This electronic thesis or dissertation has been downloaded from Explore Bristol Research, http://research-information.bristol.ac.uk

Author: Finlay, Joanna

Title: A study of polyolefin blends

General rights
Access to the thesis is subject to the Creative Commons Attribution - NonCommercial-No Derivatives 4.0 International Public License. A copy of this may be found at https://creativecommons.org/licenses/by-nc-nd/4.0/legalcode This license sets out your rights and the restrictions that apply to your access to the thesis so it is important you read this before proceeding.

Take down policy
Some pages of this thesis may have been removed for copyright restrictions prior to having it been deposited in Explore Bristol Research. However, if you have discovered material within the thesis that you consider to be unlawful e.g. breaches of copyright (either yours or that of a third party) or any other law, including but not limited to those relating to patent, trademark, confidentiality, data protection, obscenity, defamation, libel, then please contact collections-metadata@bristol.ac.uk and include the following information in your message:

• Your contact details
• Bibliographic details for the item, including a URL
• An outline nature of the complaint

Your claim will be investigated and, where appropriate, the item in question will be removed from public view as soon as possible.
A Study of Polyolefin Blends

Joanna Finlay

A dissertation submitted to the University of Bristol in accordance with the requirements of the degree of Doctor of Philosophy in the Faculty of Science

Department of Physics
July 2003
ABSTRACT

In this project three sets of isotactic polypropylene/high-density polyethylene (iPP/HDPE) blends were studied. The primary aim was to determine how physical properties such as morphology, viscosity and crystallization kinetics affect the blends' mechanical properties such as Young's (tensile) modulus, yield strength, extension to break and tensile strength. The emphasis was on the practical applications of these materials in both the manufacturing and recycling industries.

Transmission electron microscopy was used to elucidate the morphologies of the blends. It revealed that they were phase separated and that the shape, size and distribution of the phase separated domains depended on the processing conditions and on the viscosity ratios of the components. Differential scanning calorimetry demonstrated that the blends’ crystallization behaviour was highly dependent on cooling rate. At fast cooling rates the components crystallized at higher temperatures in the blends than they did on their own. At very slow cooling rates the components crystallized at lower temperatures in the blends than they did on their own. At slow cooling rates the samples were much more crystalline than at higher cooling rates.

Existing models for composite materials predict that the blends’ moduli should lie between upper and lower bounds calculated using parallel and series coupling. However, in this project, rapidly quenched blends were found to have unexpectedly high Young’s moduli that exceeded the upper bound. Conversely, slowly cooled blends were found to have moduli that fell below the lower bound. These interesting mechanical properties were attributed to crystallization effects.

Unlike modulus, tensile strength and extension to break were found to be lower in the rapidly quenched blends than in the pure components. This was attributed to poor interfacial adhesion between the components in the blends. The slowly cooled homopolymers and blends were found to be much weaker and more brittle than the rapidly quenched materials. Again, these properties were attributed to crystallization effects.
ACKNOWLEDGEMENTS

Firstly, I would like to thank Dr Mary Hill and Dr Pete Barham for their supervision, motivation and enthusiasm over the past four years. I would also like to thank Anna Halter and Jerry Hart for their useful knowledge, technical assistance and general good humour.

Thanks also go to the other members of the Polymer Group, both past and present, for making the lab an enjoyable and pleasant place to work. Thanks go to the EPSRC for providing funding for the project and to Brian Murray, Alan Swanborough and the technical staff of Thermo PRISM® (formerly PRISM®) for allowing me to use their blending equipment free of charge.

Finally I would like to thank my friends, family and myself; without whom, none of this would have been possible! This thesis is dedicated to the memory of my PC, who thoughtfully gave up the ghost during the final stages of my write-up. Long may he rest in peace!
DECLARATION

I declare that the work in this dissertation was carried out in accordance with the Regulations of the University of Bristol. The work is original except where indicated by special reference in the text and no part of the dissertation has been submitted for any other degree.

Any views expressed are those of the author and in no way represent those of the University of Bristol.

The dissertation has not been presented to any other University for examination either in the United Kingdom or overseas.

[Signature]

Joanna Finlay

July 2003
CHAPTER 3: CAPILLARY EXTRUSION RHEOMETRY

3.1 INTRODUCTION
3.2 MOTIVATION
3.3 THEORETICAL BACKGROUND
  3.3.1 Rheology and Viscoelasticity
  3.3.2 Newtonian and Viscoelastic Shear Thinning Liquids
  3.3.3 Capillary Extrusion and Poiseuille's Law of Flow
  3.3.4 Immiscible Blend Viscosities
  3.3.5 Temperature Dependence of Viscosity
3.4 EXPERIMENTAL METHODS
3.5 RESULTS
  3.5.1 Homopolymers
    3.5.1.4 Bagley Plots and End Pressure Losses
    3.5.1.5 True Shear Stress – Apparent Shear Rate
    3.5.1.6 Rabinowitsch Correction
    3.5.1.7 Viscosity
  3.5.2 Blends
    3.5.2.1 Low-Viscosity Isotactic Polypropylene/High-Density Polyethylene Blends (LViPP/HDPE)
    3.5.2.2 Medium-Viscosity Isotactic Polypropylene/High-Density Polyethylene Blends (MViPP/HDPE)
    3.5.2.3 High-Viscosity Isotactic Polypropylene/High-Density Polyethylene Blends (HViPP/HDPE)
3.6 DISCUSSION
  3.6.1 Discussion of the Blends’ Viscosities
3.7 CONCLUSIONS

CHAPTER 4: TRANSMISSION ELECTRON MICROSCOPY (TEM)

4.1 INTRODUCTION
4.2 EXPERIMENTAL TECHNIQUES
  4.2.1 Transmission Electron Microscope (TEM)
  4.2.2 Sample Preparation
4.3 EXPECTED BLEND MORPHOLOGIES
4.4 EXPERIMENTAL METHODS
4.5 RESULTS
  4.5.1 Rapidly Quenched Low-Viscosity Isotactic Polypropylene/High-Density Polyethylene (LViPP/HDPE) Blends
  4.5.2 Rapidly Quenched Medium-Viscosity Isotactic Polypropylene/High-
LIST OF TABLES

1.1 Properties of various polyethylenes and isotactic polypropylene 10
1.2 Manufacturers' data of the polymers used in my project 11
1.3 Densities of the homopolymers and blends, measured by flotation in water and isopropanol 11

3.1 Various constants used to calculate the viscosity of the homopolymers in the linear power law region 50

4.1 Morphologies obtained for each blend composition in each blend system 76

5.1 Crystallinities of the MViPP/HDPE homopolymers and blends 96
5.2 Crystallinities of the LViPP/HDPE homopolymers and blends 96
5.3 Crystallinities of the HViPP/HDPE homopolymers and blends 96
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Skeletal Structure of various different polyethylenes</td>
<td>12</td>
</tr>
<tr>
<td>1.2</td>
<td>Crystal structure of high-density polyethylene</td>
<td>13</td>
</tr>
<tr>
<td>1.3</td>
<td>Crystal structure of isotactic polypropylene</td>
<td>13</td>
</tr>
<tr>
<td>2.1</td>
<td>Variation of $\Delta G_m$ with composition $\phi_2$ at temperatures (a) $T_1$ and (b) $T_2$</td>
<td>28</td>
</tr>
<tr>
<td>2.2</td>
<td>Phase diagram constructed from figure 2.1, showing the spinodal and binodal boundaries.</td>
<td>28</td>
</tr>
<tr>
<td>2.3</td>
<td>Different forms of phase diagram indicating different levels of miscibility</td>
<td>29</td>
</tr>
<tr>
<td>2.4</td>
<td>A schematic illustration of the concentration profiles and corresponding 2D morphologies during phase separation</td>
<td>30</td>
</tr>
<tr>
<td>2.5</td>
<td>A 2D representation of a polymer solution and polymer blend, using the simple lattice model</td>
<td>31</td>
</tr>
<tr>
<td>2.6</td>
<td>Schematic representation of the fringed micelle model</td>
<td>31</td>
</tr>
<tr>
<td>2.7</td>
<td>Schematic representation of a polyethylene lamella, grown from dilute solution</td>
<td>32</td>
</tr>
<tr>
<td>2.8</td>
<td>Schematic representation of the chain folding in melt grown lamellae.</td>
<td>32</td>
</tr>
<tr>
<td>2.9</td>
<td>Polyethylene and polypropylene spherulites, viewed in an optical microscope through crossed polarizers</td>
<td>33</td>
</tr>
<tr>
<td>2.10</td>
<td>Schematic representation of a spherulite</td>
<td>33</td>
</tr>
<tr>
<td>2.11</td>
<td>Polyethylene spherulites viewed in a transmission electron microscope (TEM).</td>
<td>34</td>
</tr>
<tr>
<td>2.12</td>
<td>Polyethylene shish kebab viewed in a TEM</td>
<td>34</td>
</tr>
<tr>
<td>2.13</td>
<td>Schematic representation of the change in free energy, $\Delta G$, for homogeneous nucleation during the first stages of polymer crystallization</td>
<td>35</td>
</tr>
<tr>
<td>2.14</td>
<td>Schematic illustration of the secondary nucleation process for crystal growth</td>
<td>35</td>
</tr>
<tr>
<td>3.1</td>
<td>Schematic illustration of the ASTM test used to determine melt flow rate, MFR</td>
<td>50</td>
</tr>
<tr>
<td>3.2</td>
<td>Schematic illustration of planar shear flow</td>
<td>51</td>
</tr>
<tr>
<td>3.3</td>
<td>Idealised shear stress-shear rate plot and idealised viscosity curve for a Newtonian and shear thinning fluid</td>
<td>51</td>
</tr>
<tr>
<td>3.4</td>
<td>Idealised logarithmic plot of viscosity as a function of shear rate for a shear thinning fluid</td>
<td>52</td>
</tr>
<tr>
<td>3.5</td>
<td>Schematic illustration of the Davenport capillary rheometer</td>
<td>53</td>
</tr>
<tr>
<td>3.6</td>
<td>Bagley plots of the four homopolymers</td>
<td>54</td>
</tr>
<tr>
<td>3.7</td>
<td>Plots demonstrating the effect of the end pressure losses for the four homopolymers</td>
<td>56</td>
</tr>
<tr>
<td>3.8</td>
<td>True shear stress as a function of apparent shear rate for all four homopolymers</td>
<td>58</td>
</tr>
<tr>
<td>3.9</td>
<td>True shear stress versus apparent shear rate on a logarithmic scale</td>
<td>58</td>
</tr>
<tr>
<td>Section</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>3.10</td>
<td>True shear stress as a function of true shear rate for all four homopolymers</td>
<td>59</td>
</tr>
<tr>
<td>3.11</td>
<td>True viscosity as a function of true shear rate for all four homopolymers</td>
<td>59</td>
</tr>
<tr>
<td>3.12</td>
<td>True shear stress as a function of true shear rate for the LViPP/HDPE blends</td>
<td>60</td>
</tr>
<tr>
<td>3.13</td>
<td>True shear stress as a function of true shear rate for the MViPP/HDPE blends</td>
<td>60</td>
</tr>
<tr>
<td>3.14</td>
<td>True shear stress as a function of true shear rate for the HViPP/HDPE blends</td>
<td>61</td>
</tr>
<tr>
<td>3.15</td>
<td>True shear stress of the blends measured at a true shear rate of 1000s⁻¹</td>
<td>61</td>
</tr>
<tr>
<td>4.1</td>
<td>Micrographs taken from the surface and middle of a 10% MViPP blend sheet</td>
<td>77</td>
</tr>
<tr>
<td>4.2</td>
<td>Micrographs of the rapidly quenched LViPP/HDPE blends</td>
<td>78</td>
</tr>
<tr>
<td>4.3</td>
<td>Micrographs of the rapidly quenched MViPP/HDPE blends</td>
<td>80</td>
</tr>
<tr>
<td>4.4</td>
<td>Micrographs of the rapidly quenched HViPP/HDPE blends</td>
<td>82</td>
</tr>
<tr>
<td>4.5</td>
<td>Micrographs of the MViPP/HDPE blends cooled at 1°C/minute</td>
<td>84</td>
</tr>
<tr>
<td>4.6</td>
<td>Micrographs of the MViPP/HDPE blends cooled at 3°C/minute</td>
<td>86</td>
</tr>
<tr>
<td>5.1</td>
<td>Typical DSC trace showing three thermal transitions</td>
<td>97</td>
</tr>
<tr>
<td>5.2</td>
<td>DSC melting endotherms for the rapidly quenched MViPP/HDPE homopolymers and blends</td>
<td>98</td>
</tr>
<tr>
<td>5.3</td>
<td>Peak melting temperatures of each component in the rapidly quenched blends</td>
<td>99</td>
</tr>
<tr>
<td>5.4</td>
<td>DSC crystallization exotherms for the MViPP/HDPE homopolymers and blends cooled at 80°C/minute</td>
<td>101</td>
</tr>
<tr>
<td>5.5</td>
<td>DSC crystallization exotherms illustrating the effect of blending on the components</td>
<td>102</td>
</tr>
<tr>
<td>5.6</td>
<td>DSC crystallization exotherms for the MViPP/HDPE homopolymers and blends cooled at 1°C/minute</td>
<td>103</td>
</tr>
<tr>
<td>5.7</td>
<td>Onset crystallization temperatures for MViPP/HDPE blends, cooled at various rates from the melt</td>
<td>104</td>
</tr>
<tr>
<td>5.8</td>
<td>DSC crystallization exotherms for the LViPP/HDPE blends cooled at 80°C/minute</td>
<td>106</td>
</tr>
<tr>
<td>5.9</td>
<td>DSC crystallization exotherms for the HViPP/HDPE blends cooled at 80°C/minute</td>
<td>107</td>
</tr>
<tr>
<td>5.10</td>
<td>Onset crystallization temperatures for LViPP/HDPE blends, cooled at 80°C/minute</td>
<td>108</td>
</tr>
<tr>
<td>5.11</td>
<td>Onset crystallization temperatures for HViPP/HDPE blends, cooled at 80°C/minute</td>
<td>108</td>
</tr>
<tr>
<td>6.1</td>
<td>Idealised nominal stress-strain behaviour of a ductile polymer subjected to tensile testing</td>
<td>129</td>
</tr>
<tr>
<td>6.2</td>
<td>Nominal stress-strain curves illustrating the effect of temperature and strain rate</td>
<td>129</td>
</tr>
<tr>
<td>6.3</td>
<td>Schematic curves of true stress versus nominal strain illustrating the Considère construction</td>
<td>130</td>
</tr>
<tr>
<td>6.4</td>
<td>Schematic representations of the parallel (Voigt) and series (Reuss) models</td>
<td>130</td>
</tr>
<tr>
<td>6.5</td>
<td>WAXD patterns of the rapidly quenched MViPP/HDPE blends</td>
<td>131</td>
</tr>
</tbody>
</table>
6.6 Typical load-extension curves for the various blend systems 132
6.7 Variation of Young's modulus with composition for the rapidly quenched LViPP/HDPE blends 132
6.8 Variation of yield strength with composition for the rapidly quenched LViPP/HDPE blends 134
6.9 Extension to break values for the rapidly quenched LViPP/HDPE blends 134
6.10 Variation of tensile strength with composition for the rapidly quenched LViPP/HDPE blends 135
6.11 Variation of Young's modulus with composition for the rapidly quenched MViPP/HDPE blends 135
6.12 Variation of yield strength with composition for the rapidly quenched MViPP/HDPE blends 136
6.13 Extension to break values for the rapidly quenched MViPP/HDPE blends 136
6.14 Variation of tensile strength with composition for the rapidly quenched MViPP/HDPE blends 137
6.15 Variation of Young's modulus with composition for the rapidly quenched HViPP/HDPE blends 137
6.16 Variation of yield strength with composition for the rapidly quenched HViPP/HDPE blends 138
6.17 Extension to break values for the rapidly quenched HViPP/HDPE blends 138
6.18 Variation of tensile strength with composition for the rapidly quenched HViPP/HDPE blends 139
6.19 Variation of Young's modulus with composition for the slowly cooled MViPP/HDPE blends 139
6.20 Variation of tensile strength with composition for the slowly cooled MViPP/HDPE blends 140
CHAPTER 1: INTRODUCTION

1.1 GENERAL INTRODUCTION

Since the first fully synthetic polymers were made in the early 1900s, the growth of the polymer industry has been immense. Over the past century, polymers, or plastics as they are commonly known, have replaced many other materials in our everyday lives: packaging, containers, casing, fabrics, toys, engineering materials and spectacles are just some of the many applications of these materials. The increase in use has been due to several factors. Although polymers may be mechanically weak compared to materials such as metals and ceramics, their strength and stiffness compare favourably to these materials when their low density is considered. Also, their manufacturing costs are considerably lower than those of many other materials. Another reason for their popularity is the ease with which they are processed; polymers melt at relatively low temperatures and are ideal for moulding into intricate shapes.

