</td>
<td>48</td>
</tr>
<tr>
<td>3.2.6 Summary of Results obtained from the RDS</td>
<td>48</td>
</tr>
<tr>
<td>3.3 Rheological Characterisation using the MPR</td>
<td>49</td>
</tr>
<tr>
<td>3.3.1 Comparisons between Results Obtained using a MPR and a RDS</td>
<td>50</td>
</tr>
<tr>
<td>3.3.2 Measurement of Steady Shear Response in the MPR</td>
<td>51</td>
</tr>
<tr>
<td>3.3.3 Pressure Dependence of Dynamic Moduli</td>
<td>51</td>
</tr>
<tr>
<td>3.3.4 Measurement of Compressibility using the MPR</td>
<td>53</td>
</tr>
<tr>
<td>3.4 Summary and Conclusions</td>
<td>53</td>
</tr>
<tr>
<td>4. TRANSIENT FLOW AND PROCESSING OF HIGH DENSITY POLYETHYLENE</td>
<td>55</td>
</tr>
<tr>
<td>4.1 Transient Flow and Melt Flow Instabilities in HDPE and other Polymer Melts</td>
<td>55</td>
</tr>
<tr>
<td>4.1.1 Effect of Temperature</td>
<td>58</td>
</tr>
<tr>
<td>4.1.2 Effect of Wall Surface</td>
<td>58</td>
</tr>
<tr>
<td>4.1.3 Effect of Capillary and Slit Geometries</td>
<td>58</td>
</tr>
<tr>
<td>4.1.4 Effect of Die Diameter (D), Length (L), L/D Ratio</td>
<td>59</td>
</tr>
<tr>
<td>4.1.5 Effect of Die Entry Angle</td>
<td>60</td>
</tr>
<tr>
<td>4.1.6 Effect of Molecular Structure and Molecular Weight</td>
<td>60</td>
</tr>
<tr>
<td>4.2 Origin of the Discontinuous Flow curve and Melt Flow Instabilities</td>
<td>61</td>
</tr>
<tr>
<td>4.2.1 Summary of Literature Review</td>
<td>65</td>
</tr>
<tr>
<td>4.3 Experimental Section</td>
<td>65</td>
</tr>
<tr>
<td>4.4 Experiments Results - Capillary Geometry</td>
<td>67</td>
</tr>
<tr>
<td>4.5 Experimental Results - Flow Birefringence</td>
<td>75</td>
</tr>
<tr>
<td>4.5.1 Flow Birefringence patterns - Stable Flow Regime</td>
<td>76</td>
</tr>
<tr>
<td>4.5.2 Birefringence patterns - Periodic Oscillations, Overshoot regimes</td>
<td>78</td>
</tr>
<tr>
<td>4.5.3 Birefringence patterns - High Velocity regimes</td>
<td>80</td>
</tr>
<tr>
<td>4.5.4 Observations of Flow Disturbances near the Wall</td>
<td>81</td>
</tr>
<tr>
<td>4.5.5 Discussion of Capillary and Flow Birefringence Results</td>
<td>86</td>
</tr>
<tr>
<td>4.6 Summary and Conclusions</td>
<td>88</td>
</tr>
<tr>
<td>5. THE MODELLING OF TRANSIENT FLOW IN THE MULTIPASS RHEOMETER</td>
<td>91</td>
</tr>
<tr>
<td>5.1 Introduction</td>
<td>91</td>
</tr>
<tr>
<td>5.2 Derivation of the Model</td>
<td>92</td>
</tr>
<tr>
<td>5.3 Experimental Observations of Capillary Flow</td>
<td>95</td>
</tr>
<tr>
<td>5.4 Solution of Differential Equation</td>
<td>96</td>
</tr>
<tr>
<td>5.5 Comparison of Experimental and Predicted Results</td>
<td>97</td>
</tr>
<tr>
<td>5.6 Summary and Conclusions</td>
<td>102</td>
</tr>
<tr>
<td>6. THE TRANSIENT FLOW AND PROCESSING OF POLYOLEFIN ELASTOMER</td>
<td>103</td>
</tr>
<tr>
<td>6.1 Transient Flow and Melt Flow Instabilities of Metallocene Polymers</td>
<td>103</td>
</tr>
<tr>
<td>6.1.1 Summary of Literature Review</td>
<td>105</td>
</tr>
<tr>
<td>6.2 Experimental Section - Capillary Flow Experiments</td>
<td>105</td>
</tr>
<tr>
<td>6.2.1 Characteristics of Pressure Build-up of POE</td>
<td>106</td>
</tr>
<tr>
<td>6.3 Flow Regimes of POE</td>
<td>111</td>
</tr>
<tr>
<td>6.4 Flow visualisation Observations for POE</td>
<td>115</td>
</tr>
<tr>
<td>6.4.1 Flow Visualisation - Plane Polarised Light</td>
<td>116</td>
</tr>
<tr>
<td>6.4.2 Flow birefringence Observations</td>
<td>122</td>
</tr>
</tbody>
</table>
6.5 Characteristics of the DPB effect .............................. 124
   6.5.1 Determination of a Master Curve for the DPB effect .... 124
   6.5.2 Long Term Stability of the Wall Slip layer .... 126
   6.5.3 Reversal of DPB Effect Using Oscillatory Shearing Conditions .. 127
6.6 Hypothesis for Delayed pressure build-up effect ................. 128
6.7 Summary and Conclusions ........................................... 134

7. TRANSIENT FLOW AND PROCESSING OF LINEAR LOW DENSITY POLYETHYLENE ......................... 137
   7.1 Transient Flow and Melt Flow Instabilities in LLDPE ......... 137
      7.1.1 Processibility of LLDPEs ................................. 138
      7.1.2 Effect of Die Length, Diameter and L/D Ratio ......... 139
      7.1.3 Mechanisms of Instability ............................... 140
      7.1.4 Summary and Findings of Literature Review ............ 141
   7.2 Experimental Section ............................................ 142
   7.3 Experimental Results - Capillary Geometry .................. 142
      7.3.1 Characteristics of Pressure Build-up of LLDPE ....... 146
   7.4 Flow Birefringence Results .................................... 148
   7.5 Summary and Conclusions ....................................... 151

8. CONCLUSIONS AND FUTURE WORK ..................................... 155

APPENDIX A FLOW BIREFRINGENCE ...................................... 159
APPENDIX B MATLAB PROGRAM CODE .................................. 165

LIST OF FIGURES .................................................. 167
BIBLIOGRAPHY ...................................................... 173
1. Introduction

In this chapter, the background, current manufacturing technology, a wall characteristics are being presented. Those problems of wall flow channels are also. In this basic, three different approaches in order to understand their flow characteristics exhibited by each of them.

1.1 Background to the

This chapter is concerned with the theory of flow in three different pipe configurations. Consider the flow experiments in which the flow was occurring during.

Polyethylene being used at elevated temperatures and high velocities was an excellent plastic characterized by good elastic properties and a high degree of wear resistance. The use of polyethylene in the manufacture of plastic pipes was becoming more common. This improvement of process equipment was to many manufacturers in the improved equipment and process. The demand for polyethylene products increased as the manufacturing process improved over the years, and so did the number of polyethylene
1. Introduction

In this chapter, the background, aims and objectives of this thesis are introduced. Due to changes in the manufacturing technology, a wide range of polymers with different end properties and processing characteristics are being produced. The processibility of polymers such as polyethylenes can be inhibited due to presence of melt flow instabilities, which can change in nature from one type of polyethylene to the other. In this thesis, three different types of polyethylenes have been studied using a Multipass rheometer in order to understand their rheological and processing behaviour and establish the type of flow instabilities exhibited by each of these polyethylenes.

1.1 Background to the Thesis

This thesis is concerned with the characterisation and understanding of the capillary flow rheology of three different polyethylene melts using a newly developed two-piston capillary rheometer called the Multipass Rheometer (Mackley et al., 1995). In particular, transient flow experiments have been carried out to study the processability and the instabilities occurring during the flow of these polyethylenes.

Polyethylenes belong to a class of polymers called thermoplastics, which melt at elevated temperatures and can therefore be repeatedly moulded using conventional techniques such as extrusion and blow moulding (Stevens, 1989). Polyethylenes are characterised by good end properties such as durability, inertness and reasonable strength and are being increasingly used for producing disposable materials such as packaging film. In order to meet the ever-increasing demand, it has been estimated that 35 million tonnes of polyethylene were being synthesised in the 1990s (Oxley, 1992). The expansion in the manufacture of polyethylene has brought about the need for the development and improvement of processes employed to convert them into useful products. This has led to many innovations in the manufacturing technology leading to polyethylenes with improved end properties and processibility. Apart from the recognition of an increasing demand for polyethylene products, these innovations are guided by the necessity to make the manufacturing process as viable as possible in the face of increasing competition. Hence, over the years, one of the main thrusts of research has been the manufacture of new varieties of polyethylenes, which can be employed in a number of areas and which
have improved end properties. The following section covers the different types of polyethylenes that are being manufactured and their associated physical properties.

1.1.1 Classification of Polyethylenes

Polyethylenes can be divided into low density and high density products. The differences in the densities of polyethylenes are due to different levels of branching and consequently different levels of crystallinity in the solid state (Monrabal, 1987). A wide range of polyethylenes have been synthesised having differing molecular weights (MW), molecular weight distributions (MWD), branching characteristics and also by copolymerisation using higher olefins like butene, octene and hexene as comonomers.

The first few grams of polyethylene were synthesised in 1933 by Fawcett and Gibson of ICI in 1933 (McMillan, 1979), while carrying out high pressure reaction (between ethylene and benzaldehyde) kinetic studies. The first major milestone in the commercial manufacture of polyethylene was also devised by ICI and involved the use of high pressure technology (140-300 MPa) to synthesise LDPE, which is a polyethylene with long side chains. A major limitation of LDPE is its low stiffness and it has a low melting temperature due to its high level of long-chain branching (LCB). The emergence of HDPE in the 1950s, was due to the development of Ziegler-Natta catalyst technology (Young, 1981), which can polymerise ethylene under milder pressure conditions. HDPE is a pure linear polymer with a high degree of crystallinity and has a higher density, stiffness and melting temperature than LDPE.

The next major development was the introduction of Linear Low Density Polyethylenes (LLDPE) in the late 1970s (Young, 1981). LLDPEs are copolymers of ethylene with α-olefins (such as butenes, hexenes, octenes) and were also manufactured using Ziegler catalysts (Stevens, 1989). LLDPEs have certain advantages over LDPEs because they are in general tougher and as a consequence have become dominant in the application of polyethylenes to the packaging industry. Also, they are mainly composed of linear chains with some proportion of the chains exhibiting short chain branching (SCB).

Recently, in the 1990s, one of the major innovations in the polyethylene manufacture technology has been the introduction of the Single-site metalloocene catalysts to manufacture polyethylenes with narrow MWDs (Martino, 1995), which are referred to
as metallocene polyethylenes. This new technology, in principle enables a better control of the physical properties of the polyethylene resin. Similar to LLDPEs, these metallocene polyethylenes can be comonomers of ethylene with \( \alpha \)-olefins, and have superior processing properties such as higher melt flow indices (MFI), lower heat seal temperature, bubble stability, clarity and impact resistance as compared to conventional LLDPEs (Grande, 1998).

It is now possible to manufacture PE resins to specifically suit various end applications by controlling its molecular structure. Despite these innovations in the manufacturing process, it has been observed that all these types of polyethylenes are affected by the presence of melt flow instabilities during extrusion, which can impose a limit on the rate of production of polyethylene extrudates. The nature of flow instabilities varies greatly from one type of polymer to the other, even to the extent that widely different instabilities can be observed for different types of polyethylenes. In the following section, the processability and instabilities observed during the flow of polyethylenes are described.

### 1.1.2 Polyethylene Processing and Melt Flow Instabilities

Polyethylenes can be processed using a variety of techniques such as extrusion, moulding, blowing and die casting. Extrusion is an important technique used to process polyethylene melts in order to obtain profiles and films (see for example, Dealy and Wisbrun, 1995). In extrusion, the polyethylene melt is forced through a die to obtain an end product or extrudate of the desired shape. When extrusion is carried out above a certain critical output rate, the extrudate emerging from the die can be affected by the presence of defects. These defects may range in severity from small-scale deformations on the surface to large-scale gross distortions extending into the bulk of the extrudate (see for example, Becker et al., 1990 and Venet and Vergnes, 1997). These extrusion defects arise due to the presence of instabilities in the flow of the melt and are hence referred to as *Melt Flow Instabilities*. The nature, onset and propagation of these instabilities vary from one type of polymer to the other (Petrie and Denn, 1976). In addition, the form and origin of these instabilities can be very sensitive to the type of polyethylene and are also influenced by the boundary conditions of flow (Wang and Drda, 1997 and Piau et al., 1995 and Denn, 1990).
In general, over a range of shear rates, the scale and nature of these instabilities also change, resulting in extrudates, which exhibit a wide range of both superficial and bulk distortions. Based on the visual characteristics of the extrudates, four different flow regimes have been observed for progressively increasing flow rates, which are (see for e.g. Becker et al., 1990 and Denn, 1990 and Larson, 1992)

- **Stable flow regime**: The extrudate is smooth, transparent and undistorted
- **Regime of Surface instabilities**: The extrudates show a matte appearance and small scale high frequency surface roughness, which in its severe form has also been referred to as *Sharkskin* in many papers (first reported by Clegg, 1957)
- **Stick-Slip regime**: The extrudates show alternate regions of smooth and rough patches which accompany the pressure fluctuations in the system
- **Regime of Gross instabilities**: The extrudates are irregular and the distortion extend into the bulk which are also referred to as *Gross melt fracture* (Petrie and Denn, 1976). The distortions could be regular resulting in helical or wavy extrudates or they could be irregular in nature.

![Figure 1.1: Examples of instabilities affecting polymer melts (Petrie and Denn, 1976)](image)

In general, not all the unstable flow regimes, which have been listed above, are observed for all types of polymers and the nature of the instabilities appears to vary considerably from linear polymers to branched polymers. Some examples of the type of instabilities observed for polymer melts is shown in Figure 1.1. In the case of HDPE, with increasing shear rate, all the four flow regimes listed above can be observed. Another
important feature is a discontinuity in the flow curve (wall shear stress versus apparent shear rate) of linear polymers such as HDPE (Bagley et al., 1958) and polybutadiene (Vinogradov et al., 1972, Yang et al., 1998) resulting in the non-uniqueness of wall shear stress for a range of apparent shear rates. However, neither polystyrene (which has linear chains) nor linear silicones (Benbow et al., 1961) show a discontinuity in the flow curve. In the case of branched polyethylenes such as LDPE, the extrudates directly change from smooth ones to those having large scale defects with increasing shear rates and they also do not show the discontinuity which characterises the flow curve of linear polyethylenes like HDPE (Wales, 1969). For LLDPEs, initially smooth extrudates are obtained followed by extrudates, which show small-scale surface defects followed by larger scale defects. LLDPEs can also show the presence of a discontinuous flow curve similar to HDPEs, depending on their MW and MWD. Therefore, it can be seen that the nature and complexity of the instabilities observed varies considerably from one type of polymer to the other and shows a great dependence on the molecular structure, MW and MWD of the polymers (Vinogradov et al., 1972). The observed Melt Flow Instabilities can be initiated either at the die entry, exit or along the length of the die (Petrie and Denn, 1976) and are also dependent on a number of experimental parameters such as temperature, material of construction of the die and die geometry.

Despite a considerable amount of literature available on Melt Flow Instabilities, there still exists some ambiguity as far as the terms such as Sharkskin and Gross melt fracture, which are used to describe melt flow defects and deformations are concerned. There is also not a clear consensus on the origin of instabilities during the flow of polymers and the mechanism governing the propagation of instabilities. It is also not very clear why there is a considerable difference in the instabilities exhibited by polyethylenes, which differ in terms of their molecular structure (branching) and other molecular parameters such as MW and MWD.

1.2 Polyethylene Samples and Experimental Apparatus

The broad aim of this thesis is to study the rheology and processing of certain polyethylenes with a view to gain a better understanding of the general processability and flow instabilities that affect the extrusion of polyethylene melts and correlate these observations with molecular structure. Three polyethylenes have been used for
Introduction

experimental purposes and they can be mainly distinguished in terms of their branching characteristics. These are High Density Polyethylene (HDPE), Polyolefin Elastomer (POE) and Linear Low Density Polyethylene (LLDPE). A brief description of these three polyethylenes is given below.

1.2.1 High Density PolyEthylene (HDPE)

High density Polyethylene (HDPE) is a linear polymer and it is usually polymerised with a broad MWD. Compared to other polyethylenes like LDPEs and LLDPEs, HDPE is harder and less flexible and has a higher density. HDPE has a highly crystalline structure because of the linear nature of the chains (Figure 1.2) and is manufactured using the Ziegler Natta catalyst technology (Stevens, 1989) which produces isotactic polymers of high purity. These catalysts have reaction sites of varying activity, which give rise to chains of differing lengths resulting in a resin with a large polydispersity index (PI).

\[
\begin{array}{c}
\text{Figure 1.2 : Schematic molecular chain structure of HDPE}
\end{array}
\]

1.2.2 Polyolefin Elastomer (POE)

Polyolefin Elastomer (POE) (Figure 1.3), is an ethylene-octene copolymer, and is manufactured using Single site metalloocene catalysts (Chowdhury and Moore, 1995) having reaction sites of uniform activity. This facilitates the synthesis of polymer chains with similar characteristics such as chain length and level of branching giving rise to a narrow MWD. This technology permits greater control over the polymerisation process and the polymers synthesised exhibit desirable characteristics such as increased toughness and clarity as compared to LLDPEs manufactured using the conventional Ziegler catalyst technology. The molecular structure of POE consists of short chains (of hexane) attached to a polyethylene backbone.
1.2.3 Linear Low Density Polyethylene (LLDPE)

Linear Low Density Polyethylene (LLDPE) consists of linear chains and also of chains having short hexane side branches. It is manufactured using a Ziegler-Natta type catalyst and is less flexible and transparent than POE. It consists of both linear and branched chains and can be considered as a blend of POE and HDPE (Gabriel et al. 1997). LLDPE is manufactured using a catalyst having reaction sites with at least two levels of activity. The chains of LLDPE catalysed by one of these sites are linear similar to that of HDPE, while the other active site gives rise to a copolymer of ethylene and octene with uniformly distributed side chains similar to POE (Figure 1.4). The lengths of LLDPE chains differ giving rise to a resin with a significant polydispersity index.

From the description of the resins given above, it can be seen that LLDPE is structurally equivalent to a mixture of HDPE and POE; i.e. LLDPE may be considered as a blend of HDPE and POE. Hence, any rheological effect in LLDPE can be tentatively attributed to the sum of contributions of its linear and branched copolymer parts. So if a particular rheological effect can be observed in HDPE because of its linear molecular
structure, the same effect can be observed to a lower magnitude in LLDPE. Similarly, any effect on the rheology of POE due to its branched chains can also be perceived to a reduced extent in LLDPE. Thus, by using two PEs with distinct molecular characteristics and one PE in between, it has been attempted to carry out a systematic study of the effects of short chain branching (or its absence) on the rheology and instabilities occurring during the flow of these polyethylenes.

1.2.4 The Multipass Rheometer

The Multipass Rheometer (MPR) is the main device used to study the rheology and processing of the three polyethylenes. The MPR is a two piston capillary rheometer and has been recently developed by Mackley et al. (1995) in the University of Cambridge and is capable of operating over a range of pressures, temperatures and shear rates.

The MPR is different from other conventional capillary rheometers because it has a constrained geometry, which can fully contain the melt with the result that there are no free surface extrudates and the same sample can be repeatedly processed to carry out a number of experiments. The presence of a free surface at the exit of a capillary can cause additional instability effects, which result in structural deformation of the emerging extrudate (Cogswell, 1972). Therefore, the flow of a polymer melt in the MPR is free from complications arising due to the presence of a free surface at the exit of conventional capillary rheometers.

1.3 Objectives and Structure of the Thesis

The objective of this thesis is to carry out a detailed study of the rheology and processing behaviour of three different types of polyethylenes, HDPE, POE and LLDPE, which have a distinct molecular structure. Experiments have been carried out on these polyethylenes using both a conventional rheometer and the MPR.

These polyethylenes have been rheologically characterised using a rotational rheometer called the Rheometrics Dynamic Spectrometer (RDS) with a parallel plate geometry. The MPR is also used to carry out rheological measurements similar to those obtained from the RDS and the results obtained from the MPR have been verified with those obtained from conventional rheometers (RDS and the Gottfert capillary rheometer).
The processing and steady shear behaviour of these polyethylenes was studied using the MPR. The time dependent flow rheology and flow instabilities such as pressure oscillations exhibited by polyethylene melts were also studied. The experiments carried out on the MPR include both capillary flow measurements and flow visualisation using a slit geometry.

In addition to experimental observations, a model has been developed to predict the time dependent (or transient) flow behaviour including flow instabilities of polyethylene melts. This model enhances the understanding of factors governing the transient flow rheology and unstable flow of polyethylene melts.

From a study of processing behaviour for the three polyethylenes, the flow regimes observed over a wide range of shear rates have been identified. It has been attempted to link the processing behaviour including flow instabilities observed with the molecular architecture of the polyethylene melts.

The thesis is divided into seven further chapters, which are as follows. The background and techniques used for rheological characterisation and flow birefringence are given in Chapter 2. In Chapter 3, the results from the structural and rheological characterisation of the polyethylene samples using chromatographic techniques and RDS respectively are presented. Some of the preliminary measurements carried out using the MPR have also been discussed. In chapter 4, the study of the transient flow rheology of HDPE using a capillary geometry and complementary flow visualisation experiments using a slit geometry are described. Results of a similar study for POE and LLDPE are presented in chapter 6 and chapter 7 respectively. In chapter 5, a model is developed to describe the transient flow of polyethylene melts in the MPR its predictions are compared with the experimental measurements of HDPE. Chapter 8 provides an overview of results obtained, discussions and conclusions of this thesis.
2. Rheological Chara...
2. **Background to Rheology and Experimental Techniques**

This chapter introduces the general rheological principles, theory and techniques used in the thesis. The Maxwell model of linear viscoelasticity is discussed and extended to describe non-linear viscoelasticity using the K-BKZ integral constitutive model coupled with the Wagner damping function. In subsequent sections of this chapter, the experimental apparatus and techniques used are described. The rheometers used for experimentation are the Multipass Rheometer (MPR), a capillary rheometer and the Rheometrics Dynamic Spectrometer (RDS), a rotational rheometer. The RDS has been used to carry out dynamic (oscillatory) experiments and steady shear experiments at low shear rates. The MPR has been used to carry out both capillary measurements and flow visualisation in a slit geometry. The concluding section of this chapter introduces the flow birefringence technique and its application to flow situations.

2.1 **Rheological Characterisation of Polymers**

Rheology is a branch of science concerned with the manner in which materials deform when they are subjected to forces (see for e.g. Dealy and Wissbrun, 1995). It is important to have a good rheological description of polymers in order to understand their behaviour in a processing situation and this includes the knowledge of their viscoelastic and steady shear behaviour. When a material is subjected to a deforming stress, it responds by means of some structural rearrangements within itself. If the rate of deformation is proportional to the deforming force, the material is considered to be purely viscous. On the other hand, if the magnitude of deformation is proportional to the deforming force, then the material is considered to be purely elastic. Polymers exhibit a behaviour which is somewhere in between these two extremes, and are hence regarded as viscoelastic materials (see for e.g. Tschoegl, 1989).

The viscoelastic nature of a polymer can be studied from two viewpoints depending on the magnitude, kinematics and frequency of the strain imposed on the sample (Dealy, 1992). These are linear viscoelasticity, where the stress response can be modelled by coupling linear viscous and elastic elements, and non-linear viscoelasticity, where the linear elements are no longer adequate to model the stress response.
2.1.1 Linear Viscoelasticity

Several models have been proposed to describe the flow behaviour of viscoelastic materials ranging from a simple extension of the Newton’s law of viscosity to molecular models of great mathematical complexity (Rosen, 1987). They can be broadly classified into two categories; “mechanical analogues” and “molecular” models which look into the micro-level details (Aklonis, 1983). In this study, a simple model based on a mechanical analogue of a polymer system is used to predict the rheological behaviour of a polymer in simple shear situations.

An elastic or Hookean solid can be represented by a mechanical model in the form of a spring (Figure 2.1) and the constitutive equation of a linear elastic or Hookean solid is given by

\[ \tau = G\gamma \]

where \( \tau \) is stress, \( G \) an elastic modulus and \( \gamma \), shear strain.

![Figure 2.1: Linear elastic model](image)

Similarly, a linear viscous or Newtonian liquid can be represented by a dashpot (Figure 2.2) and its constitutive equation can be given in terms of shear stress \( \tau \) and shear rate \( \dot{\gamma} \).

\[ \tau = \eta \dot{\gamma} \]

where \( \eta \), the viscosity is constant.

![Figure 2.2: Linear viscous model](image)
The behaviour of viscoelastic materials such as polymer melts cannot be sufficiently described by using just a spring or a dashpot, but can be adequately represented by a combination of springs and dashpots. In order to predict the linear viscoelastic response of a polymer melt, a combination of a spring and dashpot in series (first proposed by Maxwell), which is commonly referred to as a Maxwell element is used (Figure 2.3).

![A Maxwell element represented by a spring and dashpot in series](image)

In a Maxwell element, both the spring and dashpot experience the same stress, which is given by $\tau$.

Eqn. 3
$$\tau = \tau_{\text{spring}} = \tau_{\text{dashpot}}$$

The total strain on the system is given by the sum of the strains on the spring and the dashpot.

Eqn. 4
$$\gamma = \gamma_{\text{spring}} + \gamma_{\text{dashpot}}$$

Differentiating Eqn. 4 with respect to time gives the total rate of deformation

Eqn. 5
$$\dot{\gamma} = \dot{\gamma}_{\text{spring}} + \dot{\gamma}_{\text{dashpot}}$$

The total rate of deformation can be rewritten as follows,

Eqn. 6
$$\frac{d\gamma}{dt} = \frac{1}{G} \frac{d\tau}{dt} + \frac{\tau}{\eta}$$

or rearranged as

Eqn. 7
$$\dot{\tau} = \eta \dot{\gamma} - \frac{\eta}{G} \dot{\gamma} = \eta \dot{\gamma} - \lambda \dot{\tau},$$

where the quantity $\lambda = \eta/G$ has the dimensions of time and is called as the relaxation time of a Maxwell element, when it is subject to a stress relaxation test.

In one form of stress relaxation test, the applied strain can be defined mathematically using a step function and the resultant stress is monitored as a function of time, while the strain is held constant. When a strain ($\gamma_0$) is instantaneously applied to a Maxwell element (Figure 2.3), the spring initially responds to a stress equal to $G\gamma_0$. The
solution of the differential equation (Eqn. 6) with \( \dot{\gamma} = 0 \) and initial conditions, \( \tau = G\gamma_0 \) at \( t = 0 \) shows that stress undergoes a first-order exponential decay given by

\[
\tau(t) = G\gamma_0 \exp\left(-\frac{t}{\lambda}\right)
\]

A term called the relaxation modulus \( G(t) = \frac{\tau(t)}{\gamma_0} \) can be defined as

\[
G(t) = \frac{\tau(t)}{\gamma_0} = G \exp\left(-\frac{t}{\lambda}\right)
\]

The relaxation time \( \lambda \), is the time constant for exponential decay.

The stress relaxation data of polymer melts in the linear viscoelastic region cannot be quantitatively described by a single value of \( G \) and \( \lambda \), i.e. the decay in stress is not a single exponential effect. Therefore, a generalised Maxwell model (see for e.g. Rosen, 1993) is used to describe the stress-relaxation experiment, where a combination of \( N \) different Maxwell elements in parallel is used to represent a polymer melt system (Figure 2.4).

\[
G(t) = \sum_{i=1}^{N} G_i \exp\left(-\frac{t}{\lambda_i}\right)
\]

The stress relaxation in the generalised Maxwell model, where all the individual Maxwell elements are subjected to the same constant strain, \( \gamma_0 \), is given by a summation of the stress responses of the individual Maxwell elements

\[
\tau(t) = \sum_{i=1}^{N} \gamma_0 \sum_{i=1}^{N} G_i \exp\left(-\frac{t}{\lambda_i}\right)
\]

and the overall relaxation modulus \( G(t) \) is represented as

\[
G(t) = \sum_{i=1}^{N} G_i \exp\left(-\frac{t}{\lambda_i}\right)
\]

It has been demonstrated that between five and ten pairs of \( G_i \) and \( \lambda_i \) values are reasonably capable of describing the linear viscoelastic response of most polymer melt systems (see...
for e.g. Baumgaertel and Winter, 1989 and Mackley et al., 1994). The set of values given by $G_i$ and $\lambda_i$ are called as the relaxation spectrum of the material.

In order to determine the stress at a given time $t$, Eqn. 7 is integrated to give

**Eqn. 12**

$$\tau(t) = \int_{-\infty}^{t} G(t-t')\gamma dt'$$

where $t$ represents the present time and $t'$ the past time. The relaxation modulus is represented in terms of the relaxation spectrum and therefore the stress response at a given time $t$, is given by,

**Eqn. 13**

$$\tau(t) = \sum_{i=1}^{N} G_i \exp\left(-\frac{t-t'}{\lambda_i}\right)\gamma_{t'}$$

Eqn. 13 is integrated again and the shear stress, $\tau(t)$ can be rewritten as follows

**Eqn. 14**

$$\tau(t) = \sum_{i=1}^{N} \left(\frac{G_i}{\lambda_i}\right)\exp\left(-\frac{t-t'}{\lambda_i}\right)\gamma(t,t')dt'$$

where $\gamma(t,t')$ is the past strain between $t$ and $t'$ given by

**Eqn. 15**

$$\gamma(t,t') = \int_{t'}^{t} \gamma dt'$$

The time dependence of the stress response of a polymer melt can be written in terms of a memory function $m(t-t')$

**Eqn. 16**

$$m(t-t') = -\frac{\partial G(t-t')}{\partial(t-t')} = \sum_{i=1}^{N} \left(\frac{G_i}{\lambda_i}\right)\exp\left(-\frac{t}{\lambda_i}\right)\gamma(t,t')$$

The Maxwell model of linear viscoelasticity is only valid to describe the rheological response of a polymer melt, which is subjected to small strains and strain rates. The linear viscoelastic response of a polymer melt can be predicted using its relaxation spectrum, which can be obtained from the stress relaxation modulus when it is subjected to small step strains. The relaxation spectrum can also be determined from small amplitude oscillatory strain experiments, which is described in the following section.

### 2.1.1.1 Determination of the Viscoelastic Parameters

Frequency response analysis is a powerful technique to derive the viscoelastic parameters of a polymeric system (Rosen, 1993). If a sinusoidal strain $\gamma = \gamma_0 \sin(\omega t)$ is applied to a
linear spring, where stress is proportional to the applied strain, i.e. \( \tau = G\gamma \), the resulting stress is given by

\[ \text{Eqn. 17} \quad \tau = G\gamma \sin (\omega t) \]

and is in-phase with the applied strain.

In the case of a linear dashpot, where the stress is proportional to the rate of strain, i.e. \( \tau = \gamma \dot{\gamma} \), the resulting stress given by

\[ \text{Eqn. 18} \quad \tau = \gamma \omega \gamma \cos (\omega t) \]

is 90° out of phase with the applied strain.

Since a viscoelastic material represented by a Maxwell element, exhibits an intermediate behaviour, the resultant stress is out of phase with the applied strain by an angle, \( \delta \), which is between 0 and 90°. The resultant stress can also be resolved into an in-phase(\( \tau' \)) and an out of phase component(\( \tau'' \)), which can be mathematically written in terms of a complex number.

\[ \text{Eqn. 19} \quad \tau = \tau' + i \tau'' \]

The applied strain can also be represented in terms of a complex number

\[ \text{Eqn. 20} \quad \gamma = \gamma' + i \gamma'' \]

where \( \gamma' = |\gamma| \) and \( \gamma'' = 0 \). Correspondingly, and in-phase or storage modulus can be defined by

\[ \text{Eqn. 21} \quad G' = \frac{\tau'}{\gamma} \]

and an out-of-phase or loss modulus can be defined by

\[ \text{Eqn. 22} \quad G'' = \frac{\tau''}{\gamma} \]

A complex viscosity \( \eta^* \) can also be defined as follows

\[ \text{Eqn. 23} \quad \eta^* = \eta' - i \eta'' = \tau / \dot{\gamma} \]

Consider the integral representation of the stress response derived for a Generalised Maxwell model, which is given in Eqn. 13. This can be converted to give the stress response of a single Maxwell element, which is subjected to a small amplitude sinusoidal strain (\( \gamma = \gamma_0 \sin (\omega t) \)).

\[ \text{Eqn. 24} \quad \tau(t) = G \gamma_0 \left[ \cos (\omega t) - \frac{1}{\omega} \sin (\omega t) \right] \int_{-\infty}^{t} \exp \left( -\frac{t-t'}{\lambda} \right) \cos (\omega t') \, dt' \]

This integral can be solved and the stress response of a single Maxwell element is given
by

Eqn. 25

\[ \tau(t) = \frac{G' \omega \lambda^2}{1 + \omega^2 \lambda^2} \sin(\omega t) + \frac{G'' \omega \lambda^2}{1 + \omega^2 \lambda^2} \cos(\omega t) \]

Therefore, the storage and loss modulus of a single Maxwell element is given by

Eqn. 26

\[ G' = \frac{\tau'}{\gamma} = \frac{G \omega^2 \lambda^2}{1 + \omega^2 \lambda^2} \]

Eqn. 27

\[ G'' = \frac{\tau''}{\gamma} = \frac{G \omega \lambda^2}{1 + \omega^2 \lambda^2} \]

The corresponding expression for the loss angle \( \delta \) is given by

Eqn. 28

\[ \tan \delta = \frac{G''}{G'} = \frac{1}{\omega \lambda} \]

The storage and loss modulus of a polymer system represented by a generalised Maxwell model consisting of \( N \) Maxwell elements is obtained by adapting the expressions derived for a single Maxwell element.

Eqn. 29

\[ G'(\omega) = \sum_{i=1}^{N} \frac{G_i \lambda_i^2 \omega^2}{1 + \lambda_i^2 \omega^2} \]

Eqn. 30

\[ G''(\omega) = \sum_{i=1}^{N} \frac{G_i \lambda_i \omega}{1 + \lambda_i^2 \omega^2} \]

and the magnitude of a complex viscosity, \( \eta^* \) is given by

Eqn. 31

\[ |\eta^*| = \frac{1}{\omega} \sqrt{(G')^2 + (G'')^2} \]

The values of \( G' \) and \( G'' \) can be experimentally measured from the stress response of a material subjected to a small amplitude oscillatory strain. The relaxation spectrum \( (G_i, \lambda_i) \) can then be calculated from the experimentally determined values of \( G' \) and \( G'' \) using a non-regularisation procedure (see for e.g. Ferry, 1980). The relaxation spectrum can also be obtained from the stress relaxation data when the system is subjected to small step strains. Using the relaxation spectrum, it is possible to predict the linear viscoelastic response of a polymeric system.

### 2.1.2 Non-linear Viscoelasticity

Many processing phenomena that are of practical and scientific importance cannot be described using the model of linear viscoelasticity. These include simple flow situations such as steady shear at higher shear rates. Examples of non-linear effects include the dependence of the relaxation modulus on the strain magnitude and the shear thinning nature of the viscoelastic material. Unlike linear viscoelastic behaviour, there is no
universal quantitative model available to describe non-linear viscoelastic behaviour of polymeric systems (Dealy and Wissbrun, 1995).

The stress response predicted by Eqn. 13 includes a memory function and does not account for the shear thinning response observed in polymer melts at high steady shear rates. In order to incorporate non-linearity, a class of strain-dependent constitutive equations, which are referred to as the K-BKZ type equations were introduced (see e.g. Dealy and Wissbrun, 1995 and Larson, 1988). Wagner (1976) developed a single integral K-BKZ type equation to account for the generalised non-linear behaviour of a polymer melt of the form

\[ \tau(t) = \int_{-\infty}^{t} m(t-t') h(I_1, I_2) C^{-1}(t', t) \, dt' \]

where \( h(I_1, I_2) \) is called the strain-dependent damping function and \( C^{-1}(t', t) \) is the Finger strain tensor (for a detailed explanation see Larson, 1988), which gives the strain evaluated at time \( t' \) with reference to its configuration at time \( t \). \( I_1 \) and \( I_2 \) are scalar invariants of the Finger strain tensor and Cauchy strain tensor respectively. The expressions for the Cauchy strain tensor \( C(t', t) \) and Finger strain tensor \( C^{-1}(t', t) \) in simple shear are given by

\[ C(t', t) = \begin{bmatrix} 1 & -\gamma(t,t') & 0 \\ -\gamma(t,t') & 1 + \gamma(t,t')^2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \]

\[ C^{-1}(t', t) = \begin{bmatrix} 1 + \gamma(t,t')^2 & -\gamma(t,t') & 0 \\ -\gamma(t,t') & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \]

Hence, the scalar invariants of the Finger and Cauchy tensor in simple shear are

\[ I_1 = I_2 = 3 + \gamma^2 \]

The damping function proposed by Wagner (1976) is of the form

\[ h(I_1, I_2) = \exp(-k\sqrt{I_1 + I_2(1-\beta) - 3}) \]

where \( k \) is a constant and \( \beta \) is another non-linear parameter which is irrelevant in simple shear because, \( I_1 = I_2 \).

A complete derivation of these expressions can be obtained from Larson (1988). The strain-dependent exponential damping function \( h(I_1, I_2) \) is one of the simplest...
representations available for introducing the non-linearity character of a polymeric system. This damping function is solely dependent on the strain applied while the memory function is independent of the strain and only varies in time. Therefore, the same memory function (Eqn. 16) derived using small amplitude oscillatory experiments can be used to describe the non-linear behaviour of the system. Substituting Eqn. 35 into Eqn. 36, the damping function $h(I_1, I_2)$ can be written as follows,

\[ h(I_1, I_2) = h(\gamma) = \exp(-k|\gamma(t,t')|) \]

where $k$, the damping factor is an empirical parameter, which quantifies the level of non-linearity of the polymeric system and $|\gamma(t,t')|$ is the magnitude of past strain between time $t'$ and $t$. If $k = 0$, the material is linear viscoelastic and behaves as a Newtonian fluid in steady shear. The non-linear damping function is included in Eqn. 14 to obtain the following integral constitutive equation

\[ \tau(t) = -\sum_{i=1}^{N} \left( \frac{G_i}{\lambda_i} \right) \exp\left( \frac{t-t'}{\lambda_i} \right) \exp(-k|\gamma(t,t')|) \gamma(t,t') \, dt' \]

Eqn. 38 can be used to predict the shear stress response of a system to a non-linear strain. In steady shear, the strain function is of the form (see for e.g. Mackley et al., 1994)

\[ \gamma(t,t') = -k\dot{\gamma}_0 (t-t') \]

When Eqn. 39 is substituted into Eqn. 38, the integral can be solved to give an analytical expression for the shear stress response $\tau$, as a function of shear rate $\dot{\gamma}_0$:

\[ \tau(\dot{\gamma}_0) = \sum_{i=1}^{N} \frac{G_i \dot{\gamma}_0}{\lambda_i (1 + k\lambda_i^2 \dot{\gamma}_0^2)} \]

The damping factor, $k$ can be determined using the stress relaxation modulus obtained from linear and non-linear step strains. In a step-strain experiment, the polymer sample is subjected to an instantaneous (or step function) deformation, and the resultant stress is measured as a function of time to give the shear stress relaxation modulus $G(t)$.

The strain history of the melt can be expressed as follows,

for $t < 0$ \hspace{1cm} $\gamma = -\gamma_1$

for $t > 0$ \hspace{1cm} $\gamma = 0$

Substituting the expressions for strain history in Eqn. 38, the integral can be solved to obtain the following expression for the relaxation modulus $G(\gamma_1, t)$.
Eqn. 41
\[ G(\gamma_1, t) = \frac{\tau(t)}{\gamma_1} = \exp(-k \gamma_1) \sum_{i=1}^{N} G_i \exp(-t/\lambda_i) \]

where \( \tau(t) \) is the value of shear stress after a step strain of magnitude \( \gamma_1 \). If the step-strain is small, i.e. in the linear region, the relaxation modulus can be written as

Eqn. 42
\[ G(\gamma_0, t) = \sum_{i=1}^{N} G_i \exp(-t/\lambda_i) \]

where \( \gamma_0 \) is a linear step-strain. The damping factor \( k \), can be obtained from the ratio of the relaxation modulus at large (non-linear) and small (linear) strains

Eqn. 43
\[ \exp(-k \gamma_1) \frac{G(\gamma_1, t)}{G(\gamma_0, t)} \]

The relaxation spectrum of a polymer melt can be determined using either the stress relaxation modulus for linear step strain or using the small amplitude oscillatory strain experiments as explained in the earlier section. The steady shear stress response of a polymer melt in the region of non-linear viscoelasticity can then be predicted using its relaxation spectrum (\( G_0, \lambda_0 \)) and damping factor, \( k \).

### 2.2 Experimental Apparatus and Techniques

The rheological characterisation of the polyethylene samples were carried out using two types of rheometers; a Rheometrics Dynamic Spectrometer (RDS), which is a rotational rheometer and a Multipass Rheometer (MPR), which is a two-piston capillary rheometer. The RDS has been used to carry out the frequency response analysis for polymer melts in order to determine the storage and loss modulus, which are used to calculate the relaxation spectrum. It has also been used to determine the damping factor \( k \), by carrying out step-strain experiments for both linear and non-linear strains. The MPR is mainly used to study the rheological behaviour of polymer melts at larger strains and strain rates, which cannot be achieved using a RDS. The MPR has also been used to visualise the flow of polymer melts using the flow birefringence technique.

An introduction to these two rheometers, the calculation of rheological parameters from their measurements and a description of the use of the flow birefringence technique is given in the following sections.

#### 2.2.1 The Rheometrics Dynamic Spectrometer (RDS)

The RDS, a rotational rheometer, is a controlled strain instrument, i.e. the material is
subjected to a measured value of strain (or strain rate) and the stress response of the sample is monitored. The material under study is subjected to shear deformations using two concentric plates, which are separated by a specified distance (≈ 1 mm). The lower fixture is operated using a stepper motor, which can impart steady or oscillatory motions and step-strains to the sample. The polymer sample is compression moulded into a thin sheet of uniform thickness (1 mm), by melting polymer pellets. The sample was stamped out of this sheet in the shape of a circular disc having the same diameter as that of the parallel plates (= 25 mm). The quantities measured during an experiment were the torque on the upper plate and the total normal force required to maintain a constant gap width (h). A schematic representation of the RDS geometry is shown in Figure 2.5.

![Figure 2.5: Schematic representation of the parallel plate geometry of a RDS](image)

The RDS can be used to perform both dynamic and steady shear experiments for a range of strain and strain rates respectively. These results were used to determine the relaxation spectrum of the sample using an in-built RHECALC (RHEometrics Enhanced CALCulation program) software. It has also been used to carry out step strain experiments in order to determine the damping factor, k. The specification of the RDS is given in Table 2.1.

<table>
<thead>
<tr>
<th>Plate Diameter</th>
<th>25 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gap Width (recommended)</td>
<td>0.5 - 2 mm</td>
</tr>
<tr>
<td>Frequency range</td>
<td>0.00001 - 500 radians per second</td>
</tr>
<tr>
<td>Strain rate range</td>
<td>0.001 - 100 radians per second</td>
</tr>
<tr>
<td>Operating temperature range (Oven range)</td>
<td>Ambient to +600 °C</td>
</tr>
<tr>
<td>Normal Force Rebalance Transducer</td>
<td>+ 2 kg compression and -1.2 kg tension</td>
</tr>
</tbody>
</table>
2.2.2 The Multipass Rheometer (MPR)

The Multipass Rheometer is a two piston capillary rheometer developed in the University of Cambridge by Mackley et al. (1995). An advantage of the MPR over the RDS is its ability to study flow of materials such as polymer melts in a fully enclosed environment under high shear rate conditions similar to those employed during industrial processing. A schematic diagram of the MPR is shown in Figure 2.6. The MPR consists of a top and bottom barrel through which two pistons enter the system. In between the barrels is a test section, which can either be a capillary or a slit of required dimensions. The pistons can be moved either separately or synchronously to perform experiments involving both steady and oscillatory rheological measurements. Two pressure transducers on each side of the test section monitor the pressure changes in the system. There are two thermocouples on either side of the test section to detect the temperature of the system. Both the pistons are driven by means of a servo-hydraulic controller, which is operated, from a PC using LabVIEW; a graphical development package designed for controlling instruments and for data acquisition. Data acquisition consists of reading piston positions, pressure traces from both the transducers and the thermocouple readings. Oil is circulated through the different test sections using an oil heater and circulator to attain the desired temperature in the rheometer.

The bottom barrel is placed over the bottom piston and fixed to a movable platform. Solid polymer pellets are loaded into the bottom barrel and heated to a desired melt temperature. The test section is then fixed to the bottom barrel and loaded with polymer pellets, which are also then melted. Subsequently, the top barrel is fitted onto the test section and filled with polymer pellets, which are also subsequently melted. Finally, the movable platform is raised to meet the top piston that enters into the top barrel to form a fully constrained system. One of the pistons is moved inward to eliminate air in the system through a bleed valve present in both the top and bottom barrels. The pistons are moved either towards or away from each other to attain a suitable system pressure.

The central test section of the MPR can be either a capillary geometry for rheological measurements or a slit geometry for flow visualisation. The technical specification of the MPR is given in Table 2.2. The MPR can be easily adapted to perform capillary measurements over a wide range of shear rates up to 10,000 s⁻¹. In order to perform these measurements, a central test section has been designed in the form
of a capillary holder, where capillaries of different diameters, lengths and entry angles can be inserted, thus enabling experimentation over a wide range of shear rates.

Figure 2.6: Capillary flow configuration of the Multipass Rheometer

The pistons of the MPR can be operated in a number of ways. They can be moved independently towards each other to pressurise the sample before experimentation or to perform compressibility measurements. They can also be moved together in a steady or oscillatory motion to carry out steady shear or dynamic measurements respectively. The operation of the MPR in all the modes mentioned are discussed in greater detail in the following sections.

Table 2.2: Technical specifications of the MPR

<table>
<thead>
<tr>
<th>Material of construction</th>
<th>Stainless steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barrel/Piston diameter</td>
<td>1.2 (10^2) m</td>
</tr>
<tr>
<td>Sample volume</td>
<td>15 - 30 (10^{-6}) m(^3)</td>
</tr>
<tr>
<td>Piston velocity</td>
<td>5 (10^{-4}) - 0.1 m/s</td>
</tr>
<tr>
<td>Frequency</td>
<td>0.01 - 100 Hz</td>
</tr>
<tr>
<td>Wall strain</td>
<td>10 - 10000% (8 mm capillary diameter)</td>
</tr>
<tr>
<td>Wall shear rate</td>
<td>0.1 (s^{-1}) lower limit of (8 mm capillary diameter)</td>
</tr>
<tr>
<td></td>
<td>3 (10^3) (s^{-1}) upper limit of (1 mm capillary diameter)</td>
</tr>
<tr>
<td>Maximum piston displacement</td>
<td>3 (10^4) m</td>
</tr>
<tr>
<td>Range of operating pressures</td>
<td>0.1 - 250 MPa</td>
</tr>
<tr>
<td>Range of operating temperatures</td>
<td>Ambient - 200 °C</td>
</tr>
</tbody>
</table>
• Measurement of Compressibility

In order to explain certain time dependent experimental observations that are reported in this thesis, it is necessary to determine the compressibility of the polyethylene melts. The compressibility, $\chi$, of a material under isothermal conditions can be defined as

$$
\chi = \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = - \left( \frac{\partial \ln V}{\partial P} \right)_T
$$

where, $V$ is the volume occupied, $P$ is the pressure and $T$ is the temperature in the system (see for e.g. Ferry, 1980). In order to measure the compressibility of a polymer melt, a capillary of the same radius as that of the barrel (i.e. 6 mm) was used as the test section of the MPR. This gives a flow geometry equivalent to a tube without any constrictions. The melt in this tube can be compressed by moving one of the pistons inwardly. This reduces the volume occupied by the melt and is accompanied by a corresponding pressure increase in the system. The slope of a plot of ln (volume) occupied by the melt versus system pressure, is then used to calculate the compressibility over a pressure range of 1 to 25 MPa.

• Steady Shear Mode of Operation

The MPR is used to carry out steady shear experiments over a wide range of shear rates. In the steady mode of operation, the sample in the assembly is made to flow through the test section and the pressure difference across the test section is determined from the readings of the top and bottom pressure transducer. For a piston velocity, $v_p$, and barrel radius $R$, the flow rate through the barrel is $Q_m$ is given by

$$
Q_m = \pi R^2 v_p
$$

With a capillary radius $r$, the wall shear rate, $\dot{\gamma}_w$, for a Newtonian fluid is given by

$$
\dot{\gamma}_w = \frac{4Q_m}{\pi r^3}
$$

In the case of shear thinning fluids, the wall shear rate is underestimated and can be corrected using the Rabinowitsch correction (see for e.g. Rosen, 1993), which depends on the deviation of the $Q-\Delta P$ curve,

$$
\dot{\gamma}_w = \frac{1}{\pi r} \left[ \frac{3Q_m + \Delta P \frac{dQ_m}{d\Delta P}}{3Q_m} \right]
$$

For a slit geometry of width $W$, depth $D$ and length $L$, the wall shear rate $\dot{\gamma}_w$ for a Newtonian fluid is given by
The wall shear stress \( \tau_w \) is related to the pressure difference \( \Delta P \) across a capillary test section.

\[
\tau_w = \Delta P \frac{r}{2L}
\]

and a slit test section

\[
\tau_w = \Delta P \frac{W}{2L}
\]

Accurate results can be obtained by correcting the pressure difference (\( \Delta P \)) for pressure losses at the ends of the capillary.

For steady shear measurements, the pistons can be operated either in a **Multipass** mode or in a **Single pass** mode. In the **Multipass** mode, the pistons are moved for a given amplitude and a constant velocity in one direction. The pressure difference across the capillary increases to reach a steady value. After the piston stroke, a delay time is introduced and the pressure difference across the capillary diminishes. Then the pistons are moved for the same amplitude and with the same velocity in the reverse direction giving rise to a similar pressure difference across the capillary, followed by a similar delay period. This piston stroke is then repeated for a number of times such that the sample has “multiple passes” through the capillary. This mode is useful to study the evolution of parameters measured over a period of time or to obtain average values of the experimental parameters over a number of passes. In addition, time dependent pressure evolution and relaxation measurements can be carried out by operating the MPR in the **Multipass** mode. A typical pressure difference profile obtained for the capillary flow of POE in the MPR in the **Multipass** mode is shown in Figure 2.7.

The change in the position of the top and bottom piston, top barrel pressure, and bottom barrel pressure with time have been recorded, though only the bottom piston position and pressure difference trace has been shown for the sake of clarity. The upper portion of Figure 2.7 shows the displacement of the bottom piston in the following sequence; down stroke -delay time -up stroke. The pistons are moved for an amplitude of \( 1.0 \times 10^{-2} \) m with a piston velocity of \( 1.0 \times 10^{-2} \) m/s and the delay time between strokes is fixed as 2 seconds. The pressure difference across the capillary increases to reach a steady value with the down stroke, undergoes relaxation during the delay time and in the
up-stroke the pressure difference across the capillary builds up in the opposite direction. In this case, the pressure difference is of the order of 40 bar or 4 MPa.

![Figure 2.7: The pressure difference traces obtained for a Multipass experiment on HDPE T = 180 °C, capillary, L = 40 mm, D = 4 mm, Half Entry angle = 45°, \( v_p = 1.5 \times 10^{-2} \text{ m/s} \), \( A = 1.5 \times 10^{-2} \text{ m} \)](image)

In addition to the Multipass mode, it is possible to investigate the time dependent steady shear behaviour in greater detail by moving the pistons in a Single pass mode. In the Single pass mode, as in the Multipass mode, both the pistons are moved together in the same direction only once with a certain velocity (corresponding to a certain shear rate) and amplitude (corresponding to a certain shear strain). As a result, pressure difference across the (capillary or the slit) test section generally rises to reach a steady state. When the pistons stop moving, this pressure difference across the test section undergoes relaxation. The advantages of the Single pass mode of operation includes better resolution of data over the duration of the experiment and the machine can also be used to closely study the relaxation of pressure after a steady shear experiment. Equivalent experiments can be carried out for both upward and a downward movement of the pistons and this feature enables easy repetition of experiments using the same sample by alternately moving the pistons upwards and downwards. A majority of the experiments described in this thesis have been carried out on the MPR using the Single pass mode.

- **Oscillatory Mode of Operation**

The MPR has also been used to carry out small amplitude oscillatory strain measurements in order to determine the storage and loss modulus of the polymer samples. These measurements have been compared to the results obtained from a RDS to confirm the validity of the experimental data obtained using the MPR.
The polymer sample is subjected to small amplitude harmonic or oscillatory deformations, and the dynamic moduli is calculated from the phase angle $\delta$ between the applied strain and the measured pressure difference. The maximum wall shear strain $\gamma_w$ for a Newtonian fluid is given by

$$\text{Eqn. 51} \quad \gamma_w = \frac{4V}{\pi r^3}$$

where $V$ is the volume displacement resulting from a centre to peak stroke, $x_{\text{max}}$ of the piston i.e. $V = \pi R^2 x_{\text{max}}$.

A typical pressure difference profile generated during the small amplitude sinusoidal movement of the pistons is shown in Figure 2.8. The upper part of the graph shows the displacement of the bottom piston which is in the form of a sine wave of a certain amplitude and frequency. The corresponding pressure difference across the capillary is shown in the bottom portion of the graph. The pressure difference signal is also sinusoidal in nature and out of phase with the displacement of the pistons.

![Figure 2.8](image)

**Figure 2.8**: The pressure difference traces for a small amplitude sinusoidal movement of pistons for POE, $T = 180^\circ \text{C}$, straight tube, $L = 8.2 \times 10^{-2} \text{ m}$, $D = 1.2 \times 10^{-2} \text{ m}$

The phase difference between the imposed oscillatory strain and resulting oscillatory stress are calculated using a cross-correlation method where the values of applied strain and resulting stress magnitudes are also determined (see for e.g. Smits et al., 1991). The expressions for storage and loss moduli can be derived to give

$$\text{Eqn. 52} \quad G' = \frac{r^4 \Delta P_{\text{max}}}{8 L R x_{\text{max}}^3} \cos \delta$$
where \( r \) is the radius and \( L \) is the length of the capillary test section. The barrel radius is represented by \( R \) and \( \delta \) is the phase difference between the imposed sinusoidal strain and measured value of the maximum pressure difference (\( \Delta P_{\text{max}} \)), which is of the order of 20 bar or 2 MPa in Figure 2.8. A complete derivation of all the formulae listed above can be found in a publication about the MPR (Mackley et al., 1995). The LabVIEW program, which is used to control the MPR, determines the value of the loss tangent, \( \tan \delta \) and consequently the values of storage and loss moduli, \( G' \) and \( G'' \).

It can be seen that the MPR is a versatile instrument and has the capability to carry out a variety of measurements over a range of shear strains, frequencies, shear rates, pressures and temperatures. It can also be used to monitor the time dependent events during processing of samples which is one of the important aspects of this thesis. The MPR can also be used to carry out flow visualisation experiments (such as flow birefringence) using a specially designed test section, called the Optic cell. A background to flow birefringence and the experimental set-up used to carry out flow birefringence measurements on the MPR are given in the next section.

### 2.3 Background to Flow Birefringence Technique

Most of the experimental measurements described in this thesis are concerned with the rheological and processing data obtained from capillary flow measurements carried out using the MPR. However, some additional studies have also been done using optical techniques including flow birefringence. In this section, the technique of flow birefringence is briefly described.

When a transparent isotropic material such as a polymer melt is subjected to mechanical stresses it becomes optically anisotropic. This phenomenon is called stress birefringence or photoelastic effect and was first reported for crystals by Brewster in 1815 (Born and Wolf, 1969). The application of flow birefringence to determine the rheology of polymeric fluids is a technique, which has been widely used. (see for e.g. Ahmed et al., 1993, Kalogrianitis and van Egmond, 1997, White and Baird, 1988). Birefringence is mathematically expressed as the difference between the principal refractive indices within a material. The effect of stress can be observed by viewing a stressed layer of polymer
melt between crossed polarisers. In doing so, both bright and dark fringes can be seen and these fringes are contours of equal principal stress difference (PSD) (Fuller, 1990).

The fringes can be seen at maximum intensity in any given region of the pattern only if the principal axes of the stress system in this region are at 45° to the directions of the light waves transmitted by the polariser. When the principal axes of the stress are parallel to the directions transmitted by the polariser, the fringes disappear and the field of view becomes black. Thus the directions of the axes of the stress system can be determined by rotating the crossed polarisers, while the magnitude of the shearing stress can be obtained from the order of the fringes.

For optical flow birefringence measurements on materials such as polymer melts (birefringence \( \Delta \), of the order of \( 10^{-5} - 10^{-4} \)), the use of polarisers and counting of fringes are adequate to determine the stress distribution in the flow field. For measuring birefringences of the order of \( 10^{-7} \) and greater, compensators such as Ehringhaus or de Senarmont need to be used (Born and Wolf, 1969). A description of some of the optical terms introduced in this section and a mathematical description of flow birefringence are given in Appendix A.

### 2.3.1 Interpretation of Flow Birefringence Patterns

Han and Drexler (1973) have clearly illustrated the use of flow birefringence technique to obtain a quantitative measure of the stress distribution in flowing melts. Each band (black and white) in a birefringence pattern corresponds to a locus of points with a constant principal stress difference (PSD). In order to determine the order of the fringes, it is necessary to know how the fringes develop in the slit.

The fringes tend to emerge from the front corners of a slit entrance and develop from the two corners towards the centre line of the slit. When the two fringes having the same numerical order meet at the centre of the slit, they combine with each other. As the flow rate increases, this combined fringe splits into two and the two parts move simultaneously in different directions. One part of the fringe moves downstream into the slit length and the other part moves into the upstream reservoir. In slits, the fringes tend to straighten out as they move further away from the slit entrance. The point where the fringes have left the entrance region and have become parallel lines corresponds to the fully developed flow section. The other part of the originally combined fringe moves further into the upstream reservoir as the flow rate is increased. The fringe grows with a slight curvature on its sides and with a flat centre section which contains a small
indentation. As the flow rate is increased, this fringe moves further away from the slit entrance. Each subsequent fringe grows in the same manner as the first fringe. The order of the fringes increases with the distance from the centre line of the slit.

The technique of flow birefringence has been used extensively on an extruder within the Polymer and Fluids group in the University of Cambridge to obtain a quantitative description of the stress distribution of the flow field (see for e.g. Ahmed et al. 1993, Rutgers, 1998). Apart from its usefulness in quantitatively determining the stress distribution in the slit, flow birefringence observations have been used to make qualitative observations of complex rheological behaviour such as flow instabilities in polymer melts (Tordella, 1969) and Vinogradov et al., 1975) and for analysis of stresses for components obtained by injection moulding (Janeschitz-Kriegl, 1983). In this thesis, the flow birefringence technique has been used to make qualitative observations of the flow field in the slit.

2.3.2 Flow Birefringence in the MPR

In order carry out flow visualisation observations on the MPR, a special central test section called the Optic cell has been designed (Figure 2.9). The Optic cell has a main cubic shaped body into which two die blocks can be inserted at opposite faces to form a slit of required dimensions. Two quartz windows are inserted through the other two opposite faces and are flush with the slit formed. Oil circulation channels through the cell are used to heat up the polymer pellets to a desired temperature. Flow birefringence (FB) for a flowing polymer melt is carried out by passing light through the Optic cell in a direction perpendicular to the flow and along a plane transverse to the flow.

![Figure 2.9: Schematic diagram of the Optic cell showing the die blocks and transparent quartz windows](image)

The flow birefringence apparatus used for experimentation is shown in Figure 2.10. The light source is a fibre optic cable and the light passes through a green monochromator to give a monochromatic diverging beam of light. This beam is then
focused and made parallel using a two convex lens assembly. The parallel beam of light then passes through an assembly of cross polarisers, which are referred to as the polariser and the analyser. The polariser is placed upstream to the light passing through the slit while the analyser is placed in the downstream direction.

Figure 2.10: Flow visualisation set-up on the MPR showing assembly of lenses, polarisers and analysers

The polariser-analyser assembly is positioned at an angle of $45^\circ$ to the direction of flow of the melt in the slit using a pre-oriented sample. The light passing through a polariser gives plane polarised light and this light passes through the slit to reach an analyser placed at the other side of the slit. The output is captured by a CCD camera and is viewed on a TV monitor and also recorded onto an S-VHS tape. In order to perform experiments with unpolarised light, the polariser and analyser are excluded from the set-up and to perform experiments only with plane polarised light, the analyser is excluded from the set-up.

2.4 Summary and Conclusions

A background to rheological characterisation of polymer melts has been given and the use of the Maxwell model coupled with the Wagner damping function has been presented. The experimental parameters needed to apply these models are the relaxation spectrum and damping factor, $k$ and these parameters are determined using the RDS, a parallel plate rotational rheometer.
A newly developed capillary rheometer, the Multipass Rheometer (MPR), which can be used to carry out both steady shear and dynamic rheological measurements, has been described. The MPR can also be used to monitor the time dependent flow of the polymer melt through a capillary and a slit geometry over a wide range of shear rates. In addition, the principles of flow birefringence, its application to flow situations and the flow birefringence set-up on the MPR have also been given.
3. Structural and Rheological characterisation of HDPE, POE and LLDPE

In this chapter, measurements carried out to characterise the molecular structure and rheological behaviour of three polyethylene samples are described. The characterisation of the molecular structure of the three polymers were carried out using chromatographic techniques. The rheological characterisation of the three polyethylene samples was carried out using the RDS and is used to determine the parameters required to predict their steady shear response. Also, the dynamic and steady shear properties of the three polyethylenes have been compared. The measurements carried out using the MPR were validated with those obtained from the RDS. The compressibility of the PE melts and the pressure dependence of dynamic properties were also measured using the MPR.

3.1 Introduction to Characterisation of Polyethylene Samples

The rheological and mechanical properties of polymers are strongly influenced by the morphology of the polymer chains. The end properties of a polymer are strongly dependent on its molecular weight (MW) and molecular weight distribution (MWD). Therefore, the characterisation of the molecular structure of polymers is useful, as it can contribute towards the understanding of their rheological behaviour. Chromatographic techniques were used in order to elucidate the molecular structure and molecular weight distribution of these polyethylenes. The rheological characterisation of the three polyethylene samples have been carried out using a RDS and a MPR.

3.1.1 Characterisation of Molecular Structure

The molecular characterisation of the three polyethylenes was carried out using the Gel Permeation Chromatography (GPC) technique. The GPC technique provides information about the MW and MWD of the polymer chains. However, it does not reveal the presence of branched chains and the level of branching in the polymer chains. In order to overcome this shortfall, a relatively new technique called Temperature Rising Elution Fractionation (TREF) was also used to clarify the molecular structure and branching
nature (Monrabal, 1994) of polymer systems. The results from the GPC have been supplied by the Dow Chemical Company in Terneuzen, Netherlands while the TREF results have been obtained from a publication of Gabriel et al. (1998).

The GPC apparatus consists of a packed column generally made up of highly cross-linked polystyrene beads with a distribution of pore sizes in the range of 10 - 10⁵ nm (Young, 1981). The polymer solution passes through the column and the solvent goes through and around the beads. The smaller polymer molecules permeate through the pores in the beads and their flow through the column is retarded. Larger molecules which are unable to enter the pores pass through the column faster than the smaller molecules (Young, 1981). The separation of chains of different molecular weights is carried out on the basis of their hydrodynamic radius to generate the MWD and the GPC columns are calibrated using standard polymers of known MW and MWD.

The distribution of molecular weights of HDPE, POE and LLDPE obtained from the GPC are shown in Figure 3.1, Figure 3.2 and Figure 3.3 respectively. The parameters calculated from these plots are presented in Table 3.1.

![Figure 3.1: GPC trace of HDPE indicating a broad MWD](image)

HDPE has a relatively broad MWD indicating that it is made up of chains of widely differing lengths giving it a high polydispersity index (PI = 8). The MWD of Polyolefin Elastomer (POE) on the other hand is much narrower indicating that it is made up of chains of similar molecular mass which gives it a low polydispersity index (PI = 1.3). The GPC traces of LLDPE show that it has relatively broad MWD as compared to POE, but is
less polydisperse (PI = 2.22) than HDPE.

![Figure 3.2: GPC trace of POE indicating a narrow MWD](image)

![Figure 3.3: GPC trace of LLDPE indicating a reasonably narrow MWD](image)

| Table 3.1: Molecular parameters of the polyethylenes measured using the GPC technique |
|-----------------------------------|--------|--------|
| HDPE    | POE    | LLDPE  |
| Mn      | 22900  | 98100  | 54800  |
| Mw      | 183000 | 127000 | 122000 |
| PI      | 8      | 1.3    | 2.22   |
The basis of separation of the polymer fractions in TREF is their crystallinity. The unbranched chains constitute the crystalline part and all the co-monomer units, diluents and polymer end-groups are regarded as non-crystallising parts of the polymer. The analysis was carried out by monitoring the change in the concentration of a polymer solution during crystallisation initiated by temperature reduction. The process involves a stepwise fractionation carried out by precipitation starting at temperatures at which there are no crystalline components in the polymer solution. As the temperature reduces, the most crystalline fraction made up of molecules with zero or very few branches will precipitate initially. This is followed by precipitation of fractions of increasing branching content with a decrease in temperature, ending up with a fraction that was not crystallised (mainly highly branched material) and hence remains in solution.

The TREF results for HDPE and POE indicate that they are both homogeneous materials with respect to chain branching. It also shows that HDPE is an unbranched polymer while POE is a uniformly branched polymer. The TREF trace obtained for LLDPE is shown in Figure 3.4. It can be clearly seen that LLDPE is not homogeneous but is in fact made up of two main components. The first component is linear polyethylene (similar to HDPE) and the second component consists of short chain branched molecules (similar to POE). Also, the linear fraction is distinctly higher by a factor of two as compared to the branched fraction. Therefore, LLDPE can be regarded as a blend of POE and HDPE in the ratio of 1:2 (Gabriel et al., 1998).

![Figure 3.4: Temperature Rising Elution fractionation (TREF) trace for LLDPE indicating the presence of linear and branched chains in the ratio of 2:1](image-url)
LLDPE can be a suitable medium to observe the properties of both branched and linear polymer chains because the effect of both types of chains will be reflected in its rheology. This in turn could enhance the understanding of the effect of molecular structure on the rheology of linear and branched polymers. Consider the steady shear flow curves (shear stress versus shear rate) of the three polymers shown in Figure 3.5. These flow curves have been obtained using a Göttfert capillary rheometer and have also been supplied by The Dow Chemical company. The flow curve of HDPE is the lowermost curve and as reported in many studies, it is distinctly discontinuous, made up of two monotonically increasing branches (Benbow and Lamb, 1963). The uppermost flow curve is that of POE and it is continuous and monotonously increasing in nature. The middle flow curve is that of LLDPE and is slightly discontinuous and is also made up of two monotonically increasing branches. The flow curve of LLDPE is also predicted by the weighted addition of the flow curves of the HDPE and POE in the following manner.

\[
\tau_{\text{LLDPE}} = 0.67 \times \tau_{\text{HDPE}} + 0.33 \times \tau_{\text{POE}}
\]

This prediction is plotted as a solid line and can be seen to coincide with the experimentally determined flow curve of LLDPE. Therefore, it may be inferred that the rheology of HDPE and POE are additive in nature.

Figure 3.5: Experimentally determined flow curves of the three polyethylene samples using the Göttfert capillary rheometer at \( T = 180 \, ^\circ \text{C} \) using a capillary of \( L/D = 20/1 \) and half entry angle = 90° and the predicted flow curve of LLDPE using an addition rule.
3.2 Rheological Characterisation of Polyethylene samples

The polyethylene samples have been rheologically characterised to determine the parameters for the Wagner integral constitutive equation (described in chapter 2) using the protocol proposed by Mackley et al. (1994). In order to achieve this, small amplitude dynamic strain and step strain experiments are carried out using a RDS. All the results shown in the following sections have been obtained at a temperature of 180 °C.

3.2.1 Determination of the linear Viscoelastic Region

In order to determine the linear viscoelastic region, the polymer melt samples are subjected to oscillatory strains at a given frequency. In the linear viscoelastic region, the values of $G'$, $G''$ and $\eta^*$ are unchanged with respect to the magnitude of imposed strain.

The three polymer samples were subjected to a range of strains over four decades from 0.05 to 500% and the change in the values of $G'$, $G''$ (and hence $\eta^*$) are measured. These experiments are carried out at a frequency of 15 rad/s for HDPE and POE and 5 rad/s for LLDPE (Figure 3.6 a, b and c). The linear region is estimated to extend up to 70 % strain for HDPE, 50% strain for POE and 80% for LLDPE. Beyond the linear region, the values of $G'$ and $G''$ start to decrease indicating the onset of shear thinning (non-linear) behaviour. All the three polymers show higher values of loss modulus as compared to the storage modulus and therefore the contribution to complex viscosity is mainly due to the loss modulus. This is because at low frequencies, the polymer behaves in a predominantly viscous manner.
Figure 3.6: Small amplitude oscillatory strain sweep carried out using a RDS for a) HDPE b) POE and c) LLDPE at $T = 180 \, ^\circ C$
3.2.2 Determination of the Relaxation Spectrum

The relaxation spectrum of the polyethylene samples was obtained from the dynamic moduli, \( G'(\omega) \) and \( G''(\omega) \), by determining the best fit values of the relaxation spectrum \( (G_i, \lambda_i) \) for Eqns 29 and 30, using a number of numerical techniques (see for e.g. Baumgaertel and Winter, 1989, Kamath and Mackley, 1990).

\[
G'(\omega) = \sum_{i=1}^{N} \frac{G_i \lambda_i^2 \omega^2}{1 + \lambda_i^2 \omega^2}
\]

Eqn. 29

\[
G''(\omega) = \sum_{i=1}^{N} \frac{G_i \lambda_i \omega}{1 + \lambda_i^2 \omega^2}
\]

Eqn. 30

The dynamic moduli of the polyethylene samples are measured over a range of frequencies, by subjecting them to small amplitude oscillatory strain. A value of strain is chosen such that it lies in the linear region of the polyethylene melts, which was determined from the strain sweep experiments.