Of all the synthetic polymers, polyolefins are the most widely used and this is one of the reasons why I have studied these materials. Olefins are hydrocarbons whose molecules contain a pair of carbon atoms linked together by a double bond. They are mostly derived from natural gas or from low molecular weight constituents of petroleum. Olefin molecules can be represented by the chemical formula \( \text{CH}_2=\text{CHR} \), where R represents a hydrogen atom or hydrocarbon group of varying composition. As the repeating unit of a polymer their chemical structure can be represented as \( -[\text{CH}_2-\text{CHR}]_n- \). The composition and structure of R will determine the properties of the polymer. Polyethylene (where R is a hydrogen atom) and polypropylene (where R is a methyl group) are the most widely available polyolefins and come in various different forms.

Before discussing the different forms of polyethylene and polypropylene it is necessary to define the terms molecular weight and polydispersity. Molecular weight, otherwise known as relative molecular mass, is equal to the number of repeat units in the macromolecular chain multiplied by the molecular weight of the repeat unit. Molecular weight is a dimensionless quantity and is a number typically in excess of 10,000. By multiplying the numerical value of molecular weight by the units g mol\(^{-1}\), it can be converted into the equivalent value of molar mass. For example, a polymer with a molecular weight of 50,000 has a molar mass of 50,000 g mol\(^{-1}\). For most polymers the number of repeat units varies between the chains, leading to a molar mass distribution. For
convenience the molar mass distribution is characterised in terms of molar mass averages. These averages are known as the weight average molar mass, $M_w$, and the number average molar mass, $M_n$:

$$M_w = \frac{\sum NiMi^2}{\sum NiMi} \quad (1.1) \quad \text{and} \quad M_n = \frac{\sum NiMi}{\sum Ni} \quad (1.2)$$

where $Ni$ is the number of chains of molar mass $Mi$.

The ratio $M_w/M_n$ is known as the polydispersity index, $p$. Polymers typically have a polydispersity of $p = 1.5 - 5$. If, however, all of the chains are the same length, i.e. $p = 1$, the polymer is termed monodisperse. (N.B. Throughout the rest of this chapter the term molecular weight is used interchangeably with the number average molar mass.)

The properties of polymers in the molten state are highly influenced by molecular weight. A polymer melt consists of essentially randomly coiled macromolecular chains; the higher the molecular weight, the longer the chains and the more entanglements there will be. Hence melt flow properties such as viscosity are highly dependent on molecular weight.

In industry polymers are processed in the molten state using a variety of methods such as compression moulding, extrusion, blow moulding, injection moulding and thermoforming. In compression moulding the polymer is melted and pressed into a film or mould. During extrusion the material is melted in a barrel and then forced through an opening (die) to form sheets or fibres. Blow moulding involves extruding or injecting a tube of molten polymer into a mould; the polymer tube is then blown from the inside until it fills the mould. In injection moulding the polymer is forced into the mould at a very high pressure. The mould is kept at a given temperature while the polymer crystallizes; the mould is then opened and the finished article is ejected. Thermoforming is the general term used for the process of making plastic parts from a flat sheet of plastic through pressure and temperature. When choosing any of these processing methods molecular weight must be carefully considered as certain grades of polymer are more suited to some processes than others. For example, blow moulding generally requires higher molecular weight materials than injection moulding. During blow moulding the extruded polymer tube must be self-supporting as it is blown into the mould. If the viscosity of the polymer is too low, the tube may be unable to hold its shape, making it difficult to blow. For injection moulding a low viscosity polymer is more suitable, as it flows into the mould more easily than a high viscosity polymer.
Molecular weight also influences the properties of polymers in the solid state such as tensile modulus and tensile strength (both of which generally increase with increasing molecular weight). Again, different grades of polymer are used for different applications. For example, stiff, strong polymers with very high molecular weights are used in orthopaedic implants; polymers with lower molecular weights are often used in disposable food packaging.

Returning to the different forms of polyolefins, polyethylene (PE) can be classified according to its density and degree of chain branching. If polyethylene is composed of essentially linear molecules (with very few chain branches) it is known as high-density polyethylene (HDPE) – see figure 1.1. HDPEs are available in a variety of molecular weights, ranging from roughly 10,000 to 500,000. Linear polyethylenes with molecular weights in the region of 3,000,000 to 6,000,000 are termed ultra high molecular weight polyethylenes (UHMWPE).

Polyethylenes with chain branching include low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE) and very low-density polyethylene (VLDPE). The skeletal structures of these are shown in figure 1.1. LDPEs have a tree-like structure with irregular branches that vary greatly in length. LDPEs typically have 30 short chain branches (1-3 carbon atoms long) and 30 long chain branches (tens of carbon atoms long) per 1000 backbone carbon atoms. LLDPEs and VLDPEs have short chain branches (1-3 carbon atoms long); their frequency can range from 1-100 branches per 1000 backbone carbon atoms.

Linear polyethylenes are generally denser and more rigid than the branched versions as the lack of branching allows the polymer chains to pack closely together, resulting in a dense, highly crystalline material. Note that UHMWPE is less crystalline than HDPE because of its very long chains and resulting entanglements. Branched polyethylenes are less crystalline and therefore more flexible than their linear counterparts. The variety of properties that can be achieved by varying the molecular weight, density and degree of chain branching means that polyethylenes can be used in numerous applications, some of which are listed in table 1.1. On the negative side, some polyethylenes - especially HDPE- can be highly susceptible to environmental stress cracking; this means that certain fluids, for instance liquid detergents, can initiate premature cracking and embrittlement of the material whilst it is under stress. Elevated temperatures tend to accelerate this cracking.

Polypropylene (PP) is classified according to its tacticity. Tacticity refers to the positioning of the methyl groups on the hydrocarbon backbone. Isotactic PP has all the groups on the same side of the hydrocarbon chain, syndiotactic PP has them on alternate sides, and atactic PP has them positioned randomly. The only widely available commercial form of polypropylene is isotactic, as it has the greatest ability to crystallize (atactic does not crystallize at all). Isotactic polypropylene shares
some of the properties of high-density polyethylene, but it is generally stiffer and has a higher melting temperature. However, it is more sensitive to oxidation, has lower impact strength and a higher glass transition temperature (around -10°C compared to -100°C for HDPE) meaning that its uses are limited at low temperatures. Polypropylene has numerous end uses, some of which are listed in table 1.1.

Other factors that can vary between different grades of polymer are the type and number of additives. When polymers are manufactured in bulk the materials are not pure; additives may be present, which act as heterogeneous nucleating agents. These additives aid the crystallization process by providing many nucleation sites, and allow the materials to crystallize at higher temperatures than they otherwise would. These factors affect the final characteristics of the material such as the size of the crystals and the degree of crystallinity, which can in turn have a profound effect on the materials' optical and mechanical properties. Nucleating agents are often specifically chosen to suit the material being processed; they can be inorganic additives such as talc or silica, organic compounds such as salts or colour pigments, or copolymers such as ethylene/acrylic esters. These agents - generally in powder form - are distributed uniformly throughout the polymer during melt processing and are usually present in quantities of 0.1% or less. Foreign bodies such as dust and dirt in the processing machinery may also act as heterogeneous nucleating agents.

The polymer industry is always looking to improve existing materials at low cost. By varying factors like density and molecular weight and by introducing additives, the properties of a polymer can be tailored to suit specific applications. Another way in which this is accomplished is by physically blending two or more polymers together. Blending is the equivalent of alloying in metals and is usually achieved by melt mixing followed by extrusion. Melt mixing typically involves placing pellets of each material (in the desired proportions) into an extruder. The extruder melts the pellets and mixes them using a screw mechanism. Once mixed the blended material is ejected through a die, quenched into a cold water bath and collected. The extruder is similar to a giant food processor or mincing machine. For thermodynamic reasons most polymers are immiscible in the melt, meaning that polymer blends are almost always phase separated materials. The aim of blending is to combine the attractive qualities of the constituent polymers and improve the deficient properties of one or more of the components. For example, when a soft, rubbery polymer like polybutadiene is introduced into a hard, brittle plastic like polystyrene, the resulting phase separated material is more elastic than the pure polystyrene, impact-resistant and protected against cracking.

Nearly all polymers are incompatible; this means that they do not produce materials with desirable properties when blended. Poor properties often result from a lack of good interfacial adhesion
between the immiscible components in the blend. It must be noted that the term 'incompatibility' is not the same as immiscibility; polymers may be compatible despite being immiscible, like the polybutadiene/polystyrene blends mentioned above. When polymers are incompatible, materials known as 'compatibilizers' may be added in order to promote mixing and to control the morphology and properties of the final material. Di-block co-polymers are commonly used as compatibilizers. Each block in the co-polymer reacts or mixes with one of the blend’s components; because of this the co-polymer tends to situate itself along the interfacial boundaries thus improving the adhesion between the components.

Another way in which polymer blending could be potentially useful is in the recycling of plastics. Currently, recycling plastic waste can often cost more than manufacturing virgin materials and is therefore commercially unpopular. As mentioned above different types of polymers are nearly always incompatible and must be separated before recycling is possible. Although this may be achieved, for instance, by separating the materials according to their density, this becomes difficult when the polymers belong to the same family and have similar densities - as is the case for polyethylene and polypropylene. Recycling may therefore involve reusing polyethylene contaminated with polypropylene; i.e. a polyethylene/polypropylene blend. If these materials could be processed in such a way as to produce desirable mechanical properties, blending could prove to be very useful in the recycling business.

Given that polyethylene and polypropylene are the most widely used polymers and chemically the simplest, the properties of these materials when blended have received a lot of attention. Some researchers choose to concentrate on their physical properties such as phase behaviour, structure and morphology, crystallization, etc.; while others look at their rheological properties (i.e. melt flow properties); others still, concentrate on their mechanical properties. Despite the numerous studies on polyethylene/polypropylene blends, authors continue to report contradictory findings. For instance, some found that adding small amounts of polyethylene to polypropylene could change the polypropylene’s crystallinity and hence its mechanical properties (Lovinger and Williams, 1980; Noel III and Carley, 1975). Conversely, others (e.g. Wenig and Meyer, 1980) reported that the crystallization of polypropylene was unaffected by the presence of polyethylene. Some authors (e.g. Bains et al., 1994) reported that by closely matching the viscosities of the component polymers, particularly good mechanical properties could be achieved, while others (e.g. Gunderson and Chilcote, 1991) did not find a link between the viscosity ratio of the components and the blends’ mechanical properties. Veenstra et al. (2000) reported that morphology could have an effect on a blend’s final properties and that changing from one type of morphology to another could improve the blend’s mechanical performance.
The examples given above are just some of many conflicting results and views. In order to resolve some of these issues I have studied various properties of isotactic polypropylene/high-density polyethylene (iPP/HDPE) blends. My interest has centred on the mechanical properties of the blends as these determine their end uses and are the most significant from a commercial viewpoint. The most interesting and important result of my study is the observation that under certain processing conditions blends can be produced that have higher Young's (tensile) moduli than any of the existing models of composite materials predict. The rest of my project has concentrated on finding an explanation for this behaviour. I have achieved this by varying the processing conditions of the samples (including the cooling rate) and by using various experimental techniques to characterise the blends. I looked at the effect that viscosity can have on a blend's properties by studying three different blend systems with components of varying viscosity ratios. I then used transmission electron microscopy (TEM) to examine the morphologies of the blends cooled at different rates. I also used differential scanning calorimetry (DSC) to study the melting and crystallization behaviour of the materials cooled at different rates. Finally, I employed wide angle X-ray diffraction (WAXD) to determine whether molecular orientation was present in the samples used for mechanical testing. This was a different approach from those of the authors mentioned above, who only used one or two techniques to characterise their blends. My aim was to ascertain how a range of factors affect each other and which, if any, are the most important in determining the mechanical properties of the blends.

From this detailed investigation, I deduced that crystallization effects were the most probable cause of the unexpectedly high Young's moduli. Further, by varying the crystallization conditions of my blends, I believe that I have found a possible explanation as to why many previous works disagree with each other.

In the following section, details of the materials used are given, along with a description of how the blends were prepared. The final section of this chapter provides an outline to the rest of the thesis.

1.2 MATERIALS

The polyethylene used in this project was a linear high-density polyethylene (HDPE). The most common crystalline structure of HDPE is orthorhombic and has two chains per unit cell. The cell parameters are \( a = 0.7148 \text{nm}, b = 0.4946 \text{nm} \) and \( c = 0.254 \text{nm} \) - see figure 1.2. The polypropylene used in this project was the isotactic form (iPP). The most common crystalline structure of iPP is the \( \alpha \)-phase (\( \alpha \text{iPP} \)). The \( \alpha \text{iPP} \) unit cell is monoclinic and the chains form a 3, helix. The cell parameters are \( a = 0.665 \text{nm}, b = 2.096 \text{nm}, c = 6.5 \text{nm} \) and \( \beta = 99^\circ 80 \) - see figure 1.3. Polypropylene can also form a \( \beta \)-phase and a \( \gamma \)-phase (see e.g. Lotz and Wittmann, 1996).
Three grades of polypropylene (iPP) were supplied by Borealis and a high-density polyethylene (HDPE) was supplied by BP Chemicals. These homopolymers were supplied as small pellets and the manufacturers' data is given in table 1.2 below. The polypropylenes were named according to their relative viscosities. (N.B. low melt flow rate implies high viscosity; viscosities were not available from the manufacturers and had to be measured - see Chapter 3.) Talc had been used as a nucleating agent in the polypropylenes, although the proportions of talc added were not stated in the manufacturer's data. The type and amount of nucleating agent added to the HDPE were not available in the manufacturer's data.

1.2.1 Blend Preparation
Three sets of blends were prepared by blending each of the isotactic polypropylenes with the high-density polyethylene; the blends were named:

- Low-viscosity isotactic polypropylene/high-density polyethylene (LViPP/HDPE),
- Medium-viscosity isotactic polypropylene/high-density polyethylene (MViPP/HDPE),
- High-viscosity isotactic polypropylene/high-density polyethylene (HViPP/HDPE).

The polymers were blended by melt mixing in a PRISM® miniature co-rotating twin-screw extruder. Mixtures of iPP and HDPE beads, to a total of 200g, were weighed in appropriate quantities for each blend composition. Blends were labelled according to their percentage composition (by mass) of iPP, thus a 10% blend contained 10% iPP and 90% HDPE by mass. For each set of polymers, blends of 10, 30, 40, 50, 60, 70 and 90% iPP were prepared. In order to ensure that all of the samples had been prepared in the same way, the homopolymers were also passed through the extruder.

The twin-screw extruder had a screw diameter of 16 mm and a barrel length/diameter ratio of 25:1. It was operated at 200 rpm. The barrel could be set to different temperatures along its length, though due to work dissipated the actual temperatures experienced by the melt may have been slightly higher than those set. The first section was set to 100°C, the central section to 200°C and the die to 200°C. The extruded blend was quenched into a cold water bath (~20°C), and then pelletized. Studying the blends after being extruded once (using TEM and DSC) showed that the components were very unevenly distributed and that the scale of the phase separated domains was of the order of millimetres. As the samples used for mechanical testing were only 0.3 mm thick (see below), a sample that was nominally 50% iPP, might have contained different proportions of each material depending on how it was cut. To ensure that the components were more evenly mixed and that the scale of phase separation was suitable for the mechanical tests, the blends were passed through the extruder twice. This had the effect of reducing the size of the phase separated domains to the order of microns (Finlay et al., 2001).
After examining the blends in the transmission electron microscope I found that the 100% HViPP was contaminated with a small amount of HDPE. During preparation, each blend percentage was passed through the extruder twice before changing directly to the next composition. On changing compositions about a metre of extrudate was discarded before the new blend was collected. When the 100% blend was extruded the first time, a small amount of the 90% blend must have been present which then became evenly distributed throughout the polypropylene during the second extrusion. By studying several micrographs of the nominal 100% blend, I estimated the percentage of polyethylene to be <0.5%. As a result, this blend was renamed 99.5% HViPP and a new 100% blend was made which was not contaminated.