The change in the values of the dynamic moduli with frequency are shown in Figure 3.7. These experiments have been carried out at a 15% strain magnitude. It can be seen that at the higher frequency end, the values of both \( G' \) and \( G'' \) seem to be decreasing. This behaviour must be an artefact, because the values of \( G' \) never decrease with increasing frequency (see for e.g. Dealy and Wissbrun, 1995). This artefact could have emerged because of the limitations of the RDS while trying to impart high frequency deformations. The relaxation spectrum \( (G_i, \lambda_i) \) is determined using RHECALC software available in the RDS using a non-linear fitting procedure. For this procedure, eleven time constants are chosen which are equally spaced between \( 10^{-1} \) and \( 10^{3} \) seconds. The software then performs a non-linear regression fit to give a best set of \( G_i \) values for the selected set of \( \lambda_i \) values (Figure 3.8 a, b and c). In some cases, the values of \( G_i \) determined using this procedure are very small, and can therefore be safely neglected.

The relaxation spectrum is then used to recalculate the values of the storage and loss moduli over a range of frequencies (using Eqns 29 and 30) and is compared with the experimentally determined values of the dynamic moduli (Figure 3.9 a, b and c). The fitted curve is consistent with the experimental data, indicating that the relaxation spectrum can be reliably used to predict the linear viscoelastic response of the material. This is not unexpected since a total of sixteen parameters have been used to recalculate the frequency response. However, it ensures that the non-regularisation procedure is adequate for converting the frequency response into a relaxation spectrum.
Figure 3.7: Small Amplitude Frequency sweep using RDS for a) HDPE b) POE and c) LLDPE, T = 180 °C
Structural and Rheological characterisation of HDPE, POE and LLDPE

![Graphs showing relaxation spectra of HDPE, POE, and LLDPE](image)

Figure 3.8: Relaxation spectrum of a) HDPE b) POE and c) LLDPE computed from the Small Amplitude frequency sweep data
Figure 3.9: Recalculation of dynamic moduli using the relaxation spectrum and its comparison with the measured dynamic moduli of a) HDPE b) POE and c) LLDPE using the RDS, $T = 180 \, ^\circ C$
3.2.3 Determination of the Damping Factor, $k$

A quantitative characterisation of the non-linear response (i.e. value of $k$) of polymer melts has been obtained by carrying out step strain experiments at different magnitudes of strains. The damping factor, $k$ is calculated by taking the ratio of relaxation modulus at large (non-linear) and small (linear) strains as given in Eqn.43

\[
\exp(-k |\gamma|) = \frac{G(\gamma_{\infty}, t)}{G(\gamma_0, t)}
\]

A step strain refers to the instantaneous application of a strain, but in practice, the imposed strain is not instantaneous and it takes a finite time for the motor to generate this deformation. In a step strain experiment, the motor of the RDS applies a high rate of deformation. As the value of the imposed strain becomes larger, the motor takes an even longer time to apply the strain. The application of 50% and 100% strains are reasonably instantaneous whereas for 200% and 300% strains, it takes a finite amount of time (about 0.1 seconds) before the entire strain can be imposed.

The step strain response of the polyethylene melts for a number of linear and non-linear strains have been plotted together in Figure 3.10 a, b, and c. The relaxation modulus is found to be independent of the imposed strain magnitude for linear strains ($\gamma_0$). The step strain response for small (linear) strains is also predicted using the relaxation spectrum (Eqn. 11). This prediction is plotted as a dashed line and is found to be in reasonable agreement with the experimentally determined relaxation modulus for all the three polyethylenes.

As the strain magnitude is increased beyond the linear region, the relaxation modulus data obtained successively fall below the linear relaxation modulus curve. The relaxation modulus curves are parallel to each other over a period of two decades from 0.1 seconds to 10 seconds and can be considered to be separable in time and strain over this period. Using Eqn. 43, the ratio of the relaxation modulus is fitted with magnitude of strain to determine the damping factor, $k$ of the polyethylene melts. The values of $k$ calculated for HDPE, POE and LLDPE are 0.4, 0.15 and 0.34 respectively.
Figure 3.10 Stress relaxation data for linear and non-linear step strains measured on a RDS at $T = 180 \, ^\circ C$ and prediction of stress relaxation for linear step strains of a) HDPE b) POE and c) LLDPE
3.2.4 Steady Shear Rate Response

The steady shear stress response of the three polyethylene melts were measured using a RDS and the results are shown in Figure 3.11 a, b and c. The measured steady shear stress of the polymer sample increases with increasing shear rate until a shear rate of about \(10 \text{ s}^{-1}\). Beyond this shear rate, the data obtained exhibits anomalous behaviour, where the measured shear stress shows a sudden decrease followed by a gradual increase. At this point, it can be visually observed that the free surface between the plates is distorted and a major portion of the sample is ejected from the gap between the plates. Hence, the data obtained beyond this point is not representative of the steady shear behaviour of the polymer.

The reason for this effect may be the break-up of adhesive bonds between the material and the plates at higher shear rates and is referred to as “edge-fracture” phenomenon. A similar effect has been observed at a comparable shear stress of \(5.0 \times 10^4 \text{ Pa}\) in a cone and plate rheometer and has been attributed to the elasticity of the melt by Hutton in 1969 (Larson, 1992). This is one of the major limitations of rotational rheometers, which prevents its use at higher shear rates. This problem does not occur in a capillary rheometer and in particular a MPR, which has a constrained sample volume.

The steady shear response of the polyethylene melts in simple shear is predicted from the relaxation spectrum \((G_i, \lambda_i)\) and damping factor, \(k\) using Eqn 40. The steady shear response for linear systems is also predicted using Eqn. 40 with \(k = 0\). The predictions of the steady shear response are compared with the experimental results (Figure 3.11 a, b and c). It can be seen that both these predictions compare reasonably well with the experimental data for a limited range of shear rates (up to \(10 \text{ s}^{-1}\)). However, the predictions of the Generalised Maxwell model coupled with the Wagner damping factor, \(k\) show a better fit at higher shear rates, where the polyethylenes start to exhibit the onset of shear-thinning behaviour.
Figure 3.11: Steady shear response measured on a RDS at $T = 180 \, ^{\circ}C$ and prediction of steady shear response using the Maxwell model of linear viscoelasticity and Maxwell model coupled with the Wagner damping factor of a) HDPE b) POE and c) LLDPE.
3.2.5 Determination of Zero-Shear-Rate Steady Flow Viscosity

The apparent Newtonian viscosity, $\eta(\dot{\gamma})$ of the three polyethylene melts has been obtained from the steady flow curve and the zero-shear-rate steady flow viscosity, $\eta_0$ is determined by extrapolating the values of $\eta(\dot{\gamma})$ as $\dot{\gamma}$ tends to zero (Figure 3.12) and also from the measured low frequency limit of $|\eta^*|$, 

$$|\eta^*(\omega \to 0)| = \eta_0 = \eta(\dot{\gamma} \to 0)$$

It can be seen from Figure 3.12, that the zero-shear-rate-steady flow viscosity, $\eta_0$ of HDPE is much higher than the other two polymers while LLDPE appears to have a slightly higher value of $\eta_0$ than POE. This is consistent with the GPC results, which indicate that HDPE has a much higher MW than POE and LLDPE, and LLDPE has a higher molecular weight as compared to POE. However, these values of $\eta_0$ are not very reliable, due to the lack of data at very low shear rates and frequencies giving rise to errors during extrapolation.

![Figure 3.12 Extrapolation of the apparent Newtonian viscosity determined from steady shear flow curves for HDPE, POE and LLDPE to determine values of $\eta_0$ at $T = 180 \degree C$](image)

3.2.6 Summary of Results obtained from the RDS

Using the RDS, the rheological behaviour of the three PE samples have been characterised with reasonable success. Some interesting trends can be observed from the results obtained for the three polyethylenes. POE for instance has uniformly branched
chains and shows a smaller linear region than the other two resins while LLDPE, which has both linear and branched chains shows a higher linear region than HDPE, which is made up only of linear chains. A comparison of the values of damping factor $k$ calculated from the step strain curves, indicates that POE is the least shear-thinning followed by LLDPE and then HDPE. A summary of the results obtained from the rheological characterisation of the polyethylene samples using the RDS is provided in Table 3.2.

The Maxwell model of linear viscoelasticity was found to be adequate in calculating the relaxation spectrum of the polyethylene samples. The steady shear response of the polyethylene melts predicted using the Maxwell model of linear viscoelasticity coupled with the Wagner damping factor, $k$ was found to be in good agreement with the experimental data for lower shear rates. Above a shear rate of 10 s$^{-1}$, reliable data could not be obtained for the polyethylenes using a RDS. In order to carry out experiments above these shear rates, capillary rheometers such as the Multipass Rheometer are needed.

<table>
<thead>
<tr>
<th>RDS observations</th>
<th>HDPE</th>
<th>POE</th>
<th>LLDPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear region (% strain)</td>
<td>70%</td>
<td>50%</td>
<td>80%</td>
</tr>
<tr>
<td>Zero shear steady flow viscosity $\eta_0$ from the frequency sweep</td>
<td>$3 \times 10^5$ Pas</td>
<td>$1.2 \times 10^4$ Pas</td>
<td>$2 \times 10^4$ Pas</td>
</tr>
<tr>
<td>Zero shear steady flow viscosity $\eta_0$ from the steady shear flow curves</td>
<td>$3.5 \times 10^5$ Pas</td>
<td>$2 \times 10^4$ Pas</td>
<td>$2 \times 10^4$ Pas</td>
</tr>
<tr>
<td>Wagner Damping coefficient $k$</td>
<td>0.40</td>
<td>0.17</td>
<td>0.34</td>
</tr>
<tr>
<td>Steady shear response measurable up to</td>
<td>$8$ s$^{-1}$</td>
<td>$8$ s$^{-1}$</td>
<td>$8$ s$^{-1}$</td>
</tr>
</tbody>
</table>

### 3.3 Rheological Characterisation using the MPR

The Multipass Rheometer (MPR) is a two piston capillary rheometer and is suitable for both steady shear and dynamic rheological measurements. Although the MPR has a number of potential advantages, it is a relatively new rheometer and it is advisable to check the results of the MPR with established rheometers. The results of some of the rheological experiments, which were obtained using a RDS and repeated using a MPR, were compared with each other. This is done to ensure that the results obtained using the MPR are consistent with those obtained from well established, conventional rheometers.
In comparison to the RDS, the MPR can be used at much higher shear rates. The advantages of a confined sample volume of the MPR are evident while measuring melt compressibility and the pressure dependence of the dynamic moduli. In the following sections, the experimental results of a range of experiments performed using the MPR are presented. These measurements highlight the versatility of the MPR for carrying out experiments, which are in general not possible using conventional rotational and capillary rheometers. These experimental results are presented for POE and have been obtained at a temperature of 180 °C using a capillary test section with the same diameter as the barrels of the MPR, which eliminates end effects.

### 3.3.1 Comparisons between Results Obtained using a MPR and a RDS

The results of a small amplitude oscillatory strain experiment performed over a range of frequencies on POE, using both a MPR and a RDS are shown in Figure 3.13. These experiments were performed at 20 % strain over a frequency range between 0.1 and 500 rad/s. It can be seen that there is a reasonable match between the data obtained using a RDS and a MPR, especially at the higher frequencies, indicating that the MPR is suitable for carrying out dynamic small strain oscillatory experiments over a wide range of strains and frequencies. However, the RDS is a well established machine and is more convenient and faster to use than a MPR for performing these types of measurements. For example, the assembly and cleaning up of a MPR takes much longer than that of a RDS. Nevertheless, a MPR has an advantage over a RDS because it can provide a confined environment for testing samples, which are sensitive to degradation.

![Figure 3.13: Comparison of the small strain dynamic measurement over a range of frequencies for POE at a strain of 20% and T = 180 °C](image-url)
3.3.2 Measurement of Steady Shear Response in the MPR

The steady shear response of POE has been studied using the MPR and the data obtained has been compared with the results obtained at lower shear rates from the RDS and higher shear rates from a Gottfert\(^1\) capillary rheometer as shown in Figure 3.14. The prediction of the steady shear behaviour using the Maxwell model of linear viscoelasticity coupled with the Wagner damping factor, \(k\) is also shown in Figure 3.14. The apparent shear rate of the data obtained using the capillary rheometers were not modified using the Rabinowitsch correction (see for e.g. Dealy and Wissbrun, 1995) and the error bars of the MPR data points are of the order of 5%.

In general, at low shear rates, there is reasonable agreement between the data obtained from the RDS and the MPR. Using capillaries of smaller diameters in the MPR, it is also possible to experiment at higher shear rates, similar to those achieved using the Gottfert capillary rheometer.

![Figure 3.14: Comparison of the steady shear response of POE measured using a MPR with a test section of D = 1.2 \(10^2\) m, L = 8.2 \(10^2\) m at T = 180°C with data obtained from RDS and Gottfert rheometer](image)

3.3.3 Pressure Dependence of Dynamic Moduli

The MPR is used to study the pressure dependence of the rheological properties such as the storage and loss modulus of the polymer melt. The ambient pressure in the system is set by moving the pistons in order to either pressurise or decompress the polymer melt.

---

\(^1\) The steady shear measurements for POE using the Gottfert capillary rheometer have been supplied by The Dow Chemical Company, Terneuzen, Netherlands.
Then, the pistons are moved in an oscillatory manner to impart a small amplitude oscillatory strain to the polymer sample. This results in an oscillatory pressure difference across the system, which is compared with the imposed oscillatory piston displacement to determine the storage and loss moduli of the melt (as described in Mackley et al., 1995). In general, with an increase in pressure, a corresponding increase in the values of the moduli is observed.

The pressure dependence of storage modulus and loss modulus of POE measured using the MPR is shown in Figure 3.15. The pistons impart an oscillatory strain of 33% magnitude with a frequency of 10 rad/s. It can be seen that the values of $G'$ and $G''$ increase linearly with pressure corresponding to a net change of about 40% over a pressure range of 0 - 25 MPa. Similar experiments have also been performed on HDPE and LLDPE using the MPR. The values of $G'$ and $G''$ were found to increase by approximately 20% over 0 - 25 MPa for both HDPE and LLDPE which is much lower than the 40% increase in the values of $G'$ and $G''$ over the same range of pressure for POE. A similar increase (about 20%) in the values of dynamic moduli has been previously reported for a different LLDPE with the MPR by Mackley and Spitteler (1996).

![Figure 3.15: The change in the dynamic moduli of POE over a range of system pressures measured using a MPR, strain = 33%, frequency = 10 rad/s, T = 180 °C using a test section, D = 1.2 $10^{-2}$ m, L = 8.2 $10^{-2}$ m](image_url)

The increase in the values of the viscoelastic moduli with change in pressure and temperature have been extensively reported in Ferry (1980). The level of change of dynamic moduli and other viscoelastic properties with system pressure and temperature
has been associated with a change in free volume of the polymer melt. The free volumes of the polymer melt are comparable to their densities. The density of POE is 860 kg/m$^3$, while the densities of HDPE and LLDPE are much higher at 1000 kg/m$^3$ and 990 kg/m$^3$ respectively.

### 3.3.4 Measurement of Compressibility using the MPR

The constrained geometry of the MPR allows the measurement of compressibility of polymer melts. The compressibilities of HDPE, POE and LLDPE were measured under identical conditions using the MPR. The melt compressibility of POE was determined as $1.37 \times 10^{-9}$ Pa.s$^{-1}$ from the slope of a plot of $\ln$(Volume) versus pressure, which is shown in Figure 3.16. The compressibility values of HDPE and LLDPE were found to be identical to that of POE within limits of experimental error ($< 5\%$). Melt compressibility can have a considerable effect on the rate of pressure build-up across the capillary and this aspect will be investigated in greater detail in chapter 5.

![Figure 3.16](image)

Figure 3.16: Change in $\ln$(Volume) occupied with system pressure measured on the MPR to determine the compressibility of the POE, $T = 170 \, ^\circ \text{C}$, test section $D = 1.2 \, 10^{-2} \, \text{m}$, $L = 8.2 \, 10^{-2} \, \text{m}$

### 3.4 Summary and Conclusions

In this chapter, the structural and rheological characterisation of the three polyethylenes have been presented. The molecular characterisation results have clearly distinguished the molecular architecture of the three polyethylenes. HDPE has a higher MW and a broader MWD, while the MW of POE is smaller and it has a much narrower MWD.
LLDPE has an intermediate MW and MWD. Also, the TREF results show that LLDPE can be considered to be a blend of HDPE and POE in the ratio of 2:1. The rheological characterisation of the three polyethylenes mirror a number of aspects seen in their molecular characterisation. For instance, the zero-shear-rate steady flow viscosity, $\eta_0$, determined from the dynamic frequency response and steady shear response of HDPE is higher than that of LLDPE, which in turn is higher than that of POE and in accordance with their MWs.

A comparison of the values of the damping coefficient, $k$, indicate that the shear thinning effects are higher for HDPE and lower for POE with an intermediate value for LLDPE. The Maxwell model of linear viscoelasticity coupled with the Wagner damping factor is found to be adequate to describe the steady shear flow behaviour of the polyethylene melt.

The comparison of the results obtained using the RDS and MPR for both dynamic and steady shear measurements indicate that the MPR is capable of performing reliable rheological measurements over a much larger range of shear rates. The MPR also has the capability to perform experiments to determine the variation in the rheological properties with change in temperature and pressure. The variation of the dynamic moduli with pressure is much higher for POE as compared to HDPE and LLDPE, which could be due to a higher free volume of POE as compared to LLDPE and HDPE. The compressibilities of the three polyethylenes have also been measured on the MPR and have been found to be identical to each other. In general, the flow and steady shear behaviour of the three polyethylenes appear to be reasonably similar and it is not possible at this point to distinguish any unique or individual flow characteristics between the three polymers.
4. Transient Flow and Processing of High Density Polyethylene

In this chapter, a review of literature concerning transient flow and flow instabilities observed in polymer melts and in particular linear polymers such as HDPE are presented. In a subsequent discussion of MPR capillary flow data, four different flow regimes including one regime showing periodic pressure oscillations will be identified. Flow visualisation experiments have been carried out for HDPE using a slit geometry on the MPR. More details about these flow regimes come to light from these flow visualisation experiments performed under similar shear rate conditions as the capillary flow experiments.

4.1 Transient Flow and Melt Flow Instabilities in HDPE and other Polymer Melts

A flow that is developing and changing in time is called as a transient flow. Transient flow of polymer melts is a wide-ranging subject covering the time dependent response of polymer melts to a variety of strain and strain rates. Examples of transient flow include experiments such as frequency response analysis, single and multi-step shear strain, start-up and cessation of steady flow, creep and recoil experiments. (Hatzikiriakos and Dealy, 1994, Dealy and Wissbrun, 1995).

Transient flow behaviour can also be observed during the “steady” shear extrusion of polymer melt. Extrusion behaviour of polymer melts is generally analysed by considering the fluid to be incompressible. Rudin and Vlasschaert (1971) have observed a significant change in the apparent density of a polymer melt during extrusion. In addition, the time required for the polymer melt to achieve a steady pressure difference in a capillary rheometer, operating at constant piston speed can be very long in some cases and can result in inaccurate estimations of the melt viscosity (Hatzikiriakos and Dealy, 1994).

Transient flow behaviour may also manifest as flow instabilities during extrusion, resulting in pressure fluctuations and are in some cases accompanied by extrudates having a non-uniform cross-section (see for e.g. Tordella, 1958). The MPR can be used to study
the transient flow behaviour of polymer melts both during flow start-up, relaxation and steady shear flow. A detailed review of the instabilities affecting polymer melts such as HDPE is given in the following sections.

The capillary flow extrusion of HDPE shows a number of transient features that increases in complexity with an increase in flow rate. Over a certain range of shear rates, the scale and nature of these instabilities also change, resulting in extrudates exhibiting a wide range of deformities. These instabilities were first reportedly observed by in 1945 by Nason (as mentioned by Petrie and Denn, 1976) and have been extensively studied since then by a number of researchers (for e.g. Bagley et al., 1958, Lupton and Regester, 1965, Huseby, 1966, Benbow and Lamb, 1963 and more recently Kalika and Denn, 1987, Wang and Drda, 1996a, 1997 and Yang et al., 1998).

Extrudate distortions can be divided into two main classes. These are the small-scale surface distortions (SSSD), which is referred to in many papers as Sharkskin (first reported by Clegg, 1957) and a large-scale roughness referred to as Gross melt fracture (Benbow and Lamb, 1963). Gross fracture can also result in regular large amplitude helical distortions in the extrudate (Petrie and Denn, 1976). Sharkskin or SSSD always occurs at relatively lower shear rates and can develop into Gross melt fracture at higher shear rates. SSSD has been distinguished from more severe distortions by classifying it as a surface roughness that changes the extrudate diameter by no more than one percent and consists of semi-regular cracks or ridges running perpendicular to the flow axis (see for e.g. El Kissi and Piau, 1990). Gross fracture is characterised as an extrudate distortion of an order greater than say 10% of its diameter and can be a result of chaotic and irregular flow patterns (see for e.g. Petrie and Denn, 1976). Benbow and Lamb (1963) also postulated that SSSD was initiated at the die exit, while Gross melt fracture was a result of unstable flow within the die. Flow birefringence experiments by Vinogradov et al. (1972) supported the theory that SSSD was associated with high local stresses at the point where the polymer melt emerges from the die.

The flow behaviour of linear polymers such as HDPE has been mainly studied using capillary rheometers in two different modes [a] controlled piston speed and [b] controlled pressure mode (Petrie and Denn, 1976). The most striking feature observed during controlled piston speed mode of operation is the presence of a non-monotonous flow curve (wall shear stress vs. apparent shear rate), where a range of wall shear stresses exhibit a non-unique dependence on apparent shear rate, i.e. a particular value of wall
shear stress can exist at more than one shear rates (Figure 4.1). The flow of HDPE melts in this range of shear rates is characterised by periodic pressure fluctuations (Tordella, 1958). This flow regime is also referred to as the *Stick-slip* regime implying the alternative sticking and slipping of the melt in the capillary, giving rise alternate smooth and rough portions on the extrudate surface.

\[ \ln (\text{Shear stress}) \rightarrow \ln (\text{Shear rate}) \rightarrow \]

![Figure 4.1: Schematic illustration of the discontinuous flow curve observed for HDPE in the Controlled piston-speed mode of operation](image)

In the controlled pressure mode of operation, the flow curve (apparent shear rate vs. wall shear stress) is again discontinuous in nature and a small increase in the pressure difference results in a substantial jump or *Spurt* in the volumetric flow rate (Figure 4.2). Therefore, this regime is also referred to as the *Spurt* regime (first reported by Bagley et al., 1958). The corresponding extrudates obtained in this case are smooth and do not show the presence of distortions either on a surface level or in its bulk. The shear stress at which the discontinuity occurs is the same irrespective of the mode of operation.

\[ \ln (\text{Shear rate}) \rightarrow \ln (\text{Shear stress}) \rightarrow \]

![Figure 4.2: Schematic illustration of the discontinuous flow curve observed for HDPE in the Controlled pressure mode of operation](image)

The *Spurt* effect has been subsequently studied by a number of researchers (see for e.g. Vinogradov et al., 1972 and Wang and Drda, 1996a). The critical shear stress at which
this discontinuity occurs is generally of the order of 0.2 MPa, depending mainly on the molecular characteristics of the polymer melt and also marginally on a number of other factors such as temperature, material of construction of the die, die geometry (see for e.g. Durand et al., 1996). These factors are described in greater detail in the following sections.

4.1.1 Effect of Temperature

The temperature dependence of the Stick-slip effect of HDPE has been studied in considerable detail by Blyler and Hart (1970), Vinogradov (1981) and Wang et al. (1996b). Wang et al. (1996b) have studied the characteristics of this transition over a range of temperatures from 160 °C to 260 °C and found that the magnitude of discontinuity of the flow curve does not change with temperature. They found that the critical shear stress (τc) at which the stick-slip transition occurred increased linearly with temperature from 200 °C to 260 °C by 10%. The change in critical stress being rather small, many investigators have claimed it to be independent of temperature (from review by Boudreaux and Cuculo, 1977). Below 200 °C, Wang et al. (1996b) observed that the linear relationship between critical shear stress and temperature was not satisfied, and referred to this effect as a low temperature anomaly.

4.1.2 Effect of Wall Surface

Ramamurthy (1986) performed extrusion experiments in a capillary rheometer for a variety of HDPE and LLDPE resins. He emphasised upon the importance of the nature of polymer-wall interface and its effect on extrudate appearance by using capillaries made from different metals. Kalika and Denn (1987) also reported similar findings. Hatzikiriakos and Dealy (1991) have used a sliding plate rheometer to study slip behaviour as a function of only shear stress and interface conditions in the absence of entrance effects and with no pressure gradients. In experiments using FE coated metal plates slip was calculated to occur at a critical shear stress, which varied with the nature of the polymer/wall interface. They concluded that this slip was a result of adhesive failure occurring at this interface. They have reported similar trends for a study carried out using a capillary geometry (Hatzikiriakos and Dealy, 1993).

4.1.3 Effect of Capillary and Slit Geometries

The capillary geometry has been widely for the study of transient flow behaviour of
polymer melts and some work has also been carried out using slit geometries. Studies into the influence of geometry on melt flow instabilities have revealed variable results. In the case of silicones (linear and branched), den Otter (1970) reported that melt fracture occurred at the same shear rate and shear stress in capillaries and slits within limits of experimental error. Wales (1969) also reported that the onset of irregular flow takes place at about the same wall shear stress in both capillaries and slits for HDPE. Other polymers such as polystyrene (PS) (which is linear) and LDPE (polymers with long chain branching) failed to show any irregularity in slit flow for the wall shear stresses at which melt fracture was observed in capillary flow. In contrast, Vlachopoulos and Chan (1977) found that extrudate distortion in a slit geometry could be observed at relatively low flow rates as compared to that for capillary geometries for HDPE, LDPE and polystyrene. They believed that the restricting influence of the two edges in a slit produced a higher flow rate in the midsection of the die. Hence the polymer in the middle of the slit is flowing at a higher shear rate than that near the edges resulting in it swelling excessively or buckling upon emergence from the slit leading to a large amplitude ripple on the surface. Tordella (1956) also proposed a similar suggestion.

4.1.4 Effect of Die Diameter (D), Length (L), L/D Ratio

Durand et al. (1996) have reported that for the discontinuous flow curve of HDPE, the data obtained from experiments carried out using dies of different diameters superimpose on top of each other for the first branch of the flow curve. However, in the case of the second branch of the flow curve, they found that the data obtained was more sensitive to the die diameter, indicating the presence of wall slip. Other studies by Ramamurthy (1986) and Kalika and Denn (1987) also suggested the presence of slip along the die length from a diameter dependence of the flow curve.

With an increase in capillary length, pressure oscillations accompanying the Stick-slip effect, were found to appear at higher shear rates with smaller amplitudes (Han and Lamonte, 1971 and Durand et al., 1996). This could happen because the residence time of pressure oscillations in a shorter capillary would not allow the same degree of damping as obtained using a longer capillary. den Otter (1970), observed that the severity of extrudate distortion for linear polymers such as HDPE increased with an increase in the capillary length.
Durand et al. (1996) found that for an orifice die, (i.e. L/D = 0), neither the oscillating flow regime nor a slope change was detected along the flow curve, although the extrudate was distorted above a certain shear rate. These observations indicate that flow instabilities could be initiated in the die entry region and therefore the die entry region could play an important role in determining the nature of these instabilities. Similar results were also obtained by Li et al. (1986) for HDPE and LLDPE. The period of pressure oscillations accompanying the stick-slip effect was found to increase with an increase in the amount of melt in the reservoir of the rheometer (Lyngaae-Jorgenson and Marcher, 1985), and does not depend on the capillary length (den Otter, 1970).

4.1.5 Effect of Die Entry Angle

The pressure oscillations observed for linear polymers such as HDPE began at the same time in a tapered entry die as they did in a flat entry die (Petrie and Denn, 1976). Also, the apparent shear rate at which the extrudates became visibly distorted was higher for a tapered die entry as compared to a flat entry die (Bagley and Schreiber, 1961 and Han and Lamonte, 1971). This was explained by Petrie and Denn (1976) due to an increased acceleration of flow of the melt into the capillary entrance due to the presence of a solid wall, consequently speeding up the cycles of compression and decompression at the die entry. This in turn, leads to pressure fluctuations of higher frequency. den Otter (1970, 1975) observed that the frequency of pressure oscillations was strongly influenced by die entry shape and not die length. Based on this result, he believed that an instability was initiated at the die entry region and it had a significant influence on the melt fracture observed for HDPE.

4.1.6 Effect of Molecular Structure and Molecular Weight

Branched polymers such as LDPE (Wales, 1969) do not show discontinuous flow curves, which can be observed for linear polymers such as HDPE (Bagley et al., 1958) and polybutadiene (Vinogradov et al., 1972, Yang et al., 1998). However, neither PS (which is linear) nor linear silicones (Benbow and Howells, 1961 and den Otter, 1970) show a discontinuity in the flow curve. LDPE and PS also failed to show any irregularity in flow through a slit at wall shear stresses, where melt fracture was observed in a capillary geometry.

Flow visualisation experiments for linear polymers showed that converging flow in the die entry region filled up all the available space, while for branched polymers such
as LDPE, there was a dead space near the die entry region occupied by recirculating vortices (Bagley and Birks, 1960 and den Otter, 1970). den Otter (1970), also reported that for a series of linear silicones, recirculating flow vortices could be observed in the die entry region only for low molecular weight (MW) polymers, but not for the high MW polymers. Vinogradov (1973) commented that while the Spurt effect and the accompanying phenomena were in general observed for high MW linear polymers, they can be observed with greater clarity in high MW, narrow MWD linear polymers.

Blyler and Hart (1970) observed that the first branch of discontinuous flow curves observed for linear polymers such as HDPE, depends on its MW, while the second branch was found to be independent of MW (and depends on die diameter). With a decrease in the MW of HDPE, the magnitude of discontinuity between the two branches of the flow curve decreased, and there was an increase in the critical shear stress at which this transition occurred (Wang and Drda, 1996a and Blyler and Hart, 1970).

### 4.2 Origin of the Discontinuous Flow curve and Melt Flow Instabilities

The debate on the origin of the discontinuous flow curve, melt flow instabilities and associated extrudate distortions for linear polymers have been centred around the occurrence of [1] a bulk failure i.e. a non-monotonous constitutive equation or [2] an adhesive failure i.e. interfacial slip at the Wall (from reviews by Pearson, 1969, Petrie and Denn, 1976 and Larson, 1992). Wall slip as the name suggests is due to a violation of the conventional no-slip boundary condition and results in a finite velocity at the wall which depends on the shear stress (Hill et al., 1990). The flow instabilities could also be initiated at [3] the die exit region and [4] die entry region. Therefore, four possible sites were identified for the initiation of instabilities. These sites are denoted in the following schematic diagram (Figure 4.3).

**Figure 4.3**: Schematic diagram showing four different sites for initiation of instabilities in a die during extrusion of a polymer melt.
Site 1) Flow instabilities are a consequence of the existence of a non-monotonic flow curve and are therefore constitutive in nature, occurring in the bulk of the polymer melt.

Site 2) Flow instabilities are a result of polymer-wall interactions and originate at a region near the walls of the capillary, leading to slipping of the polymer or Wall slip.

Site 3) Flow Instabilities originate at or near the die exit region - Exit effect

Site 4) Flow instabilities originate in the die entry region - Entry effect.

1. Constitutive Instability Theory

A constitutive instability has been suggested to occur because of the existence of a non-monotonic constitutive equation relating the shear stress and the shear rate, i.e. the constitutive equation is inherently unstable. The Doi and Edwards (1979) theory predicts a non-monotonic shear stress-shear rate curve, which will result in a constitutive instability. The stress minimum observed for high shear rates is accounted by the transition of the melt to a Rouse-like or unentangled flow behaviour when the shear rate reaches a value roughly equal to $1/\lambda_{\text{Rouse}}$, where $\lambda_{\text{Rouse}}$ is the longest Rouse relaxation time. Theories involving constitutive equations predict the formation of a thin layer near the wall where the shear rates are higher causing the material in the bulk to move in a plug-like manner (McLeish and Ball, 1986).

Over a series of publications in the seventies and the eighties, Vinogradov and co-workers (1972, 1973, 1981 and 1983) further developed the constitutive instability theory to explain the presence of Melt Flow Instabilities. They proposed that above a critical shear stress, the polymer melt undergoes an irreversible transition from a fluid state to a forced high elastic state. As a result, the adhesion of polymers to the surface of solids (metal wall) decreases and under certain shear rate conditions it leads to slipping at the wall. The critical deformation rates at which the transition from fluid to a highly elastic state occurs, depends very strongly on the MW of the polymers and is greatly influenced by their MWD. With a widening of MWD, the transition of the polymers from the one physical state to the other extends over an increasing range of deformation rates in which the polymers exhibit both fluidity and signs of the high elastic state giving rise to a discontinuous flow curve.

2. Wall Slip Theory

The presence of Wall slip was hypothesised to occur either at the polymer/metal wall
interface or at a polymer-polymer interface near the wall. In order to understand the interactions at the wall-polymer interface, studies were carried out by coating the metal walls with a FE (see for e.g. Ramamurthy, 1986, Kalika and Denn, 1987, Rudin, et al., 1990, Hatzikiriakos and Dealy, 1991, 1993, Piau et al., 1995, Xing et al., 1996b, Wang and Drda, 1996a, 1997). These researchers observed that the phenomenon of pressure oscillations accompanying the stick-slip regime could be made to disappear by using this coating. Ramamurthy (1986) carried out film blowing studies using linear polyethylenes and observed that a change in the material of construction of the die played a major role in extrudate distortion. He promoted the concept that extrudate distortion was due to a breakdown in adhesion at the polymer/wall interface, and therefore, the promotion of better adhesion at the walls would lead to extrudates, which are free of distortions. Kalika and Denn (1987) also supported this concept. Piau et al. (1995) and Wang and Drda (1996a and 1997) have explained the discontinuous flow curve and other effects accompanying the stick-slip or spurt transition using a theory for highly entangled polymer systems proposed by Brochard and de Gennes (1992). In this theory, it was hypothesised that high molecular weight flexible polymer chains adsorb strongly at many sites on a metallic wall to form a high density layer at the wall. These chains in turn go on entangling with the long and flexible chains in the bulk thus resulting in a continuous network of chains covering the entire flow field at low stress levels. Slip occurs at high stress levels because of a cohesive fracture of the bulk polymer, which disentangles from and slips over the layer of polymer chains near the wall. Wang and Drda (1996a) have explained these effects by taking into consideration the level of entanglement observed in polymer melts, as this transition was observed only for highly entangled polymers such as HDPE and not for less entangled polymers such as polystyrene and PolyDiMethylSiloxane (PDMS) (Piau et al., 1995) of comparable MW. This theory is called the coil-stretch transition theory (Brochard and de Gennes, 1992).

Wang and Drda (1996a, 1997) have postulated that the stick-slip (Spurt) effect observed during the controlled pressure mode of operation is due to a flow-induced chain entanglement-disentanglement, also referred to as a coil-stretch transition occurring at the first interfacial molecular layer near the wall. They explained that the lack of a stick-slip transition, when the surface of a die was coated with a
fluoroe lastomer (FE) was due to a complete wall slip occurring at the melt/FE interface. This was attributed to an absence of adsorbed chains at the FE interface.