Because of the various complicated mechanisms operating in the twin-screw extruder it is extremely difficult to calculate the strain rate experienced by the melt. I estimate the shear (strain) rate to be in excess of 1000s\(^{-1}\). When MViPP and HViPP were blended with the HDPE, the extrudate was very smooth, however when the LViPP was blended with the HDPE, the extrudate exited in spurts and was very distorted; the die swell was considerably larger for the LViPP/HDPE blends. This observation will be discussed further in Chapter 3.

1.2.2 Sheet Preparation

For many of the tests (e.g. the tensile tests), pellets were not suitable. The pellets were therefore made into sheets, 0.15m square and 0.3mm thick, by compression moulding in a hot press at 200°C between aluminium plates. The pellets were placed between the plates in the middle of a square aluminium spacer (to give the aforementioned dimensions) and were then placed in the hot press using an initial pressure of 0.9MPa and a final pressure of 4.5MPa. When the pressure became stable at 4.5MPa (after 10 minutes) the press was released. As the cooling rate in the hot press could not be controlled, the sheets were cooled in various reproducible ways. Rapid quenching - a technique commonly used by polymer manufacturers - was achieved by dropping the sheets into cold water at 20°C. Two different slow cooling rates were achieved by leaving the sheets to cool outside the hot press, and inside the hot press with the power switched off. The average rates of cooling between 140°C and 100°C (the temperature region in which the crystallization took place) were measured using a thermocouple (placed in the middle of the polymer samples, between the metal spacers) attached to a chart recorder. The cooling rates were found to be approximately 100°C, 3°C and 1°C/minute respectively. When the thermocouple was removed, it was always found to be embedded in the centre of the sample. It must be noted that due to the temperature gradient throughout a sheet, the outside will have cooled faster than the middle: the values given above most likely represent the slowest cooling rate throughout the sheet.

I was particularly interested in the properties of blends that had been rapidly quenched in a water bath, as this technique closely resembles the way polymers are manufactured in industry. I
therefore studied the properties of all three sets of blends after rapid quenching. The materials cooled slowly from the melt were only interesting from a purely scientific viewpoint, as such materials would take too long to process in industry. The slow cooling rates were only applied to the medium-viscosity isotactic polypropylene/high-density polyethylene (MViPP/HDPE) blends.

1.2.3 Density Measurements
When referring to the blends throughout the thesis the mass fraction is generally used. However, for mechanical models, volume rather than mass fraction is needed. In order for this to be calculated, the densities of the homopolymers and blends were measured by flotation in mixtures of water and isopropanol. Because the densities of the homopolymers are very close in value, the numerical values for the mass and volume fractions for each blend are very similar. For example, a rapidly quenched 50% MViPP, named according to mass, is 50.4% according to its volume. The densities are given in Table 1.3.

1.3 ORGANISATION OF THESIS

The rest of the thesis is primarily organised according to experimental technique. Each experimental chapter includes its own theory section and literature review. In Chapter 2, some of the theories that are relevant to the whole project, rather than a specific technique, are reported. The main topics of Chapter 2 are phase separation and crystallization. In Chapter 3 the melt viscosities of the individual components and of the blends, measured by capillary extrusion rheometry, are given. Chapter 4 presents the morphologies of the rapidly quenched and slowly cooled homopolymers and blends; pictures were obtained using a transmission electron microscope (TEM). TEM was used to reveal information about the size and shape of the crystalline lamellae. It also revealed information that other techniques could not about the phase behaviour of the blends including the size, shape and distribution of the phase separated components within the blends. Chapter 5 details the differential scanning calorimetry (DSC) results. DSC was used to study the phase behaviour of the samples quenched rapidly from the melt and the crystallization behaviour of the samples cooled at various rates, including rapid quenching and slow cooling. The final, and most important, experimental chapter - Chapter 6, presents the mechanical properties of all the blends and their components determined by tensile testing. Wide-angle X-ray diffraction results (taken in collaboration with another PhD student) are also reported in this chapter. In Chapter 7, a summary of the experimental chapters is given along with a general discussion of the results. Finally, conclusions and suggestions for future work are given in Chapter 8.
Table 1.1 Properties of various polyethylenes and isotactic polypropylene

<table>
<thead>
<tr>
<th>Class</th>
<th>Density (kgm(^{-3}))</th>
<th>Crystallinity (%)</th>
<th>Melting Point (°C)</th>
<th>Properties</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultra high molecular weight polyethylene (UHMWPE)</td>
<td>935-950</td>
<td>40-75</td>
<td>135-138</td>
<td>Strongest, stiffest and toughest PE. Highly resistant to abrasion and wear.</td>
<td>Medical equipment and implants. Bullet-proof vesting.</td>
</tr>
<tr>
<td>Linear low-density polyethylene (LLDPE)</td>
<td>915-930</td>
<td>60-85</td>
<td>120-125</td>
<td>More flexible than UHMWPE and HDPE. High impact strength. Better ESCR than HDPE or LDPE.</td>
<td>Film, moulding, pipes, cables, toys and vacuum packaging.</td>
</tr>
<tr>
<td>Low-density polyethylene (LDPE)</td>
<td>910-925</td>
<td>50-70</td>
<td>115-120</td>
<td>Similar properties to LLDPE. More glossy than LLDPE</td>
<td>Bin liners and supermarket carrier bags.</td>
</tr>
<tr>
<td>Very low-density polyethylene (VLDPE)</td>
<td>890-900</td>
<td>30-40</td>
<td>100-105</td>
<td>Most flexible PE. Highly tear resistant.</td>
<td>Frozen food packaging. Shrink wrap</td>
</tr>
</tbody>
</table>
### Table 1.2 Manufacturers’ data of polymers used.

<table>
<thead>
<tr>
<th>Code</th>
<th>High-density polyethylene (HDPE)</th>
<th>Low-viscosity iPP (LViPP)</th>
<th>Medium-viscosity iPP (MViPP)</th>
<th>High-viscosity iPP (HViPP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>HD6070</td>
<td>XP171SC</td>
<td>P123FE</td>
<td>M9</td>
</tr>
<tr>
<td>Number Average Molecular Weight, $M_N$</td>
<td>11,000</td>
<td>58,900</td>
<td>77,400</td>
<td>100,000</td>
</tr>
<tr>
<td>Weight Average Molecular Weight, $M_w$</td>
<td>72,000</td>
<td>208,000</td>
<td>377,000</td>
<td>380,000</td>
</tr>
<tr>
<td>Polydispersity Index, $p$</td>
<td>6.5</td>
<td>3.5</td>
<td>4.8</td>
<td>3.8</td>
</tr>
<tr>
<td>Tacticity (%)</td>
<td>N/A</td>
<td>89.01</td>
<td>93.21</td>
<td>90.96</td>
</tr>
<tr>
<td>Melt Flow Rate, MFR, (g/10min) ASTM D1238</td>
<td>7.6 (180°C/2.16g)</td>
<td>37 (230°C/2.16g)</td>
<td>3 (230°C/2.16g)</td>
<td>2.4 (230°C/2.16g)</td>
</tr>
</tbody>
</table>

### Table 1.3 Densities in kg/m³ of the homopolymers and blends measured by flotation in water and isopropanol. (Error ±1 kg/m³)

<table>
<thead>
<tr>
<th>Blend (%iPP)</th>
<th>0</th>
<th>10</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>90</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rapidly quenched LViPP/HDPE</td>
<td>975</td>
<td>975</td>
<td>972</td>
<td>971</td>
<td>969</td>
<td>967</td>
<td>966</td>
<td>963</td>
<td>961</td>
</tr>
<tr>
<td>Rapidly quenched MViPP/HDPE</td>
<td>975</td>
<td>975</td>
<td>973</td>
<td>972</td>
<td>971</td>
<td>969</td>
<td>968</td>
<td>965</td>
<td>963</td>
</tr>
<tr>
<td>Rapidly quenched HViPP/HDPE</td>
<td>975</td>
<td>975</td>
<td>973</td>
<td>972</td>
<td>971</td>
<td>970</td>
<td>969</td>
<td>967</td>
<td>966</td>
</tr>
<tr>
<td>MViPP/HDPE cooled at 3°C/min</td>
<td>980</td>
<td>978</td>
<td>976</td>
<td>975</td>
<td>974</td>
<td>973</td>
<td>972</td>
<td>970</td>
<td>969</td>
</tr>
<tr>
<td>MViPP/HDPE cooled at 1°C/min</td>
<td>983</td>
<td>980</td>
<td>977</td>
<td>976</td>
<td>974</td>
<td>973</td>
<td>972</td>
<td>971</td>
<td>971</td>
</tr>
</tbody>
</table>
High-density polyethylene (HDPE)

Low-density polyethylene (LDPE)

Linear low-density polyethylene (LLDPE)

Very low-density polyethylene (VLDPE)

Figure 1.1 Skeletal structures of various different polyethylenes.
Figure 1.2 The crystal structure of orthorhombic high-density polyethylene.\([-\text{CH}_2 - \text{CH}_2\text{]_n}\) (a) General view of unit cell. (b) Projection of unit cell parallel to the chain axis. Adapted from Young and Lovell (1991).

Figure 1.3 The crystal structure of monoclinic isotactic polypropylene (\(\alpha\text{IPP}\)).\([-\text{CH}_2 - \text{CH}_2\text{]_n}\): (a) 3, helix. (b) Projection along the chain axis, two unit cells are shown here. Adapted from Young and Lovell (1991).
CHAPTER 2: PHASE BEHAVIOUR AND CRYSTALLIZATION OF POLYMER BLENDS: BACKGROUND THEORIES

2.1 INTRODUCTION

As stated in Chapter 1, each experimental chapter in this thesis deals with a different technique and includes its own theory section. This chapter introduces phase separation in polymer solutions and blends, and polymer crystallization as these topics are relevant to all the techniques used and cannot be limited to only one chapter.

2.2 PHASE SEPARATION

Polymer blends are composite materials composed of two or more different polymers, which are not chemically bonded to each other. Knowledge of the compatibility and miscibility of the components is essential in predicting and controlling a blend’s properties. For thermodynamic reasons mixtures of different polymers are often immiscible in the melt, i.e. the melt is phase separated into co-existing phases of differing compositions. When the scale of phase separation is on a molecular level the blend components are termed miscible, i.e. the melt is composed of a single homogeneous phase. However, polymer mixtures are not usually miscible over the entire temperature and composition range available; for example, for a given composition the components may be miscible or immiscible depending on the temperature of the melt - this is known as partial miscibility. The following section deals with polymer phase diagrams and the thermodynamics of mixing. Some of the theories discussed first deal with polymer solutions (as these systems are more simple) and are then developed to include polymer blends.

In practical terms a necessary, but not sufficient, test for miscibility in a polymer blend prepared at a certain temperature is the existence of a single glass transition temperature (Paul and Newman, 1978; Sperling, 1997). More generally a blend is termed miscible if all techniques used to study it, such as microscopy and calorimetry, show a single-phase material. Practical ways of determining phase separation are discussed in later chapters.
2.2.1 Conditions for Miscibility

Classically the thermodynamics of polymer blending can be expressed in terms of the Gibbs free energy change, $\Delta G_M$, for mixing two substances at a temperature $T$:

$$\Delta G_M = \Delta H_M - T\Delta S_M$$  \hspace{1cm} (2.1)

where $\Delta H_M$ is the enthalpy change on mixing and $\Delta S_M$ is the entropy change on mixing. The value of $\Delta G_M$ and its variation with composition depends on the competition between the configurational entropy and the energy associated with the interaction of the mixture components.

A negative $\Delta G_M$ is a sufficient condition for partial, but not necessarily complete, miscibility. In an ideal solution $\Delta H_M$ is zero. In polymer blends, interactions between the chains are usually unfavourable making $\Delta H_M$ positive, however, in some cases there are specific attractive interactions - such as hydrogen bonding - that make $\Delta H_M$ negative. For a mixing process, $\Delta S_M$ is positive, however it is smaller for a polymer-polymer mixture than for a mixture of simple liquids as the long chains prevent a large amount of disorder from occurring. A condition for complete miscibility at a given temperature is that the variation of $\Delta G_M$ with composition, $\phi$, must be concave with no inflection point, i.e.:

$$\left( \frac{\partial^2 \Delta G}{\partial \phi^2} \right)_{P,T} > 0$$  \hspace{1cm} (2.2)

Figure 2.1 shows $\Delta G_M$ as a function of composition, $\phi_2$, at temperatures (a) $T_1$ and (b) $T_2$. At temperature $T_1$ mixing is complete over the entire composition range as is evident by considering any point on the curve. If a mixture of composition $\phi_{2a}$ were to phase separate into compositions $\phi_{2a'}$ and $\phi_{2a''}$ the resulting $\Delta G_M$ would be positive; in this case demixing is not favoured.

The situation at temperature $T_2$ is more complex as two minima and two inflection points are present. In this case three types of phase stability are possible: stable, unstable and metastable, and the mixture is termed partially miscible. In the stable regions $0<\phi_2<\phi_{2b'}$ and $\phi_{2b''}<\phi_2<1$ the curve is concave as in figure 2.1(a) and the mixture is miscible. In the unstable region $\phi_{2a}<\phi_2<\phi_{2a''}$ the curve is convex, i.e.:

$$\left( \frac{\partial^2 \Delta G}{\partial \phi^2} \right)_{P,T} < 0$$  \hspace{1cm} (2.3)
The unstable region lies between the points of inflection, known as the spinodal points defined by:

\[
\frac{\partial^2 \Delta G}{\partial \phi^2} = 0
\]  

(2.4)

Spinodal decomposition has no nucleation free energy barrier. It refers to the process that occurs in the unstable region, by which small fluctuations in composition grow until the system becomes stable and the two co-existing phases have the binodal compositions \( \phi_{2b}' \) and \( \phi_{2b}'' \). The general condition for equilibrium between the two co-existing phases is that for each component, the chemical potential \( \mu = (\partial \Delta G/\partial \phi)_{P,T} \) must be the same in both phases, i.e.:

\[
\mu_1' - \mu_1^0 = \mu_1'' - \mu_1^0
\]  

(2.5a)

and

\[
\mu_2' - \mu_2^0 = \mu_2'' - \mu_2^0
\]  

(2.5b)

where the primes and double primes denote the different phases and \( \mu_i^0 \) is the chemical potential of component \( i \) in its standard state. Equations 2.5a and b are satisfied when two points on the curve have a common tangent, as is the case for the binodal points \( \phi_{2b}' \) and \( \phi_{2b}'' \) in figure 2.1(b).

Finally, the metastable region lies where \( \phi_{2b}' < \phi_2 < \phi_{2b}'' \) and \( \phi_{2s}' < \phi_2 < \phi_{2s}'' \). Phase separation into the binodal compositions is thermodynamically favoured, but will give rise to an increase in \( \Delta G_M \). For phase separation to occur this free energy barrier must be overcome.

### 2.2.2 Phase Diagrams

A phase diagram is constructed by plotting the spinodal and binodal points at varying temperatures as a function of composition, see figure 2.2. The spinodal curve sets the boundary of the unstable region and the binodal curve sets the boundary of the metastable region. The point where the spinodal and the binodal curves intersect is known as the critical point, associated with the critical temperature, \( T_{cr} \), and the critical composition \( \phi_{cr} \). A critical point can be located by applying the condition:

\[
\frac{\partial^2 \Delta G}{\partial \phi^2} = 0
\]  

(2.6)

In figure 2.2 the critical temperature is termed the upper critical solution temperature (UCST) as above this temperature all compositions are miscible. Mixtures can also exhibit a lower critical
solution temperature (LCST), as illustrated in figure 2.3(c); in this case all compositions below this temperature are miscible. Polymer blend phase diagrams may take many forms; figure 2.3 shows some examples.