The experimental observation of instabilities and accompanying Wall slip vary with the type of polymer involved. Changes in the level of branching, molecular weight, molecular weight distribution have a major influence on the type of instabilities and level of slip detected for polyethylenes indicating that the phenomenon of Wall slip is strongly governed by the constitutive properties of the polymer melt.

3. Exit effect

Small-scale surface distortions (SSSD) is one of the types of instability observed for the extrusion of polymers such as LLDPE and HDPE. The presence of SSSD was attributed to an acceleration of the polymer melt in the die exit region due to a change in the boundary conditions from the die wall to a free surface (see for e.g. Kurtz, 1984, and 1994). It was proposed that an increase in the stress levels at the exit above a critical value led to a coil-stretch transition in the exit region, resulting in an extrudate which shows high frequency surface defects (Wang et al., 1996b) or SSSD. A detailed review of this phenomenon is provided in chapter 7.

4. Entry Flow Instabilities

The presence of a discontinuous flow curve and pressure oscillations observed for HDPE are attributed to the interactions at the polymer/wall interface. But the presence of extrudate distortions and melt fracture were explained with a different mechanism. Piau et al. (1995) proposed that above a certain stress level at the entrance region, higher than the critical stress level for stick-slip transition, an upstream flow instability originates and influences the entire flow field.

This instability was observed as a vibration of the fluid along the flow streamlines with a clearly identified frequency. It was then transported downstream along the entire die, giving the extrudate the shape of a helix for axisymmetric dies or a sinusoid for 2D dies. The frequency associated with the helicity was found to be the same as that of the triggering upstream instability. As the flow rate was increased, additional modes were introduced in the upstream instability, which results in a loss of axisymmetry and leads to a disorderly flow field. This may cause a fluctuation in the local stress levels generate some singular sites, where the stress levels are larger than the critical shear stress, thus triggering slip. The severity of these distortions increased while frequency reduced with an increase in the molecular weight of the polymer.
Wang and Drda (1997) proposed that the abrupt entry of a polymer melt into a die introduced an extremely strong converging flow. This results in an unstable conformation at the die entrance, which might probably produce fluctuations in the flow rate and lead to extrudate distortions.

4.2.1 Summary of Literature Review

In summary, the findings and conclusions of researchers, whose work were referred in this chapter have identified four possible regions for the initiation of instabilities. While there is some evidence to suggest that some instabilities are initiated at specific sites resulting in certain types of instabilities, there is no unified or universal theory available at this point, which can convincingly explain the presence of all these transient effects and extrudate instabilities. On the other hand, the phenomenon of flow instabilities is very complex and may not be a result of one single effect. A number of instabilities observed could be explained as a combination of the effects listed above.

4.3 Experimental Section

The transient flow behaviour of HDPE was studied using a MPR with a capillary geometry and complementary optical observations were carried out using a slit geometry. The results from both these types of experiments were used to conclude about the nature of instabilities and the mechanism behind the discontinuous flow curve of HDPE.

The MPR has a fully constrained geometry and mainly differs from conventional capillary rheometers because of the absence of a free surface at the exit of the capillary. The absence of a free surface at the exit of a capillary may or may not affect the transient flow behaviour and flow instabilities of HDPE. However, it enables the elimination of one of the possible sources for the initiation of flow instabilities. Also, the fully defined boundary conditions of a MPR make it easier to carry out an analysis of the transient flow behaviour of the melt through a capillary. Unlike conventional rheometers, no extrudates are obtained using a MPR and this is a disadvantage because the direct observation of extrudates can provide a lot of information about the flow field inside the die.

The conditions under which capillary and slit flow experiments have been carried out are listed in Table 4.1. The dimensions of the capillary geometry and slit geometry used are shown in Figure 4.4. All the capillary flow experiments were carried out at 180 °C and all the slit flow experiments were carried out at 170 °C. The optical experiments using a slit geometry were performed at a lower temperature because of some limitations.
in the oil circulation system of the MPR. The system pressure was maintained at 3 MPa before the start of all experiments in order to ensure consistency of experimental conditions. It is not expected that a change in system pressure of the order of a few MPa would have a significant effect on the experimental data (Mackley and Spitteler, 1996).

In the steady shear experiments, the pistons were moving in the single-pass mode. The change in pressure difference across a capillary or a slit with time was measured, both when the pistons were moving and when they had stopped moving.

| Table 4.1: Experimental Conditions for capillary flow measurements of HDPE |
|-----------------------------|-----------------------------|
| Linear Polymer | High Density Polyethylene (HDPE) |
| Temperature | 180 °C or 170 °C |
| Capillary geometry dimensions | L = 10⁻² m, D = 10⁻¹ m, Entry angle = 90° |
| Slit geometry dimensions | H = 1.2 10⁻² m, D = 10⁻¹ m, W = 10⁻³ m |

The cross sectional area of flow in the slit is 1.0 10⁻³ x 1.0 10⁻³ m. In this configuration, the flow through the slit cannot be considered to be 2-D planar flow. The W : D ratio of the slit required for carrying out experiments under similar conditions of shear rate (of the order of 1000 s⁻¹) would mean using a slit width of dimensions of the order of 100 µm. This is not suitable because it is very difficult to obtain an accurate measurement of the slit width, leading to significant errors in estimating shear rates. Since the primary objective of these experiments were to observe the flow rather than to model it, the slit configuration listed in Table 4.1 can be considered to be adequate.

The set-up of flow birefringence experiments using a slit geometry using the set-up has been described in chapter 2. In this set-up, plane polarised light is passed through the polymer melt flowing through a slit and the emerging light beams are converged using an analyser to generate a FB pattern, which is recorded on S-VHS tapes. These
recordings had a frame rate of 24 frames per second and the sample rate on the pressure transducer was typically of the order of about two to ten points per second. The camera was focused along one end of the slit, which alternately acted as the entrance, and exit of the slit. Therefore all the recordings consist of one end of the slit and one-third of the slit length near that end. Using image capture software (Adobe Premier, version 4) and a video capture card; individual pictures were obtained from these recordings.

4.4 Experiments Results - Capillary Geometry

Single-pass experiments were performed for a range of piston velocities from $1.0 \times 10^{-1}$ to $1.0 \times 10^{-2}$ m/s (corresponding to a shear rate of 100 - 10,000 s$^{-1}$) using a capillary geometry. In most of these experiments, the pressure difference across the capillary increased in time to reach a steady value. In some cases, the pressure difference across the capillary showed fluctuations and did not reach a steady value. The results from all these experiments were collected and used to determine the experimental flow curve of HDPE (mean steady pressure difference across the capillary versus piston velocity), shown in Figure 4.5.

![Figure 4.5: Steady state flow curve of HDPE determined from single-pass experiments in the MPR](image)

$T = 180\, ^\circ C$, capillary, $L = 1.0 \times 10^{-2}$ m, $D = 1.0 \times 10^{-1}$ m, Half Entry angle = 45\(^\circ\)

The corresponding wall shear stress and apparent shear rate are also indicated along the second Y and second X axes respectively. The error bars for pressure difference measurements were lower than 5% and are therefore not plotted on the graph. The flow
Transient Flow and Processing of High Density Polyethylene

curve consists of two branches and a range of piston velocities in between, where the steady pressure difference cannot be determined because of the fluctuating nature of the pressure traces. The nature of the flow curve is consistent with those reported by others researchers using conventional capillary rheometers (see for e.g. Durand et al., 1996). The flow curve can be divided into four regimes, identified from the time dependent, pressure difference data. These flow regimes were indicated on the flow curve as regimes, 1, 2, 3 and 4.

- **Stable Flow** Regime

  A *Stable flow* regime can be observed for the steady shear flow of HDPE at lower shear rates (or piston velocities). This regime can be observed for all shear rates in the first branch of the flow curve shown in Figure 4.5. The profile of pressure difference versus time for this regime is characterised by the rapid rise of the pressure difference across the capillary to reach a steady value. The cessation of piston movement is accompanied by a relaxation of the pressure difference across the capillary.

![Figure 4.6: A pressure difference profile in Stable flow regime for HDPE in the MPR, T = 180 °C, Capillary, L = 1.0 10⁻² m, D = 10⁻¹ m, Half Entry angle = 45°, v_s = 1.0 10⁻⁷ m/s, A = 8.0 10⁻⁴ m](image)

An example of a typical pressure profile obtained for an experiment carried out at a shear rate in the *Stable flow* regime is shown in Figure 4.6. This experiment was carried out at a piston velocity of 1.5 10⁻¹ m/s, corresponding to a flow rate of 1.6 10⁻⁷ m³/s and an apparent shear rate 1700 /s. The pressure difference across the capillary increases from zero to reach 15 MPa in approximately four seconds.
In order to understand the pressure difference trace shown in Figure 4.6, consider a schematic representation of the flow curve shown (pressure difference versus flow rate) in Figure 4.7. The flow rate, \( \alpha_1 \), is the upper extremity of the first branch of the flow curve and \( \beta_1 \) is the corresponding point on the second branch of the flow curve which has the same pressure difference as \( \alpha_1 \). The flow rate at the lower extremity of the second branch of the flow curve is represented by \( \beta_2 \) and \( \alpha_2 \) is the point on the first branch of the flow curve which has the same pressure difference as \( \beta_2 \).

The imposed rate of displacement of volume in the barrels due to the movement of the pistons is given by \( Q_A \). When the pistons move in a downward direction, the polymer melt is pushed towards the capillary constriction in the upper barrel. Initially the flow rate of polymer melt through the capillary is very low because the polymer above the capillary is getting compressed. As the polymer melt accumulates at the capillary entrance, the pressure increases and the flow rate of melt through the capillary also increases. When steady flow condition is achieved, the rate of the volume displacement in the barrel and the flow rate of melt in the capillary are equal leading to a steady pressure difference corresponding to \( \Delta P_A \) across the capillary. This type of flow behaviour is observed for all rates of volume displacements in the barrels from 0 to \( \alpha_1 \).

When the pistons stop moving, the steady pressure difference across the capillary decreases leading to a pressure equalisation between the top and bottom barrels. This relaxation of pressure across the capillary may be due to a combination of viscoelastic relaxation of the stressed melt and the flow of polymer melt through the capillary into the lower barrel under the influence of the pressure difference across the capillary.

- **Periodic Oscillations** Regime

In a *Periodic Oscillations* regime, the pressure difference across the capillary increases to reach a certain value and then oscillates periodically about this value. An example of
a typical pressure profile obtained for an experiment carried out in the *Periodic Oscillations* regime is shown in Figure 4.8. This experiment was carried out at a piston velocity of $2.0 \times 10^{-3}$ m/s (corresponding to a flow rate of $2.1 \times 10^{-7}$ m$^3$/s and an apparent shear rate $2304$ s$^{-1}$). The pressure difference across the capillary increases from zero to reach $16.5$ MPa in approximately one second. This regime can be observed for all flow rates between $\alpha_1$ and $\beta_2$. The oscillations are always observed between two constant limits of pressure difference in a given experimental set-up. In this case, the pressure oscillations are of the order of $2.5$ MPa and take place between $16.5$ MPa and $14$ MPa. The period of these oscillations was generally of the order one second in this set-up and decrease with an increase in the flow rate. The period of oscillations also shows a slight dependence on the volume of polymer melt in the barrels.

![Pressure profile](image)

*Figure 4.8: A pressure difference profile in a Periodic Oscillations regime for HDPE in MPR, $T = 180 \degree$ C, Capillary, $L = 1.0 \times 10^{-1}$ m, $D = 1.0 \times 10^{-3}$ m, Half Entry angle = $45\degree$, $v_p = 2.0 \times 10^{-3}$ m/s, $A = 1.5 \times 10^{-2}$ m

This flow behaviour can be qualitatively understood by considering a schematic representation of the flow curve (Figure 4.9). The imposed rate of displacement of volume in the barrels due to the movement of the pistons is given by $Q_1$, and it can be seen that the pressure difference corresponding to $Q_1$ is not defined on the flow curve. When the pistons start moving with a constant velocity in the downward direction, the melt in the upper barrel is compressed, leading to a time dependent pressure rise across the capillary and the flow rate of the melt in the capillary increases from $0$ to $\alpha_1$. At $\alpha_1$, the melt reaches the threshold of the unstable regime. This leads to a spurt in the flow rate.
from $\alpha_1$ to $\beta_1$, which lies along the second branch of the flow curve. In order to obtain a steady flow of the melt through the capillary, the rate of volume displacement in the barrel and the flow rate of the melt through the capillary needs to be equal (in this case equal to $Q_0$). When the flow rate in the capillary is equal to $\beta_1$, which is higher than $Q_0$, it results in a decompression of the melt in the top barrel leading to a reduction in pressure. Therefore, the pressure difference and flow rate through the capillary decreases from $\beta_1$ to $\beta_2$, where the melt again reaches the threshold of the unstable regime. The flow rate reduces further by crossing over to $\alpha_2$, which lies along the first branch of the flow curve. Now the flow rate of the melt in the capillary is $\alpha_2$, which is lower than $Q_0$. This leads to a build-up of melt at the mouth of the capillary resulting in a compression of the melt. The flow rate and the pressure difference across the capillary increases from $\alpha_2$ to $\alpha_1$ and the above described process repeats itself leading to a limit cycle and periodic pressure oscillations. These oscillations are sustained as long as the pistons are moving and polymer melt is displaced from the barrels into the capillary. On cessation of piston movement, pressure equalisation between the top and bottom barrels occurs leading to a flow through the capillary section followed by an associated time dependent pressure relaxation.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure49.png}
\caption{Schematic representation of Periodic Oscillations regime}
\end{figure}

\begin{itemize}
\item **Overshoot** Regime
\end{itemize}

An Overshoot regime occurs at higher piston velocities (shear rates) after the Periodic Oscillations regime. In this regime, the pressure difference across the capillary rapidly increases to give an overshoot to finally reach a steady value. An example of a typical pressure profile obtained for an experiment carried out in the Overshoot regime is shown in Figure 4.10.
Transient Flow and Processing of High Density Polyethylene

The pressure difference across the capillary increases from zero to reach 16.5 MPa in less than one second. The overshoot regime is observed for flow rates between $\beta_1$ and $\beta_2$. The maximum pressure difference obtained is 16.5 MPa similar to that observed in the Periodic Oscillations regime and the magnitude of the overshoot decreases as the flow rate increases from $\beta_2$ to $\beta_1$.

![Figure 4.10: A pressure difference profile in the Overshoot regime for HDPE in the MPR, T = 180 °C, Capillary, L = 1.0 $10^{-2}$ m, D = 1.0 $10^{-3}$ m, Half Entry Angle = 45°, $v_p$ = 2.4 $10^{-1}$ m/s, A = 1.5 $10^{-2}$ m](image)

The flow behaviour can be understood from the schematic flow curve shown in Figure 4.8. The imposed rate of displacement of volume in the barrels due to the movement of the pistons is given by $Q_c$. When the pistons start moving with a constant velocity in the downward direction, the melt in the upper barrel is compressed, leading to a time dependent pressure increase and flow rate of the melt in the capillary from 0 to $\alpha_1$. At $\alpha_1$, the melt reaches the threshold of the unstable regime. This leads to a spurt in the flow rate from $\alpha_1$ to $\beta_1$, which lies along the second branch of the flow curve. In order to obtain a steady flow of the melt through the capillary, the rate of volume displacement in the barrel and the flow rate of the melt through the capillary needs to be equal (in this case equal to $Q_c$). When the flow rate in the capillary is equal to $\beta_1$, which is higher than $Q_c$, it results in a decompression of the melt leading to a reduction in pressure. Therefore, the pressure difference and the corresponding flow rate through the capillary decrease from $\beta_1$ to $\Delta P_c$ and to $Q_c$ respectively. At this point, the flow rate of the melt through the
capillary is equal to $Q_c$ leading to a steady pressure difference of $\Delta P_c$ across the capillary. This regime can be observed for all flow rates on the second branch of the flow curve from $\beta_1$ to $\beta_2$. On cessation of piston movement, pressure equalisation between the top and bottom barrels occurs leading to a flow through the capillary section giving an associated time dependent pressure relaxation as observed earlier.

![Figure 4.11 Schematic representation of Overshoot regime](image)

- **High velocity** Regime

A High velocity regime can be observed at very high piston velocities (or shear rates) after the Overshoot regime. In this regime, the pressure difference across the capillary initially rises rapidly followed by a decrease in the rate of rise of the pressure difference to finally reach a steady plateau. Two different rates of rise of pressure difference can be seen and the flow regime is referred to as the High velocity regime. A typical pressure profile for an experiment carried out in this regime is given in Figure 4.12. This experiment is carried out at a piston velocity of $2.9 \times 10^{-3}$ m/s (corresponding to a flow rate of $2.1 \times 10^{-1}$ m$^3$/s and an apparent shear rate $3340$ s$^{-1}$). The pressure difference across the capillary increases from zero to reach $17$ MPa in approximately two seconds.

The flow behaviour can be understood from the schematic flow curve shown in Figure 4.13. The imposed rate of displacement of volume in the barrels due to the movement of the pistons is given by $Q_0$. When the pistons start moving with a constant velocity in the downward direction, the melt in the upper barrel is compressed, leading to a time dependent pressure rise across the capillary and the flow rate of the melt in the capillary increases from $0$ to $\alpha_1$. At $\alpha_1$, the melt reaches the threshold of the unstable regime. This leads to a spurt in the flow rate from $\alpha_1$ to $\beta_1$, which lies on the second branch of the flow curve. In order to obtain a steady flow of the melt through the capillary, the rate of volume displacement in the barrel and the flow rate of the melt through the capillary needs to be equal (in this case equal to $Q_0$).
When the flow rate in the capillary is equal to $\beta_1$, which is lower than $Q_0$, it results in further compression of the melt in the top barrel leading to an increment in pressure. Therefore, the pressure difference and the corresponding flow rate through the capillary increases from $\beta_1$ to $\Delta P_0$ and to $Q_0$ respectively. The second branch is less steep than the first branch of the flow curve and therefore the increase in pressure and flow rate is slower giving rise to a pressure profile where two different rates of build-up of pressure are observed. At this point, the flow rate of the melt through the capillary is equal to $Q_0$ leading to a steady pressure difference corresponding to $\Delta P_0$ across the capillary. This regime can observed for all the rates of volume displacement on the second branch of the flow curve from onwards. On cessation of piston movement, pressure equalisation between the top and bottom barrels occurs leading to a flow through the capillary section giving an associated time dependent pressure relaxation as observed.

Figure 4.12: A pressure difference profile in the High Velocity regime for HDPE in the MPR, $T = 180^\circ C$, Capillary, $L = 1.0 \times 10^{-2}$ m, $D = 1.0 \times 10^{-3}$ m, Half Entry angle = $45^\circ$, $\eta_p = 2.9 \times 10^{-3}$ m/s, $A = 1.5 \times 10^{-2}$ m

Figure 4.13: Schematic representation of High velocity regime
These are the four flow regimes observed for the capillary flow of HDPE. The range of shear rates for which these regimes can be observed in HDPE at 180 °C for this experimental set-up are listed in Table 4.2.

Table 4.2: Range of shear rates for the four flow regimes at 180 °C

<table>
<thead>
<tr>
<th>Regime</th>
<th>Range of shear rates at 180 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stable Flow regime</td>
<td>0 - 1800 s⁻¹</td>
</tr>
<tr>
<td>Periodic Oscillations regime</td>
<td>1800 - 2800 s⁻¹</td>
</tr>
<tr>
<td>Overshoot regime</td>
<td>2800 - 3800 s⁻¹</td>
</tr>
<tr>
<td>High Velocity regime</td>
<td>3800 s⁻¹ upwards</td>
</tr>
</tbody>
</table>

It can be clearly seen that these flow regimes arise as a result of the discontinuity in the flow curve of HDPE. In order to gain a better understanding of the mechanism behind these instabilities, the visual observation of the flow of HDPE over these shear rates was performed. One point of particular interest is the crossover of the melt from one branch of the flow curve to the other one. Also, optical experiments enable the observation of any secondary phenomena occurring during flow, which are not reflected in the pressure traces obtained from the capillary flow experiments. In the following section, the experimental observations obtained from the flow birefringence experiments on HDPE are presented.

4.5 Experimental Results - Flow Birefringence

The technique of flow birefringence was used to study the distribution of stress in the flow field of HDPE. A description of the flow birefringence technique and the optical set-up on the MPR are described in Chapter 2. Flow birefringence provides information about the stress distribution and also allows the observation of melt flow to a limited extent in the slit.

Single-pass experiments were carried out at a temperature of 170 °C for a range of piston velocities from 1.0 \(10^4\) to 1.0 \(10^5\) m/s (corresponding to a shear rate of 100 - 10,000 s⁻¹) for HDPE to study the evolution of flow birefringence patterns with time. In these experiments, the change in pressure difference across the slit with time was also simultaneously monitored. The four different flow regimes identified for capillary flow can also be observed during the flow of HDPE through a slit. These flow regimes were observed at lower shear rates in slit flow experiments as compared to the capillary flow experiments due to the difference in temperatures of both the set-ups.

In the following sections, flow birefringence patterns observed for the Stable flow...
regime and also during the transition of the melt from one branch of the flow curve to the other during the other three flow regimes are presented. The birefringence patterns have also been compared with the pressure difference profiles. Apart from these, some birefringence patterns showing flow disturbances near the walls of the slit are also shown.

4.5.1 Flow Birefringence patterns - Stable Flow Regime

In a Stable flow regime, the pressure difference across the slit increases in time to reach a steady value. Therefore, the birefringence patterns obtained after the pressure difference has reached a stable value is also unchanging. However, when the flow is developing in the slit or when there are pressure oscillations, it is possible to observe the evolution of the fringe patterns with time. The flow birefringence patterns showing the change in stress build-up with time for flow in the Stable flow regime is shown in. The evolution of fringes at the entry and one-third along the length of the slit and at the exit and one-third of the slit upstream to the exit are presented. The evolution of the corresponding pressure difference trace obtained from the pressure transducers is also plotted alongside to the pictures. It can be seen that the pressure difference across the slit increases in time to reach a steady value. In general, it can be observed that as the pressure difference across the slit increases, the fringes in the slit entry region also increase in number. In order to follow this increase in pressure, one of the fringes in the entry region, indicated by a red square is monitored.

The first row of birefringence patterns were obtained at 0.0 seconds at the beginning of the experiment and show the dark flow field, when the melt is at rest. The pressure difference was zero and no fringes were observed in the slit. As the pistons started moving, fringes started to develop at the corners of the slit in the entry region and moved downstream along the length of the slit. The following three rows show the fringes at 2.2, 5.8 and 7.9 seconds of the experiment, when the pressure difference across the slit increases from zero to reach 3, 6.5 and 8.5 MPa respectively. When the flow was fully developed, a stable birefringence pattern was observed in the slit as shown in the fifth row obtained at 13.8 seconds. The pressure difference across the slit rises to reach a stable value of 9 MPa. Correspondingly at the exit, the fringes become parallel to each other along the length of the slit and the number of these parallel fringes increases with time to reach a stable profile. This behaviour of the fringes is consistent with the pressure difference profile obtained from the pressure transducers.
Figure 4.14: The stress birefringence pattern and the pressure difference profile in the Stable Flow regime $T = 170^\circ C$, slit, $L = 1.0 \times 10^{-2} m$, $D = 1.0 \times 10^{-2} m$, $W = 1.0 \times 10^{-3} m$
4.5.2 Birefringence Patterns - *Periodic Oscillations, Overshoot* regimes

The common feature observed during the flow of HDPE in the *Periodic Oscillations, Overshoot* and *High Velocity* regimes through a capillary, was the transition of the melt from the first branch of the flow curve to the second. This transition is instantaneous and is accompanied by a subsequent increase or decrease in the pressure difference across the capillary. These flow regimes were observed for the flow of HDPE through a slit geometry. The evolution of the birefringence pattern with time for a single-pass experiment carried out in the *Periodic Oscillations* regime is shown in Figure 4.15. The evolution of fringes at the slit entry and a one-third along the length of the slit and at the exit and one-third of the length of the slit upstream of the exit are presented. The corresponding pressure difference profile obtained from pressure transducers also shown alongside these pictures. The movement of one of the fringes is again followed by marking it with a red dot in order to track the change in pressure in the slit entry region.

The first row of pictures were obtained at 0.6 seconds after the pistons have started moving and the pressure difference at this time is 6 MPa. As the pressure difference across the slit increases, the flow rate of the melt through the slit increases leading to an increase in the number of fringes in the slit. The next two rows have been obtained at 1.26 and 1.96 seconds, where the pressure difference across the slit increases to 9.5 MPa and eventually to 13.5 MPa respectively. The corresponding number of fringes in the slit also increases from two to five and six fringes respectively. The fringe, marked with the red dot moves downstream along the slit for 1.96 seconds till the value of pressure difference reaches its maximum value of 13.5 MPa corresponding to point $\alpha_1$ on the flow curve.

At this point, the melt crosses over to the second branch of the curve to point $\beta_1$. This transition from one branch of the flow curve to the next is faster than $1/24^{th}$ of a second and could not be captured using the image capture utility. When the melt has crossed over from the first branch of the flow curve to the second, the fringe marked by the red dot retracts and moves in the upstream direction indicating a reduction in pressure. This can be seen clearly in the fourth and fifth rows obtained at 2.07 and 2.16 seconds, where the pressure difference across the capillary decreases by 2.5 MPa from 13.5 MPa to 12 MPa and 11 MPa respectively.
Figure 4.15: The stress birefringence pattern and pressure difference profile in the Periodic Oscillations regime $T = 170^\circ C$, $\text{slit } L = 1.0 \times 10^{-3} \text{ m}$, $D = 1.0 \times 10^{-1} \text{ m}$, $W = 1.0 \times 10^{-4} \text{ m}$, $v_p = 1.0 \times 10^3 \text{ m/s}$, $A = 2.0 \times 10^2 \text{ m}$
The magnitude of discontinuity in the flow curve obtained from experiments carried out using a slit geometry at 170 °C is of the order of 2.5 MPa similar to that obtained at 180 °C using a capillary flow geometry. Corresponding observations at the slit exit show that the fringes were initially parallel to the slit wall move inwards towards the centre of the slit and converge at the middle of the slit with a decrease in pressure.

The increase in the pressure difference across the slit to $\alpha_1$ is observed as an increase in the number of the fringes in the slit. At $\alpha_1$, the system crosses over to the second branch of the flow curve and the pressure difference across the slit starts to decrease from $\beta_1$ to $\beta_2$, which is indicated by a decrease in the number of fringes. As the system undergoes further periodic oscillations, the fringes in the entry region move downstream and upstream of the flow direction, when the pressure difference across the capillary increases and decreases respectively. At the exit, the fringes move towards and away from the centre of the slit with increase and decrease in pressure difference respectively.

The Periodic Oscillations regime is followed by the Overshoot regime, which is characterised by the presence of an overshoot followed by a steady pressure difference across the slit. The birefringence patterns obtained for flow in the Overshoot regime are similar to those in Figure 4.15 and are therefore not shown here. At the slit entry, the pressure difference across the capillary increases, which is reflected in an increase in the number of fringes. When the pressure difference reaches its maximum value $\alpha_1$, it is accompanied by a transition from the first branch to the second branch of the curve to $\beta_1$. This is followed by a decrease in the pressure difference across the slit along the second branch of the flow curve to a certain value between 13.5 MPa and 11 MPa. Subsequently, the pressure difference across the slit is constant, indicated by a stable fringe pattern.

4.5.3 Birefringence patterns - High Velocity regimes

The final flow regime observed for HDPE is the High velocity regime. In capillary flow, this regime is characterised by a pressure difference profile, which initially shows a rapid increase up to $\alpha_1$ followed by a slower rise in pressure difference to reach a steady pressure difference across the capillary. At the slit entry, as seen before for the Periodic Oscillations regime, the pressure difference across the slit increases reflected in an increase
in the number of fringes. When the pressure difference reaches the value $\alpha_1$, the number of fringes increases to a maximum followed by a cross over to the second branch of the flow curve. The pressure difference across the slit then increases along the second branch of the flow curve to reach a stable value. The increase in pressure difference across the slit for this experiment is of the order of 14 MPa. The pressure difference levels in this regime were much higher than those observed earlier and results in very high flow rates of the melt through the slit, which is also reflected in the abundance of the fringes in the slit.

![Figure 4.16: The stress birefringence pattern and pressure difference profile in the High Velocity regime at the entry and exit of the slit.](image)

4.5.4 Observations of Flow Disturbances near the Wall

The phenomenon of transition of the melt from the first branch of the flow curve to the second is dominated by flow disturbances, which can be clearly observed near the exit of the slit for the Periodic Oscillations and the Overshoot regime. In order to describe these flow effects, consider the flow birefringence pictures obtained at the entry and the exit of the slit for an experiment carried out in the Overshoot regime. These pictures have been captured in a space of one second at the times indicated in the individual pictures. The pressure difference profile obtained from the pressure transducers is shown in Figure 4.17.

This pressure difference profile is typical of the Overshoot regime, and the pressure difference increases to reach 13.5 MPa within 2.5 seconds and subsequently reduces to and remains reasonably stable around 10.8 MPa within 3 seconds. Small pressure fluctuations can be observed when the pressure difference is at 10.8 MPa. These fluctuations are absent when the experiment is carried out using a capillary geometry. This could be because of the better uniformity of temperature across the whole assembly of barrels and the capillary section. As compared to a capillary geometry, the heat
distribution in an Optic cell is not very uniform because it has removable quartz windows and die inserts.

![Graph showing pressure difference profile](image)

**Figure 4.17:** The pressure difference profile for flow in the Overshoot regime of HDPE, $T = 170^\circ\text{C}$, slit, $L = 1.2\ 10^{-7}\ \text{m}$, Depth = $1.0\ 10^{-3}\ \text{m}$, $W = 1.0\ 10^{-7}\ \text{m}$, $v_f = 8.0\ 10^{-5}\ \text{m/s}$, $A = 2.0\ 10^{-7}\ \text{m}$

The fringe pattern in the slit entry corresponding Figure 4.17, evolves in time to give fringes, which move in the downstream direction and eventually become parallel to the walls of the slit. The picture shown in Figure 4.18 was obtained at the slit entry region, when the pressure difference across the slit reaches its maximum value, 13.5 MPa. The corresponding observations at the slit exit are shown in greater detail in Figure 4.19. The fringes increase in number as the pressure difference across the capillary reaches its maximum value, point $\alpha_1$. The white arrow in these pictures indicates the direction of flow of the melt.

At this point, a disturbance can be seen to originate at a point about two slit widths downstream of the slit entry causing the fringes at that point to become distorted. The arms of the U-shaped fringes, which were earlier parallel to the wall, start to broaden and end into the walls of the slit as shown in Figure 4.20. The disturbance originates near the entrance of the slit and causes a distortion of the downstream flow field resulting in a loss of symmetry of fringes near the exit of the slit (Figure 4.21).
Figure 4.18: The birefringence pattern at the entry of the slit in the Overshoot regime showing U-shaped fringes parallel to the walls of the slit. 
\[ T = 170 \, ^\circ C, \text{ slit, } L = 1.0 \times 10^{-2} \, m, D = 1.0 \times 10^{-3} \, m, W = 1.0 \times 10^{-1} \, m \text{ at } v_o = 8.0 \times 10^{-3} \, m/s, A = 2.0 \times 10^{-3} \, m \]

Figure 4.19: The birefringence pattern at the exit of the slit in the Overshoot regime showing the build-up of fringes with time as the pressure difference reaches its maximum value.
\[ T = 170 \, ^\circ C, \text{ slit, } L = 1.0 \times 10^{-2} \, m, D = 1.0 \times 10^{-3} \, m, W = 1.0 \times 10^{-1} \, m \text{ at } v_o = 8.0 \times 10^{-3} \, m/s, A = 2.0 \times 10^{-3} \, m \]

Figure 4.20: The birefringence pattern at the entry of the slit in the Overshoot regime showing start of the disturbance leading to broadening of U-shaped fringes.
\[ T = 170 \, ^\circ C, \text{ slit, } L = 1.0 \times 10^{-2} \, m, D = 1.0 \times 10^{-3} \, m, \text{ at } v_o = 8.0 \times 10^{-3} \, m/s, A = 2.0 \times 10^{-3} \, m \]

Figure 4.21: The birefringence pattern at the exit of the slit in the Overshoot regime showing a loss of symmetry in fringes.
\[ T = 170 \, ^\circ C, \text{ slit, } L = 1.0 \times 10^{-2} \, m, D = 1.0 \times 10^{-3} \, m, \text{ at } v_o = 8.0 \times 10^{-3} \, m/s, A = 2.0 \times 10^{-3} \, m \]
Meanwhile, at the entry region, all the U-shaped fringes broaden and end discontinuously at the walls of the slit. The fringes also start to show disturbances, which originate in the form of ripples near the surface of the slit (Figure 4.22). The distortion of the flow field arising from the ripples continues in the form of a wave. The intensity of this wave can be seen from the ripples near the surface of the slit. The propagation of this wave along the length of the slit is shown in Figure 4.23.

The fringe pattern in the upstream region of the slit remains reasonably stable for the remainder of the experiment and the fringes remain broadened as shown in Figure 4.24. The wave propagates along the length of the slit and moves towards the downstream region. The time required for this wave to propagate along the length of the slit is of the order of half a second. In the end, the wave completely disappears and a stable fringe pattern can be observed at the exit of the slit (Figure 4.25).

After this wave has completely passed through the slit, a stable fringe pattern can be observed in the downstream part of the slit. However, there are small-scale perturbations at the surface of the slit, which persist for the remainder of the flow of the melt along the length of the slit. Unfortunately, the resolution of the camera is not good enough to distinctly capture these perturbations and as a result they can't be seen with great clarity. This effect is clearly observed in the motion video clip, but cannot be resolved with clarity in the individual picture stills shown in Figure 4.26.

The fringes in the entry region of the slit remain broadened and end discontinuously at the walls of the slit. In the exit region, the fringes appear to be concentrated near the walls of the slit rather than be spread uniformly across the slit. These fringe patterns appear to indicate that the melt flowing through the slit has a plug flow profile and is slipping near the walls of the slit.

Figure 4.22: The birefringence pattern at the entry of the slit in the Overshoot regime showing broadened U-shaped fringes ending discontinuously into the walls of the slit, $T = 170 ^\circ C$, slit, $L = 1.0 \times 10^{-7} \text{ m}$, $D = 1.0 \times 10^{-4} \text{ m}$, $W = 1.0 \times 10^{-7} \text{ m}$ at $v_p = 8.0 \times 10^{-3} \text{ m/s}$, $A = 2 \times 10^{-3} \text{ m}$
In the Periodic Oscillations regime, the pressure oscillations can be observed by a periodic repetition of the fringes moving downstream and upstream respectively to the flow direction. Another important characteristic is the flow disturbance, which originates
from the surface of the slit which propagates in the form of a wave each time there was a transition of the melt from the first branch to the second branch of the flow curve. In the case of the Overshoot regime, where there is only a single transition from the first branch of the flow curve to the second, this flow disturbance can be observed during the transition. It is also not possible to distinguish this effect for flow in the High Velocity regime using the present experimental set-up. This could be either due to the fact that this effect does not occur or because the time scales of an experiment in the High Velocity regime is of the order of one second or lower, which makes it difficult to distinguish this effect.