2.2.3 Mechanisms of Phase Separation

Two mechanisms for phase separation are spinodal decomposition and nucleation and growth. Spinodal decomposition occurs in the unstable region of figures 2.1(b) and 2.2, where phase separation occurs spontaneously. Initially there are small-amplitude concentration fluctuations that increase with time. A new phase is created by an uphill diffusion process of molecules from regions of low concentration to regions of high concentration (negative diffusion coefficient). In the early stages, a fine bicontinuous morphology (both components form continuous phases) is formed and the composition changes with time. At the intermediate stages the morphology coarsens and the composition changes with time. In the final stages, the composition remains constant and the morphology continues to coarsen until the phases are discontinuous. Figure 2.4(a) shows the kinetic mechanism by which spinodal decomposition occurs and shows a schematic diagram of the changing morphology over time.

Nucleation and growth occurs in the metastable region indicated in figures 2.1(b) and 2.2. In this region the formation of a nucleus requires an initial activation energy, which must come from a finite temperature penetration, $\Delta T$, into the binodal region. The concentration in the immediate vicinity of the nuclei is low; the nuclei grow into droplets via a downhill diffusion process, where molecules diffuse from regions of high concentration to low concentration (positive diffusion coefficient). The droplets grow with time but their composition remains the same as that of the nuclei. As the droplets grow they will form a dispersed structure similar to the final stages of spinodal decomposition. Figure 2.4(b) shows the mechanism by which nucleation and growth occurs and also shows the morphology coarsening with time.

In both spinodal decomposition and nucleation and growth, the phases tend to coarsen or ripen with time. During ripening the domain sizes increase and may also change shape. Phase ripening is known to occur via two different methods; these are Brownian coalescence (Fortelny et al., 1988; Jang et al., 1984; Laverty et al., 1996; van Gisbergen and Meijer, 1991) and Ostwald Ripening (Hill and Barham, 1995; Mirabella, 1995; Mirabella and Barley, 1995; Ostwald, 1901; Sheng et al., 1997). In simple terms, Brownian coalescence involves small droplets approaching each other as a result of Brownian motion and coalescing to form larger droplets. During the process of Ostwald ripening, small droplets (which are thermodynamically less stable than larger ones) dissolve and diffuse towards the larger droplets. Hence the larger droplets grow at the expense of the smaller ones. Both Brownian coalescence and Ostwald ripening predict that the growth (or ripening) rate is proportional to the cube root of the time spent in the melt.
2.2 Thermodynamic Models of Mixing

Thermodynamic theories of mixing arose from the need to predict the phase behaviour of mixtures, as discussed in section 2.2.2. The three main theories are the classical theory, the statistical theory and the equation-of-state theories. The classical theory for the Gibbs free energy ($\Delta G_m = \Delta H_m - T\Delta S_m$), introduced in section 2.2.1, makes few assumptions about the size, shape and relative positions of the molecules. The statistical thermodynamic theory arranges all the molecules on a lattice and calculates the entropy by counting the number of molecular arrangements in space. This theory assumes that all the molecules are the same size and that the system is incompressible, i.e. no holes are allowed in the lattice. The well-known Flory-Huggins theory develops the simple lattice theory by considering polymer solutions, where the solvent and polymer molecules are different sizes; the theory then considers the interactions between the molecules. The equation-of-state theories take into account the relationship between temperature, pressure and volume, and unlike the statistical thermodynamic theory, assume that the system is compressible. The equations-of-state theories are, however, beyond the scope of this thesis and will not be discussed further.

2.2.4.1 Simple Lattice Theory

The statistical thermodynamic theory for an ideal solution ($\Delta H_m=0$) calculates the entropy, $\Delta S_m$, by counting the number of ways of arranging solvent and solute molecules on a lattice. Detailed derivation gives the Gibbs free energy to be:

$$\Delta G_m = -RT[n_1 \ln X_1 + n_2 \ln X_2]$$

(2.7)

Polymer solutions and blends are not ideal for two reasons - the difference in size of the solvent and solute molecules and the connectivity of the polymer chains; as a result the simple lattice theory fails to predict realistic thermodynamic properties for mixtures containing polymers.

2.2.4.2 Flory-Huggins Lattice Theory

Flory (1942) and Huggins (1942a,b,c) independently proposed a modified lattice theory which sets out to predict $\Delta G_m$ for the formation of polymer solutions. It considers the polymer molecules to be chains of segments, $x$, where each segment is equal to the size of a solvent molecule. On this basis, polymer and solvent molecules can be placed in a three-dimensional lattice consisting of identical cells, where each cell is occupied by a solvent molecule or a chain segment. Each polymer molecule is placed in the lattice so that its chain segments occupy a continuous sequence of $x$ cells, see figure 2.5(a). The theory was modified by Scott (1949) and Tompa (1949) to describe polymer blends by considering the solvent to be a polymer molecule with $x_1$ chain segments and the solute to be another polymer molecule of $x_2$ chain segments, see figure 2.5(b).
By considering the number of ways of arranging \( N \) solvent molecules and \( N \) solute molecules in a lattice of \( N = x_1N_1 + x_2N_2 \) cells, a new term for \( \Delta S_M \) can be derived:

\[
\Delta S_M = k_B \ln \left[ \left( \frac{N}{x_1N_1} \right)^{N_1} + \left( \frac{N}{x_2N_2} \right)^{N_2} \right]
\]

(2.8)

which simplifies to:

\[
\Delta S_M = -R \left[ n_1 \ln \phi_1 + n_2 \ln \phi_2 \right]
\]

(2.9)

where \( \phi_1 \) and \( \phi_2 \) are the volume fractions of solvent and solute respectively and are given by \( \phi_1 = x_1n_1 / (x_1n_1 + x_2n_2) \) and \( \phi_2 = x_2n_2 / (x_1n_1 + x_2n_2) \). \( x_i \) represents the number of equivalent segments in the species; for a monomeric solvent this will be 1 and for a polymer, this will be roughly equal to the number of repeat units.

The second development in the Flory-Huggins theory accounts for the intermolecular interactions - specifically the replacement of \([1,1]\) and \([2,2]\) interactions with \([1,2]\) interactions upon mixing. The interaction energy, \( \Delta w_{12} \), is given by:

\[
\Delta w_{12} = 2w_{12} - w_{11} - w_{22}
\]

(2.10)

If the system is a filled lattice with \( Z \) nearest neighbours, the dimensionless \( \chi_{12} \), known as the interaction parameter can be introduced:

\[
\chi_{12} = \frac{Z \Delta w_{12}}{2RT}
\]

(2.11)

In the original Flory-Huggins theory, \( \chi_{12} \) was assumed to be purely enthalpic; however, the theory was later modified to assume that \( \chi_{12} \) is a free energy term containing both enthalpic, \( \Delta w_{h12} \), and entropic, \( \Delta w_{s12} \), terms:

\[
\Delta w_{12} = \Delta w_{h12} - T\Delta w_{s12}
\]

(2.12)

The original Flory-Huggins theory could only predict the existence of the UCST in a phase diagram; however, by considering the enthalpic contribution to be temperature dependant the existence of a LCST could also be predicted.
Detailed derivation gives the Flory-Huggins equation for the Gibbs free energy change of mixing to be:

\[ \Delta G_M = RT \left[ n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \chi_1 \phi_1 \phi_2 \right] \]  

(2.13)

2.3 POLYMER CRYSTALLIZATION

Crystallization is the process whereby an ordered structure is produced from a disordered phase, usually a melt or dilute solution; melting can be considered as the opposite of this process. The ability of some polymers to crystallize has been recognised for many years as they exhibit first order transitions (melting) and show X-ray diffraction patterns characteristic of crystalline materials. The extent to which polymers crystallize depends on their molecular structure. Polymers rarely form completely crystalline materials as a consequence of their long chains and resulting entanglements; they are normally, at best, only semi-crystalline. Polymers with large amounts of chain branching such as branched polyethylene (LDPE) are less likely to crystallize than linear polymers such as linear polyethylene (HDPE). The degree of crystallinity of LDPE is typically 50-60\% compared to HDPE, which is typically 70-90\% crystalline. For polymers with regularly spaced pendant groups such as polypropylene, tacticity is crucial. For instance, in isotactic polypropylene the flexible carbon backbone can twist into a helical shape to incorporate the bulky side groups, as seen in Chapter 1, section 1.2. By adopting this crystalline form, polypropylene can achieve crystallinities of 50-60\%. However, in atactic polymers the randomly placed side groups cannot be incorporated into a crystal structure at all and the polymers are completely amorphous. Although polymers with bulky side groups like isotactic polypropylene can crystallize, their chains cannot pack very closely together meaning that their packing density is lower than those without side groups, such as HDPE.

The degree of crystallinity and the size and arrangements of the crystals all have a profound effect on the physical and mechanical properties of the polymer. Besides chemistry, many other factors affect the rate and extent to which crystallization can occur; amongst these factors are processing conditions (including rate of cooling), the presence of orientation in the melt and the melt temperature. Another important factor is the presence of additives, which can act as nucleating agents in the polymers.

2.3.1 Crystal Structure

Crystalline solids consist of regular, repeated, three-dimensional arrays of atoms. The repeating unit is known as the unit cell and the crystals are made up of stacks of these cells. The crystals formed by polymers are different from those formed by small molecules as the basis of the crystal
is only a part of the molecule, rather than the whole molecule (Wunderlich, 1973; Phillips, 1990). The crystals formed are thin platelets or lamellae with typical dimensions of 10-20 nm thick and 10µm long. The atoms are joined together by strong covalent bonds along the macromolecular chains and by weak intermolecular forces (van der Waals or in some cases hydrogen bonding) between the chains. As a result, polymer crystals are highly anisotropic. Like all crystals they contain defects; these include edge dislocations, screw dislocations and point defects. Defects resulting from molecular structure will also arise and are associated with chain ends and side groups.

2.3.2 Thermodynamics of Polymer Crystallization
When considering polymer crystallization the first question to address is why polymers crystallize? A system is in equilibrium when the Gibbs free energy, \( G = H - T S \), is a minimum. A polymer melt consists of randomly coiled and entangled chains; this gives a much higher entropy, and hence lower \( G \), than if the molecules are extended chains. When cooling to temperatures below the melting temperature, \( T_m \), the polymer molecules may crystallize, forming an ordered structure. Although crystallization leads to a reduction in entropy, \( S \), it also leads to a reduction in enthalpy, \( H \). If the resulting \( \Delta G \) is lower for the crystallized material than for the melt, crystallization will be thermodynamically favoured. However, this can only be applied to processes that occur quasi-statically. In practice, especially in industrial applications, polymers are often cooled very quickly from the melt. In this situation crystallization is controlled by kinetics; the rate of nucleation and growth then becomes important. In some cases it is possible to cool so quickly from the melt that crystallization does not occur at all and a completely amorphous material is formed. In such cases, crystallization can normally be induced by annealing the polymer at a temperature above the glass transition temperature.

2.3.3 Crystal Lamellae and Chain Folding
The second question to address is how polymers crystallize? X-ray diffraction work in the early 1900s showed that generally, polymers did not crystallize fully; this was deduced because their X-ray diffraction patterns consisted of both crystalline and amorphous parts. Much of the early work on polymer crystallization concentrated on crystals grown from dilute solution as they have a higher degree of perfection than melt grown crystals. In dilute solution, molecules are thought to be isolated coils and their crystallization is not hindered by entanglements, etc. Early theories viewed polymer crystals as fringed micelles, in which crystalline regions are separated by disordered amorphous regions; chains meander from an amorphous region through a crystallite and back into the amorphous region, binding the whole mass together, see figure 2.6. The modern view of chain folding was first introduced by Storks (1938). He concluded that chains of trans-polyisopropene had to fold back and forth; however, his proposal went largely unnoticed by the scientific community. Almost twenty years later, three papers published independently by Keller (1957), Till
(1957) and Fischer (1957) reported that single crystals of polyethylene could be grown from solution. These crystals were 10 nm thick platelets with regular facets and with the chain direction perpendicular to the lamellar surface. The thicknesses of the lamellae were very much less than the length of the polymer chains. This led Andrew Keller to postulate that the chains must fold back and forth into the crystal. Chain folding has since been found to be present in both solution and melt grown crystals.

Figures 2.7 depicts a schematic illustration of a polyethylene lamella, grown from dilute solution. A typical feature of a lamellar crystal is its low thickness-to-width ratio, with values ranging from 0.01-0.001. The lamellar thickness, \( l_c \), is defined as the length of the shortest crystal dimension. A fold surface free energy, \( \sigma_f \), or a lateral surface free energy, \( \sigma_L \), is associated with each lamellar surface. As we have already seen, polymer crystals do not generally adopt the lowest free energy conformation - where the chains are fully extended - but prefer to adopt a chain folded conformation. As a result polymer crystals are non-equilibrium structures. The melting point of an equilibrium crystal, \( T_m^0 \), is defined as the temperature at which the Gibbs free energy change on crystallization is zero, hence \( T_m^0 = \Delta H_m^0 / \Delta S_m^0 \), where \( \Delta H_m^0 \) and \( \Delta S_m^0 \) are the enthalpy and entropy of fusion respectively. At temperatures below \( T_m^0 \) there is a driving force for crystallization. The difference in temperature between \( T_m^0 \) and the crystallization temperature, \( T_c \), is known as the supercooling, \( \Delta T \). During the 1980s (Barham et al., 1985) it was shown that the initial lamellar thickness, \( l_c \), depends only on the degree of supercooling and can be defined as:

\[
l_c = \frac{C}{\Delta T} + \delta l \tag{2.14}
\]

where \( C \) and \( \delta l \) are constants.

As the crystals are non-equilibrium structures they have the potential to minimise their free energy - usually by crystal thickening. Thickening can occur via solid state diffusion of the polymer chains, or by partial melting/dissolution and re-crystallization. One solid state diffusion mechanism for thickening was proposed by Dreyfus and Keller (1970). It involves a fold being pulled into the crystal creating a defect known as a fold dislocation. The dislocation propagates through the crystal until the fold eventually doubles in size.

The equilibrium melting point of a crystal, \( T_m^0 \), as defined above relates to an infinitely large crystal. In practice polymer crystals melt at temperatures below \( T_m^0 \), due to the free energies associated with their surfaces and to defects within them. The melting point of a polymer can be described by the Thompson-Gibbs equation:
In practice, melting occurs over a range of temperatures, as polymers contain crystals of differing thickness and perfection.

The exact nature of chain folding has been a subject of much debate; see for example Faraday Discussions (1979). Ideally the molecules fold back and forth with tight hairpin turns - this is known as the adjacent re-entry model. Another model, known as the switchboard model (Flory, 1962), sees the chains re-entering randomly into the lamella with loose folds. These two models represent limiting cases; in reality systems may combine elements of both. Crystals grown from dilute solution produce isolated monolayer lamellae. In this case it is thought that a given molecule is contained in only one crystal and a considerable degree of adjacent re-entry is likely (as in figure 2.7). Crystals grown from more concentrated solutions produce multilayer crystal aggregates in which the degree of chain folding is reduced. The amorphous material is thought to be located at the lamellar surfaces and the amount of amorphous material will depend on the nature of the chain fold (random re-entry will produce more amorphous material) and the number of chain ends. Melt crystallization produces lamellae with similar thickness-to-width ratios as solution grown lamellae. A characteristic feature of melt grown lamellae is their stacking in alternate layers with amorphous material. The current model of the chain folding in melt grown lamellae is illustrated in figure 2.8. It shows that some adjacent re-entry is thought occur, but the crystal surfaces are mostly associated with tie molecules, chain ends, cilia and loose folds.

It must be noted that although the earliest crystallization experiments produced polymer crystals with regular facets, subsequent work has shown that this is not generally the case and that crystals grown at higher temperatures tend to have curved rather than linear faces.