**4.5.5 Discussion of Capillary and Flow Birefringence Results**

Four distinct flow regimes were identified from the time dependent, pressure difference traces for the capillary flow of HDPE. All the available literature mentions the presence of four flow regimes for HDPE, which were classified depending on the nature of the extrudates obtained, as described in chapter 1. There is some degree of overlap between both these forms of classifications. The stable flow regime identified from the pressure difference traces covers both the stable flow regime and regime of small scale surface distortions regime identified from the nature of the extrudates. The regime of Periodic Oscillations coincides with the Stick-slip regime, where the extrudates show alternate smooth and rough portions. The regime of Gross Instabilities, where the extrudates show bulk distortions can correspond to both the Overshoot and High Velocity regimes.

The flow disturbance, which is distinctly observed in the flow birefringence patterns of the Periodic Oscillations and the Overshoot flow regimes could be an indication of an entry instability arising due to the elongation and breakdown of the melt at the entry of the slit due to high levels of stress in the entry region. Such effects have been reported in literature by a number of authors for the flow of linear polymers (Vinogradov et al. 1978, 1981, Piau et al., 1995). Vinogradov (1981) have studied the flow birefringence patterns, where an entrance instability was initiated during the flow of a linear polymer such as polybutadiene. They observed that the entire flow field became distorted and this distortion clearly originated in the entry region of the slit and was present for the entire flow period. The characteristics of the flow disturbance wave observed for HDPE in the MPR are similar to the entry flow instability described by Piau.
et al. (1995) and could therefore be one kind of entry instability. In the flow birefringence observations shown for HDPE, it appears that the instability was initiated at the walls of the slit, slightly downstream to the slit entrance, although it is very difficult to pinpoint the exact site of origin of this instability. But the reasonably stable fringe pattern in the entry region suggests that the instability might originate slightly downstream in the die land region. The instability propagates in the form of a wave along the length of the slit and eventually disappears at the slit exit. These observations suggest that this instability may not be the entry instability referred to by Vinogradov (1981) or Piau et al. (1995). Since this instability was found to initiate at the walls of the slit when the pressure difference reaches its maximum value, i.e. point \( \alpha_1 \), it may be a manifestation of the stick-slip phenomenon accompanying the transition of the melt from the first branch to the second branch of the flow curve.

The flow through the slit becomes fully developed slightly downstream to the slit entrance and the maximum wall shear stress in the slit can be obtained at this length. As the pressure difference across the capillary builds up to \( \alpha_1 \), a coil-stretch transition could be initiated at this point in the slit. This transition could lead to a slip of the melt near the walls and a Spurr in the flow rate of the melt in the slit due to a disentanglement between the chains in the bulk and the chains which are adhered to the metallic walls. The slip of the melt near the walls can be observed by the broadening of the fringes which end into the wall similar to the observations reported by Vinogradov et al. (1978) for polybutadiene. The coil-stretch transition could lead to an instantaneous increase in the flow rate of the melt through the slit, resulting in a distortion of the flow field and loss of symmetry of the fringes in the downstream portion of the slit. The melt compressibility could be an important factor determining the magnitude of this transition because it is an indication of the capacity of the melt to store elastic energy (Pearson, 1969). When the pressure difference builds up to \( \alpha_1 \), crosses over to \( \beta_1 \) and then decreases, it leads to a decompression of the system. As a result, some of the elastic energy stored in the melt could be dissipated in the form of a wave and results in a distortion of the fringes.

This energy is dissipated as the pressure difference and flow rate through the slit decreases, causing the flow disturbance observed to disappear. In the Periodic Oscillations regime, the transition from point \( \alpha_1 \) to point \( \beta_1 \) is periodically observed and
accompanying by a periodic wave like flow disturbance. The amount of energy dissipated during each crossover is the same because the amplitude of pressure difference is the same for each oscillation. The extrudates of HDPE are characterised by alternate smooth and rough portions on its surface, when periodic pressure oscillations were present in the system (Durand et al., 1996). Hence, the periodic flow disturbance observed in the slit, which is initiated during the transition from the first branch of the flow curve to the second could result in an extrudate with alternate rough and smooth surfaces.

The *Overshoot* regime is characterised by a wave like flow disturbance accompanying the transition of the melt from the first branch of the flow curve to the second. This wave propagates through the slit and disappears as the pressure difference and flow rate of the melt through the slit decreases. This is followed by a stable fringe pattern indicating a steady pressure difference across the slit. The fringes in the entry region remain broadened and end discontinuously at the walls of the slit, indicating that the melt could be flowing in the form of a plug and continuously slipping along the length of the slit. This observation is a direct confirmation that flow of the melt in the second branch of the flow curve could be accompanied by slip, which has also been indirectly concluded by a number of researchers (see for e.g. Wang and Drda, 1997) from the diameter dependence of data for the second branch of the flow curve.

In case of the *High Velocity* regime, the crossover from the first branch of the flow curve to the second branch is followed by a further increase in the pressure difference (or further compression of the melt) to reach a steady value. Unlike the *Periodic Oscillations* or *Overshoot* regime, there is no decompression in the system following the crossover to the second branch of the flow curve. Therefore, the elastic energy stored in the melt may not be dissipated during the piston stroke and hence the wave like distortion of the fringes may not be observed.

### 4.6 Summary and Conclusions

The transient flow behaviour of HDPE was studied on the MPR using a capillary and a slit geometry. Four flow regimes have been identified from the pressure difference traces obtained for capillary flow experiments. These regimes can be observed with increase in shear rate and have been named as the *Stable Flow, Periodic Oscillations, Overshoot and High Velocity* flow regimes. A flow curve in terms of pressure difference versus piston
velocity was determined from the time dependent pressure measurements for HDPE. This flow curve is discontinuous and consists of two branches, which are separated by an unstable flow regime.

Flow birefringence measurements were carried out for HDPE in a slit geometry test section having transparent windows. The flow of HDPE in a slit geometry appears to be similar to its flow in a capillary geometry with respect to the pressure difference profiles obtained. The four regimes observed in capillary flow have also been observed for the flow of HDPE through a slit. In the Stable Flow regime, a stable flow birefringence pattern can be observed in the slit. In case of the Periodic Oscillations and Overshoot flow regimes, flow birefringence patterns were obtained during the transition of melt from the first branch to the second branch of the flow curve.

The transition from the first branch to the second branch of the flow curve is also marked by the presence of a flow disturbance, which appears to originate near the walls of the slit, slightly downstream of the slit exit. This disturbance propagates in the form of a wave along the walls of the slit and disappears at the slit exit. It causes a distortion of the downstream flow field resulting in a loss of symmetry of the fringes. This phenomenon can be observed during the transition of the melt from the first branch of the flow curve to the second for the Periodic Oscillations and Overshoot regime. It was difficult to distinguish the presence of this phenomenon in the High Velocity regime. The flow in the second branch of the flow curve are accompanied by fringes, which no longer remain parallel to the walls of the slit in the upstream region. These fringes tend to remain broadened and end at the walls of the slit.

It has not been possible to comment on the presence of surface and bulk defects occurring in HDPE melts, which have been extensively reported in literature, because of the absence of extrudates in a Multipass Rheometer. The four flow regimes identified for HDPE have been explained due to the presence of a discontinuous flow curve. The mechanism behind the presence of the discontinuous flow curve and the Periodic Oscillations regime could not be conclusively established from this study. The observations of the flow birefringence patterns in a Periodic Oscillations and Overshoot regime lend support to the theory of coil-stretch transition proposed by Brochard and de Gennes (1992) and extended by Piau et al. (1995) and Wang and Drda (1997).
5. The Modelling of Transient Flow in the Multipass Rheometer

In this chapter, a model with no adjustable parameters is developed to predict the transient capillary flow behaviour of a polymer melt in a MPR. The significant parameters of this model include the flow curve of the melt and melt compressibility. The predictions of this model were compared to the experimentally determined time dependent pressure traces for the steady shear capillary flow in all the four flow regimes of HDPE.

5.1 Introduction

This chapter is devoted to the derivation of a model to describe and predict the transient flow behaviour of a polymer melt including pressure oscillations and overshoots in the MPR (also available as a publication by Ranganathan et al., 1999). The experimental measurements carried out for polymer melts using the MPR, show that it takes a finite time for the pressure difference across the capillary to build-up and reach a steady value. After the pistons have stopped moving, it again takes a finite time for the pressure difference across the capillary to relax. Therefore, there are significant time scales involved in the transient flow of a polymer melt through a capillary.

A number of models, varying in terms of their approach and complexity have been proposed to predict the transient flow of polymer melts such as HDPE. Most of these models include a viscoelastic constitutive equation coupled with a wall slip boundary condition and a compressibility parameter. Georgiou and Crochet (1994a, b) have used a numerical finite element approach to model the flow of a compressible fluid using non-Newtonian viscous constitutive equations. Adewale and Leonov (1997) have developed a model along similar lines, which include both molecular and rheological parameters. Hatzikiriakos and Dealy (1992) have developed a simpler power law model consisting of seven parameters, including melt compressibility to predict the pressure transients.
observed in capillary flow. Molenaar and Koopmans (1994) have formulated a relaxation-oscillation type model, which was initially proposed by Weill (1980), to describe the flow of HDPE through a simple capillary rheometer assembly. The Molenaar and Koopmans model consists of two coupled differential equations and melt compressibility and can be used to predict the pressure difference profiles obtained for the different flow regimes observed for a HDPE melt. The predictions of this model have been fitted to experimental results by Durand et al. (1996) using an arbitrary undefined parameter and therefore the application of this model is limited to a qualitative prediction of capillary flow behaviour.

The boundary conditions of capillary flow in the MPR are different to that of a conventional capillary rheometer due to the absence of free surfaces at the exit of the capillary. Also, melt volume and boundary conditions within a MPR are fully defined. The development of a model to describe capillary flow of a polymer melt in the MPR follows a similar approach to the Molenaar and Koopmans (1994) model and has been used to predict the time dependent capillary flow of a polymer melt for a given flow rate. Furthermore, the fully defined upstream and downstream boundary conditions of the MPR coupled with a reformulation of the problem, enable modelling the flow of polymer melts without having to resort to the use of any semi-arbitrary adjustable parameters.

5.2 Derivation of the Model

The Multipass Rheometer (MPR), as described in chapter 2, is a two piston capillary rheometer with a capillary test section positioned between the two barrels. A schematic diagram of the MPR is shown in Figure 5.1. The sample is fully constrained by two pistons, which move simultaneously in the same direction with a velocity, \( v_p \). The top and bottom barrels are represented by subscripts \( t \) and \( b \) respectively. The pressure and volume in the barrels are represented by \( P \) and \( V \) respectively. The capillary radius and length are \( r \) and \( L \) respectively and the internal radius of both barrels is \( R \). The rate of volume displacement of the melt in the barrels due to the movement of the pistons is represented by \( Q_m \) and \( Q_c \) is the flow rate of the melt through the capillary.

Consider the top barrel and capillary assembly filled with a polymer melt of density, \( \rho \) and compressibility, \( \chi \) as shown in Figure 5.2. A mass balance across the top barrel and capillary yields,
Eqn. 56 \[ \frac{d}{dt}(V \rho) + Q_c \rho = 0 \]

The volume of the capillary can be neglected while taking the mass balance (generally ratio of capillary and barrel radius is 1:12)

Expanding the differential equation, Eqn. 56 gives,

Eqn. 57 \[ \frac{dV}{dt} \rho + \frac{dp}{dt} + \frac{Q_c \rho}{V_t} = 0 \]

The density, \( \rho \) of the polymer melt can be related to the pressure, \( P_t \) in the top barrel using compressibility, \( \chi \) of the polymer melt

Eqn. 58 \[ \frac{1}{\rho} \frac{dp}{dt} = \chi \frac{dP_t}{dt} \]

Substituting Eqn. 58 in Eqn. 57 gives
The volume of top barrel, $V_t$ decreases in time as the piston moves downward into the top barrel with a velocity, $v_p$ and the change in $V_t$ with time is given by

Eqn. 60
$$\frac{dV_t}{dt} = -\pi R^2 v_p = -Q_m$$

Substituting Eqn. 60 into Eqn. 59 gives

Eqn. 61
$$-Q_m + V_t \frac{dP_t}{dt} + Q_c = 0$$

which can be rewritten as

Eqn. 62
$$\frac{dP_t}{dt} = \frac{1}{\chi V_t} \left( Q_m - Q_c \right)$$

Eqn. 62 gives the relationship between the change in top barrel pressure $P_t$ in terms of barrel and capillary flow rates, compressibility and volume of the top barrel. A similar relationship has been derived for the change in pressure $P_b$ and volume $V_b$ in the bottom barrel.

Eqn. 63
$$\frac{dP_b}{dt} = \frac{1}{\chi V_b} \left( Q_c - Q_m \right)$$

Subtracting Eqn. 63 from Eqn. 62 gives

Eqn. 64
$$\frac{dP_t}{dt} - \frac{dP_b}{dt} + \frac{d\Delta P}{dt} = \frac{1}{\chi} \left( \frac{1}{V_t} + \frac{1}{V_b} \right) \left( Q_m - Q_c \right)$$

where $\Delta P$ is the pressure difference across the capillary. Substituting for $Q_m$ from Eqn. 60 gives

Eqn. 65
$$\frac{d\Delta P}{dt} = \frac{1}{\chi} \left( \frac{1}{V_t} + \frac{1}{V_b} \right) \left( \pi R^2 v_p - Q_c \right)$$

The polymer melt flows into the capillary with a flow rate $Q_c$, given by

Eqn. 66
$$Q_c = \pi r^2 v_{cap}$$

where $v_{cap}$ is the mean velocity of the melt in the capillary section. The flow in the capillary takes a finite amount of time to become fully developed and this is reflected in the build-up of pressure difference across the capillary. In a single-pass experiment, the melt tries to reach and maintain a capillary flow rate equal to the rate of volume displacement in the barrel. Hence, in a fully developed flow,
When this relation is substituted into Eqn. 65, it yields

\[ \frac{d\Delta P}{dt} = 0 \]

which satisfies the equation of mass conservation. The resulting solution is a steady \( \Delta P \) or pressure difference across the capillary whose value is defined by the experimental flow curve for that value of \( Q_m \). If the system cannot reach a state of stability, i.e. \( Q_m \neq Q_c \), then the equation of mass conservation is not satisfied and the system does not reach a steady pressure difference across the capillary. This can lead to periodic pressure fluctuations. This type of flow can be observed in the *Periodic Oscillations* regime.

In order to solve Eqn. 65, it needs to be converted into a differential equation with one dependent variable, i.e. \( \Delta P \) needs to be expressed in terms of \( Q_c \), the flow rate of the melt through the capillary. The experimental steady state flow curve of the system is in terms of \( \Delta P \) versus \( Q_m \). At steady state, \( Q_m = Q_c \) and hence the flow curve can be written in terms of \( \Delta P \) and \( Q_c \).

### 5.3 Experimental Observations of Capillary Flow

The experimental observations for the capillary flow of molten HDPE in the MPR have been discussed in chapter 4. The time dependent capillary flow of HDPE for a range of flow rates have been studied and four different flow regimes have been identified. The flow curve of HDPE (Figure 5.3) consists of two branches with a section in between where the flow behaviour of HDPE is considered to be unstable.

In this unstable region, a steady pressure difference across the capillary cannot be obtained because of the fluctuating nature of the pressure traces. Four parameters can be identified from the discontinuous flow curve shown in Figure 5.3 which are \( \alpha_1, \alpha_2, \beta_1 \) and \( \beta_2 \) and the two monotonically increasing branches of the flow curve can be fitted by a power-law model. Using these parameters and melt compressibility values, Eqn. 65 is solved to predict the time dependent pressure difference across the capillary for all the four flow regimes of HDPE.
5.4 Solution of Differential Equation

The two branches of the flow curve of HDPE are expressed in terms of a power-law relation of the form, \( Q_m = a_1 (\Delta P)^{b_1} \). Using this power-law relationship between \( \Delta P \) and \( Q_m \), Eqn. 65 can be solved using the initial and boundary conditions listed in Table 5.1.

For the first branch of the flow curve

Eqn. 69

\[ Q_c = a_1 (\Delta P)^{b_1} \]

and for the second branch of the flow curve,

Eqn. 70

\[ Q_c = a_2 (\Delta P)^{b_2} \]

Hence Eqn. 65 can be rewritten as

Eqn. 71

\[ \frac{d\Delta P}{dt} = X \left( \frac{1}{V_t} + \frac{1}{V_b} \right) \left\{ \pi R^2 v_p - a_1 (\Delta P)^{b_1} \right\} \]

Eqn. 71 is a differential equation with a single dependent variable \( \Delta P \), where \( a_i \) and \( b_i \) were determined from the experimental flow curve. The piston velocity, \( v_p \) is imposed on the system and \( V_t \) and \( V_b \) are the barrel volumes which change in time depending on the value
of \( v_p \) in the following manner,

\[
\begin{align*}
\text{Eqn. 72a} & \quad V_t &= V_{t0} - \pi R^2 v_p t \\
\text{Eqn. 72b} & \quad V_b &= V_{b1} + \pi R^2 v_p t
\end{align*}
\]

The unknown parameter in this equation is compressibility, \( \chi \) of HDPE, which has been experimentally measured using the MPR. The value of compressibility measured for HDPE at 180 °C is \( 1.37 \times 10^{-9} \) (Pa\(^{-1}\)). The compressibility, \( \chi \) can be taken as a constant and \( R \), \( r \), \( v_p \), and \( L \) are fixed for a given single-pass experiment. Eqn. 71 is solved with a numerical solver package MATLAB, with a second order Runge-Kutta method and has been used to predict the time dependent profiles for the flow of the HDPE melt in the MPR in all the four regimes. The typical values of numerical parameters used for the solution of the model are given in Table 5.2.

### 5.5 Comparison of Experimental and Predicted Results

The model has been reasonably successful in predicting the time dependent pressure profiles for all the four regimes and has also been used to predict the change in flow rate of the melt through the capillary, \( Q_c \) with time (see Figures 5.5 - 5.8). For a detailed comparison, the time dependent profiles in each of the four regimes have been split up into three sections, which are as follows:

- **The pressure build-up section**
  
  This is the initial part of the time dependent pressure profile. The predicted pressure build-up profile has the same characteristics as that of the experimentally observed profile. The model is able to predict this pressure build-up across the capillary, although it predicts a slightly higher rate of pressure difference build-up across the capillary than that experimentally observed. This discrepancy is reduced as we move from regime 1 to regime 4 (as can be seen from Figures 5.5 - 5.8). The predicted flow rate through the capillary in all the four regimes has similar characteristics as the build-up of pressure difference across the capillary.

- **The fully developed flow section**
  
  This is the middle part of the time dependent pressure profile where the pressure difference across the capillary corresponds to a fully developed flow condition. In
regime 1 (Figure 5.4), the model is able to accurately predict the value of steady pressure difference across the capillary. This is expected, because the experimental steady state flow curve has been used in the model. The predicted flow rate through the capillary \( Q_c \) also increases from zero to reach a final steady value similar to the pressure difference, which is equal to the rate of volume displacement of the melt in the barrel due to the movement of the pistons.

In the case of the *Periodic Oscillations* regime (Figure 5.5), the model was able to predict the frequency of periodic oscillations with reasonable accuracy. The frequency of these oscillations predicted by the model was also found to be highly sensitive to small changes in the values of melt compressibility. The amplitude of these oscillations was obtained directly from the upper and lower limits of the first branch and the second branch respectively of the experimental steady state flow curve. The model was also able to closely reconstruct the shape of these experimental oscillations. The predicted flow rate through the capillary \( Q_c \) showed instantaneous changes in its value whenever there was a crossover from one branch of the flow curve to the other.

In the *Overshoot* regime (Figure 5.6), the model gives a good prediction of the pressure overshoot and the subsequent steady pressure difference across the capillary. The flow rate of the melt through the capillary also shows an overshoot corresponding to the overshoot observed in the pressure difference profile.

Finally, in the *High Velocity* regime (Figure 5.7), where two distinct rates of rise of pressure were observed, the model was able to predict the final value of the steady pressure difference with good accuracy, but the crossover from one rate of pressure increase to the second rate pressure increase is not very pronounced. The corresponding predicted flow rate of the melt through the capillary jumps instantaneously to a higher value when there is a cross-over from the first branch of the flow curve to the second and continues to increase thereafter until it reaches a steady state value.

- **The pressure relaxation section**

  This is the third and final part of the time dependent pressure profile obtained from a single-pass experiment. In a single-pass experiment, when the piston movement...
ceases, there is a substantial pressure difference across the capillary that relaxes over a finite period of time. This pressure relaxation could be a result of flow of melt through the capillary leading to pressure equalisation in both the barrels. Also, since HDPE is a viscoelastic material, some amount of viscoelastic relaxation (similar to that observed during a stress relaxation test) may also be expected after cessation of piston movement. When the predictions of the model were compared with the experimental observations, it can be seen that the model is remarkably successful in predicting the pressure relaxation behaviour. However, the model does not account for viscoelastic relaxation of the melt and the kinetics of pressure relaxation in the model are solely governed by melt compressibility. Therefore, melt compressibility not only governs the build-up of pressure but also plays a dominant role in the relaxation of the pressure difference across the capillary, while the contribution due to viscoelastic relaxation appears to be negligible. Particle tracking observations of the melt in a slit geometry during the relaxation of pressure difference have also confirmed that there is a significant flow of the melt through the slit.

![Graph showing comparison of experimental and predicted pressure differences over time.](image)

**Figure 5.4:** Comparison of the predictions of the model with experimental data for HDPE in the Stable flow regime at 180°C for a capillary of L = 1.0 × 10^{-2} m, D = 1.0 × 10^{-3} m and Half Entry angle = 45°.
Figure 5.5: Comparison of the predictions of the model with experimental data for HDPE in the Periodic Oscillations regime at 180 °C, capillary of $L = 1.0 \times 10^{-3}$ m, $D = 1.0 \times 10^{-3}$ m and Half Entry angle = $45^\circ$

Figure 5.6: Comparison of the predictions of the model with experimental data for HDPE in the Overshoot regime at 180 °C for a capillary of $L = 1.0 \times 10^{-3}$ m, $D = 1.0 \times 10^{-3}$ m and Half Entry angle = $45^\circ$
Figure 5.7: Comparison of the predictions of the model with experimental data in the High Velocity regime for HDPE at 180°C for a capillary of L = 1.0 × 10⁻² m, D = 1.0 × 10⁻³ m and Half Entry angle = 45°.

Table 5.1: Initial and boundary conditions used in modelling the four flow regimes

<table>
<thead>
<tr>
<th>Flow regime</th>
<th>During piston movement</th>
<th>After cessation of piston movement</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$t = 0, \Delta P = 0, v_p = v_p$</td>
<td>$t = t, \Delta P = \Delta P, v_p = 0$</td>
</tr>
<tr>
<td>for flow rates $0 - \alpha_1$</td>
<td>$Q_c = a_1^{*}(\Delta P)^{b_1}$</td>
<td>$Q_c = a_1^{*}(\Delta P)^{b_1}$</td>
</tr>
<tr>
<td>2</td>
<td>$t = 0, \Delta P = 0, v_p = v_p$</td>
<td>$t = t, \Delta P = \Delta P, v_p = 0$</td>
</tr>
<tr>
<td>for flow rates $\alpha_1 - \beta_1$</td>
<td>$Q_c = a_1^{<em>}(\Delta P)^{b_1}$ for $Q_c &lt; \beta_1$ and $Q_c &gt; \beta_2$, $Q_c = a_2^{</em>}(\Delta P)^{b_2}$ for $Q_c &gt; \alpha_2$ and $Q_c &lt; \alpha_1$, $Q_c = a_1^{*}(\Delta P)^{b_1}$</td>
<td>$Q_c = a_2^{<em>}(\Delta P)^{b_2}$ for $Q_c &gt; \alpha_2$ and $Q_c &lt; \alpha_1$, $Q_c = a_1^{</em>}(\Delta P)^{b_1}$</td>
</tr>
<tr>
<td>3</td>
<td>$t = 0, \Delta P = 0, v_p = v_p$</td>
<td>$t = t, \Delta P = \Delta P, v_p = 0$</td>
</tr>
<tr>
<td>for flow rates $\beta_2 - \beta_1$</td>
<td>$Q_c = a_1^{<em>}(\Delta P)^{b_1}$ for $Q_c &lt; \alpha_1$, $Q_c = a_2^{</em>}(\Delta P)^{b_2}$ for $Q_c &gt; \beta_1$ and $Q_c &gt; \beta_2$, $Q_c = a_2^{*}(\Delta P)^{b_2}$</td>
<td>$Q_c = a_2^{<em>}(\Delta P)^{b_2}$ for $Q_c &gt; \alpha_2$ and $Q_c &lt; \alpha_1$, $Q_c = a_1^{</em>}(\Delta P)^{b_1}$</td>
</tr>
<tr>
<td>4</td>
<td>$t = 0, \Delta P = 0, v_p = v_p$</td>
<td>$t = t, \Delta P = \Delta P, v_p = 0$</td>
</tr>
<tr>
<td>for flow rates $\beta_1$ and onwards</td>
<td>$Q_c = a_1^{<em>}(\Delta P)^{b_1}$ for $Q_c &lt; \alpha_1$, $Q_c = a_2^{</em>}(\Delta P)^{b_2}$ for $Q_c &gt; \beta_1$, $Q_c = a_2^{*}(\Delta P)^{b_2}$</td>
<td>$Q_c = a_2^{<em>}(\Delta P)^{b_2}$ for $Q_c &gt; \alpha_2$ and $Q_c &lt; \alpha_1$, $Q_c = a_1^{</em>}(\Delta P)^{b_1}$</td>
</tr>
</tbody>
</table>
5.6 Summary and Conclusions

Four time dependent flow regimes were identified from the experimental data obtained using the MPR, and each of these regimes had a characteristic pressure difference profile. The nature of time dependent pressure build-up and relaxation is similar in each case, but the regimes differ from each other due to the presence of periodic oscillations or overshoots.

It has not been necessary to include adjustable arbitrary parameters in the model because of the fully constrained geometry of the MPR and therefore the model can be used to obtain a quantitative prediction of the flow behaviour of a polymer melt using only its compressibility value and steady shear flow curve. The prediction of the time dependent pressure profiles for capillary flow of HDPE in the four regimes was found to be reasonably accurate. In particular, the model was able to predict the pressure relaxation after flow with remarkable accuracy. Direct particle tracking observations and model predictions indicate that the relaxation of pressure difference was predominantly due to the flow of the melt through the capillary leading to pressure equalisation in both the barrels, i.e. a compressibility effect. Therefore, it may be concluded that compressibility effects should be included while describing the time dependent pressure behaviour of polymer melts during flow through a constriction.

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Table 5.2: Typical values of numerical parameters

<table>
<thead>
<tr>
<th>( \lambda )</th>
<th>( 1.37 \times 10^{-9} ) (Pa)(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_t, V_b )</td>
<td>( 7.5 \times 10^{-6} ) m(^3)</td>
</tr>
<tr>
<td>( R )</td>
<td>( 6 \times 10^{-3} ) m</td>
</tr>
<tr>
<td>( r )</td>
<td>( 5 \times 10^{-3} ) m</td>
</tr>
<tr>
<td>( a_1 )</td>
<td>( 9.68 \times 10^{23} )</td>
</tr>
<tr>
<td>( b_1 )</td>
<td>( 2.3886 )</td>
</tr>
<tr>
<td>( a_2 )</td>
<td>( 1.6 \times 10^{19} )</td>
</tr>
<tr>
<td>( b_2 )</td>
<td>( 1.7056 )</td>
</tr>
</tbody>
</table>
6. **The Transient Flow and Processing of Polyolefin Elastomer**

This chapter begins with a review of the literature available on the rheology and processing of metallocene catalysed polymers. Then, the results for steady shear experiments carried out on POE using a MPR are presented. Steady shear capillary flow experiments were repeated using the same sample of POE in order to study the effect of shearing on its rheology. Flow visualisation experiments were also carried out for POE in a slit geometry, using both unpolarised and plane polarised light. These observations reveal the presence of a surface layer near the walls of the slit, which is different from the polymer in the bulk. Finally, a hypothesis was proposed in order to try to explain the distinct nature of the pressure difference profiles observed for POE, which were different to those observed for HDPE.

6.1 Transient Flow and Melt Flow Instabilities of Metallocene Polymers

Polyolefin Elastomer (POE) is a random ethylene-octene copolymer with a narrow molecular weight distribution as compared to HDPE and LLDPE. This polymer was manufactured by The Dow Chemical Company, using newly developed metallocene catalysts. Metallocene catalysts have reaction sites of uniform activity and this technology is referred to as the Constrained Geometry Catalyst Technology (CGCT) (see Martino, 1992). The improved features of polymers manufactured using this technology have been the focus of a number of papers (see for e.g. Martino, 1992, Chowdhury and Moore, 1993). As this type of polymer has only been recently introduced into the market, there is a limited information available in literature about their rheology.

The first reported study on the rheological characteristics of polymers synthesised using metallocene catalysts was carried out by Chien et al. (1992). They studied the dynamic viscoelastic properties of a metallocene catalysed polypropylene melt. A more detailed study of metallocene catalyzed high density polyethylene (m-HDPEs) was carried out by Vega et al. (1996). These m-HDPEs were characterised by a narrow MWD (P1 of the order of 2) and a total absence of short (SCB) or long (LCB) chain branching. They compared the results of a range of m-HDPEs of different MWs
with conventionally catalysed HDPEs (c-HDPE) of similar MWs. In general, they observed that the viscosities of the m-HDPEs were much higher than that of c-HDPEs. They have suggested that above a critical molecular weight ($M_c$), the structure and configuration of chains of m-HDPEs are different as compared to that of c-HDPEs, which gives rise to a more entangled system and a higher melt viscosity for m-HDPEs. In the case of m-HDPEs, they also reported a higher relaxation strength ($G'_r$) for longer values of relaxation times $\lambda_r$, as compared to c-HDPE, while at shorter relaxation times, the values of $G'_r$ are identical for both polyethylenes.

In general, it was concluded that m-HDPEs were difficult to process as compared to c-HDPEs and exhibited the presence of melt flow instabilities at relatively low shear rates (see for e.g. Vega et al., 1996 and Muñoz - Escalona et al., 1997). Vega et al. (1996) reported the onset of Small-Scale Surface Distortions (SSSD) and stick-slip effect below a shear rate of 10 s$^{-1}$ and a critical shear stress of 0.1 MPa for the onset of SSSD, which is independent of temperature (over a range of 160 - 180 °C). Muñoz - Escalona et al. (1997) observed that blending of a higher MW m-HDPE with increasing amounts (> 50% by weight) of a low MW m-HDPE, increased the apparent shear rates for the onset of the SSSD and stick-slip effects. They have therefore concluded that the presence of a low MW polymer acts as a processing aid for a high MW polymer.

Hatzikiriakos et al. (1997) have carried out capillary flow experiments for two metallocene catalysed LLDPEs (m-LLDPEs) and have compared their findings with a conventional LLDPE (c-LLDPE). They observed that in contrast to c-LLDPEs, the capillary extrusion of m-LLDPEs showed large pressure transients and it was necessary to go through multiple loads of the polymer melt before a steady state could be obtained. They also observed that m-LLDPEs showed SSSD initially during extrusion, but once the extrusion reached a steady state, these defects could not be observed and smooth extrudates were obtained. They found that similar to c-LLDPEs, the flow curves of m-LLDPEs also showed a diameter dependence indicating the presence of slip in the system. They used the Mooney analysis (see for e.g. Dealy and Wissbrun, 1995) and calculated slip velocities of very high magnitudes, which suggested the presence of a plug-flow velocity profile. In comparison, the calculated slip velocities of c-LLDPEs were much smaller. Deeprasertkul et al. (1998) have studied the characteristics of steady shear extrusion (Monsanto capillary rheometer in a controlled pressure mode) of three metallocene catalysed LLDPEs (m-LLDPEs) of similar MWDs ($Pl = 2$) with differing
MWs and Melt Indices (MI). They observed that the flow curve of the three m-LLDPEs showed SSSD over a range of shear stresses from 0.41 - 0.44 MPa. Unlike HDPEs, which show a discontinuity in the flow curve, m-LLDPEs do not exhibit a clear discontinuity in their flow curve. They also reported another discontinuous transition region at a higher value of shear stress similar to those reported for conventional LLDPEs (Kurtz, 1984).

6.1.1 Summary of Literature Review

It can be summarised from the literature reviewed above that the rheology of the m-polymers is very different as compared to similar polymer synthesised using conventional techniques. In general, m-polymers appear to have higher viscosities as compared to c-polymers. The onset of instabilities such as SSSD were observed at lower shear rates suggesting that these m-polymers are more difficult to process as compared to c-polymers. The most distinct observation was about the transient nature of flow and flow instabilities in the m-polymers. In this respect, it is useful to study the processing behaviour of m-polymers such as POE using a MPR. This is because, the MPR can be advantageously used for repeating experiments using the same polymer volume because of its constrained flow geometry. This feature makes it possible to systematically study the effect of shearing on a given sample volume and characterise its transient flow behaviour. The results obtained from the rheology and processing behaviour of POE, studied in a MPR are presented in the following section.

6.2 Experimental Section - Capillary Flow Experiments

The transient flow behaviour of POE has been studied in a capillary geometry using a MPR. Three different capillary configurations, referred to as A, B and C were used to carry out steady shear experiments and the specifications of these capillaries are listed in Table 6.1. These experiments have been carried out at either at 180 °C or at 170 °C and that will be appropriately indicated with the results. Capillary flow experiments have been carried out in single-pass mode over a wide range of apparent shear rates from 0.1 to 12,000 s⁻¹. These experimental results are presented by separating them into a number of series. Each series of single-pass experiments were carried out using the same POE sample. Before the start of each experiment, the system pressure was adjusted to 3 MPa, in order to maintain consistent experimental conditions. In each series, the first experiment was carried out by moving the pistons in either in an upward or downward
direction. The change in pressure difference across the capillary, both when the pistons were moving and when they have stopped moving were measured. Following this, the system pressure was again checked and adjusted to 3 MPa. The next experiment was carried out by moving the pistons in the opposite direction as compared to the first experiment. Typically, the time between two successive experiments is less than one minute. The same process is repeated and a number of experiments were carried out for the same POE sample to form a series of experiments.

<table>
<thead>
<tr>
<th>Capillary</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length (L)</td>
<td>$1.0 \times 10^{-2}$ m</td>
<td>$4.0 \times 10^{-2}$ m</td>
<td>$1.0 \times 10^{-2}$ m</td>
</tr>
<tr>
<td>Diameter (D)</td>
<td>$1.0 \times 10^{-2}$ m</td>
<td>$8.0 \times 10^{-2}$ m</td>
<td>$1.0 \times 10^{-2}$ m</td>
</tr>
<tr>
<td>Entry angle</td>
<td>$45^\circ$</td>
<td>$45^\circ$</td>
<td>$90^\circ$</td>
</tr>
<tr>
<td>Shear rate range studied</td>
<td>$50 - 12,000$ s$^{-1}$</td>
<td>$0.1 - 100$ s$^{-1}$</td>
<td>$50 - 12,000$ s$^{-1}$</td>
</tr>
</tbody>
</table>

6.2.1 Characteristics of Pressure Build-up of POE

The steady shear extrusion of metallocene catalysed polymers are reported to exhibit irreproducible behaviour during the initial periods of extrusion (see for e.g. Muñoz-Escalona et al., 1997 and Hatzikiriakos et al., 1997). In order to study the reproducibility of steady shear data of POE, single-pass experiments were carried out for a range of shear rates from 100 - 10,000 s$^{-1}$ using capillary A at 180 °C (which will be referred to as Series 1). In series 1, pressure traces from successive single-pass experiments carried out at a piston speed of $1.0 \times 10^4$ m/s are compared with each other. In all the figures shown below, the change in the pressure difference and the piston position are plotted as a function of time.