2.3.4 Crystal Aggregates

When polymers crystallize from the melt, the lamellar crystals form aggregates - the most common type being the spherulite. Spherulites are not unique to synthetic polymers or long chain molecules and occur in minerals, vitamins, ice, and even elements such as selenium (Ryschenkow and Faivre, 1988). Figures 2.9(a) and (b) show examples of polyethylene and polypropylene spherulites viewed through an optical microscope between crossed polarizers. The characteristic Maltese Cross extinction pattern arises from the coincidence of the principal axes of the crystal with the extinction direction of the polarizer and analyser. It has been shown that the b crystal axis is radial in polyethylene spherulites and the a and c crystallographic directions are tangential and circumferential. Some polymers, for instance the polyethylene in figure 2.9(a), show regular concentric bands: this has been attributed to a regular twist in the radiating lamellae. The reason for
this twist is unknown although some have speculated that it may originate from screw dislocations (Schultz and Kinloch, 1969; Patel and Basset, 1991). Figure 2.10 shows a schematic diagram of the orientation of molecules and lamellae inside a spherulite.

Spherulites form by nucleation at different points in the sample. They are only spherical in shape during the early stages of growth. During the latter stages of crystallization the spherulites impinge on their neighbours. When all the spherulites within a sample are nucleated at the same time, the boundaries will be straight; however, when they are nucleated at different times, they will be different in size and the boundaries will be hyperbolic. The radial growth rate of spherulites is dependent on the viscosity of the melt. Nucleation rate (which can be increased by the presence of additives) and growth rate together determine the size and number of spherulites: slow nucleation and fast growth result in a small number of large spherulites whereas fast nucleation and slow growth result in a large number of smaller spherulites. Materials having a larger spherulitic morphology are usually more brittle. In the early stages of crystal growth, before spherulites impinge, the overall rate of crystallisation can be written (Mandelkern, 1964):

\[ X_C(t) = \gamma X_{CS} \left( \frac{\rho_C}{\rho} \right) \left( \frac{4\pi}{3} GR^3 t^3 \right) \] (2.16)

where \( X_C(t) \) is the weight fraction or degree of crystallinity at time \( t \), \( \gamma \) is the number of nuclei per unit volume or nucleation density, \( X_{CS} \) is the degree of crystallinity of the spherulite which is assumed to be independent of radius, \( \rho_C \) and \( \rho \) are the spherulitic and bulk densities, and \( GR \) is the radial growth rate i.e. the rate of change of the spherulitic radius, \( dr/dt \). It is found that the rate soon decreases from the \( t^3 \) dependance due to spherulitic impingment.

Electron microscopic studies helped to reveal the internal structure of spherulites. (Bassett et al., 1978a,b, 1981, 1984) Figure 2.11 shows polyethylene spherulites as seen in an electron microscope. The centre of a spherulite consists of either a common nucleation point for several crystals, or the nucleation point of a single lamellar crystal. The crystals grow initially as aggregates called sheaves, containing parallel crystals that subsequently splay out. The skeletal structure of a spherulite is formed through the growth of dominant lamellae, which are thought to grow from the purest and highest molecular weight material. It is the growth of these crystals, known as primary crystallization, which defines the spherulitic growth front observed optically. The dominant lamellae splay apart and branch to form a spherical entity. Behind the growth front there is secondary crystallization into subsidiary lamellae. Secondary crystallization is slow and the initial rapid crystallization is normally dominated by primary crystallization. Segregation into dominant and subsidiary lamellae is most easily observed in spherulites grown at low supercoolings. Since it is the widely spaced dominant lamellae that form the spherulite skeletal
structure, the reason for spherulitic growth is not one of filling space efficiently. A mechanism is required for the splaying and branching of the dominant lamellae that leads to the formation of spherulites rather than stacks of parallel lamellae. It seems likely that the mechanism for spherulitic growth in polymers may have some features in common with the growth of non-polymeric materials. However, Bassett and Olley (1984) suggested that the splaying of dominant lamellae is caused by cilia (partly attached molecules), which increase the pressure in the inter-lamellar regions; this cannot happen in low molecular weight materials.

Polymers may also form axialites. Their structure is somewhere between that of a single crystal and a spherulite. To a crude approximation, axialites can be considered as spherulites in the early stages of growth. The large-scale structure of a polymer depends on molecular weight and crystallization temperature. At a given crystallization temperature the structure of a polymer, such as polyethylene, changes from axialitic to spherulitic with increasing molecular weight. The spherulitic structure becomes increasingly irregular at higher temperatures. Ultra high molecular weight polyethylene (UHMWPE) has randomly arranged lamellae and therefore does not form axialites or spherulites.

Another form of crystalline aggregate is the Shish Kebab (a term coined by Pennings and Keil, 1965). These form when crystallization occurs during flow. They consist of extended chain backbones, which nucleate epitaxial overgrowths of lamellae - see figure 2.12. Other types of crystal aggregates can sometimes be observed in polymers, such as row-nucleated structures, dendrites and densely branched morphologies.

2.3.5 Kinetic Crystal Growth Theories
In kinetic theories the thickness of the crystal that grows at a given temperature is that which maximises the overall transformation rate, not that which minimises the free energy. The driving force for crystallization is related to the supercooling. The different theories aim to explain and predict the experimentally observed variation of crystal thickness with temperature, given earlier by equation 2.14 and the observed temperature dependence of growth rate, \( GR \):

\[
GR \propto \exp\left(-\frac{K}{T\Delta T}\right)
\]  

(2.17)

where \( K \) is a constant within a given growth regime.

2.3.5.1 Nucleation Theory
Before discussing the various kinetic theories it is necessary to introduce the nucleation theory. Crystallization can be divided into two stages: nucleation and growth. Nucleation is either homogeneous or heterogeneous. During homogeneous nucleation in a polymer solution or melt
there are small density fluctuations, during which small volumes may take a structure close to that of the solid crystalline form. As the temperature of the solution/melt is lowered below the melting temperature, small crystal nuclei may become stable and grow. The condition for stable growth is that an increase in volume of a nucleus will result in a reduction of the Gibbs free energy, $G$. There are two contributions to the free energy: the creation of a crystal surface, with an associated surface energy, results in an increase in $G$, whereas the incorporation of molecules into a crystal, results in a decrease in $G$. In the early stages of nucleation, when the surface-to-volume ratio of the nucleus is high, the overall value of $G$ increases because of the rapid increase in surface energy. As the nucleus grows, the surface-to-volume ratio decreases and there is a critical nucleus size above which $G$ starts to decrease - eventually the free energy will be less than that of the original melt and the nucleus will be stable, see figure 2.13.

If there are foreign bodies present, such as chemical additives, dust particles or the walls of a containing vessel, the balance of the free energy will be affected and the rate of nucleation will be increased. This is known as heterogeneous nucleation. Many commercial polymers have specific additives in order to manipulate the crystallization process and control various properties of the polymer. At present it is somewhat of a mystery as to the mechanisms of these nucleating agents; as a result, searching for effective nucleating agents is more or less an empirical process. Although homogeneous nucleation has been studied in detail from a theoretical viewpoint, in practice nucleation is nearly always heterogeneous. The formation of a nucleus, whether homogeneous or heterogeneous, is known as primary nucleation; nucleation rate is dependent on the supercooling and crystal growth proceeds via secondary nucleation.

2.3.5.2 Secondary Nucleation Theory

The secondary nucleation theory arose from the need to explain why chains fold rather than adopting the lowest free energy conformation of extended chains. The model in its simplest form was first presented by Lauritzen and Hoffman (1960, 1961) and shortly afterwards by Frank and Tosi (1961). Secondary nucleation considers the growth of a layer of crystal on an infinitely flat substrate of perfect crystal, see figure 2.14(a). The molecule is considered to lie inside a box whose lateral sides have a free energy $\sigma_L$ and fold surfaces have a free energy $\sigma_F$. The first step is the laying down of a molecular strand on the smooth crystal substrate, which is followed by the subsequent addition of further segments through the process of chain folding - see figure 2.14(b). The model considers the changes in the free energy as each strand lies down. The deposit of the first strand causes the initial large increase in the free energy, $2bL\sigma_L$ (due to the new lateral surfaces created) reduced by a fraction ($\psi$) of the free energy of crystallization, $\psi abL\Delta G$. The remainder of the free energy of crystallization for the first strand, $(1-\psi)abL\Delta G$, is released on the other side of the first maximum. As the strand folds, a new fold surface is created, with a free energy cost of $ab\sigma_F$, again reduced by a fraction of the free energy of crystallization, $\psi abL\Delta G$. 

26
As it lies down next to the first strand, no new side surface is created so it is energetically downhill until it reaches the end of the first strand and folds back again. The process is then repeated as more strands are added. Provided that $l_c > 2\sigma / \Delta G$, the overall free energy will decrease as more strands are added. Eventually the free energy change is negative and a stable secondary nucleus will have been formed.

Rate equations for the initial step and the subsequent forwards and backwards steps (illustrated in figure 2.14(b)) can be written and an expression for the crystal thickness, $l_c$, can be derived:

$$l_c = \frac{2\sigma e T_m^0}{\Delta H_m^0 \Delta T} + \delta l$$

(2.18)

Clearly this expression is in agreement with equation 2.14, and can also be re-arranged to give the Thompson-Gibbs equation 2.15.

For the past forty years the Lauritzen-Hoffman theory has been under modification in order to remove some of the incorrect assumptions and over simplistic arguments. One of the most significant modifications was introducing reptation into the model (Hoffman et al., 1979). The modification was driven by the suggestion made by Yoon and Flory (1977), that regular tight chain folding was prohibited by the long times needed for the entangled molecules to re-arrange. Later modifications addressed the problem that crystals which have been grown from the melt at high temperatures have curved rather than straight edges, see Mansfield (1988), Hoffman and Miller (1989).

The Lauritzen-Hoffman theory considers the free energy barrier to be purely enthalpic. A more recent kinetic theory proposed by Sadler and Gilmer (1984) suggests that the free energy barrier is mostly entropic. The Sadler-Gilmer theory accounts for the observation of curved crystal faces but does not provide information on the mechanisms of growth or describe different growth regimes. As this theory is not the main concern of this thesis, it will not be discussed further.
Figure 2.1 Variation of $\Delta G_M$ with composition $\phi_2$ at temperatures (a) $T_1$ and (b) $T_2$. Reproduced from Young and Lovell (1991).

Figure 2.2 Phase diagram constructed from figure 2.1. Reproduced from Young and Lovell (1991).
Figure 2.3 Different forms of phase diagram (a) total miscibility, (b) UCST, (c) LCST, (d) and (e) a combination of UCST and LCST and (f) total immiscibility.
Figure 2.4 A schematic illustration of the concentration profiles and corresponding 2D morphologies during phase separation: (a) spinodal decomposition and (b) nucleation and growth. Adapted from Sperling (2001).
Figure 2.5 (a) A 2D representation of a polymer solution: polymer (black) and solvent (grey) molecules are placed on a lattice consisting of identical cells, each polymer molecule is placed so that its chain segments occupy a continuous sequence of cells. (b) A 2D representation of a polymer blend: polymer 1 (black) and polymer 2 (grey) are placed on the lattice so that both occupy a continuous sequence of cells.

Figure 2.6 The fringed micelle model; each chain meanders from crystallite to crystallite, binding the whole mass together.
Figure 2.7 Schematic representation of a polyethylene single crystal grown from dilute solution. The diagram shows the molecules folding back and forth with tight hairpin turns. In reality, the molecules may also have loose folds.

Figure 2.8 Schematic representation of a polymer that has been grown from the melt. There are tie molecules, chain ends, cilia, loose folds and tight hairpin folds. (Reproduced from Phillips, 1994)
Figure 2.9 (a) polyethylene and (b) polypropylene spherulites viewed in an optical microscope through crossed polarizers.

Figure 2.10 Schematic illustration of a spherulite. The dominant lamellae branch, and in this case twist, in phase: this gives rise to the observed banding.
Figure 2.11 Electron micrographs of high-density polyethylene crystallized at two different supercoolings: (a) low supercooling and (b) high supercooling. The scale bars represent one micron. Figure (a) shows one large spherulite and clearly illustrates the dominant and subsidiary lamellae (illustrated schematically in figure 2.10). Figure (b) shows several spherulites and clearly illustrates the characteristic banding.

Figure 2.12 Electron micrograph of a shish kebab. The scale bar represents 0.2 microns. (Courtesy of Mary Hill).
Figure 2.13 Schematic representation of the change in free energy, $\Delta G$, for homogeneous nucleation during the first stages of polymer crystallization.

Figure 2.14 Schematic illustration of the secondary nucleation process for crystal growth (a) crystal lamella and (b) the free energy map of crystallization.
CHAPTER 3: CAPILLARY EXTRUSION RHEOMETRY

3.1 INTRODUCTION

This chapter deals with the measurements of viscosities of the four homopolymers and of the blends. Melt flow rates of the homopolymers are given in the manufacturers' data in Chapter 1: table 1.2. Melt flow rate, MFR\(^1\), is often used in industry to characterise a polymer melt; low melt flow rate implies high viscosity. In a standard ASTM test (see figure 3.1) melt flow rate is determined at a single temperature by means of extrusion and is equal to the number of grams of material extruded in 10 minutes. In the ASTM test, the weight of the load on the molten sample is 2.16 kg, with a corresponding shear stress of 1.94x10^4 Pa. For HDPE the standard processing temperature is 180°C and for iPP the temperature is 230°C. Although the ASTM test is a simple and quick method of quality control, it has its limitations; MFR only represents a single point on a viscosity curve, it therefore does not accurately describe a polymer’s properties over a range of shear rates and temperatures. In the following sections the well-known fact that the viscosity of a polymer melt is highly dependent on the temperature and the rate of extrusion will be illustrated. As HDPE and iPP are extruded at different temperatures in the ASTM test, a direct comparison between them cannot be made. It was therefore necessary to measure the viscosities of the homopolymers and some of the blends over a range of extrusion (shear) rates at 200°C – the temperature at which the blends were processed throughout the project.

In the following section the motivation for studying viscosity is discussed, along with the findings of other authors. In section 3.3 the relevant theories are introduced and sections 3.4 to 3.7 detail the experimental methods, results, discussion and conclusions.

3.2 MOTIVATION

The main reason for studying the melt flow properties of the homopolymers and blends was to investigate the effect of the viscosities of the component phases on the mechanical and physical properties of the blends. A common measure used in the study of polymer blends is the viscosity

\(^1\) Melt flow rate, MFR, is the term used for polypropylene. For other polymers, such as polyethylene, the term melt flow index, MFI is used. For simplicity, melt flow rate will be used throughout the thesis.
This is the ratio of the viscosity of one component to the other. The effect of viscosity ratio on the morphology and mechanical properties of immiscible polymer blends has been the subject of several previous investigations. Some authors believe the fineness of the dispersion of one phase in the other (i.e. the size and number of inclusions) to be an important factor in determining mechanical properties (Bains et al., 1994; Rudin, 1980; Wu, 1987). These authors generally found that the closer the viscosity ratio was to unity when blending, the finer the initial dispersion of the inclusions was, however, they did not consider the effect of phase ripening on the blends' morphologies. Another factor that has been studied is the extent to which the two phases interpenetrate each other (i.e. how diffuse the interface is). Authors such as Bains et al. (1994) and Kim and Burns (1990) found that in PP/PE blends, the closer the viscosity ratios were to unity, the more diffuse the interface boundaries were.

Intuitively, it seems likely that more diffuse the interface is, the stronger the interfacial adhesion between the components will be. Interfacial adhesion will almost certainly have an effect on the blends' mechanical properties. Also, from a manufacturing point of view, the blends are more likely to be extruded smoothly if the components have similar viscosities. Given the factors mentioned above it seems that the best mechanical properties should be achieved by blending two polymers with closely matching viscosities. Indeed Bains et al. (1994) found that the modulus of isotactic polypropylene/linear low-density polyethylene blends (iPP/LLDPE) showed increases of up to 50% above a simple additive law of mixtures when the viscosity of the components closely matched. However Gunderson and Chilcote (1991) found that the melt flow rate of iPP had little effect on the mechanical properties of its blends with HDPE. Neither of these studies looked at the viscosities of the blends themselves, just at the individual components. In a study by Liang and Ness (1997) on the melt flow properties of isotactic polypropylene/high-density polyethylene blends (iPP/HDPE) and isotactic polypropylene/low-density polyethylene blends (iPP/LDPE) it was found that the viscosities of the blends did not obey a simple additive mixing rule. The viscosities of the blends were lower than expected and in some cases fell below the viscosity of both components. Liang and Ness attributed the low viscosities to poor adhesion between the components but did not report how these results related to morphology or mechanical properties.