The same polymer sample was passed through the capillary approximately 30 times. The results from the fourth, seventh, ninth, fifteenth and thirtieth experiments of series 1 are compared with each other. The main points of comparison are the maximum steady pressure difference of each experiment and the time taken to reach this pressure difference. Another point of discussion is the nature of pressure fluctuations observed in these experiments. For the fourth pass of series 1, shown in Figure 6.1, the pressure difference across the capillary rises to around 9.5 MPa in a period of 10 seconds and then shows regular pressure fluctuations (with a period of approximately 4 seconds) about that value. The amplitude of these fluctuations is of the order of 1.2 MPa and were characterised by a rapid increase followed by a gradual decrease in pressure with time.
Figure 6.1: Series I, Pressure difference profile for single-pass experiment no. 4 for POE, $T=180^\circ C$, Capillary, $v_p = 1.0 \times 10^{-4} \text{ m/s}$, $A = 1.0 \times 10^{-2} \text{ m}$

Figure 6.2: Series I, Pressure difference profile for single-pass experiment no. 7 for POE, $T=180^\circ C$, Capillary $A$, $v_p = 1.0 \times 10^{-4} \text{ m/s}$, $A = 3.0 \times 10^{-3} \text{ m}$

Figure 6.3: Series I, Pressure difference profile for single-pass experiment no. 9 for POE, $T=180^\circ C$, Capillary $A$, $v_p = 1.0 \times 10^{-4} \text{ m/s}$, $A = 3.0 \times 10^{-3} \text{ m}$
The pressure difference traces from the seventh and the ninth passes of series 1 are shown in Figure 6.2 and Figure 6.3 respectively. As seen before in Figure 6.1, the pressure difference across the capillary increases to reach a mean value of 9 MPa and is accompanied by regular pressure fluctuations (of amplitude 1.5 MPa and a period of the order of 7 seconds) around this value. The nature of pressure fluctuations observed however differ from those seen in Figure 6.1, where the fluctuations were characterised by a gradual rise accompanied by a sharp drop in the value of the pressure difference. It should be noted that these fluctuations are extremely erratic in nature and are therefore difficult to reproduce. The general trends of pressure build-up and time dependence are reproducible.

By the fifteenth pass (Figure 6.4), the mean steady value of the pressure difference across the capillary decreases to a value around 8.5 MPa in 15 seconds. In the thirtieth pass of series 1 (Figure 6.5), the pressure difference profile is remarkably different from that seen before for the fourth pass (Figure 6.1). The mean pressure difference across the capillary is of the order of 7.5 MPa. Also, it takes approximately 30 seconds for the pressure difference across the capillary to reach a steady value. The pressure difference traces from the seventh and the ninth passes of series 1 are shown in Figure 6.2 and Figure 6.3 respectively. As seen before in Figure 6.1, the pressure difference across the capillary increases to reach a mean value of 9 MPa and is accompanied by regular pressure fluctuations (of amplitude 1.5 MPa and a period of the order of 7 seconds) around this value. The nature of pressure fluctuations observed however differ from those seen in Figure 6.1, where the fluctuations were characterised by a gradual rise accompanied by a sharp drop in the value of the pressure difference. It should be noted that these fluctuations are extremely erratic in nature and are therefore difficult to reproduce. The general trends of pressure build-up and time dependence are reproducible.
Single-pass experiments similar to the ones described above for series 1 were repeated using a new POE sample with capillary C. In these series of experiments similar to that observed for series 1, the maximum steady pressure difference across the capillary decreases, while the time taken to reach this value increases with each successive experiment. Again, as observed in series 1, pressure fluctuations can be observed which tend to diminish in magnitude with each successive experiment. These fluctuations do not appear to have a fixed frequency or amplitude.

In order to systematically study the pressure build-up characteristics of POE, successive single-pass experiments (Series 2) were carried out using capillary A at 180 °C (Series 2). The results from ten successive experiments carried out at a piston speed of 2.0 $10^3$ m/s and amplitude of $1.5 \times 10^2$ m are presented in Figure 6.6. It can be observed that
with each successive pass, the initial rate of build-up of pressure difference across the capillary progressively decreases. For the latter experiments, the differences in pressure traces are not very distinct from one experiment to the other. Another important observation is that the pressure fluctuations and maximum steady pressure difference also decrease in magnitude with each successive experiment. In the first pass, the pressure difference across the capillary increases up to 15.5 MPa in twenty-five seconds of flow and shows five pressure oscillations of the order of 1 MPa. The second, third and fourth passes also exhibit pressure differences of the order of 15.5 MPa and show four pressure oscillations of the order of 1 MPa. The subsequent six passes show pressure differences of the order of 14.5 MPa and show pressure oscillations of the order of 1 MPa.

As compared to the first pass, each of the successive passes shows a lower maximum steady pressure difference for the same apparent wall shear rate, during the build-up of pressure difference across the capillary. This could imply that the same polymer melt is flowing under a lower pressure difference during subsequent experiments for the same apparent wall shear rate. In the section of the pressure difference traces, showing a rapid build-up of pressure difference, the curves are more or less parallel to each other for all the single-pass experiments, indicating that the rate of pressure build-up is similar following the initial period of slower rate of pressure build-up. This
phenomenon of delay in build-up of pressure difference across the capillary in the initial
stages of capillary flow will be hence referred to as the *Delayed Pressure Build-up (DPB)*
effect. The salient feature of this pressure difference profile is that the polymer melt
flows through the capillary under a lower pressure difference during the initial flow
period and in the later period, the flow through the capillary is across a much greater
pressure difference.

In summary, the data obtained from experiments performed on the same sample
appears to change with successive single-pass experiments. The steady shear rheology of
POE shows a substantial dependence on its shear history. While certain trends such as
reduction in the final pressure difference across the capillary with successive passes are
reproducible, the nature of the pressure fluctuations observed is not consistent. These
pressure fluctuations tend to vary a great deal from one experiment to the other and it has
not been possible to characterise these pressure fluctuations or attribute them to a
discontinuity in the flow curve. This effect is similar to that observed by Hatzikiriakos
*et al.* (1998), who had to extrude multiple batches of m-LLDPEs before they could get a
stable pressure trace. In order to gain a better understanding of flow of the polymer melt
in this initial period where it exhibits the *DPB* effect, flow visualisation experiments have
been carried out using a slit geometry with the Optic Cell.

### 6.3 Flow Regimes of POE

A flow curve of POE was determined from single-pass experiments performed over a
range of shear rates. This flow curve is not totally representative of the flow of POE
because of the influence of shear history on the pressure build-up characteristics of POE.
A flow curve of POE (in terms of wall shear stress versus apparent wall shear rate) is
determined over a range of shear rates from 0.1 to 10,000 s\(^{-1}\) at a temperature of 170 \(^\circ\)C
using two capillaries, B and C (Figure 6.7). Although data from two different capillaries
are presented together, the Bagley end correction (see for e.g. Aklonis, 1983), which
would be different for different capillaries has not been carried out. This is because of the
ambiguity in determining the value of the final pressure difference, as explained earlier.
The apparent wall shear rates are also not corrected with the Rabinowitsch equation (see
for e.g. Dealy and Wissbrun, 1995).

This flow curve can be differentiated into two different flow regimes depending on
the absence or presence of the *Delayed Pressure Build-up (DPB)* effect. The first regime
can be seen at lower shear rates, where the pressure difference traces of repetitive single-
pass experiments do not appear to exhibit the DPB effect. The second regime is seen at higher shear rates, where POE exhibits the DPB effect.

![Flow curve for POE in terms of shear stress versus apparent shear rate obtained using two capillaries, B and C at T = 170 °C](image)

**Stable Flow** Regime

The change in pressure difference with time for a single-pass experiment carried out at a relatively low shear rate of 1.6 s⁻¹ using capillary B, is shown in Figure 6.8. The steady pressure difference obtained for this experiment is approximately 0.65 MPa. The pressure difference traces for four single-pass experiments carried out at a shear rate of 1.6 s⁻¹ are shown in Figure 6.9. It can be clearly observed that these pressure difference traces do not exhibit a significant DPB effect.

The pressure traces shown in Figure 6.9 do not seem to exhibit any significant pressure fluctuations. At these low pressures, the noise levels of the pressure traces are an order of magnitude lower than the magnitude of the actual pressure trace. Therefore it is difficult to identify and distinguish any genuine pressure fluctuations from noise in the pressure transducer readings. The level of noise can be detected from the pressure fluctuations observed during the initial three seconds of the experiment, when pistons have not begun moving. This regime of shear rates will be referred to as the **Stable flow** regime for POE and it extends approximately to a shear of 1.6 s⁻¹ at 170 °C. These pressure traces are similar to those obtained for the **Stable flow** regime of HDPE. The apparent wall shear stress corresponding to this shear rate is of the order of 33 kPa.
Figure 6.8: Series 6, Pressure difference profile in Stable flow regime for POE, $T = 170 \degree C$, capillary B, $v_p = 7.0 \times 10^4 \text{ m/s, A} = 1.7 \times 10^{-2} \text{ m}$

Figure 6.9: Series 6, Comparison of pressure difference profiles of four single-pass experiments for POE, $T = 170 \degree C$, capillary B, $v_p = 7.0 \times 10^4 \text{ m/s, A} = 1.7 \times 10^{-2} \text{ m}$

**Delayed Pressure build-up effect Regime**

Above a shear rate of $1.6 \text{ s}^{-1}$, POE exhibits the Delayed Pressure build-up effect and pressure difference traces are accompanied at times by pressure fluctuations of the order of magnitude of 1 MPa. Therefore, this flow regime is called the Delayed Pressure Build-up effect regime.

Unlike the Periodic Oscillations regime for HDPE, where the pressure traces oscillate with fixed amplitude over a certain range of shear rates, the pressure fluctuations of POE are erratic in nature and may be observed both during and after the build-up of pressure difference across the capillary.
The pressure traces obtained for shear rates higher than 2000 s\(^{-1}\) up to a shear rate of 5000 s\(^{-1}\) were reasonably smooth and did not exhibit the presence of fluctuations. Figure 6.10 shows the pressure difference trace for a single-pass experiment carried out at a shear rate of 3300 s\(^{-1}\), where the pressure difference across the capillary increases and reaches a maximum stable value of the order of 26 MPa. The pressure difference curve is smooth and does not show any fluctuations. The initial sharp increase in pressure (in a period less than 0.1 seconds) is due to an acceleration of the pistons when they start moving and can be observed for all polymer melts in the MPR. Following this period, the pistons start to move with the desired velocity and POE shows a DPB effect. Beyond an apparent wall shear rate of 5000 s\(^{-1}\), experiments could not be carried out using this capillary, because of the limitations in the accuracy of the movement of the pistons of the MPR.

It has been shown that POE does not show the DPB effect at lower shear rates. This effect is manifested when the wall shear stress is in excess of 33 kPa, as estimated from the flow curve. It may also be concluded from the pressure difference traces exhibiting the DPB effect (in say, Figure 6.6), that POE starts to slip at a pressure difference of 1.5 MPa, which corresponds to an approximate wall shear stress of 36 kPa. Under the assumption that the DPB effect observed for POE is associated with slip of POE at a critical wall shear stress, a new experimental protocol was used to independently ascertain the approximate wall shear stress at which POE starts to slip. In this protocol, POE melt within the MPR was not initially pressurised and a single-pass experiment was
carried out at a shear rate in the DPB regime. The pressure traces for a single-pass experiment performed for a piston velocity of $1.0 \times 10^4$ m/s is shown in Figure 6.11. In the first twelve seconds, after the pistons have started moving, the polymer melt in the system is slowly compressed. The pressure in the top barrel and the pressure difference across the capillary gradually increases to reach a value of approximately 1.1 MPa.

As the pistons move further, the pressure difference across the capillary starts to decrease indicating the onset of slip. This is followed by a rapid build-up of pressure difference to a value around 8 MPa. This experiment independently identifies the wall shear stress at which POE starts to exhibit the DPB effect to be of the order of 30 kPa. This value is comparable to the value of 33 kPa determined from the flow curve shown in Figure 6.7. Hence it may be suggested that the steady shear flow of POE may involve a stick-slip-stick transition in comparison to a stick-slip transition observed for HDPE. The mechanism behind the existence of the DPB effect could be slip and in order to investigate this mechanism, flow visualisation experiments were carried out for POE.

![Figure 6.11: Change of pressure in top and the bottom barrels of a MPR for a single-pass experiment performed at ambient pressure, capillary C, $T = 170 \, ^{\circ}C$, $v_p = 1.0 \times 10^4$ m/s; $A = 8.0 \times 10^{-3}$ m](image)

### 6.4 Flow visualisation Observations for POE

The flow behaviour of POE was studied using a slit geometry in the MPR with an experimental set-up similar to that used for carrying out flow birefringence measurements on HDPE (as described in chapter 2). However, minor modifications were made to this set-up and apart from flow birefringence experiments, where a polariser and an analyser are used, experiments were also carried out using unpolarised and plane polarised light
without an analyser. The conditions under which the flow visualisation experiments (Series 3) were performed are listed in Table 6.2.

In this section, results from flow visualisation experiments carried out at a piston velocity of $1.0 \times 10^{-1}$ m/s and an amplitude of $8.0 \times 10^{-1}$ m are presented. The flow visualisation experiments were carried out using all the three configurations described in Table 6.3. These experiments were recorded on a S-VHS cassette and individual pictures were captured using a video capture card. All the sets of flow visualisation pictures shown in this section will contain frames from the following time intervals: $t = 0$, $2.02$, $2.05$, $2.23$, $3.02$ and $4.00$ seconds.

Table 6.2: Experimental Conditions

<table>
<thead>
<tr>
<th>Slit geometry specifications</th>
<th>Temperature</th>
<th>170 °C</th>
</tr>
</thead>
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<tr>
<td>Slit Dimensions</td>
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<td></td>
</tr>
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<td>Depth (D)</td>
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<td></td>
</tr>
<tr>
<td>Length (L)</td>
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<td></td>
</tr>
<tr>
<td>Width (W)</td>
<td>$1.0 \times 10^{-3}$ m</td>
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</tr>
</tbody>
</table>

Table 6.3: Flow visualisation set-ups

<table>
<thead>
<tr>
<th>Experimental Set</th>
<th>Polariser</th>
<th>Analyser</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>×</td>
</tr>
<tr>
<td>2</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>3</td>
<td>√</td>
<td>√</td>
</tr>
</tbody>
</table>

6.4.1 Flow Visualisation – Plane Polarised Light

In the second experimental set-up, plane polarised light was passed through POE flowing in the slit and an analyser was not placed at the other end of the slit. As a result, flow birefringence patterns, which are formed by the interference of beams of plane polarised light converging at the analyser, cannot be observed. However, this flow set-up was used to detect any heterogeneity or differences in flow field that may arise due to shearing or other factors. The pictures obtained during the first four seconds of flow of POE at the entry and exit of the slit are shown in Figure 6.12. At the exit, it can be clearly seen that a continuous layer emerges from near the walls at the end of the slit, which subsequently settles along the sides at the slit exit. This layer is observed only during the initial few seconds of flow and the presence of this layer cannot be distinguished during entry flow.
Figure 6.12: Series 3, Flow visualisation using polarised light in Set-up 2

\[ T = 170 \, ^\circ\text{C}, \quad v_p = 1.0 \times 10^3 \, \text{m/s}, \quad \text{Slit}, \quad L = 1.2 \times 10^{-2} \, \text{m}, \quad W = 1.0 \times 10^{-1} \, \text{m}, \quad D = 1.0 \times 10^{-1} \, \text{m}. \]
This effect is clearly not visible when the flow observations were carried out using unpolarised light. The pictures captured for flow visualisation experiments using unpolarised light for POE at the entry, exit and along the length of the slit are shown in Figure 6.13. These pictures do not show any abnormalities in the flow through the slit and POE. This configuration does not provide any insight into the mechanism behind the DPB effect, although it does confirm that there is no obvious segregation of POE in the flow field.

A semi-schematic illustration of the emergence of this layer from the exit of the slit is shown in Figure 6.13. In this particular experiment, the time taken for the emergence of this layer is of the order of two seconds. A comparison of the length of the observed layer with the dimensions of the slit width indicates that the length of this layer could be of the order of a few millimetres. It is important to note that the DPB effect is observed during capillary flow experiments for a period of the order of a few seconds, under similar conditions of shear rate. The observation of this layer under plane polarised light could be an indication that polymer chains near the walls of the slit have a different orientation as compared to the chains present in the bulk of the slit.
Figure 6.13: Series 3, Flow visualisation in Set-up -1 using unpolarised light,
\[ T = 170^\circ \text{C}, \quad \nu_p = 1.0 \times 10^{-3} \text{ m/s}, \quad \text{Slit, } L = 1.2 \times 10^{-6} \text{ m}, \quad W = 1.0 \times 10^{-3} \text{ m}, \quad D = 1.0 \times 10^{-3} \text{ m}. \]
The Transient Flow and Processing of Polyolefin Elastomer
Figure 6.14: Semi-schematic illustration of the emergence of a layer at the exit of the slit for POE, 
$T = 170 \, ^{\circ}C$, $v_f = 1.0 \times 10^{-3} \, m/s$, Slit, $L = 1.2 \times 10^{-2} \, m$, $W = 1.0 \times 10^{-2} \, m$, $D = 1.0 \times 10^{-2} \, m$. 

The Transient Flow and Processing of Polyolefin Elastomer
6.4.2 Flow Birefringence Observations

Flow birefringence measurements were carried out for POE using the third experimental set-up described in Table 6.3. The fringe patterns at the entry and exit region of the slit are shown in Figure 6.15. The layer that is observed for the second experimental set-up, at the exit of the slit in Figure 6.12 can be seen here as a continuous black layer. This layer settles along the sides of the slit exit and cannot be clearly observed as it is obscured by the presence of fringes.

The first row of pictures shows POE at a state of rest in the slit. The next two pictures show polymer melt flowing through the slit. However, it is interesting to note that no fringes could be observed in the entry region, although the polymer melt was flowing through the slit. The corresponding fringes at the exit were also not very well defined. In the 4th, 5th and 6th rows, the fringes started to develop and propagated downstream along the length of the slit. Correspondingly, a layer could be seen to emerge from the exit of the slit.

The pressure difference profiles observed during capillary flow (see for e.g. Figure 6.6) in the DPB effect regime, indicates that POE is initially flowing under a much lower pressure difference. The absence of fringes in the initial few seconds could be an indication of flow under a lower pressure difference during the initial few seconds. The subsequent development of the fringe pattern in the slit could be an indication of a rapid increase in pressure difference across the slit. The initial absence of birefringence fringes in the entry region could be explained due to slip of the polymer at the entry of the slit, and the subsequent appearance of fringes could be explained due to the polymer sticking to the walls. The time for which a layer could be observed at the exit of the slit also coincided with the absence of fringes in the entry region. This layer will be referred to as a Wall slip layer.
Figure 6.15: Series 3, Flow birefringence observations on POE with Set-up 3, 
$T = 170 \, ^\circ \text{C}$, $v_p = 1.0 \times 10^{-3} \, \text{m/s}$, Slit, $L = 1.2 \times 10^{-2} \, \text{m}$, $W = 1.0 \times 10^{-1} \, \text{m}$, $D = 1.0 \times 10^{-1} \, \text{m}$
6.5 Characteristics of the DPB effect

In the previous section, the Delayed Pressure Build-up effect was observed for the steady shear of POE. In order to understand the DPB effect and to explore its characteristics, a range of experiments were carried out on POE using the MPR. The pressure traces obtained from experiments carried out in the DPB effect regime were compared in order to determine a master curve. Also, the stability of the DPB effect in time and when POE is subjected to oscillatory shearing is studied.

6.5.1 Determination of a Master Curve for the DPB effect

In the DPB effect, an initial slower rate of pressure build-up is followed by a rapid increase in the rate of pressure build-up. Consider a series (series 4) of single-pass experiments carried out over a range of piston velocities from $1.0 \times 10^4$ to $9.0 \times 10^7$ m/s (Figure 6.16). All these pressure difference profiles belong to the DPB effect regime. In this series, experiments were performed in the order of increasing piston velocity. With an increase in piston velocity, the time taken to reach the maximum steady pressure difference decreases, while the maximum steady pressure difference across the capillary increases.

![Figure 6.16 Series 4, Single-pass experiments carried out for a POE sample using capillary A, T = 180 °C, A = 8.0 \times 10^{-3} m](image)

Figure 6.16 Series 4, Single-pass experiments carried out for a POE sample using capillary A, T = 180 °C, A = 8.0 \times 10^{-3} m

In order to compare the traces from these experiments, the pressure difference values (obtained during the period where the pistons were moving) for each of these
experiments were normalised by their respective maximum steady pressure difference values. The time scale shown in the X-axis for each of these experiments were converted into a length scale by multiplying it with their respective piston velocities. The plot of normalised pressure difference ($\Delta P/\Delta P_{\text{max}}$) versus a length scale (i.e. time * piston velocity) is plotted in Figure 6.17. It can be seen that all the normalised pressure difference traces fall on a master curve. The two rates of build-up of pressure difference seen in Figure 6.17 can be differentiated using two linear approximations. It is difficult to attribute any physical meaning to the calculated length scale of 4.5 mm. This length scale may be related to the geometry of the capillary and further experiments need to be carried out to confirm this suggestion.

![Figure 6.17: Series 4, Master curve for DPB effect determined from pressure difference profiles of single-pass experiments plotted in Figure 6.16.](image)

In the flow visualisation experiments described in the previous section, a layer can be observed at the slit exit, which appears to have a length equal to a few millimetres. Therefore, it may be hypothesised that a layer of finite length (in the order of a few millimetres and named as the Wall slip layer) is formed near the entry of the capillary. The length of this layer will be referred to as the Wall slip layer length. Therefore, it may be concluded that the Wall slip layer length and the DPB effect appears to be independent of shear rate or time. All the pressure traces in the DPB effect appear to exhibit this effect to a similar extent irrespective of shear rate.
6.5.2 Long Term Stability of the Wall Slip layer

In order to investigate the stability of the DPB effect and Wall slip layer, a series (series 5) of single-pass experiments were carried out using capillary A at a piston velocity of $1.0 \times 10^3$ m/s. The pressure difference profiles for five different single-pass experiments which have carried out at a piston velocity of $6.0 \times 10^4$ m/s, over a period of two days are shown in Figure 6.18. The first pressure trace, which is identified by the legend 'pre' was obtained after the POE sample starts to exhibit the DPB effect. The pressure difference increases slowly and then rapidly builds up to reach a maximum value of 19 MPa. Following this experiment, the polymer system was cooled down to room temperature and allowed to rest overnight for sixteen hours. Then the system temperature was raised again to 180 °C and the ambient pressure in the system was raised to 3 MPa. Further single-pass experiments, (denoted by prefix 'post') were carried out. The first single-pass experiment carried out following this rest period does not exhibit the same magnitude of DPB effect as compared to the 'pre' pressure difference profile. However, the three subsequent experiments exhibit the DPB effect to the same extent as seen for the 'pre' experiment.

![Figure 6.18: Series 5, Comparison of the pressure difference profiles of single-pass experiments carried out for a POE sample over a period of 16 hours, $T = 180^\circ\text{C}$, $v_p = 6.0 \times 10^4$ m/s, $A = 8.0 \times 10^{-3}$ m](image)

In summary, by allowing the system to rest for a long period (as compared to the period of a single-pass experiment) reduces the magnitude of the DPB effect to a certain extent. However, on resumption of shearing, the system rapidly reverts back to its original state and exhibits DPB effect to the same extent as seen for the first experiment.
This series of experiments indicates with reasonable confidence that a POE sample, which was modified by repeated shearing, remains reasonably stable over a long period of time despite solidification of the melt and its subsequent melting.

### 6.5.3 Reversal of DPB Effect Using Oscillatory Shearing Conditions

In order to support the hypothesis about the existence of a *Wall slip layer*, another series (series 6) of experiments was performed using the MPR. All the experiments in this series were performed using capillary C at a temperature of 170 °C. The piston velocity was set at 1.0 \(10^{-3}\) m/s (corresponding to an apparent shear rate of 1152 s\(^{-1}\)) and amplitude of the piston stroke is 1.0 \(10^{-2}\) m. The pressure difference traces for the 6\(^{th}\), 8\(^{th}\), 12\(^{th}\) and 14\(^{th}\) pass of this series are shown in Figure 6.19.

![Figure 6.19: Series 6, Effect of high frequency shearing on pressure difference profiles seen for POE, \(T = 180 \, ^\circ\text{C}, v_p = 6.0 \times 10^{-4} \, \text{m/s}, A = 8.0 \times 10^{-3} \, \text{m}\)](image)

The pressure difference trace of the 6\(^{th}\) pass exhibits the *DPB* effect. After the 6\(^{th}\) pass, the POE sample is subjected to continuous shearing in a multipass mode with a piston velocity of 2.0 \(10^{-2}\) m/s and an amplitude of 2.0 \(10^{-3}\) m. This corresponds to a shear rate of magnitude 20,000 s\(^{-1}\), which is twenty times higher than the shear rate of the earlier single-pass experiment. The sample was sheared at this high shear rate for a period of 500 seconds, which was chosen arbitrarily. Following this, another single-pass (8\(^{th}\)) experiment was carried out under similar shearing conditions as that of the 6\(^{th}\) pass. It can be seen that the pressure trace of the 8\(^{th}\) pass does not exhibit the *DPB* effect any more. Also, the value of the final pressure difference obtained was of the order of 10.5 MPa as compared to 9.5 MPa, obtained for the 6\(^{th}\) pass. Therefore, it appears that the *DPB* effect
has been eliminated and the delay in pressure build-up coupled with a reduction in final steady pressure difference cannot be observed. Further single-pass experiments (12th and 14th pass) were carried out in the same assembly and the pressure difference traces from these experiments progressively show an increase in the DPB effect coupled with a gradual decrease in the final value of pressure difference across the capillary.

This series of experiments supports the earlier proposed hypothesis about the existence of a Wall slip layer and may be interpreted as follows. The Wall slip layer develops along the walls of the capillary during successive single-pass experiments and is accompanied by the DPB effect. When a POE sample in the capillary is subjected to rapid shearing in alternating directions, the Wall slip layer is disturbed. The following single-pass experiments do not exhibit the DPB effect. However, the Wall slip layer again builds up along the walls of the capillary and the latter single-pass experiments show a gradual increment of the DPB effect. In summary, subjecting POE to oscillatory shearing at very high shear rates can reverse the DPB effect.

### 6.6 Hypothesis for Delayed pressure build-up effect

The following details on the rheology of POE can be inferred from the experiments described above.

- The build-up of pressure is delayed with each successive single-pass experiments through the same capillary (Figure 6.6), leading to the conclusion that shear history of POE has a significant effect in altering the rate of pressure difference build-up before it eventually reaches a steady state.

- In the initial period of subsequent single-pass experiments, POE flows under a lower pressure difference as compared to the first pass and this could be an indication of the presence of slip in the system. If POE is indeed slipping in the initial period, then following that period it sticks again and the pressure difference builds up rapidly. Hence, for the initial period of the piston stroke there must be some factor altering the flow of POE, and following the initial period, this factor no longer has an effect on the flow.

- From the flow visualisation experiments, it may be concluded that over a certain length of the slit, the POE melt near the walls of the slit has a different orientation as compared to its bulk. This material near the walls emerges from the slit during the initial period of the single-pass experiment only, and it settles down along the walls at the exit of the slit. This material is referred to as the Wall slip layer. It may be
concluded from flow birefringence observations that POE may be slipping during the initial few seconds of flow, which is consistent with the observations of the pressure difference profiles obtained in capillary flow.

From all these experimental results shown above, a number of questions emerge such as

What is the Wall slip layer made up of?

There are two possibilities to explain the composition of the Wall slip layer.

1. One possible explanation is that a gel fraction comprising of higher molecular weight chains has accumulated near the entrance of the capillary. The Wall slip layer can be considered to be reasonably stable from the experiments shown in section 6.5.2 and 6.5.3. The stability of the layer over long rest periods and its rapid regeneration after shearing at high shear rates supports the gel fraction theory. When POE is not flowing, the flow field observed using plane polarised light is very homogeneous and this layer can be distinguished only when there is flow in the system. However, one of the main features of this polymer is that it has a narrow molecular weight distribution. So the formation of a gel fraction composed of higher molecular weight fractions of the melt does not seem very feasible.

2. The second possibility is that the layer could be composed of a fraction of POE (may also include unreacted side chains) having a lower MW than the rest of the system. Again, it may be argued that POE being a polymer with a narrow MWD, the differences in the MW of the chains may not significant. If the separation of the polymer into different weight fractions is the main factor leading to the formation of this layer and its associated effects, then it would be expected that a polymer such as HDPE should also display such effects and because of its higher MWD, these effects would be further enhanced. But HDPE does not show the DPB effect.

The extrusion of a blend of a polyethylene such as HDPE with a fluorooelastomer (FE) has been studied by a number of researchers (see for e.g. Rudin et al., 1990, Kazatchkov et al., 1995 and Xing et al., 1996b). It was observed that the addition of FE to a polyethylene melt in concentrations of the order of 500 ppm, led to a reduction in the apparent melt viscosity and delayed the onset of instabilities to much higher shear rates. This phenomenon was attributed to the migration of FE molecules to the walls of the die to form a new bulk polymer/wall interface. It was hypothesised that
the velocity of the melt in the die changes from a parabolic type profile to a more blunt, plug-flow like profile because of the lubricating nature of the polymer/wall interface, which leads to a reduction in the pressure difference across the die. A similar mechanism could be happening during the flow of POE, where a very low molecular weight fraction of POE could migrate towards the surface and form a layer at the wall. Because of its narrow MWD, this fraction could be very small and comparable with FE concentration of 500 ppm.

**What is the slip mechanism?**

In comparison to POE, the flow curve of HDPE is discontinuous in nature and the pressure traces for a range of shear rates in the stick-slip regime are accompanied by periodic pressure fluctuations. This transition was suggested to occur because of an effect called as the coil-stretch transition (Brochard and de Gennes, 1992), resulting in a slip of the bulk polymer chains at the interface of chains, adsorbed to the metal walls, producing a discontinuity in the flow curve.

The stick-slip transition has been extensively studied by researchers (see for e.g. Piau et al., 1995 and Wang and Drda, 1997), using both metal dies and metal dies coated with a FE. They reported that the Stick-slip transition was shifted to a lower wall shear stress, when the experiments were performed in a FE coated metal die. In order to explain this effect, Wang and Drda (1997) have proposed the following hypothesis. The FE coating at the die walls forms a weakly adsorbing surface of low energy. Therefore, the chains of polymer melt at the surface of FE coating are weakly adsorbed onto this layer. Hence with a small increase in the stress, the weakly adsorbed chains desorb and slip across the FE wall resulting in slip at the wall-polymer interface.

In contrast, for a metal die, there is a stationary layer of polymer chains strongly adsorbed onto the metal walls. Here, above a critical stress, the bulk polymer chains disentangle from the polymer layer at the wall, resulting in slip at a polymer/polymer interface. The pressure trace of obtained for POE during the initial period of the DPB effect is similar to that obtained for slip of the melt at the FE/polymer interface, suggesting that the wall slip layer may not strongly entangled with the layer of POE adsorbed at the metal wall. But the most striking fact about the flow of POE is the subsequent sticking, characterised by an increase in the pressure difference, which is in contrast to the flow of a polymer melt through a die coated with a FE.
The following mechanism is proposed to explain the delayed pressure build-up taking into consideration the experimental results described in the earlier section and the theories proposed in literature. A schematic illustration of this hypothesis is provided in Figure 6.20. When POE is loaded in the MPR, a layer of POE chains adsorbs strongly on the metal surface of the capillary. The bulk polymer chains are strongly entangled with the polymer chains adsorbed at the surface. The no-slip boundary condition is satisfied and the flow of POE is similar to the flow of HDPE in a stable flow regime.

With successive single-pass experiments, the direction of the piston stroke is reversed. The POE being highly viscous, the capillary flows are at very low Reynolds numbers, i.e., flow is laminar (e.g., a shear rate of 1000 s⁻¹ in this geometry corresponds to a Re < 10). Hence, it can be assumed that the same material which was displaced during one downward stroke is pushed upwards to its initial position with the following upward stroke (of the same amplitude) because of the absence of inertial effects. Since the DPB effect seems to be enhanced with shear, it may be assumed that with increased shearing, there is a layer of POE accumulating at the wall which may be different from the bulk in terms of its molecular weight and orientation. This layer, which is referred to as the Wall slip layer, may be formed at the walls of the capillary in the entry region, where the stresses are higher than the rest of the capillary. The Wall slip layer could be weakly entangling with both the bulk of POE and the stationary POE layer at the die wall. This segregation effect could be enhanced by repeatedly shearing POE and the Wall slip layer starts to accumulate in the capillary.

At very low wall shear stresses (say < 30 kPa), the segregated layer does not slip over the stationary polymer layer at the die wall. When the stresses exceed 30 kPa, slip occurs at the interface between the segregated layer and the stationary polymer layer at the wall due to disentanglement of polymer chains in the Wall slip layer. This leads to a flow of POE over a lower pressure difference across the capillary. This layer slips in the entry region and moves down along the length of the slit. When this volume of melt emerges at the slit exit, the Wall slip layer can be discerned from the bulk using polarised light.

Subsequently, the molten POE in the barrel (which does not show segregation) enters the neck of the capillary. This stationary polymer layer at the wall is strongly entangled with this volume of POE. As the pressure difference across the capillary is very small, the flow rate of the melt through the capillary is very low as compared to the
rate of piston displacement in the barrel. This in turn leads to a rapid build-up of pressure
difference across the capillary (the rate of which is governed by melt compressibility)
resulting in an increase in the flow rate of POE through the capillary to reach steady state
giving a stable value of pressure difference across the capillary.

This phenomenon is repeated at the other end of the capillary when the pistons
move in the opposite direction displacing the *Wall slip layer* back to its initial position. It
can be seen from Figure 6.6, that the *DPB* effect gradually increases in with each
successive pass to reach a steady state, leading to the suggestion that repeated shearing of
the system results in the formation and build-up of the *Wall slip layer*.
Initially, the polymer chains are adsorbed to the walls of the capillary and entangled with the chains in the bulk.

On shearing, the polymer chains in the bulk remain entangled with the chains adsorbed on the walls.

On repeated shearing, certain type polymer chains are segregated near the walls.

At low stresses, the segregated layer near the walls remains entangled with the chains adsorbed at the walls.

When stresses > 30 kPa, the layer disentangles from chains adsorbed at the wall causing the DPB effect.

When the layer exits the slit, the new polymer chains get entangled with the chains adsorbed at the walls, leading to a build-up of pressure.

Figure 6.20: Schematic diagram illustrating the hypothesis proposed to describe the flow of POE during steady shear flow and during the Delayed Pressure Build-up effect.
6.7 Summary and Conclusions

The flow behaviour of POE melt was studied over a range of shear rates using three different capillaries. The pressure build-up during a single-pass experiment was found to be dependent on the shear history of the melt for shear rates above 1.6 s\(^{-1}\). The flow of POE shows an initial lower apparent viscosity followed by a rapid increase in apparent viscosity during a single-pass experiment, which is referred to as the Delayed pressure build-up effect. The flow visualisation experiments reveal the presence of layer at the exit of the slit, which has a different orientation to the bulk of the melt and is referred to as a Wall slip layer. The pressure difference profiles of experiments carried out in the DPB effect regime lie on a master curve indicating that the DPB effect is independent of time or shear rate at which the experiment has been carried out. The time for which the DPB effect is observed has been shown to be a function of piston displacement velocity. Finally a hypothesis was proposed to explain the occurrence of the DPB effect.

The experimental results obtained and the proposed hypothesis seem to suggest that the flow of POE at higher shear rates is characterised by slip above a critical wall shear stress (of the order of 30 kPa) for a certain length, followed by an increase in the pressure difference (or sticking) of melt. In comparison, the flow of HDPE through a capillary is characterised by initial sticking and then undergoes a transition to a slip state at a critical wall shear stress, leading to a discontinuity in the flow curve. This discontinuity gives rise to periodic pressure oscillations for a range of shear rates. Some of the pressure traces for POE also show pressure fluctuations, although these fluctuations are not very regular or reproducible.

Therefore, the flow of POE through a capillary may be a combination of polymer/polymer interactions near the wall between two different types of polymer chains. The first type of chain is a weakly entangling polymer, which remains entangled to the stationary polymer layer (adsorbed at the metal wall) for very low wall shear stresses (up to 30 kPa). An increase in the wall shear stress results in slip due to disentanglement, leading to flow at low pressure differences or lowered apparent viscosities. The second type of chain is more strongly entangled with the POE chains adsorbed to the metal wall. Therefore, it does not disentangle from the stationary polymer layer at the wall at low wall shear stresses. This leads to flow of the polymer at higher pressure differences across the capillary and a higher apparent viscosity. In comparison to HDPE, where capillary flow above a certain critical shear rate is characterised by a stick
slip transition, POE appears to undergoes a stick-slip transition above a certain critical shear rate followed by a slip-stick transition.

In conclusion, there are a number of aspects which have not been resolved about the flow of POE, when it exhibits the Delayed pressure build-up effect and the nature of the Wall slip layer seen during flow visualisation experiments. The results from various experiments have helped in gaining a better insight into the nature of the Delayed pressure build-up effect and to explore its characteristics. The time dependent flow behaviour of POE appears to be influenced by its shear history and therefore cannot be predicted using the model developed in Chapter 5. In this model, the kinetics of pressure build-up and relaxation of the polymer melt are predicted using the steady state flow curve and melt compressibility.

The ability of the MPR to repeatedly shear the same sample volume has been very advantageous in the study of POE and many of the characteristics determined about the rheology of POE would not have emerged if a conventional rheometer had been used.
7. Transient Flow and Processing of Linear Low Density Polyethylene

In this chapter, a review of literature about the transient flow and flow instabilities observed for LLDPE are covered. In particular, the phenomenon of and the proposed mechanisms behind the presence of small-scale surface defects are covered. The experimental results obtained for the steady shear flow of LLDPE in the MPR are then presented. A flow curve was determined from steady shear capillary experiments and is characterized by a significant change in slope. Also, for a small range of shear rates, the time dependent pressure difference profiles exhibited fluctuations. Further, flow birefringence experiments were carried out for LLDPE for a similar range of shear rates. The results from the experiments carried out for LLDPE are also compared with those obtained for HDPE and POE.

7.1 Transient Flow and Melt Flow Instabilities in LLDPE

Linear Low Density Polyethylene (LLDPE) was developed in the late seventies as an alternative to Low Density Polyethylene (LDPE) because it is a low-pressure process and offers improved end properties (Rosen, 1993). LLDPE has been shown to be a heterogeneous polymer blend consisting of linear polyethylene chains and ethylene-\(\alpha\)-olefin copolymer chains with short chain branching (SCB), where its rheological properties are dependent on its composition (Munstedt et al., 1998). LLDPE is increasingly used in film blowing applications and other conventional applications of LDPE. The production rates of LLDPE, however, are hampered by the appearance of surface defects at high shear rates (see for e.g. Constantin, 1984, Sornberger et al., 1987 and Xing and Schreiber, 1996a).

Constantin (1984) and Sornberger et al. (1987) have studied the change in extrudate characteristics of LLDPEs of different molecular weights with increasing shear rates. They observed that the extrusion of higher MW LLDPEs showed four flow regimes with increasing shear rates. These include a Stable Flow regime, which shows smooth extrudates followed by the SSSD regime showing extrudates with small-scale surface
Transient Flow and Processing of Linear Low Density Polyethylene

defects (SSSD) (see for e.g. Kurtz, 1984). This regime was followed by the stick-slip regime, where the extrudate showed alternate smooth and rough patches and the flow curve was discontinuous in nature. Finally, this LLDPE also showed a Gross Melt Fracture regime, where the distortion of extrudates was more severe. In comparison, LLDPEs with lower MW did not show the stick-slip regime. They initially exhibited a Stable Flow regime with smooth extrudates followed by a SSSD regime. This was directly followed by the Gross Melt Fracture regime. Somberger et al. (1987) also carried out flow birefringence measurements for LLDPEs. They observed that the birefringence patterns obtained for Stable Flow and SSSD regimes did not show any qualitative differences. In the case of some LLDPEs, a second stick-slip regime could also be observed at very high shear rates, which results in an extremely severe distortion of the extrudate as compared to the first stick-slip transition (Wang et al., 1996b). Ramamurthy (1986) and Kalika and Denn (1987) reported two critical shear stresses for LLDPE; one for the onset of SSSD regime and another for the onset of gross distortion. Hatzikiriakos and Dealy (1993) observed that LLDPE extrudates show SSSD in the range of wall shear stresses between 0.18 MPa 0.25 MPa at 180 °C. They observed the stick-slip regime for a range of wall shear stresses between 0.35 - 0.4 MPa. Kurtz (1992) observed that the frequency of SSSD ranged from 10 Hz for high MW LLDPEs at low shear stress conditions to over 400 Hz for low MW during high shear stress conditions.

Along with the flow regimes and extrudate distortions, a unique feature could be observed during the steady shear flow of LLDPE. The slope of the apparent flow curve (log-log plot of apparent shear rate and wall shear stress) shows a sharp change for the onset of SSSD (see for e.g. Kurtz, 1984, Ramamurthy, 1986, Kalika and Denn, 1987, Wang et al., 1996b). Ramamurthy (1986) carried out the Mooney analysis for LLDPE capillary flow data and reported that the onset of non-zero slip velocity coincided with the onset of SSSD and a sharp change in slope of the flow curve.

7.1.1 Processibility of LLDPEs

Extrusion of LLDPE through a fluoroelastomer (FE) coated die improved its processibility by eliminating SSSD (see for e.g. Hatzikiriakos and Dealy, 1993, Hatzikiriakos et al., 1995, Piau et al., 1995 and Rutgers, 1998). The most commonly used FEs were Teflon, Viton (from Dupont) and Dynamar (from 3M). Wang and Drda (1997) observed that
LLDPEs, which exhibited a *stick-slip* transition during extrusion through a metal die, underwent the same transition at a lower critical wall shear stress when extruded through a FE coated die. It was also reported that SSSD were suppressed during extrusion through a die when it was coated with FE individually at the die exit (Wang et al., 1996b) and the die entry region (see for e.g. Moynihan et al., 1990). Moynihan et al. (1990) have suggested that such an observation could be attributed to the migration of the FE from the entry region to the die exit.

Xing and Schreiber (1996a) suggested that FEs, which were blended into LLDPE, improved their processibility at high shear rates by reducing the apparent melt viscosity. Rudin et al. (1990) observed that the benefits of adding FEs to LLDPE became apparent only after finite periods of extrusion. They propose that FEs delay the onset of flow instabilities by migrating to the die walls and act as a die lubricant rather than an adhesion promoter between the flowing melt and die wall.

Wang et al. (1996b) reported that when a FE coating was applied in the die, the sharp change of the slope of the flow curve remained, while SSSD of the extrudate were eliminated. They concluded that the slope change was influenced by events occurring over a finite region near the die exit, whereas SSSD was a result of a free surface instability originating exactly at the die exit.

### 7.1.2 Effect of Die Length, Diameter and L/D Ratio

The effect of die diameter on the flow curve of LLDPE has been studied to establish the presence of slip in the die. Ramamurthy (1986) and Hatzikiriakos and Dealy (1995) observed that the flow curves of LLDPE obtained using dies of different diameters were a function of die diameter above a certain shear rate, which was observed for HDPE. On the other hand, Wang et al. (1996b) did not observe a diameter dependence of the flow curves of LLDPE. Kurtz (1992) observed that the frequencies of the SSSDs were unaffected by die diameter, although the depth of these distortions was found to be a strong function of die diameter.

Moynihan et al. (1990) and Xing and Schreiber (1996a) observed that for LLDPEs, SSSD appeared in a capillary die at higher shear rates, with an increase in the L/D ratio of the capillary. Somberger et al. (1987) also observed that SSSD evolved into a *stick-slip* effect at higher shear rates with an increase in the L/D ratio of the capillary. Moynihan et
al. (1990) believed that SSSD was affected by the die entry region and therefore was observed at higher shear rates with an increase in the L/D ratio of the capillary. He also reported that an increase in die gap for slit dies led to more severe SSSD for the same shear stress for LLDPE. This was attributed to an increased bulk velocity and acceleration of LLDPE in the die.

### 7.1.3 Mechanisms of Instability

A number of mechanisms were proposed to describe the instability causing SSSD and the origin of the sharp change of slope of the flow curve of LLDPE. Most of these explanations were centred on the die exit effect. In order to explain the presence of SSSD, many researchers have suggested that the polymer extrudates fracture at the die exit due to an abrupt change in boundary conditions. This change in boundary condition could lead to high stretching rates, which exceed the melt strength and result in fractured extrudates (see for e.g. Cogswell, 1977 and Kurtz, 1984, Moynihan et al., 1990). Another theory proposed that the change of slope and the onset of SSSD was due to an adhesive failure at the polymer-metal wall interface in the die land region (see for e.g. Ramamurthy, 1986, Kalika and Denn, 1987). El Kissi and Piau (1994) also support the theory that SSSD are initiated in the die exit region. In their studies, they found no evidence of wall slip in the die at the onset of SSSD, after the flow curves were corrected for entrance pressure losses and for the pressure dependence of viscosity.

Kurtz (1992) postulated that SSSD was a result of a stick-slip transition occurring at the exit corner of the die, because he detected a rapid stretching of the extrudate surface as it left the die using a high-speed video camera. Wang et al. (1996b) extended the theory of Kurtz (1992) and proposed that an unsteady boundary condition at the die exit resulted in the presence of SSSD for polymer melts such as LLDPE. They suggested that a local coil-stretch transition (Brochard and de Gennes, 1992) of the polymer chains adsorbed at the die exit caused the polymer to leave the die either in a stick state or a slip state causing a high frequency, small scale extrudate distortion or SSSD.

Wang et al. (1996b) have suggested that the sharp slope change of the flow curve of LLDPE could be a combination of partial slip in the die exit region and due to a reduction of effective viscosity in the die entry region, arising from the alignment of polymer chains. Wang and Drda (1997) reported that the sharp change in the slope of the
flow curve of LLDPE was independent of die diameter and have proposed that the presence of this slope change cannot be just a simple interfacial slip phenomenon as suggested by Ramamurthy (1986).

Tremblay (1991) and Dhori et al. (1997) proposed other mechanisms. Tremblay (1991) carried out a numerical analysis of the flow of LLDPE melt at the die exit. His calculations showed that a large negative pressure (hydrostatic tension) exists at the die exit and leads to cavitation of the polymer melt close to the die exit, resulting in interfacial failure and SSSD. Dhori et al. (1997) have proposed that SSSD could be attributed to the wetting properties of the die surface at the exit corner and not due to the exceeding of a critical stress inside the die.

### 7.1.4 Summary of Literature Review

The main features observed in the capillary flow of LLDPE are the presence of five flow regimes in general, including a SSSD regime and a stick-slip regime (see for e.g. Somberger et al., 1987). The onset of SSSD coincided with a sharp change in slope of the steady shear flow curve of LLDPE (see for e.g. Ramamurthy, 1986). The SSSD observed for LLDPE extrudates were eliminated when the walls of the die were coated with a FE (Xing and Schreiber, 1996a).

Ramamurthy (1986) and Kalika and Denn (1987) have attributed the presence of SSSD and the change in the slope of the flow curve to slip of polymer melt at the metal interface. They have reached these conclusions by carrying out Mooney analysis, which indicated a finite slip velocity in the die. On the other hand many researchers (see for e.g. Kurtz, 1984, 1992, Piau et al., 1995, Wang and Drda, 1996a) believe that SSSD and the slope change are due a change in the boundary condition at the die exit. Above a critical shear stress, this results in acceleration and stretching of polymer chains, leading to melt fracture and SSSD. Wang and Drda (1995, 1996a) have proposed that a chain entanglement-disentanglement of polymer chains (coil-stretch transition) near the walls of the die leads to a stick-slip transition resulting in a discontinuous flow curve for polymer melts such as HDPE and LLDPE. They have proposed a similar mechanism, i.e. a local entanglement-disentanglement of the polymer chains at the die exit, leads to SSSD.
7.2 Experimental Section

Although, the MPR does not provide extrudates, it is still an excellent instrument to study the steady shear rheology of LLDPE. This is because of the absence of a free surface in the MPR. As a result, it is possible to gain further insight into the origin of SSSD and slope change of the flow curve of LLDPE. The details of the experimental conditions and the results obtained for LLDPE using a MPR are presented in this section.

The experimental results obtained using a capillary geometry and complementary optical observations carried out using a slit geometry are presented. The conditions under which experiments have been carried out and the dimensions of the capillary and slit geometry are listed in Table 7.1. The capillary flow experiments were obtained at 180 °C, while the slit flow measurements were performed at 170 °C. Also, the system pressure was maintained at 3 MPa before the start of all the experiments.

<table>
<thead>
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<th>Table 7.1: Experimental Conditions</th>
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<td>Polymer</td>
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<td>Temperature of study</td>
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<td>Capillary geometry dimensions</td>
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<td>Slit geometry dimensions</td>
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The steady shear flow of LLDPE was studied over a range of shear rates in a capillary geometry with the pistons moving in a single-pass mode. The change in pressure difference across the capillary or slit with time were measured, both when the pistons were moving and when they had stopped moving. Flow birefringence observations on LLDPE were carried out in a similar manner as described for HDPE and POE. The flow birefringence observations were recorded on an S-VHS tape and individual pictures were obtained using image capture software and appropriate video capture card.

7.3 Experimental Results - Capillary Geometry

Single-pass experiments were carried out using the 1 mm diameter capillary for a range of piston velocities from 1.0 * 10^{-4} m/s to 1.0 * 10^{-2} m/s (apparent shear rate of 100 - 10,000 s^{-1}) at 180 °C. The results from these experiments were collected and used to determine the experimental flow curve of LLDPE, as shown in Figure 7.1. The error bars shown in the flow curve are of the order of 5 %. The corresponding wall shear stress and apparent shear rate are shown in the second Y and X axes respectively.
The flow curve is characterised by a significant change in slope of the curve around a piston velocity of $6.5 \times 10^{-4}$ m/s, which corresponds to an apparent wall shear rate of 750 s$^{-1}$. The change in the slope of the flow curve is a well-reported phenomenon for LLDPEs and is believed to coincide with the onset of SSSD during extrusion (see for e.g. Ramamurthy, 1986). The flow curve can also be divided into three flow regimes, which were identified from the time dependent pressure traces. These flow regimes are the **Stable Flow regime**, the **Pressure Fluctuations regime** and **High Velocity regime**. The pressure difference traces from the **Stable Flow regime** and **High Velocity regime** for LLDPE are similar to those obtained for HDPE in identically named flow regimes.

![Graph showing shear rate vs pressure difference](image)

**Figure 7.1:** Steady shear flow curve of LLDPE determined from single-pass experiments carried out in the MPR, $T = 180\,^\circ$C, capillary, $L = 1.0 \times 10^{-5}$ m, $D = 1.0 \times 10^{-3}$ m, Half Entry angle = 45$^\circ$

### Stable Flow regime

In this flow regime, the pressure difference across the capillary builds up to reach a steady value similar to the one obtained for HDPE in the **Stable flow regime**. The pressure difference profile for a single-pass experiment carried out at a piston velocity of $8.0 \times 10^{-5}$ m/s (apparent wall shear rate of 92.0 s$^{-1}$) is shown in Figure 7.2.
The pressure difference across the capillary rapidly builds up and reaches a steady value of 6.9 MPa. When the pistons stop moving, the pressure difference across the capillary undergoes relaxation due to pressure equalisation between the two barrels.

- **Pressure Fluctuations regime**
  
  In this regime, the pressure difference across the capillary builds up to reach a certain value and shows small pressure fluctuations about this value. The pressure difference profile for a single-pass experiment carried out at a piston velocity of $2.5 \times 10^{-4}$ m/s is shown in Figure 7.3. As the piston starts moving, the pressure difference rapidly builds up to reach a steady value of 11 MPa. However, a few small pressure fluctuations of the order of 0.5 MPa can be observed at this pressure difference. These fluctuations are not periodic and can be sporadically observed for a range of shear rates between 250 - 600 s$^{-1}$. The presence of these fluctuations could be an indication of a discontinuity in the flow curve, which is much smaller than that observed for the flow curve of HDPE.

- **High Velocity regime**
  
  In this flow regime, which is observed for higher piston velocities, the pressure difference across the capillary increases to reach a steady value and is similar to the pressure traces observed in the Stable Flow regime. The pressure difference profile obtained for a single-pass experiment carried at a shear rate of 11520 s$^{-1}$ is shown in Figure 7.4. The pressure difference across the capillary increases rapidly and reaches a steady value of 27.5 MPa. The pressure difference profile obtained is smooth and similar to that obtained in the Stable Flow regime.

  In summary, the pressure difference traces obtained for LLDPE over a range of shear rates tend to be smooth and regular, except for a small range of shear rates where the pressure traces show small non-periodic fluctuations.
Figure 7.2: A pressure difference profile in the Stable Flow regime for LLDPE in the MPR.
T = 180 °C, capillary, L = 1.0 \times 10^{-2} \text{ m}, D = 1.0 \times 10^{-3} \text{ m}, \text{Half Entry angle}=45^\circ, v_p=8.0 \times 10^{-5} \text{ m/s}, A=3.0 \times 10^{-3} \text{ m}

Figure 7.3: A pressure difference profile in the Pressure Fluctuations regime for LLDPE in the MPR.
T = 180 °C, capillary, L = 1.0 \times 10^{-2} \text{ m}, D = 1.0 \times 10^{-3} \text{ m}, \text{Half Entry angle}=45^\circ, v_p=2.5 \times 10^{-4} \text{ m/s}, A=3.0 \times 10^{-3} \text{ m}
7.3.1 Characteristics of Pressure Build-up of LLDPE

The pressure difference profiles from three successive single-pass experiments (pass numbers three, four and five) carried out on the same sample of LLDPE are shown in Figure 7.5. The rest time between each of these experiments is of the order of thirty seconds, which is also the time required to set up the next experiment. The time taken to reach a steady pressure difference is marginally slower for the second and third pass, as compared to the first pass. However, the values of the steady pressure difference are similar for all three single-pass experiments. This could be an indication of the presence of the Delayed pressure Build-up (DPB) effect in LLDPE. Unlike POE, in the case of LLDPE, this effect is not very pronounced. The pressure difference traces of LLDPE do not appear to be greatly influenced by its shear history and the delay in the build up of pressure differences profiles in Figure 7.5 of the order of 100 milliseconds.

For purposes of comparison, three pressure difference profiles obtained by repeating single-pass experiments on the same sample of HDPE are shown in Figure 7.6. It can be observed that the pressure traces are fully reproducible and do not exhibit any presence of the DPB effect.
Figure 7.5: A Comparison of the pressure difference profiles of three single-pass experiments for LLDPE, $T=180\, ^\circ C$, capillary, $L=1.0 \times 10^{-2} \, m$, $D=1.0 \times 10^{-1} \, m$, Half Entry angle=45°, $v_p=2.0 \times 10^{-2} \, m/s$, $A=1.5 \times 10^{-2} \, m$.

Figure 7.6: Comparison of pressure difference profiles from three single-pass experiments for HDPE, $T=180\, ^\circ C$, capillary, $L=1.0 \times 10^{-2} \, m$, $D=1.0 \times 10^{-1} \, m$, Half Entry angle=45°, $v_p=3.0 \times 10^{-3} \, m/s$, $A=1.5 \times 10^{-2} \, m$. 

7.4 Flow Birefringence Results

In this section, the results from flow birefringence experiments carried out on LLDPE are presented. These experiments were carried out between a range of shear rates from 1.0-1000 s\(^{-1}\). For purposes of comparison, two pictures from flow birefringence experiments carried out at two widely different shear rates are shown in Figure 7.7 and Figure 7.8. These pictures show the fringes over one-third the length of the slit both in the entry and exit region. The fringe pattern obtained for the flow birefringence experiment carried out at a piston velocity of 1.0 \(10^4\) m/s are shown in Figure 7.7. This fringe pattern has good clarity and is well developed in the entry and exit region similar to the observations of Somberger et al. (1987). The fringes develop at the corners of the slit entry region and become parallel to the slit walls.

![Figure 7.7: A Flow birefringence fringe pattern obtained for LLDPE, T = 170 °C, slit, L = 1.2 \(10^2\) m, W = 1.0 \(10^{-2}\) m, D = 1.0 \(10^{-2}\) m, vp = 1.0 \(10^2\) m/s, A = 5.0 \(10^3\) m](image)

![Figure 7.8: A Flow birefringence fringe pattern obtained for LLDPE, T = 170 °C, slit, L = 1.2 \(10^2\) m, W = 1.0 \(10^{-2}\) m, D = 1.0 \(10^{-2}\) m, vp = 1.0 \(10^2\) m/s, A = 5.0 \(10^3\) m](image)

The birefringence pattern obtained for an experiment carried out at a piston velocity of 1.0 \(10^{-2}\) m/s is shown in Figure 7.8. The fringes were more abundant as compared to the pattern in Figure 7.7, which is expected as the flow rate in this case is
approximately one hundred times higher than that for Figure 7.7. The fringe pattern is well defined in the entry and exit region, but the fringes cannot be resolved along the length of the slit, particularly near the walls of the slit. The entire piston stroke for this experiment is completed in a period of one second. An abundance of fringes near the walls of the slit could lead to difficulties in obtaining an image of good clarity. On the other hand, a poor resolution of fringes near the slit walls could be an indication of slip, which is plausible at this shear rate (800 s⁻¹). Another possible explanation is shear heating near the walls of the slit, which may lead to a reduction in apparent viscosity and an absence of or diminishing of fringes near the slit walls. Further studies need to be carried out to establish the presence of slip or shear heating in the system.

In general, the flow birefringence pictures for LLDPE appear to be normal apart from one unusual feature. Consider an experiment carried out at a piston velocity of 1.0 \(10^3\) m/s (corresponding to an apparent wall shear rate of 80 s⁻¹). The evolution of the fringe pattern with time for an experiment performed at a piston velocity of \(10^3\) m/s is monitored at the entry and exit of the slit. The number of fringes in the slit entry region increases to reach a steady pattern. The fringe pattern obtained at 1.4 seconds after the flow has begun is shown in Figure 7.9. These fringe patterns are regular and do not show any abnormal effects at this point.

![Figure 7.9: Flow birefringence fringe pattern obtained for LLDPE at the slit entry region, T = 170 °C, slit, L = 1.2 \(10^{-2}\) m, W = 1.0 \(10^{-2}\) m, D = 1.0 \(10^{-2}\) m, \(v_p\) = 1.0 \(10^1\) m/s, A = 5.0 \(10^{-1}\) m](image)

A continuous layer (in black) can be seen to emerge (Figure 7.10) from near the walls of the slit in the exit region at 1.76 seconds. The layer fully emerges outside the slit exit and becomes fully developed, as seen from the picture captured at a time of 1.88
seconds (Figure 7.11). The fully emerged layer is very stable and can be seen during the entire duration of the piston stroke (Figure 7.12).

Figure 7.10: Flow birefringence fringe pattern obtained for LLDPE at the slit exit region, $T = 170^\circ C$, slit, $L = 1.2 \times 10^{-2} \text{ m}$, $W = 1.0 \times 10^{-3} \text{ m}$, $D = 1.0 \times 10^{-2} \text{ m}$, $v_p = 1.0 \times 10^{-1} \text{ m/s}$, $A = 5.0 \times 10^{-1} \text{ m}$

Figure 7.11: Flow birefringence fringe pattern obtained for LLDPE at the slit exit region, $T = 170^\circ C$, slit, $L = 1.2 \times 10^{-2} \text{ m}$, $W = 1.0 \times 10^{-3} \text{ m}$, $D = 1.0 \times 10^{-2} \text{ m}$, $v_p = 1.0 \times 10^{-1} \text{ m/s}$, $A = 5.0 \times 10^{-2} \text{ m}$

Figure 7.12: A flow birefringence pattern obtained for LLDPE at slit exit, $T = 170^\circ C$, slit, $L = 1.2 \times 10^{-2} \text{ m}$, $W = 1.0 \times 10^{-3} \text{ m}$, $D = 1.0 \times 10^{-2} \text{ m}$, $v_p = 1.0 \times 10^{-1} \text{ m/s}$, $A = 5.0 \times 10^{-2} \text{ m}$

When the pistons stop moving, the flow rate of the melt through the slit also diminishes and the layer starts to vanish (as seen in Figure 7.13). This indicates that the
layer can be distinguished from the bulk because during flow, it has a different orientation as compared to the melt in the bulk of the slit. The fringes near the walls of the slit and at the ends of the slit are well defined throughout the entire duration of the experiment. These observations are unlike those obtained for HDPE, where the flow field is distorted during a single-pass experiment carried out under similar conditions of shear rate.

Figure 7.13: A Flow birefringence pattern obtained for LLDPE at the slit exit region, T = 170 °C, slit, L = 1.2 \times 10^{-2} \text{ m}, W = 1.0 \times 10^{-3} \text{ m}, D = 1.0 \times 10^{-4} \text{ m}, v_p = 1.0 \times 10^{-1} \text{ m/s}, A = 5.0 \times 10^{-1} \text{ m}

In the case of experiments carried out using this set-up at very high shear rates (above 1000 s^{-1}), it is difficult to distinguish the presence of this layer at the slit exit because of the short duration of the experiments.

7.5 Summary and Conclusions

Capillary flow experiments were carried out on LLDPE for a range of shear rates using the MPR. Except for a narrow range of shear rates, the pressure difference traces were smooth and did not show the presence of fluctuations. The flow curve of LLDPE determined from the single-pass experiments shows a sharp change of slope around a piston velocity of 6.9 \times 10^{-3} \text{ m/s} (corresponding to a shear rate of 750 s^{-1}). The pressure difference profiles for a narrow range of shear rates from 250 s^{-1} to 600 s^{-1} show periodic pressure fluctuations of the order of 0.5 MPa. These observations are consistent with the previously published literature, which have been reviewed in the first section of this chapter.

The superposition of the pressure difference profiles obtained from single-pass experiments carried out on LLDPE, shows the presence of a weak Delayed Pressure Build-up effect. This effect has also been observed for POE, but the differences between
the successive pressure traces are not as striking as that observed for POE.

In the slit flow of LLDPE, the birefringence patterns were stable for the entire length of the experiment for all the range of shear rates that have been studied. However, in the case of experiments carried out at lower shear rates, a layer can be seen to emerge from near the walls at the exit of the slit, similar to that observed for POE. The time scales associated with the emergence of the layer are of the order of 100 milliseconds, while the time scales associated with the emergence of the layer in POE under similar shear rate conditions are of the order of few seconds.

The capillary flow rheology of LLDPE shows a number of similarities to the flow of HDPE and POE. The pressure fluctuations observed in the capillary flow of LLDPE are of the order of 0.5 MPa as compared to the pressure fluctuations in HDPE, which are of the order of 2.5 MPa. The distortion of the flow field, which has been distinctly observed in HDPE is absent for LLDPE and the fringe pattern at the entry and the exit of the slit are very stable. Therefore, it may be concluded that LLDPE exhibits a rheological behaviour similar to that of HDPE to a certain extent although the level of pressure fluctuations observed in LLDPE is greatly reduced as compared to HDPE.

The steady shear flow curve of LLDPE shows a sharp change in slope, which is well-documented in literature. Many researchers have observed that the change in the slope of the flow curve coincides with the onset of SSSD and have concluded that the presence of this phenomenon is an indication of the presence of SSSD in the extruded melt (Ramamurthy, 1986). Some researchers have attributed the change in slope predominantly to slip occurring at the die exit and to a limited extent to slip occurring in the die land region (Wang et al., 1996b). The slip at the die exit region is explained by the change in the boundary conditions resulting in an acceleration of the melt and results in slip above a certain critical stress is exceeded (Kurtz, 1984, 1992). The sharp change in the slope of the flow curve obtained for LLDPE using the MPR, clearly illustrates that this phenomenon cannot be solely attributed to a flow discontinuity at the exit of a die during extrusion. This is a very important conclusion and needs to be taken into consideration while proposing a mechanism to explain the presence of SSSD observed during the extrusion of LLDPE.

The observations of LLDPE and its comparison with HDPE and POE clearly indicate that LLDPE exhibits certain characteristics, which are associated with the flow of
both HDPE and POE. It is worth noting that the pressure fluctuations and instabilities observed in the flow of both HDPE and POE are significantly reduced in LLDPE. The pressure profiles of LLDPE are remarkably stable as compared to that of POE and HDPE. However, one of the main extrudate defect which has been reported for LLDPE is the presence of small scale surface defects, which is believed to arise from the acceleration of flow at the free surface leading to superficial tearing or rupture of the extrudates. Because of the absence of a free surface at the capillary exit, this effect may not be observed for the flow of LLDPE in the MPR. Therefore, while it may be concluded that the flow of LLDPE in the MPR is more stable as compared to that of POE and HDPE, it does not necessarily imply that LLDPE is an easier polyethylene to process as compared to HDPE and POE.
The experimental work described in this thesis involves a detailed study of the rheology and processing behaviour of three different types of polyethylenes, HDPE, POE and LLDPE, each of which have a distinct molecular structure. The different molecular structure of these polymers should affect their rheological behaviour and influence the type of flow instabilities exhibited by them. The steady shear behaviour, time dependent flow rheology and flow instabilities such as pressure oscillations of these three polyethylenes were studied using the MPR. The experiments carried out on the MPR include both capillary flow measurements and flow visualisation experiments using a slit geometry. It may be concluded that the rheology of these polyethylenes are vastly different, although the underlying factors behind these differences are not completely clear. The flow and instabilities observed for these three polymers appear to be governed by different mechanisms.

In the case of HDPE, which is made of linear chains, the flow curve is discontinuous and consists of two branches that are separated by an unstable flow regime. Four distinct flow regimes were identified from the pressure difference traces obtained from capillary flow experiments, namely the Stable Flow, Periodic Oscillations, Overshoot and the High Velocity regimes. The flow birefringence patterns follow the time dependent pressure traces. At the transition from the first branch of the flow curve to the second, the flow birefringence observations showed a disturbance, which appeared to originate at or near the walls of the slit, slightly downstream of the slit entry region. This disturbance propagated in the form of a wave along the walls of the slit and disappeared at the slit exit. The flow birefringence fringes observed for the second branch of the flow curve tend to broaden and were no longer seen to be parallel to the walls of the slit. This could be an indication of a plug flow profile and the presence of slip along the second
branch of the flow curve. In literature, the presence of a discontinuous flow curve and associated flow instabilities were attributed to either the existence of a non-monotonic constitutive equation or due to a change in boundary conditions inside the die. The observations of flow birefringence patterns in the Periodic Oscillations and Overshoot regime obtained using the MPR indicate the presence of slip at the walls of the slit. These observations are in accordance with the theory of coil-stretch transition proposed by Brochard and de Gennes (1992) and extended by Piau et al (1995) and Wang and Drda (1997).

In the case of POE, an ethylene-octene co-polymer with uniform SCB, the steady shear behaviour shows a number of unusual features. The pressure build-up during a single-pass experiment was observed to be dependent on its shear history even at very low shear rates (starting from 1.6 s\(^{-1}\) at 170 °C). The pressure profiles of POE showed a low initial apparent viscosity followed by a rapid increase in apparent viscosity during a single-pass experiment, which has been referred to as the Delayed pressure Build-up (DPB) effect in this thesis. The flow visualisation experiments reveal the presence of a surface layer emerging at the exit of the slit. It was possible to determine a master curve by comparing the pressure difference profiles from experiments carried out at different piston velocities, which indicated that the DPB effect was independent of time or shear rate. The presence of a master curve seems to indicate that the DPB effect may be related to a length scale associated with the capillary geometry. The DPB effect could be an indication of presence of slip in the system, although it was not possible to conclusively ascertain the reasons behind this effect. It could be explained in terms of the development of either a gel fraction of higher MW or a low MW fraction accumulating at the walls of the die. These fractions could result from a flow induced phase separation, although it is not possible to confirm any of these ideas without using other experimental techniques. The ability of the MPR to repeatedly shear the same sample volume has been very advantageous in the study of POE and many of the characteristics determined about the rheology of POE would not have emerged if a conventional rheometer had been used.

For LLDPE, which comprises of both linear and branched chains with SCB, the pressure difference traces were found to be stable in general as compared to those obtained for HDPE and POE. The flow curve of LLDPE shows a significant slope change, which is a characteristic of LLDPE. A DPB effect was also observed for the pressure difference
traces of LLDPE, although the effect was much smaller than that observed for POE. In the slit flow of LLDPE, a layer was again observed to emerge from near the walls of the slit at its exit similar to that observed for POE. In this respect, the flow behaviour of LLDPE shows similarities with the flow behaviour of POE. Also, it was possible to conclusively establish that the significant change in the slope of LLDPE flow curves is not associated with the change in boundary conditions at the die exit. Therefore, if SSSD are initiated at the die exit, they may not be the cause behind this change in LLDPE flow curves.

The capillary flow rheology of LLDPE shows a number of similarities and differences to the flow of HDPE and POE. The pressure fluctuations observed in the capillary flow of LLDPE were less regular and smaller in magnitude (of the order of 0.5 MPa) as compared to the pressure fluctuations of HDPE (of the order of 2.5 MPa). The flow birefringence patterns of HDPE distinctly show a distortion of the flow field, which cannot be seen for LLDPE. The fringes at the entry and the exit of the slit were stable in the case of LLDPE. Therefore, it may be concluded that LLDPE exhibits a rheological behaviour similar to that of HDPE with weak but finite instability effects.

A quantitative model (Ranganathan et al., 1999) was developed to predict the flow of polymer melts such as HDPE in the MPR. As a result of the fully constrained geometry of the MPR, it was possible to formulate this model without incorporating any adjustable parameters. The main parameters used in the model were the experimentally determinable melt compressibility and the steady shear flow curve. In the case of HDPE, the prediction of the time dependent pressure profiles for each of the four regimes was found to be reasonably accurate. In particular, the model was able to predict the pressure relaxation after cessation of piston movement with remarkable accuracy. This leads to the conclusion that compressibility rather than viscoelastic effects dominate time dependent pressure behaviour in capillary flow in the case of materials such as polyethylene melts.