It is not clear from the findings of other authors whether viscosity ratio plays a significant role in determining the physical and mechanical properties of polyethylene/polypropylene blends. In order to build on the work of others, such as Bains et al. and Laing and Ness, I studied the properties of three different iPP/HDPE blend systems. The blends were produced by melt mixing one grade of polyethylene (in turn) with three different polypropylenes of varying viscosities using a twin-screw extruder, to produce three sets of blends. These were:
- Low-viscosity isotactic polypropylene/high-density polyethylene (LViPP/HDPE),
- Medium-viscosity isotactic polypropylene/high-density polyethylene (MViPP/HDPE),
- High-viscosity isotactic polypropylene/high-density polyethylene (HViPP/HDPE).

The blends were labelled by their percentage composition of polypropylene. In this chapter the melt flow properties of the individual components and of the blends are presented. The significance of the effects of these results on other properties (such as morphology and mechanical properties) will be discussed in separate chapters.

3.3 THEORETICAL BACKGROUND

3.3.1 Rheology and Viscoelasticity
Rheology is the study of the deformation and flow of matter and embodies three main concepts: force, deformation and time. On deformation, most materials exhibit either viscous or elastic behaviour. In the classical theory of hydrodynamics, Newton's Law describes the properties of purely viscous fluids. Deformation in a viscous fluid is permanent and the law states that the stress applied to the material is proportional to the strain rate but independent of the strain itself. The classical theory of elasticity i.e. Hooke's Law, describes the mechanical properties of purely elastic solids. Deformation in an elastic solid is reversible and in the linear elastic region, stress is directly proportional to strain but independent of strain rate. In reality these are limiting cases; many fluids deviate from Newton's Law whilst the stress-strain relationships in many solids are much more complicated than can be described by Hooke's Law. In fact, all materials whether solid, liquid or gas can behave in an elastic or viscous way depending on the time scale on which they are observed. The elastic or viscous character of a material can be estimated (Barnes, 1989) through the Deborah number, $De$:

$$De = \frac{t_c}{\chi_r}$$  \hspace{1cm} (3.1)

where $t_c$ is a characteristic relaxation time of the material and $\chi_r$ is the characteristic time of the deformation process being observed.

When a material is subjected to mechanical work it develops stresses which do not always become immediately zero when the mechanical influence is removed. The time required for the stresses to relax is referred to as the relaxation time, $t_c$. As $De \to 0$ the viscous character predominates and as

2 N.B. the terms fluid and liquid are often used interchangeably, however a fluid is any material that flows in response to an applied force; thus, both liquids and gases are fluids.
De→∞ the elastic character predominates. Water has a relaxation time of order $10^{-13}$ seconds, which means that water will not display any form of elastic response unless it is deformed on a time scale less than this value. On the other hand, mountains tend to remember their original configurations for quite a long time; they have relaxation times of the order of $10^{13}$ seconds and only show viscous characteristics if deformed on a time scale longer than this! In fact it was the flowing of mountains that gave the 'Deborah' number its name; the term originates from a line sung by the prophetess Deborah in the Book of Judges: "The mountains melted (or flowed) before the Lord" (Judges 5:5, Old Testament, c.550 BC). Rheologists adopted Deborah's name as she knew two things: firstly that mountains flow, but secondly that they flow before the Lord and not man, for the simple reason that man, in his short lifetime, cannot see them flowing!

Polymeric liquids have relaxation times of the order of 1-10 seconds. Polymeric materials are therefore termed viscoelastic as they exhibit recoverable elastic deformation, plus irreversible viscous deformation on observable time scales. In the viscous process, applying stress allows the polymer molecules to flow past each other; removal of the stress results in permanent molecular slippage. In the elastic process, applying stress enables the long chains to be stretched out and aligned; removal of the stress allows the chains to recover to their original conformation.

### 3.3.2 Newtonian and Viscoelastic Shear Thinning Liquids

The following section describes Newton's Law in detail and how a polymeric melt deviates from Newtonian behaviour. In a Newtonian liquid, shear stress, $\sigma$, is the applied force per unit area needed to produce deformation ($\sigma = F/A$). Figure 3.2 illustrates how flow occurs when shear stress is applied across a liquid. Strain or shear rate, $\dot{\varepsilon}$, is the rate of change of velocity at which one layer of fluid passes over an adjacent layer. The shear stress is given by:

$$\sigma = \eta \left( \frac{dv_x}{dy} \right) = \eta \dot{\varepsilon} \tag{2.2}$$

where $\sigma$ is the shear stress (Nm$^{-2}$ or Pa), $\dot{\varepsilon}$ is the strain or shear rate (s$^{-1}$) and $\eta$ is the viscosity (Nsm$^{-2}$ or Pa.s).

The viscosity, $\eta$ (coefficient of the resistance to the change of form), is the ratio of the shear stress, $\sigma$, to the velocity gradient or shear rate, $\dot{\varepsilon}$. At a given temperature the viscosity of a Newtonian liquid is independent of the shear rate. A polymer melt consists of randomly coiled macromolecular chains. The number of entanglements, and hence the viscosity will increase as the molecular weight increases. Besides their molecular weight dependence, polymer melts are highly dependent on shear rate (unlike Newtonian fluids). Almost all polymer melts are shear thinning.
(pseudoplastic), i.e. the viscosity drops with increasing shear rate. The differences between Newtonian and shear thinning liquids are illustrated by the idealised curves in figure 3.3: figure (a) depicts the shear stress as a function of shear rate and figure (b) depicts the viscosity as a function of shear rate. Shear thinning can be a very dramatic effect and the viscosity may decrease by a factor of $10^3 - 10^4$. Shear thinning is a very complex phenomenon which will not be discussed in detail. In simple terms, shearing causes some alignment and stretching of the polymer molecules, enabling them to move past each other more and more easily. Shear flow can also have rotational components enabling molecules to rotate out of the stress direction. For more details on shear thinning the reader should refer to Barnes et al. (1989).

A further deviation from Newtonian behaviour is an elastic effect known as die swell. When a Newtonian liquid flows through a capillary, the diameter of the liquid jet will not change dramatically on exiting the capillary. When a molten polymer flows through a capillary, the diameter of the liquid jet (known as extrudate) will significantly expand on exiting the capillary. While die swell is a typical occurrence, it is by no means simple to describe theoretically. It is generally agreed that die swell arises from a combination of effects including relaxation of normal stresses at the exit of the capillary, temperature gradients across the capillary cross section produced by viscous heating and relaxation of the increased amount of stretching experienced by molecules inside the capillary (see, Barnes et al, 1989).

A more general term for the shear stress, which allows for non-Newtonian behaviour, is defined as:

$$\sigma = K\dot{\varepsilon}^n + \sigma_0$$

where $K$ is the consistency index (Pa·s), $n$ is the power law index and $\sigma_0$ is the yield stress. In a Newtonian fluid $n = 1$ and $\sigma_0 = 0$. In a shear thinning polymer melt (often called a power law fluid) $n < 1$ and $\sigma_0 = 0$. For a Newtonian fluid, equation 3.3 reduces to equation 3.2 making $K=\eta$.

From equations 3.2 and 3.3 it follows that viscosity is:

$$\eta = \frac{\sigma}{\dot{\varepsilon}} = \frac{K\dot{\varepsilon}^n}{\dot{\varepsilon}} = K\dot{\varepsilon}^{n-1}$$

Figure 3.4 shows an idealised viscosity-shear rate plot on a logarithmic scale. The power law described by equations 3.3 and 3.4 is only valid at certain shear rates, i.e. in the shear thinning linear region of figure 3.4. The linear region may cover several decades of viscosity. At very low shear rates the viscosity is independent of shear rate: this is termed the zero shear rate viscosity, $\eta_0$. 
At very high shear rates the viscosity may again become independent of shear rate and this is termed the infinite shear rate viscosity, $\eta_{\infty}$.

### 3.3.3 Capillary Extrusion and Poiseuille's Law of Flow

In order to measure viscosity in the laboratory, a capillary extrusion rheometer is often used. This is the simplest type of rheometer and consists of a capillary die placed in the bottom of a heated reservoir. The material is forced through the die by means of a piston moving at velocity $v$. A pressure transducer measures the pressure drop along the die, $\Delta p$, as a function of piston velocity, $v$. A schematic illustration of this type of rheometer is shown in figure 3.5. In order to use these measurements to calculate viscosity, Poiseuille's law of flow must be considered. Poiseuille's law describes the flow of liquids in pipes. It assumes that the liquid consists of concentric cylinders, with the outer cylinder stationary along the pipe wall and the inner cylinders each moving at a faster velocity until the fastest cylinder, at the centre of the pipe, is reached. The variation in velocity across the pipe, i.e. the velocity gradient, can be compared to Newton's law of viscosity, equation 3.2. In order for flow to occur, a pressure difference across the ends of the pipe is needed. Poiseuille found the volumetric flow rate, $Q$ (volume per unit time) to be dependent on the viscosity, $\eta$, the radius of the pipe, $r$, and the pressure difference across the ends of the pipe, $\Delta p$:

$$Q = \frac{\Delta p \pi r^4}{8\eta L}$$  \hspace{1cm} (3.5)

In a capillary rheometer the volumetric flow rate into the capillary, $Q$, is defined as:

$$Q = v\pi R_B^2$$  \hspace{1cm} (3.6)

where $v$ is determined by the speed of the piston and $R_B$ is the radius of the barrel reservoir.

Combining equations 3.2, 3.5 and 3.6 gives expressions for shear stress, $\sigma$, and shear rate, $\dot{\epsilon}$, that relate to the piston velocity, $v$, pressure drop, $\Delta p$, and rheometer geometry. The values obtained for shear stress and shear rate are only 'apparent' values and must be corrected for end pressure losses and non-Newtonian behaviour.

The apparent shear stress, $\sigma_{\text{APP}}$, is related to the pressure drop across the die, $\Delta p$ as follows:

$$\sigma_{\text{APP}} = \frac{\Delta p r}{2L}$$  \hspace{1cm} (3.7)
where \( r \) is the die radius and \( L \) is the capillary length.\(^3\)

A lot of energy is consumed during the extrusion of polymer melts due to the stored elastic energy and the viscous dissipation in the entrance flow, inner flow and exit flow. In general the apparent pressure drop, \( \Delta p \), is the sum of the entrance pressure drop, \( \Delta p_{en} \); die pressure drop, \( \Delta p_d \); and the exit pressure drop, \( \Delta p_{ex} \). The entrance and exit pressure drops are known collectively as the end pressure losses, \( \Delta p_{end} \), i.e.:

\[
\Delta p = \Delta p_{en} + \Delta p_d + \Delta p_{ex} = \Delta p_d + \Delta p_{end}
\]  

(3.8)

End losses can be very significant and can only be discarded if the length/radius ratio is very high, e.g. \( >100 \). To correct for the end pressure losses a Bagley analysis is performed (Bagley, 1957). Bagley assumed that the end pressure losses remain unchanged when varying the die length/radius ratio. When \( \Delta p \) is plotted as a function of \( L/r \), extrapolation to zero \( L/r \) will give the end pressure losses, \( \Delta p_{end} \). The true shear stress is then:

\[
\tau_{TRUE} = \frac{(\Delta p - \Delta p_{end})r}{2L}
\]

(3.9)

The apparent shear rate, \( \dot{\varepsilon}_{APP} \), is defined as:

\[
\dot{\varepsilon}_{APP} = \frac{4Q}{\pi r^3} = \frac{4\nu R^2}{r^3}
\]

(3.10)

The apparent viscosity, \( \eta_{APP} \), which assumes Newtonian behaviour, is therefore defined as:

\[
\eta_{APP} = \frac{\sigma_{TRUE}}{\dot{\varepsilon}_{APP}}
\]

(3.11)

To account for the non-Newtonian behaviour of polymer melts, a correction factor, known as the Rabinowitsch correction can be applied. It relates the apparent shear rate, \( \dot{\varepsilon}_{APP} \), to the true shear rate, \( \dot{\varepsilon}_{TRUE} \), in the following way:

---

\(^3\) The length/radius ratio, \( L/r \), is often expressed as the length/diameter ratio, \( L/D \), however to be consistent with the expression for shear rate, length/radius, \( L/r \), is used throughout the thesis.
where $n$ is the power-law index given in equations 3.3 and 3.4. Combining equations 3.3 and 3.12 gives:

$$
\sigma_{\text{TRUE}} = K \dot{\varepsilon}_{\text{TRUE}}^n = K \left( \frac{3n+1}{4n} \right)^n \dot{\varepsilon}_{\text{APP}}^n
$$

(3.13)

supposing that:

$$
K_{\text{APP}} = K \left( \frac{3n+1}{4n} \right)^n \Rightarrow K = K_{\text{APP}} \left( \frac{4n}{3n+1} \right)^n
$$

(3.14)

Plotting log true shear stress, $\log \sigma_{\text{TRUE}}$, against log apparent shear rate, $\log \dot{\varepsilon}_{\text{APP}}$, gives a gradient of $n$, and an intercept of $K_{\text{APP}}$. True viscosity within the power law region is defined as:

$$
\eta_{\text{TRUE}} = \frac{\sigma_{\text{TRUE}}}{\dot{\varepsilon}_{\text{TRUE}}} = \frac{K \dot{\varepsilon}_{\text{TRUE}}^{n-1}}{\dot{\varepsilon}_{\text{TRUE}}}
$$

(3.15)

The capillary extrusion rheometer is capable of obtaining shear rates of the order of $10^4 - 10^7$ s$^{-1}$. It is ideally suited to measuring the viscosity of polymers within the power law region, however it is not suited to measuring the zero shear rate viscosity, $\eta_0$, or the infinite shear rate viscosity, $\eta_{\infty}$.

It must be noted that there are actually two quantities that are termed viscosity. The quantity defined above, and usually just called viscosity, is sometimes called dynamic viscosity, absolute viscosity, or simple viscosity to distinguish it from the other quantity. The other quantity known as kinematic viscosity, $\nu$, is the ratio of the viscosity of a fluid, $\eta$, to its density, $\rho$:

$$
\nu = \frac{\eta}{\rho}
$$

(3.16)

### 3.3.4 Immiscible Blend Viscosities

In general one might expect the viscosities of the blends to follow a simple mixing rule, such as an additive mixing rule (sometimes called linearity) where:

$$
\eta_x = \phi_1 \eta_1 + \phi_2 \eta_2
$$

(3.17)
where \( \eta_B \) is the viscosity of the blend, \( \phi_1 \) and \( \phi_2 \) are the volume fractions of components 1 and 2 and \( \eta_1 \) and \( \eta_2 \) are the viscosities of components 1 and 2.

However several authors have reported a negative deviation from linearity (see e.g. Lopez Manchando et al., 2001). Some authors such as Liang and Ness (1997) found the viscosities of the blends to be lower than either of the two components. Some authors have attributed this drop in viscosity to be a result of changing from one morphology to another (Han, 1981), or to interlayer slip, (Lin, 1979). All of these authors agree that the drop in viscosity is evidence for poor compatibility between the phases.

### 3.3.5 Temperature Dependence of Viscosity

Lastly, a brief note about the temperature dependence of viscosity will be made. Viscosity is inversely proportional to, and highly dependent on temperature. In Newtonian fluids an Arrhenius-type relation is used to express the relationship between the viscosity, \( \eta \), and the temperature, \( T \):

\[
\eta = A \exp\left(\frac{B}{T}\right)
\]  

(3.18)

where \( A \) is the viscous coefficient and \( B \) is a constant relating to temperature dependence.

The Arrhenius equation is often used to describe the viscosity of polymer melts. Many attempts have been made to find a better relationship between temperature and viscosity for non-Newtonian fluids, see for example the work of Angell (1997), McKenna (1989), O'Connell and McKenna (1999) or Williams et al. (1955). However, as the temperature of the melt was not varied in this project, such relationships will not be discussed.

### 3.4 EXPERIMENTAL METHODS

Capillary extrusion experiments were performed using a Davenport capillary rheometer (Daventest Ltd.) with a Eurotherm attached to control the temperature. A schematic illustration of the Davenport can be seen in figure 3.5. Apparent shear stress, \( \sigma_{APP} \) and apparent shear rate, \( \dot{\varepsilon}_{APP} \), were calculated by measuring the apparent pressure drop across the die, \( \Delta P \), as a function of piston velocity, \( v \), at a constant temperature of 200°C. The pressure drop across the die was measured using a pressure transducer located a few millimetres upstream of the die. A temperature-measuring probe was fitted within the reservoir wall at the location of the die entrance. The barrel radius, \( R_B \), was 5mm. Stainless steel dies with capillary lengths of 5, 9, 11 and 14mm, radii of 0.5mm and entrance angle (2\( \alpha \)) of 90° were used. The range of shear rates possible using these dies
were 13.3 to 1000s⁻¹; 43 different shear rates within this range were employed. Apparent shear stress-apparent shear rate curves were recorded for all four homopolymers, i.e. high-density polypropylene, HDPE; low viscosity isotactic polypropylene, LViPP; medium viscosity isotactic polypropylene, MViPP; and high viscosity isotactic polypropylene, HViPP. Bagley plots were performed in order to determine the true shear stress, σ_TRUE, and the Rabinowitsch correction was applied in order to determine values for the true shear rate, \( \dot{\varepsilon}_{TRUE} \). Shear stress-shear rate curves for some of the blends were also recorded.

3.5 RESULTS

3.5.1 Homopolymers
The following section deals with the rheological behaviour of the four homopolymers. Each sub-section details with the various plots that must be made in order to determine the true viscosity of the materials as a function of shear rate.

3.5.1.1 Bagley Plots and End Pressure Losses
Bagley plots of the homopolymers are shown in figure 3.6 (a) HDPE, (b) LViPP, (c) MViPP and (d) HViPP. Bagley plots were made for the 43 different apparent shear rates used (ranging from 13.3 to 1000s⁻¹), however for the sake of clarity only 8 different apparent shear rates are shown in the figures. End pressure losses, \( \Delta p_{end} \), were determined by extrapolating to zero length/radius, \( L/r = 0 \). Figure 3.7 demonstrates the effect of the end pressure losses, by showing plots of the measured pressure, \( \Delta p \), end pressure losses, \( \Delta p_{end} \) and the true pressure drop along the die, \( \Delta p_d \). For all four homopolymers, apparent pressure is roughly 25% greater than true pressure proving that the end effects are very significant.

3.5.1.2 True Shear Stress - Apparent Shear Rate
True pressure, \( \Delta p_d \) (using \( L/r = 28 \)) was converted to true shear stress, \( \sigma_{TRUE} \), using equation 3.9. Figure 3.8 shows the true shear stress, \( \sigma_{TRUE} \), as a function of apparent shear rate, \( \dot{\varepsilon}_{APP} \) for all four homopolymers. It can be seen that all the homopolymers exhibit shear thinning behaviour. The shape of the polyethylene curve is different from those of the three polypropylenes, with a steeper gradient at high shear rates.
3.5.1.3 Rabinowitsch Correction

The Rabinowitsch correction, described by equations 3.12-3.14, was made by plotting log true shear stress, \( \log \sigma_{\text{TRUE}} \), against log apparent shear rate, \( \log \dot{\varepsilon}_{\text{APP}} \). Figure 3.9 shows such a plot for the four homopolymers. It can be seen that the linear power law region sets in at a shear rate of 166.67 s\(^{-1}\). The gradient, \( n \), and intercept, \( K_{\text{APP}} \), were determined from the linear region of figure 3.9 and are given in table 3.1. The table also gives values for the Rabinowitsch correction, the consistency index, \( K \), and the viscosity at high shear rates (according to equation 3.15).

3.5.1.4 Viscosity

Plots of true shear stress, \( \sigma_{\text{TRUE}} \), versus true shear rate, \( \dot{\varepsilon}_{\text{TRUE}} \), are shown in figure 3.10. By comparing with figure 3.8 it is easy to see the effect of the Rabinowitsch correction. Figure 3.11 shows the true viscosity, \( \eta_{\text{TRUE}} \), as a function of true shear rate, \( \dot{\varepsilon}_{\text{TRUE}} \).

At low shear rates i.e. <150 s\(^{-1}\), the viscosities of the four homopolymers are very similar. At shear rates of 200-300 s\(^{-1}\) the viscosity of the HDPE most closely resembles that of the MViPP. At 500-600 s\(^{-1}\) the viscosity of the HDPE closely resembles that of the HViPP. At higher shear rates, i.e. > 600 s\(^{-1}\) the HDPE has the highest viscosity followed by the HViPP, MViPP and LViPP respectively. By using the equations for viscosity, given in table 3.1, it is possible to extrapolate to even higher shear rates than those measured. At higher shear rates the HDPE is expected to have the highest viscosity, followed by the HViPP, MViPP and LViPP respectively. As stated earlier, the linear shear thinning region can cover several decades of viscosity before the infinite shear rate viscosity sets in. From the measurements in the capillary rheometer it is impossible to determine where the linear regions end in any of the four homopolymers.

3.5.2 Blends

The following section deals with the viscosities of each set of blends. To be concise, only true shear stress-true shear rate curves are shown.

3.5.2.1 Low-Viscosity Isotactic Polypropylene/High-Density Polyethylene Blends (LViPP/HDPE)

Figure 3.12 shows the true shear stress - true shear rate curves of the LViPP and HDPE homopolymers along with the 10, 40, 50, 60 and 90% blends. It shows that the blends do not behave according to a simple additive mixing rule. The blends with central compositions show negative deviation from this rule, especially at high shear rates. This is well illustrated in figure 3.15, which shows the true shear stress of the homopolymers and blends at a true shear rate of 1000 s\(^{-1}\).
3.5.2.2 Medium-Viscosity Isotactic Polypropylene/High-Density Polyethylene Blends (MViPP/HDPE)

Figure 3.13 shows the true shear stress - true shear rate curves of the MViPP and HDPE homopolymers along with the 10, 40, 50, 60 and 90% blends. Again, the blends do not behave according to a simple additive mixing rule, especially at central compositions. In some cases the blends' viscosities are lower than either of homopolymers. This is well illustrated in figure 3.15, which shows the true shear stress of the homopolymers and blends at a true shear rate of 1000s\(^{-1}\).

3.5.2.3 High-Viscosity Isotactic Polypropylene/High-Density Polyethylene Blends (HViPP/HDPE)

Figure 3.14 shows the true shear stress - true shear rate curves of the HViPP and HDPE homopolymers along with the 10, 40, 50, 60 and 90% blends. Like the other blend systems, the blends, especially those with central compositions, deviate negatively from linearity, with some blends having lower viscosities than the homopolymers—see figure 3.15.

3.6 DISCUSSION

The aim of this investigation was to determine the viscosities of the components and the blends and relate them to the physical and mechanical properties. The blending of the original components was done in a twin-screw extruder, which had a screw diameter of 16 mm and a barrel length/diameter ratio of 25:1. It was operated at 200 rpm. I estimate that the shear rate in the extruder was in excess of 1000s\(^{-1}\). However, the shearing forces present in an extruder are far more complex than in a simple capillary rheometer due to the rotating screw mechanisms. This means that only a qualitative, rather than quantitative comparison can be made between the viscosities of the materials in the twin-screw extruder and the capillary rheometer. Nevertheless, it seems reasonable to assume that the relationship between the homopolymers at high shear rates is the same in the extruder as in the capillary rheometer, i.e. the HDPE has the highest viscosity, followed by the HViPP, MViPP and LViPP respectively.

It was stated in Chapter 1 that when MViPP and HViPP are blended with HDPE, the extrudate is very smooth. However when LViPP is blended with HDPE, the extrudate exits in spurts, is very distorted and often fractures. From a manufacturing point of view such behaviour is very undesirable. The technicians at PRISM (where the blends were prepared) suggested increasing the speed of the screws as a possible way to improve the LViPP/HDPE extrudate. In order for a direct comparison to be made between all the blends, this was not attempted. In fact, by looking at the viscosity curves in figures 3.10 and 3.11, this would have been the wrong thing to do. The viscosity measurements indicate that the blends are extruded more smoothly when the components have
closely matching viscosities. I therefore predict that reducing the speed of the screws to a much lower shear rate (where the viscosities of the LViPP and HDPE are similar) should allow the LViPP/HDPE blends to be extruded smoothly.

For some of the tests the raw pellets were not suitable (e.g. tensile testing), the pellets were therefore formed into sheets using a hot press. I estimate that the shear rate in the hot press was roughly 0.1s\(^{-1}\). The capillary rheometer is not capable of measuring at such low shear rates, but by extrapolating the viscosity curves backwards, it is possible to determine that at very low shear rates the HViPP has the highest viscosity followed by the MViPP, LViPP and HDPE respectively. As mechanical tests were performed on the sheets rather than the pellets, the morphologies of the sheets were studied. Several processes were involved when making the sheets. Firstly, preparation in the extruder at high shear rates (>1000s\(^{-1}\)) and secondly, compression moulding of the sheets at low shear rates (~0.1s\(^{-1}\)). In the extruder the HViPP and HDPE have the closest viscosities whereas in the hot press the LViPP and HDPE have the closest viscosities. This means that even if the viscosity measurements are known \textit{a priori}, the morphologies and mechanical properties of the sheets are very hard to predict. The effect of viscosity on these various different properties is discussed in the following chapters.

3.6.1 Discussion of the Blends’ Viscosities
The observation that some blends have much lower viscosities than either of their components is not unexpected given the work of others, such as Liang and Ness (1997). They found that the viscosities of their iPP/HDPE blends did not follow a simple additive relationship, and in some cases the viscosities of the blends fell below the viscosities of both components. In my work, negative deviation from an additive rule is observed in all three sets of blends - especially those with central compositions. From a molecular point of view flow occurs when polymer molecules slide past each other. The ease of flow depends upon the mobility of the molecular chains and their entanglements with each other. If the adhesion between the components is poor, i.e. the interface does not contain many entanglements, it is possible that the components slip past each other in the melt; this may cause the lower than expected viscosity. If the observed drop in viscosity is due to poor adhesion between the components, this may have a profound effect on the mechanical properties of the blends. For instance, one might expect blends with central compositions to be brittle, with failure occurring at the interface. Indeed, many other studies on the mechanical behaviour of polyethylene/polypropylene blends have shown that the blends have a lower extension to break ratio than the pure components (Deanin and Chung 1993; Greco \textit{et al.}, 1980; Gupta \textit{et al.}, 1982; Lee \textit{et al.}, 1994; Lovinger and Williams, 1980; Noel III and Carley, 1975; Robertson and Paul, 1973). The mechanical properties of my blends are reported in Chapter 6. My results are in agreement with others, and show that the blends have much lower extension to break values than the pure homopolymers; the blends are especially brittle at central compositions.
3.7 CONCLUSIONS

The viscosities of the homopolymers were measured at 43 apparent shear rates ranging from 13.3 to 1000s\(^{-1}\). As expected, the homopolymers exhibit shear thinning behaviour. At high shear rates (comparable to the shear rate experienced in the twin-screw extruder), the HDPE has the highest viscosity followed by the HViPP, MViPP and LViPP respectively. At low shear rates (comparable to the shear rate experienced in the hot press), the HViPP has the highest viscosity followed by the MViPP, LViPP and HDPE respectively.

When the blends are prepared in the twin-screw extruder, the HViPP and MViPP mixes well with the HDPE, producing a smooth extrudate. However, when the LViPP is blended with HDPE, the extrudate is very poor. The viscosity measurements suggest that the poor extrudate is a result of the large difference in viscosities between LViPP and HDPE at the high shear rates experienced in the extruder. I suggest that a possible way to improve the quality of the extrudate would be to decrease the speed of the screw rotation to a lower shear rate (where the viscosity of the LViPP and HDPE were more closely matched). From a manufacturing viewpoint, a prior knowledge of the viscosity curves of different polymers could prove very useful when choosing which polymers to blend and how fast to process the material.

The viscosities of all three sets of blends were measured and found to deviate negatively from linearity. The effect is most pronounced in the 40, 50 and 60% HViPP and MViPP blends, whose viscosities are much lower than either of their components. I suggest that this behaviour is evidence of the poor interfacial adhesion between the components, especially at central compositions. I predict that this factor might play a major role in determining the mechanical behaviour. Looking forward to the mechanical properties in Chapter 6 shows this prediction to be true.
Table 3.1 Various constants used to calculate the viscosity of the homopolymers in the linear power law region.

<table>
<thead>
<tr>
<th></th>
<th>HDPE</th>
<th>LViPP</th>
<th>MViPP</th>
<th>HViPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power law index, (n)</td>
<td>(0.499 \pm 0.001)</td>
<td>(0.433 \pm 0.001)</td>
<td>(0.379 \pm 0.001)</td>
<td>(0.362 \pm 0.001)</td>
</tr>
<tr>
<td>Apparent consistency index, (K_{APP})</td>
<td>(11745 \pm 173)</td>
<td>(12901 \pm 146)</td>
<td>(23602 \pm 203)</td>
<td>(28755 \pm 430)</td>
</tr>
<tr>
<td>Rabinowitsch correction, (\left(\frac{3n+1}{4n}\right))</td>
<td>(1.251 \pm 0.013)</td>
<td>(1.328 \pm 0.015)</td>
<td>(1.401 \pm 0.018)</td>
<td>(1.441 \pm 0.100)</td>
</tr>
<tr>
<td>Consistency index, (K)</td>
<td>(10503 \pm 173)</td>
<td>(11412 \pm 146)</td>
<td>(20722 \pm 203)</td>
<td>(25237 \pm 430)</td>
</tr>
<tr>
<td>Viscosity (Pa)</td>
<td>(10503\gamma_{TRUE}^{-0.501})</td>
<td>(11412\gamma_{TRUE}^{-0.567})</td>
<td>(20722\gamma_{TRUE}^{-0.621})</td>
<td>(25237\gamma_{TRUE}^{-0.638})</td>
</tr>
</tbody>
</table>

Figure 3.1 Schematic illustration of the ASTM test used to determine melt flow rate, MFR. MFR is equal to the number of grams of material extruded in 10 minutes. The weight of the load is 2.16 kg, with a corresponding shear stress of \(1.94 \times 10^4\) Pa. The die diameter is 2.095 mm and the die length is 8 mm.
Figure 3.2 Schematic illustration of planar shear flow. The arrows represent layers of fluid. The shear rate, $\dot{\varepsilon}$, is the rate of change of velocity at which one layer of fluid passes over an adjacent layer.
Figure 3.3 (a) Idealised shear stress-shear rate plot for a Newtonian and shear thinning fluid. (b) Idealised viscosity curve for a Newtonian and shear thinning fluid. At low shear rates the shear thinning fluid acts like a Newtonian fluid.

Figure 3.4 Idealised logarithmic plot of viscosity as a function of shear rate for a shear thinning fluid. The linear region is termed the power law region and may cover several decades of viscosity. At low shear rates the viscosity is constant: this is termed the zero shear rate viscosity, $\eta_0$. At high shear rates the viscosity may again become constant: this is termed the infinite shear rate viscosity, $\eta_\infty$. 
Figure 3.5 Schematic illustration of the Davenport capillary rheometer. The polymer material is placed in the barrel and allowed to melt. The material is then forced though the die by the piston.
Figure 3.6 Bagley plots of the homopolymers (a) HDPE, (b) LViPP, (c) MViPP and (d) HViPP.
HDPE

* apparent pressure
* end pressure losses
* true pressure

---

LVIPP

* apparent pressure
* end pressure losses
* true pressure

---

(a)

(b)
Figure 3.7 Plots demonstrating the effect of the end pressure losses, by showing the measured pressure, $\Delta p$, end pressure losses, $\Delta p_{end}$ and the true pressure drop along the die, $\Delta p_d$. 
Figure 3.8 True shear stress, $\sigma_{\text{TRUE}}$, as a function of apparent shear rate, $\dot{\varepsilon}_{\text{APP}}$, for all four homopolymers.

Figure 3.9 True shear stress, $\sigma_{\text{TRUE}}$, versus apparent shear rate, $\dot{\varepsilon}_{\text{APP}}$, on a logarithmic scale.
Figure 3.10 True shear stress, $\sigma_{\text{TRUE}}$, versus true shear rate, $\dot{\varepsilon}_{\text{TRUE}}$, for all four homopolymers.