The MPR has proved to be a useful and versatile instrument for studying the rheological and transient flow behaviour of polymer melts. In the case of POE and LLDPE, the ability of the MPR to repeatedly shear a sample volume has proved to be very advantageous in determining flow characteristics such as the DPB effect. The MPR assembly was crucial in modifying the surface of a capillary wall and influence the shear history of these polyethylenes. However, for HDPE, the effect of shear history is not
Conclusions and Future Work

detectable. This is one of the major differences between HDPE and POE, which may be a result of their different chain architectures. From the work described in this thesis, it would appear that these differences emanate from differences in wall boundary conditions rather than bulk rheology effects. This is in accordance with the recent interpretations given by Piau et al., 1995, Wang and Drda (1997). Also, it has not been possible to be definitive about molecular aspects such as slip and coil-stretch transition effects, which may occur at or near the walls of the capillary (or slit).

In order to improve the understanding of these effects, further experimental studies of these polyethylenes are required. These could include experiments incorporating velocity measurements near the slit wall using techniques such as Laser Doppler Velocimetry (LDV). Also, in order to gain a better idea of the effect of molecular structure, it would be beneficial to carry out experiments with a range of polyethylenes of differing MW, MWD and branching effects. In the case of POE, it would be useful to carry out experiments with different types of capillary geometries to establish the effect of geometry on the DPB effect. Also, for POE, it would be useful to carry out experiments using a fluoroelastomer coated die and study its influence on the DPB effect. Apart from these experiments, complementary experiments performed using a conventional capillary rheometer alongside the MPR to obtain extrudates at different shear rates would provide further insight into flow conditions inside the die. Also, it would be useful to use other techniques such as spectroscopic methods to study the composition of polymer chains near the wall and in the bulk of the capillary.
Appendix A  Flow Birefringence

Terms used in Optics (Born and Wolf, 1969)

♦ **Light**: Light is a transverse vibration made up of an electric field $E$ and a magnetic field $B$, which are at right angles to each other and also perpendicular to the direction of propagation of the light ray. The three directions could be considered to form the edge of a cube. The electric field interacts strongly with the surrounding matter, and therefore its direction and amplitude are used to describe light in the form of a tensor called the dielectric tensor.

♦ **Polarised and Unpolarised light**: At any instant, the amplitude and direction of the electric field defines a point on a plane perpendicular to the direction of the light ray. When an observer looks towards the light source, this point traces a curve as the field varies. If the curve is simple and repetitive, the light is polarised and the form of the curve determines the state of polarisation. If the curve is irregular and chaotic, the light is unpolarised.

♦ **Plane polarised light**: When the electric field oscillates in amplitude, but has a fixed direction, the curve traced out is a straight line and the field remains in one plane. This light is referred to a plane or linearly polarised light (Figure AppendixA.1) and the plane is called the plane of polarisation.

♦ **Elliptically polarised light**: When both the amplitude and the direction of light change in a regular manner, and the curve traced out is an ellipse, then the light is elliptically polarised (Figure AppendixA.2).

♦ **Circularly polarised light**: When the electric field is of constant amplitude, but changes in direction, the point traces out a circle and the light is called circularly polarised light (Figure AppendixA.3).
Figure Appendix A.1: Schematic diagram illustrating a plane polarised light wave

Figure Appendix A.2: Schematic diagram illustrating an elliptically polarised light wave

Figure Appendix A.3: Schematic diagram illustrating a circularly polarised light wave

**State of polarisation:** Any state of polarisation can be considered as a combination of (or can be decomposed into) two perpendicular plane polarised waves of different amplitudes and with a specific phase difference. The addition of two such waves can be used to produce a state of polarisation. The state of polarisation also can be considered to be a combination of a right and left circularly polarised waves.
- **Polariser (and analyser):** A polariser is an assembly of crystals used to produce linearly polarised light whose direction of polarisation is known from other states of polarisation. It can also be used as an analyser to detect linearly polarised light and its angle of vibration. Generally the polariser is a uniaxial crystal which is cut into two equal parts cut along the diagonal plane, which are cemented together.

- **Extraordinary & Ordinary rays:** When a beam of light is incident in the direction L parallel to the long edge of the polarising crystal, it is split into an ordinary(o) and extraordinary(e) ray. The ordinary ray is totally reflected at the interface of the crystal towards the face DC, which is blackened and hence absorbs it. The extraordinary ray however passes through the prism with no lateral displacement and is thus linearly polarised. Thus the polariser gives linearly polarised light whose direction of polarisation is known.

![Figure AppendixA.4: A polarising crystal](image)

**Mathematical Description of Birefringence**

In order to derive the mathematical expressions for flow birefringence, consider a plane parallel crystal plate of thickness, \( h \), which is oriented such that the principle refractive indices \( n_x \) and \( n_y \) are parallel to the X and the Y axes respectively, as shown in Figure AppendixA.5 (Born and Wolf, 1969). A polariser and an analyser are placed on either side of the crystal. A beam of linearly polarised light emerging from the polariser is incident normally on plane of the crystal and is divided into two rays with different velocities of propagation. As a result, they emerge from the crystal with a certain phase difference \( \delta_n \). The components of the two rays in a certain direction are then resolved using the analyser. OX and OY represent the two mutually orthogonal directions of vibrations in the crystal.
Figure Appendix A.5: The vibration components transmitted by the polariser and the analyser

OP and OA are the directions of the vibrations that are passed by the polariser and the analyser respectively. The angle made by OP to OX is $\phi$ and the angle between OA and OP is $\chi$. The amplitude of light incident on the plate is represented by the vector OE (parallel to OP) and its components in the direction of the X and Y axes are

\begin{align*}
\text{Eqn. 73} & \quad OB = E \cos \phi \\
\text{Eqn. 74} & \quad OC = E \sin \phi
\end{align*}

The analyser transmits only the components parallel to OA as shown in Figure Appendix A.5 and have amplitudes of

\begin{align*}
\text{Eqn. 75} & \quad OF = E \cos \phi \cos (\phi - \chi) \\
\text{Eqn. 76} & \quad OG = E \sin \phi \sin (\phi - \chi)
\end{align*}

On leaving the crystal, the two components differ in phase by the amount $\delta_n$ where

\begin{equation}
\text{Eqn. 77} \quad \delta_n = \frac{2\pi n}{\lambda_n} (n_y - n_x) h
\end{equation}

The intensity obtained by the interference of the two monochromatic waves of phase difference $\delta_n$ is given by

\begin{equation}
\text{Eqn. 78} \quad I = I_x + I_y + 2\sqrt{I_x I_y} \cos \delta_n
\end{equation}

where $I_x$ and $I_y$ are the intensities (squared amplitudes) of the two waves. From the amplitudes given by Eqn. 75 and Eqn. 76, and using the identity $\cos \delta_n = 1 - 2 \sin^2 \frac{\delta_n}{2}$,

\begin{equation}
\text{Eqn. 79} \quad I = E^2 \left[ \cos^2 \chi - \sin 2\phi \sin (\phi - \chi) \sin \frac{\delta_n}{2} \right]
\end{equation}

When the analyser and the polariser are perpendicular i.e. $\chi = \pi/2$, then Eqn. 79 gives
The intensity corresponding to a given direction of incidence depends on $\phi$ and $\delta_n$ and these can be separately considered. The curves along which $\phi$ are constant are called isoclinics and those along which $\delta_n$ is constant are called as isochromatics. When the maximum shearing stress makes a certain angle with the axis of polarisation of the incident light, isoclinics can be seen as dark regions and they are independent of the plate thickness and the wavelength. When monochromatic light is used, isochromatics can be observed as regions of light interference and reinforcement, which appear as a pattern of light and black bands. Isoclinics can only be seen when plane polarised light is used and isochromatics appear when the incident light is either plane or circularly polarised. The isochromatics depend on the direction of the wave normals and on the thickness of the plate and when white light is used, the isochromatics are lines of equal colour. The curves along which the intensity is zero are called the principal isoclinics and principle isochromatics and are obtained when $\sin 2\phi = 0$ and $\sin \frac{1}{2} \delta_n = 0$.

In the case of a slit of width, $h$, the fringe order $N$ and the corresponding isoclinic angle $\phi$ at the die wall can be determined by extrapolating the values in the slit from $x = 0$ to $x < h$ to the die-wall $x = h/2$ and the shear stress $\tau_{xy}$ at any position $x$ in the slit can be determined from the shear stress at the wall. Using a stress optical coefficient, $C$, $\tau_{xy}$ can be determined from the fringe order $N$ and the isoclinic angle $\phi$. Therefore by combining the shear stress data obtained from the wall normal stress measurement, the stress distribution can be obtained from the birefringence patterns using the stress-optical relation which combines the birefringence tensor with the stress tensor.

\begin{equation}
\left. n_{xy} = C \tau_{xy} \right. 
\end{equation}

To predict simple shear flow, the following relation can be used

\begin{equation}
2\tau_{xy} = \frac{\Delta n}{C} \sin 2\phi
\end{equation}

\begin{equation}
\tau_{xy} - \tau_{xx} = \frac{\Delta n}{C} \cos 2\phi
\end{equation}

These are the mathematical expressions used to determine the stress distribution in a polymer melt flowing through a slit from the flow birefringence pattern.
Appendix B  Matlab Program Code

Matlab - ode23 Function for Solving the Differential Equation

global vp X i
C = input('Number of branches for calculations' );
i=1;
options = odeset('refine',6);
Ts = input('Time for calculation(secs) ')
y0=0;
vp=2.9e-3;
As=15e-3;
ts1=3;
ts2=As/vp;
Tn(1)=ts1;
tspre=[0 ts1];
X=input('Compressibility ') ;
[t,y]=ode23('rs',tspre,y0,options);
y1=y(:,1);
plot(t,y);
R=[t];
Q=[y1];
S=[t;y1];
j = size(R);
disp(j);
p=1;
while Q(p)<1.60e7;
p=p+1;
end;
if (R(p+1))<ts1
ts1=R(p+1);
end;
save reg(!) -ascii -tabs S;
if (C)>1
Nt=C-1;
n=1;
while (n)<Nt
i=2;
disp(' i = 2')
disp(n);
Tn(n+1)=input('time for calculation(secs) ');
Tn(1)=ts1;
disp(Tn(1))
Tn(n+1)=Tn(n)+Tn(n+1);
if (Nt-n)<1
Tn(n+1)=ts2;
end;
p = n;
tspre=[Tn(n) Tn(n+1)];
y0=1.580e7;
[t, y] =ode23('rs',tspre,y0,options);
y1=y(:,1);
plot(t,y1);
Appendix B
Matlab Program Code

Q=[ y(1); 
R=[ t, y(1); 
S=[ t];
if (n)<2
    save reg(2) -ascii -tabs R;
end
n=n+1;
if (n)>Nt
    break
else
    i=1;
    Tn(n+1)=input('time for calculation') ;
    Th(1)=ts1;
    Th(n+1)=Th(n)+Th(n+1);
    if (Nt-n)<1
        Th(n+1)=ts2;
    end
tspan1=[ Th(n) Th(n+1)];
disp(tspan1);
y0=1.39e7;
disp('going in');
[t, y] =ode23('rs', tspan1, y0, options);
yl=y(:,1);
Q=[ t,yl];
R=[ y(1); 
R=[ t];
if (n)<3
    save reg(3) -ascii -tabs Q;
end
n=n+1;
end
end
tsr=Ts-Tn(C);
vp=0;
tspan=[ Ts Tn(C) Ts]
y0=input('Initial pressure for relaxation (Pa)');
i=1;
[t, y] =ode23('rs', tspan, y0);
yl=y(:,1);
function yprime = rs(t, y);
global vp X i
Pti=20;
Pbi=2;
Vti=(35.75+((Pti+36)*pi^36)) *1e-9;
Vbi=(35.75+((Pbi+36)*pi^36)) *1e-9;
a(1)=9.68e-25;
b(1)=2.3886;
a(2)=1.6e-19;
b(2)=1.7056;
Rb=6e-3;
Qi=pi^2vp*Rb^2;
yprime=(1/X)*(1/(Vti-(Qi*t)) + 1/(Vbi+(Qi*t)))*(Qi-a(1)*(y(1))^b(1));
List of Figures and Tables

| Figure 1.1: Examples of instabilities affecting polymer melts (Petrie and Denn, 1976) | 4 |
| Figure 1.2: Schematic molecular chain structure of HDPE showing linear chains | 6 |
| Figure 1.3: Schematic molecular structure of POE showing branched chains | 7 |
| Figure 1.4: Schematic molecular structure of LLDPE showing both linear and branched chains | 7 |
| Figure 2.1: Linear elastic model | 12 |
| Figure 2.2: Linear viscous model | 12 |
| Figure 2.3: A Maxwell element represented by a spring and dashpot in series | 13 |
| Figure 2.4: Macroscopic representation of a polymer melt system | 14 |
| Figure 2.5: Schematic representation of the parallel plate geometry of a RDS | 21 |
| Figure 2.6: Capillary flow configuration of the Multipass Rheometer | 23 |
| Figure 2.7: The pressure difference traces obtained for a Multipass experiment on HDPE | 26 |
| Figure 2.8: The pressure difference traces for a small amplitude sinusoidal movement of pistons for POE | 27 |
| Figure 2.9: Schematic diagram of the Optic cell showing the die blocks and transparent quartz windows | 30 |
| Figure 2.10: Flow visualisation set-up on the MPR showing assembly of lenses, polarisers and analysers | 31 |
| Figure 3.1: GPC trace of HDPE indicating a broad MWD | 34 |
| Figure 3.2: GPC trace of POE indicating a narrow MWD | 35 |
| Figure 3.3: GPC trace of LLDPE indicating a reasonably narrow MWD | 35 |
| Figure 3.4: Temperature Rising Elution fractionation (TREF) trace for LLDPE | 36 |
| Figure 3.5: Experimentally determined flow curves of the three polyethylene samples using the Göttermann capillary rheometer at T = 180 °C using a capillary of L/D =20/1 and half entry angle = 90° and the predicted flow curve of LLDPE using an addition rule | 37 |
| Figure 3.6: Small amplitude oscillatory strain sweep carried out using a RDS for a)HDPE b) POE and c) LLDPE at T = 180 °C | 39 |
| Figure 3.7: Small Amplitude Frequency sweep using RDS for a) HDPE b) POE and c) LLDPE,T = 180 °C | 41 |
| Figure 3.8: Relaxation spectrum of a) HDPE b) POE and c) LLDPE computed from the Small Amplitude frequency sweep data | 42 |
| Figure 3.9: Recalculation of dynamic moduli using the relaxation spectrum and its comparison with the measured dynamic moduli of a) HDPE b) POE and c) LLDPE using the RDS, T = 180 °C | 43 |
Figure 3.10: Stress relaxation data for linear and non-linear step strains measured on a RDS at T = 180 °C and prediction of stress relaxation for linear step strains of a) HDPE b) POE and c) LLDPE

Figure 3.11: Steady shear response measured on a RDS at T = 180 °C and prediction of steady shear response using the Maxwell model of linear viscoelasticity and Maxwell model coupled with the Wagner damping factor of a) HDPE b) POE and c) LLDPE

Figure 3.12: Extrapolation of the apparent Newtonian viscosity determined from steady shear flow curves for HDPE, POE and LLDPE to determine values of \( \eta_0 \) at T = 180 °C

Figure 3.13: Comparison of the small strain dynamic measurement over a range of frequencies for POE at a strain of 20% and T = 180 °C

Figure 3.14: Comparison of the steady shear response of POE measured using a MPR with a test section of D = 1.2 \( 10^{-2} \) m, L = 8.2 \( 10^{-2} \) m at T = 180 °C with data obtained from RDS and Gottfert rheometer

Figure 3.15: The change in the dynamic moduli of POE over a range of system pressures measured using a MPR, strain = 33%, frequency = 10 rad/s, T = 180 °C using a test section, D = 1.2 \( 10^{-2} \) m, L = 8.2 \( 10^{-2} \) m

Figure 3.16: Change in ln(Volume) occupied with system pressure measured on the MPR to determine the compressibility of the POE, T = 170 °C, test section D = 1.2 \( 10^{-2} \) m, L = 8.2 \( 10^{-2} \) m

Figure 4.1: Schematic illustration of the discontinuous flow curve observed for HDPE in the Controlled piston-speed mode of operation

Figure 4.2: Schematic illustration of the discontinuous flow curve observed for HDPE in the Controlled pressure mode of operation

Figure 4.3: Schematic diagram showing four different sites for initiation of instabilities during extrusion of a polymer melt

Figure 4.4: Dimensions of the capillary and slit flow geometry

Figure 4.5: Steady state flow curve of HDPE determined from single-pass experiments in the MPR T = 180 °C, capillary, L = 1.0 \( 10^{-2} \) m, D = 1.0 \( 10^{-3} \) m, Half Entry angle = 45°

Figure 4.6: A pressure difference profile in Stable flow regime for HDPE in the MPR, T = 180 °C, Capillary, L = 1.0 \( 10^{-2} \) m, D = 1.0 \( 10^{-3} \) m, Half Entry angle = 45°, \( v_p = 1.0 \times 10^{-3} \) m/s, A = 8.0 \( 10^{-2} \) m

Figure 4.7: Schematic representation of Stable flow regime

Figure 4.8: A pressure difference profile in a Periodic Oscillations regime for HDPE in MPR, T = 180 °C, Capillary, L = 1.0 \( 10^{-2} \) m, D = 1.0 \( 10^{-3} \) m, Half Entry angle = 45°, \( v_p = 2.0 \times 10^{-3} \) m/s, A = 1.5 \( 10^{-2} \) m

Figure 4.9: Schematic representation of Periodic Oscillations regime

Figure 4.10: A pressure difference profile in the Overshoot regime for HDPE in the MPR, T = 180 °C, Capillary, L = 1.0 \( 10^{-2} \) m, D = 1.0 \( 10^{-3} \) m, Half Entry Angle = 45°, \( v_p = 2.4 \times 10^{-3} \) m/s, A = 1.5 \( 10^{-2} \) m

Figure 4.11: Schematic representation of Overshoot regime
Figure 4.12: A pressure difference profile in the High Velocity regime for HDPE in the MPR, \( T = 180 \, ^\circ\text{C} \), Capillary, \( L = 1.0 \times 10^{-2} \, \text{m} \), \( D = 1.0 \times 10^{-3} \, \text{m} \), Half Entry angle = 45°, \( v_p = 2.9 \times 10^{-2} \, \text{m/s} \), \( A = 1.5 \times 10^{-2} \, \text{m} \)

Figure 4.13: Schematic representation of High velocity regime

Figure 4.14: The stress birefringence pattern for Stable Flow regime at slit entry and exit, and pressure difference profile at \( T = 170 \, ^\circ\text{C} \), slit, \( L = 1.0 \times 10^{-2} \, \text{m} \), \( D = 1.0 \times 10^{-3} \, \text{m} \), \( W = 1.0 \times 10^{-3} \, \text{m} \)

Figure 4.15: The evolution of the stress birefringence pattern in the Periodic Oscillations regime at the entry and exit of the slit, and pressure difference profile \( T = 170 \, ^\circ\text{C} \), for a slit with \( L = 1.0 \times 10^{-2} \, \text{m} \), \( D = 1.0 \times 10^{-3} \, \text{m} \), \( W = 1.0 \times 10^{-3} \, \text{m/s} \), \( A = 2.0 \times 10^{-2} \, \text{m} \)

Figure 4.16: The pressure difference profile and stress birefringence pattern for flow in the High Velocity regime at the entry and exit of the slit, \( T = 170 \, ^\circ\text{C} \), slit, \( L = 1.0 \times 10^{-2} \, \text{m} \), \( D = 1.0 \times 10^{-3} \, \text{m} \), \( W = 1.0 \times 10^{-3} \, \text{m/s} \), \( v_p = 1.0 \times 10^{-2} \, \text{m} \), \( A = 2.0 \times 10^{-2} \, \text{m} \)

Figure 4.17: The pressure difference profile for flow in the Overshoot regime of HDPE, \( T = 170 \, ^\circ\text{C} \), slit, \( L = 1.2 \times 10^{-2} \, \text{m} \), Depth = 1.0 \times 10^{-2} \, \text{m} \), \( W = 1.0 \times 10^{-3} \, \text{m} \), \( v_p = 8.0 \times 10^{-4} \, \text{m/s} \), \( A = 2.0 \times 10^{-2} \, \text{m} \)

Figure 4.18: The birefringence pattern at the entry of the slit in the Overshoot regime showing U-shaped fringes parallel to the walls of the slit, \( T = 170 \, ^\circ\text{C} \), slit, \( L = 1.0 \times 10^{-2} \, \text{m} \), \( D = 1.0 \times 10^{-3} \, \text{m} \), \( W = 1.0 \times 10^{-3} \, \text{m/s} \), \( v_p = 8.0 \times 10^{-3} \, \text{m} \), \( A = 2.0 \times 10^{-2} \, \text{m} \)

Figure 4.19: The birefringence pattern at the exit of the slit in the Overshoot regime showing the build-up of fringes with time as the pressure difference reaches its maximum value, \( T = 170 \, ^\circ\text{C} \), slit, \( L = 1.0 \times 10^{-2} \, \text{m} \), \( D = 1.0 \times 10^{-3} \, \text{m} \), \( W = 1.0 \times 10^{-3} \, \text{m/s} \), \( v_p = 8.0 \times 10^{-3} \, \text{m/s} \), \( A = 2.0 \times 10^{-2} \, \text{m} \)

Figure 4.20: The birefringence pattern at the entry of the slit in the Overshoot regime showing start of the disturbance leading to broadening of U-shaped fringes, \( T = 170 \, ^\circ\text{C} \), slit, \( L = 1.0 \times 10^{-2} \, \text{m} \), \( D = 1.0 \times 10^{-3} \, \text{m} \), \( W = 1.0 \times 10^{-3} \, \text{m/s} \), \( v_p = 8.0 \times 10^{-3} \, \text{m/s} \), \( A = 2.0 \times 10^{-2} \, \text{m} \)

Figure 4.21: The birefringence pattern at the exit of the slit in the Overshoot regime showing a loss of symmetry in fringes, \( T = 170 \, ^\circ\text{C} \), slit, \( L = 1.0 \times 10^{-2} \, \text{m} \), \( D = 1.0 \times 10^{-3} \, \text{m} \), \( W = 1.0 \times 10^{-3} \, \text{m/s} \), \( v_p = 8.0 \times 10^{-3} \, \text{m/s} \), \( A = 2.0 \times 10^{-2} \, \text{m} \)

Figure 4.22: The birefringence pattern at the entry of the slit in the Overshoot regime showing broadening of the U-shaped fringes ending into the walls of the slit, \( T = 170 \, ^\circ\text{C} \), slit, \( L = 1.0 \times 10^{-2} \, \text{m} \), \( D = 1.0 \times 10^{-3} \, \text{m} \), \( W = 8.0 \times 10^{-3} \, \text{m/s} \), \( A = 2.0 \times 10^{-2} \, \text{m} \)

Figure 4.23: The birefringence pattern at the exit of the slit in the Overshoot regime showing the propagation of disturbance in the form of a wave at the exit of the slit, \( T = 170 \, ^\circ\text{C} \), slit, \( L = 1.0 \times 10^{-2} \, \text{m} \), \( D = 1.0 \times 10^{-3} \, \text{m} \), \( W = 8.0 \times 10^{-3} \, \text{m/s} \), \( A = 2.0 \times 10^{-2} \, \text{m} \)

Figure 4.24: The birefringence pattern at the entry of the slit in the Overshoot regime after the disturbance is initiated showing the fringes remaining broadened and ending into the walls of the slit, \( T = 170 \, ^\circ\text{C} \), slit, \( L = 1.0 \times 10^{-2} \, \text{m} \), \( D = 1.0 \times 10^{-3} \, \text{m} \), \( W = 1.0 \times 10^{-3} \, \text{m/s} \), \( v_p = 8.0 \times 10^{-3} \, \text{m/s} \), \( A = 2.0 \times 10^{-2} \, \text{m} \)
Figure 4.25: The birefringence pattern at the exit of the slit in the Overshoot regime showing the disappearance of wave disturbance at the exit of the slit, $T = 170^\circ C$, slit $L = 1.0 \times 10^{-2}$ m, $D = 1.0 \times 10^{-3}$ m, $W = 1.0 \times 10^{-3}$ m at $v_p = 8.0 \times 10^{-3}$ m/s, $A = 2.0 \times 10^{-2}$ m

Figure 4.26: The stable birefringence pattern at the exit of the slit in the Overshoot regime following the disappearance of the wave disturbance, $T = 170^\circ C$, slit, $L = 1.0 \times 10^{-2}$ m, $D = 1.0 \times 10^{-3}$ m, $W = 1.0 \times 10^{-3}$ m at $v_p = 8.0 \times 10^{-3}$ m/s, $A = 2.0 \times 10^{-2}$ m

Figure 5.1: Schematic representation of the capillary geometry of the MPR

Figure 5.2: The Upper barrel and capillary assembly

Figure 5.3: Steady state flow curve of HDPE, $T = 180^\circ C$, capillary, $L = 10^{-2}$ m, $D = 10^{-3}$ m, Half entry angle = 45$^\circ$

Figure 5.4: Comparison of the predictions of the model with experimental data for HDPE in the Stable flow regime at $180^\circ C$ for a capillary of $L = 10$ mm, $D = 1$ mm and Entry angle = 45$^\circ$

Figure 5.5: Comparison of the predictions of the model with experimental data for HDPE in the Periodic Oscillations regime at $180^\circ C$ for a capillary of $L = 10$ mm, $D = 1$ mm and Entry angle = 45$^\circ$

Figure 5.6: Comparison of the predictions of the model with experimental data for HDPE in the Overshoot regime at $180^\circ C$ for a capillary of $L = 10$ mm, $D = 1$ mm and Entry angle = 45$^\circ$

Figure 5.7: Comparison of the predictions of the model with experimental data in the High velocity regime for HDPE at $180^\circ C$ for a capillary of $L = 10$ mm, $D = 1$ mm and Entry angle = 45$^\circ$

Figure 6.1: Series 1, Pressure difference profile for single-pass experiment no. 4 for POE, $T=180^\circ C$, Capillary, $v_p = 1.0 \times 10^{-4}$ m/s, $A = 1.0 \times 10^{-2}$ m

Figure 6.2: Series 1, Pressure difference profile for single-pass experiment no. 7 for POE, $T=180^\circ C$, Capillary A, $v_p = 1.0 \times 10^{-4}$ m/s, $A = 3.0 \times 10^{-3}$ m

Figure 6.3: Series 1, Pressure difference profile for single-pass experiment no. 9 for POE, $T=180^\circ C$, Capillary A, $v_p = 1.0 \times 10^{-4}$ m/s, $A = 3.0 \times 10^{-3}$ m

Figure 6.4: Series 1, Pressure difference profile for single-pass experiment no. 15 for POE, $T=180^\circ C$, capillary A, $v_p = 1.0 \times 10^{-4}$ m/s, $A = 1.0 \times 10^{-2}$ m

Figure 6.5: Series 1, Pressure difference profile for single-pass experiment no. 30 for POE, $T=180^\circ C$, capillary A, $v_p = 1.0 \times 10^{-4}$ m/s, $A = 6.0 \times 10^{-3}$ m

Figure 6.6: Superposition of pressure difference profiles from single-pass experiments (Series 3) for POE $T = 180^\circ C$, Capillary A, $v_p = 2.0 \times 10^{-3}$ m/s, $A = 1.5 \times 10^{-2}$ m

Figure 6.7: Flow curve for POE in terms of shear stress versus apparent shear rate obtained using two capillaries, B and C at $T = 170^\circ C$

Figure 6.8: Series 6, Pressure difference profile in Stable flow regime for POE, $T = 170^\circ C$, capillary B, $v_p = 7.0 \times 10^{-4}$ m/s, $A = 1.7 \times 10^{-2}$ m

Figure 6.9: Series 6, Comparison of pressure difference profiles of four single-pass experiments for POE, $T = 170^\circ C$, capillary B, $v_p = 7.0 \times 10^{-4}$ m/s, $A = 1.7 \times 10^{-2}$ m
Figure 6.10: Pressure difference profile for a single-pass experiment in the DPB effect regime for POE, $T = 170^\circ C$, capillary $C$, $v_p = 3.0 \times 10^{-3}$ m/s, $A = 8.0 \times 10^{-3}$ m

Figure 6.11: Change of pressure in top and the bottom barrels of a MPR for a single-pass experiment performed at ambient pressure, capillary $C$, $T = 170^\circ C$, $v_p = 1.0 \times 10^{-4}$ m/s, $A = 8.0 \times 10^{-3}$ m

Figure 6.12: Flow visualisation using polarised light in Set-up 2, $T = 170^\circ C$, $v_p = 1.0 \times 10^{-2}$ m/s, Slit, $L = 1.2 \times 10^{-2}$ m, $W = 1.0 \times 10^{-3}$ m, $D = 1.0 \times 10^{-3}$ m

Figure 6.13: Flow visualisation in Set-up 1 using unpolarised light, $T = 170^\circ C$, $v_p = 1.0 \times 10^{-3}$ m/s, Slit, $L = 1.2 \times 10^{-2}$ m, $W = 1.0 \times 10^{-3}$ m, $D = 1.0 \times 10^{-3}$ m

Figure 6.15: Flow birefringence observations on POE using Set-up 3, $T = 170^\circ C$, $v_p = 1.0 \times 10^{-3}$ m/s, Slit, $L = 1.2 \times 10^{-2}$ m, $W = 1.0 \times 10^{-3}$ m, $D = 1.0 \times 10^{-3}$ m

Figure 6.16: Series 7, Single-pass experiments carried out for a POE sample using capillary $A$, $T = 180^\circ C$, $A = 8.0 \times 10^{-3}$ m

Figure 7.1: Steady shear flow curve of LLDPE determined from single-pass experiments carried out in the MPR, $T = 180^\circ C$, capillary, $L = 1.0 \times 10^{-2}$ m, $D = 1.0 \times 10^{-3}$ m, Half Entry angle = $45^\circ$

Figure 7.2: A pressure difference profile in the Stable Flow regime for LLDPE in the MPR, $T = 180^\circ C$, capillary, $L = 1.0 \times 10^{-2}$ m, $D = 1.0 \times 10^{-3}$ m, Half Entry angle = $45^\circ$, $v_p = 8.0 \times 10^{-5}$ m/s, $A = 3.0 \times 10^{-3}$ m

Figure 7.3: A pressure difference profile in the Pressure Fluctuations regime for LLDPE in the MPR, $T = 180^\circ C$, capillary, $L = 1.0 \times 10^{-2}$ m, $D = 1.0 \times 10^{-3}$ m, Half Entry angle = $45^\circ$, $v_p = 2.5 \times 10^{-4}$ m/s, $A = 3.0 \times 10^{-3}$ m

Figure 7.4: A pressure difference profile in the High Velocity regime for LLDPE in the MPR, $T = 180^\circ C$, capillary, $L = 1.0 \times 10^{-2}$ m, $D = 1.0 \times 10^{-3}$ m, Half Entry angle = $45^\circ$, $v_p = 3.0 \times 10^{-3}$ m/s, $A = 1.5 \times 10^{-2}$ m

Figure 7.6: Comparison of pressure difference profiles from three single-pass experiments for HDPE, $T = 180^\circ C$, capillary, $L = 1.0 \times 10^{-2}$ m, $D = 1.0 \times 10^{-3}$ m, Half Entry angle = $45^\circ$, $v_p = 3.0 \times 10^{-3}$ m/s, $A = 1.5 \times 10^{-2}$ m
List of Figures and Tables

Figure 7.7: A Flow birefringence fringe pattern obtained for LLDPE, \( T = 170 \, ^\circ C \), slit, \( L = 1.2 \times 10^{-2} \, m \), \( W = 1.0 \times 10^{-3} \, m \), \( D = 1.0 \times 10^{-2} \, m \), \( v_p = 1.0 \times 10^{-4} \, m/s \), \( A = 5.0 \times 10^{-3} \, m \)

Figure 7.8: A Flow birefringence fringe pattern obtained for LLDPE, \( T = 170 \, ^\circ C \), slit, \( L = 1.2 \times 10^{-2} \, m \), \( W = 1.0 \times 10^{-3} \, m \), \( D = 1.0 \times 10^{-2} \, m \), \( v_p = 1.0 \times 10^{-2} \, m/s \), \( A = 5.0 \times 10^{-3} \, m \)

Figure 7.9: Flow birefringence fringe pattern obtained for LLDPE at the slit entry region, \( T = 170 \, ^\circ C \), slit, \( L = 1.2 \times 10^{-2} \, m \), \( W = 1.0 \times 10^{-3} \, m \), \( D = 1.0 \times 10^{-2} \, m \), \( v_p = 1.0 \times 10^{-2} \, m/s \), \( A = 5.0 \times 10^{-3} \, m \)

Figure 7.10: Flow birefringence fringe pattern obtained for LLDPE at the slit exit region, \( T = 170 \, ^\circ C \), slit, \( L = 1.2 \times 10^{-2} \, m \), \( W = 1.0 \times 10^{-3} \, m \), \( D = 1.0 \times 10^{-2} \, m \), \( v_p = 1.0 \times 10^{-3} \, m/s \), \( A = 5.0 \times 10^{-3} \, m \)

Figure 7.11: Flow birefringence fringe pattern obtained for LLDPE at the slit exit region, \( T = 170 \, ^\circ C \), slit, \( L = 1.2 \times 10^{-2} \, m \), \( W = 1.0 \times 10^{-3} \, m \), \( D = 1.0 \times 10^{-2} \, m \), \( v_p = 1.0 \times 10^{-3} \, m/s \), \( A = 5.0 \times 10^{-3} \, m \)

Figure 7.12: Flow birefringence pattern obtained for LLDPE at slit exit, \( T = 170 \, ^\circ C \), slit, \( L = 1.2 \times 10^{-2} \, m \), \( W = 1.0 \times 10^{-3} \, m \), \( D = 1.0 \times 10^{-2} \, m \), \( v_p = 1.0 \times 10^{-3} \, m/s \), \( A = 5.0 \times 10^{-3} \, m \)

Figure 7.13: Flow birefringence pattern obtained for LLDPE at the slit exit region, \( T = 170 \, ^\circ C \), slit, \( L = 1.2 \times 10^{-2} \, m \), \( W = 1.0 \times 10^{-2} \, m \), \( D = 1.0 \times 10^{-2} \, m \), \( v_p = 1.0 \times 10^{-3} \, m/s \), \( A = 5.0 \times 10^{-3} \, m \)

Figure A.1: Schematic diagram illustrating a plane polarised light wave

Figure A.2: Schematic diagram illustrating an elliptically polarised light wave

Figure A.3: Schematic diagram illustrating a circularly polarised light wave

Figure A.4: A polarising crystal

Figure A.5: The vibration components transmitted by the polariser and the analyser

Table 2.1: The Specifications of the RDS

Table 2.2: Technical specifications of the MPR

Table 3.2: Molecular parameters of the polyethylenes measured using the GPC technique

Table 3.2: Summary of the results for the three polyethylene samples

Table 4.1: Experimental Conditions for capillary flow measurements of HDPE

Table 4.2: Range of shear rates for the four flow regimes at 180 °C

Table 5.1: Initial and boundary conditions used in modelling the four flow regimes

Table 5.2: Typical values of numerical parameters

Table 6.1: Capillary geometry specifications

Table 6.2: Experimental Conditions and Slit geometry specifications

Table 6.3: Flow visualisation set-ups

Table 7.1: Experimental Conditions
Bibliography

Bibliography


Bibliography


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