Figure 3.11 True viscosity, $\eta_{\text{TRUE}}$, as a function of true shear rate, $\dot{\varepsilon}_{\text{TRUE}}$, for all four homopolymers.
Figure 3.12 True shear stress, $\sigma_{\text{TRUE}}$, as a function of true shear rate, $\dot{\varepsilon}_{\text{TRUE}}$ for the LViPP/HDPE blends.

Figure 3.13 True shear stress, $\sigma_{\text{TRUE}}$, as a function of true shear rate, $\dot{\varepsilon}_{\text{TRUE}}$ for the MViPP/HDPE blends.
Figure 3.14 True shear stress, $\sigma_{TRUE}$, as a function of true shear rate, $\dot{\varepsilon}_{TRUE}$ for the HViPP/HDPE blends.

Figure 3.15 True shear stress of the blends at a true shear rate of 1000s$^{-1}$. The plot illustrates that the blends deviate negatively from linearity.
CHAPTER 4: TRANSMISSION ELECTRON MICROSCOPY (TEM)

4.1 INTRODUCTION

The precise morphological character of a polymer blend will determine its properties and hence end-use capabilities. The crystallinity, molecular orientation, phase behaviour etc. will all significantly affect the response of a polymer blend to external stimuli. For instance, crystallinity has a pronounced effect on the bulk mechanical properties of the material, as crystalline regions are generally stiffer than amorphous regions. When amorphous or semi-crystalline polymers are molecularly oriented, their chains, on average, point in a particular direction. The bonds along a polymer chain are strong covalent bonds whereas the bonds between chains are weak van der Waals bonds; molecular orientation therefore has a strong effect on mechanical properties. When polymers are blended, their components are usually immiscible. If this is the case, the nature of the interfaces between the components will be crucial in determining the blends' properties. Further, either by accident or by design, polymers (and their blends) may contain voids. The size and dispersion of these voids can strongly affect the properties of the material. Examining the morphology of a blend can help to back up the results of other techniques and can also reveal information about the blend that other techniques, such as DSC, cannot. For example, DSC can reveal that a blend is phase separated but does not provide information about the size, shape and dispersion of the components – factors that may be important to the bulk mechanical properties and which are immediately obvious from TEM.

In this project a transmission electron microscope (TEM) in imaging mode was used to study the morphology of the homopolymers and blends. In section 4.2, a brief description of the transmission electron microscope is given, along with a discussion about sample preparation. Section 4.3 describes the types of morphologies that one might expect to see in an isotactic polypropylene/high-density polyethylene blend system and sections 4.4 to 4.7 present the methods, results, discussion and conclusions.
4.2 EXPERIMENTAL TECHNIQUES

4.2.1 Transmission Electron Microscope (TEM)

The TEM provides information on the microstructure of polymers from the scale of a few nanometers up to that covered by the optical microscope; it is a well-established technique for the study of polymer blends (see e.g. Bassett and Vaughan, 2002; Hill et al., 1994; Montes et al., 1998). The TEM consists of an evacuated metal cylinder about two meters high with a source of illumination, a tungsten filament (the cathode), at the top. When the filament is heated and a high voltage (the accelerating voltage) is passed between it and the anode, the filament will emit electrons. These negatively charged electrons are accelerated towards an anode placed just below the filament; some of the electrons pass through a tiny hole in the anode to form an electron beam which passes down the column. The speed at which the electrons are accelerated towards the anode depends on the accelerating voltage. Using a series of lenses and apertures, the electron beam is focused onto the specimen which is clamped into a removable specimen stage, usually on a specimen grid. As the electron beam passes through the specimen, some electrons are scattered whilst the remainder are focused by the objective lens, either onto a phosphorescent screen or onto photographic film, to form an image. As the images in this project were taken at magnifications lower than those for which the limit of resolution is important, a detailed description on the resolving power of the TEM is not given. For more details see Amelinckx et al. (1978) or Joy et al. (1986).

4.2.2 Sample Preparation

Preparation of polymer blend samples for TEM is difficult and time-consuming. The natural variation in density is seldom sufficient to achieve adequate contrast; samples must be thin enough to allow the electrons to pass through (a few tens of nanometers) and any cutting must be done below Tg. Following sectioning, contrast can be achieved by staining. Alternatively, samples can be produced by etching followed by replication. Throughout this project chemical etching was used to prepare the samples. Etching degrades and partially removes the amorphous material more readily than the crystalline. The topography of the etched sample reflects the lamellar structure of the semi-crystalline polymer. The most important development in this area was due to Bassett and Hodge (1978) and Olley et al. (1979) who introduced permanganic etching, where a mixture of potassium and sulphuric acid was used as an etchant. Later recipes also contained orthophosphoric acid in order to eliminate artificial structures that occurred using the original recipe (Olley and Bassett, 1982). The permanganic acid etches the polypropylene more quickly than polyethylene meaning that, in a blend of the two, the semi-crystalline structure of the polyethylene will be more visible. Naylor and Phillips (1983) showed that agitating in an ultrasonic bath enhanced the etching process. The etching process leads to a build up of film on the surface, which can subsequently be removed by washing. The etched sample is then replicated after shadowing with metal, allowing
the surface morphology to be seen in the TEM. Polyethylene and polypropylene are highly sensitive to radiation and degrade quickly under the electron beam; the replica technique has the advantage that the specimen, which shows the surface morphology, contains none of the original polymer and is therefore not subject to change in the electron beam.

4.3 EXPECTED BLEND MORPHOLOGIES

There have been extensive studies on the morphology of various different polyethylene/polypropylene blends (Avalos et al., 1996; Blackadder et al., 1981; Galeski et al., 1984; Gupta et al., 1982; Hill et al., 1994; Lohse, 1986; Loos et al., 2000; Lovingier et al., 1980; Martuscelli et al., 1980; Montes et al., 1998; Noel III and Carley, 1984; Shanks et al., 2000; Souza and Demarquette, 2002; Steinmann et al., 2001; Wignall et al., 1982; Willems et al., 1999a). In general it is agreed that most types of polyethylene and polypropylene are immiscible, however some authors have found blends of linear low-density polyethylene (LLDPE) and isotactic polypropylene (iPP) to be partially miscible (Shanks et al., 2000). As this project deals with isotactic polypropylene/high-density polyethylene blends (iPP/HDPE), the following discussion focuses on these blends only.

Given that iPP and HDPE are always found to be immiscible in the melt, electron microscopy should reveal blend morphologies with two well-separated phases over the entire composition range. When the content of one component is low, a disperse droplet morphology should be seen, with inclusions of the minor component embedded in a matrix of the major component. These inclusions may be spherical or elongated as a result of flow of the molten sample during compression moulding in the hot press. Elongation of the component phases will be referred to as 'phase orientation' throughout the thesis. When the samples are released from the hot press, the elongated inclusions will slowly recover to a spherical shape with the driving force supplied by the minimisation of the surface free energy. The rate at which these 'morphological relaxations' occur will depend on the relative viscosities (and relaxation times) of the two melts. When the samples are quenched (roughly 5 seconds after being released from the hot press) the melt structure is 'frozen-in'; the shape of the inclusions will therefore depend greatly on the morphological relaxation times. It must be noted that phase orientation is very different from molecular orientation. Molecular orientation refers to the orientation of the macromolecular chains, rather than the elongation of the component phases. A blend may display phase orientation without being molecularly oriented.

Note that when viewing a sample in the microscope, a spherical inclusion will appear circular; however, an elongated inclusion may also appear circular if the sample is cut at right angles to the
flow direction. The size of an observed inclusion will also vary depending on how the sample is cut. The size and distribution of the inclusions will depend greatly on the processing conditions and on the viscosity of the two components. In Chapter 3, it was stated that the dispersion of one phase in another has been found by several authors to be finest when the viscosities of the components are closely matching during processing. One should therefore expect the HViPP/HDPE blends to contain the greatest number of small inclusions, and the LViPP/HDPE blends to contain the fewest, largest inclusions.

As the content of the minor phase increases, the inclusions may either become larger, or increase in number, or both. Phase inversion will occur with increasing content of the original minor component. Phase inversion is defined as the process whereby the two phases switch their function; the former matrix becomes the dispersed phase and vice versa. Phase inversion does not always occur at a definite concentration and may occur over a range of compositions. The resulting morphology over this composition range is an interpenetrating network, known as a 'co-continuous' morphology. The phase inversion point is then regarded as the centre of the co-continuous region. Whether or not co-continuous morphologies are formed may depend on the viscosity ratio of the components and on the processing conditions. The range over which the co-continuous region extends may also depend on these factors. One of the aims of my study was to see how the processing conditions and viscosity ratio affect the phase morphologies of the blends.

It was stated in Chapter 2 that polymers with essentially linear molecules, such as HDPE, have a greater ability to crystallize than polymers whose molecules have bulky side groups, such as polypropylene. It is therefore expected that HDPE will have more perfect crystals than iPP, when cooled at the same rate. The thickness of the crystals will, however, depend on the cooling rate. As shown in Chapter 2, the initial crystal thickness is inversely proportional to the supercooling, AT. Referring forward to Chapter 5: DSC shows that the supercooling is greatest in the rapidly quenched blends; hence at slower cooling rates, one would expect the crystals to be thicker than at fast cooling rates. The size and dispersion of the phase separated domains will also depend on the cooling rate; the longer the material stays in the melt, the more time it has to ripen. As discussed in Chapter 2, ripening can occur via Brownian coalescence or Ostwald ripening (or a combination of the two). In either case, ripening will cause the inclusions to increase in size but decrease in number. The ripening rate may well be different for each of the components, meaning that a polyethylene inclusion in a matrix of polypropylene may grow at a different rate than a polypropylene inclusion in a matrix of polyethylene.

Another factor that may affect the morphology is whether the polypropylene or the polyethylene crystallizes first upon cooling. In general it is assumed that polypropylene will crystallize before polyethylene due to its higher melting point. This will, however, be dependent on the rate of
cooling. The morphology of polyethylene/polypropylene blends is often studied after isothermal crystallization, just below the melting point of polyethylene, see for example Bartczak et al. (1985). In such cases the polypropylene crystallizes before the polyethylene. Fewer studies have been done on the morphology and crystallization behaviour of rapidly quenched and slowly cooled blends. Another aim of my study was to determine the how the rate of cooling affects the crystallization behaviour.

4.4 EXPERIMENTAL METHODS

A variation of the Bassett and Olley etching recipe, which has been used by the Bristol blends group for several years (Rosney, 1987; Puig, 1994; Patrick et al., 1996), was used in this project. The method was as follows:

Etching

1) Samples were made up under the appropriate crystallization conditions and cut into shapes (approximately 5mm diameter) that could be distinguished from each other and the surface to be replicated identified. Samples were clean, dry and free of acetone (as the etchant explodes on contact with acetone).

2) An etching solution was prepared by adding 10ml of concentrated sulphuric acid, c.H₂SO₄, to 10ml of orthophosphoric acid, H₃PO₄, in a strong boiling tube fitted with a quick-fit glass stopper. 0.35g of potassium permanganate, KMnO₄, was added to the acid mixture, which was then placed in an ultrasonic bath and agitated for 1 hour until a dark green solution resulted.

3) Up to four samples were then placed in the solution. As the samples floated, the side placed downwards was noted, as this would become the etched side. The tube was replaced in the ultrasonic bath and agitated for 1 hour. (The solution was active for 2 hours after mixing. Because the iPP etched faster than the HDPE, blend samples were not etched for over an hour, as the surface would have become too rough for the replica to be detached easily).

4) The samples were removed and washed in four baths (a-d). They were stirred in each bath for at least 30 seconds:
   - (a) 7:2 solution of distilled water and c.H₂SO₄, at 5°C,
   - (b) hydrogen peroxide, H₂O₂, from the fridge,
   - (c) distilled water at room temperature,
   - (d) acetone at room temperature.

5) The samples were dried and mounted, etched side up, on a glass slide with cellotape.
Replication

6) The slide was lightly shadowed with platinum/palladium, Pt/Pd, at about 30°.
7) The shadowed samples were coated with carbon at normal incidence.
8) A small amount of polyacrylic acid glue was placed on the middle of each sample and the slide was then left to dry in a desiccator for 2 days.
9) The glue (and the replica) were prised off the samples with a scalpel and placed in distilled water, the glue dissolved in 2 hours.
10) The shadowed carbon replicas were picked up with copper TEM grids and were ready for use in the TEM immediately.

As stated in Chapter 1, one grade of polyethylene was blended (in turn) with three different grades of polypropylenes to produce three sets of blends. These were named:

- Low-viscosity isotactic polypropylene/high-density polyethylene (LViPP/HDPE),
- Medium-viscosity isotactic polypropylene/high-density polyethylene (MViPP/HDPE),
- High-viscosity isotactic polypropylene/high-density polyethylene (HViPP/HDPE).

The blends were labelled by their percentage composition of polypropylene. A hot press was used to compress the blends into sheets. Surface replicas of the rapidly quenched sheets were prepared for all three sets of blends and homopolymers. Surface replicas of the MViPP/HDPE sheets cooled at 1°C and 3°C/minute were also made. Micrographs were taken using a Philips 400T TEM operating at an accelerating voltage of 100keV and a magnification of 6,000x (except for some iPP micrographs, which were taken at 10,000x magnification to show the much finer crystal structure).

4.5 RESULTS

This section is divided into four subsections. The first three subsections are dedicated to the three different sets of rapidly quenched blends and the final subsection deals with the slowly cooled MViPP/HDPE blends. Note that when looking at the samples in the TEM, many micrographs were taken from different areas of the grid. In most cases the micrograph shown in the figure is representative of the whole sample; in cases where more than one type of morphology was seen additional figures are shown.

Before presenting the results of my study, it is important to make a note about surface morphologies versus bulk morphology. In a separate study by Mary Hill, it was found that the outside surfaces of the sheets have very similar morphologies to the inside of the sheets. This is clearly demonstrated in figure 4.1, which shows micrographs taken from the outside and inside of a
10% MViPP blend sheet. This is an important observation as it confirms that my micrographs, which are taken from replicas of the sheet surfaces, are representative of the bulk samples.

4.5.1 Rapidly Quenched Low-Viscosity Isotactic Polypropylene/High-Density Polyethylene (LViPP/HDPE) Blends

Figure 4.2 shows typical micrographs obtained from rapidly quenched (a) 0%, (b) 10%, (c) 30%, (d) 30% from a different area of the sample, (e) 40%, (f) 50%, (g) 60%, (h) 70%, (i) 90% and (j) 100% LViPP/HDPE blend sheets. As expected, the TEM results show two well-separated phases for all the blend compositions studied. The polyethylene is easily differentiated from the polypropylene by its coarser crystals and characteristic banded spherulitic structure. In the pure polyethylene, spherulites with a diameter of roughly 5μm can be seen.

In the 10% blend, circular inclusions of HDPE are seen in a matrix of LViPP. The 30% blend contains some elliptical inclusions with smooth boundaries, as in figure 4.2(e), and some very long inclusions with ragged boundaries, as in figure 4.2(d). The 40% blend has very large (5-10μm) asymmetric inclusions of polypropylene with ragged boundaries. Phase inversion occurs at 50% where large circular inclusions of HDPE (5-6μm) with smooth boundaries, are present in a matrix of LViPP. The polypropylene matrix also contains very small inclusions (<1μm) of polyethylene. Within the large polyethylene inclusions there are smaller droplets of polypropylene (2-3μm). The 60, 70 and 90% blends contain circular droplets of polyethylene varying in size between 0.5-5μm. The presence of very small inclusions alongside very large ones may be the result of rapid Ostwald ripening during storage in the melt in the hot press. The morphological features of polypropylene are too small to be clear at the magnification appropriate to the blend samples; a micrograph of polypropylene taken at a higher magnification is therefore shown.

No co-continuous morphologies are observed in this blend system. Interestingly, phase orientation is only present in the HDPE rich blends. This implies that the HDPE and LViPP have different morphological relaxation times.

4.5.2 Rapidly Quenched Medium-Viscosity Isotactic Polypropylene/High-Density Polyethylene (MViPP/HDPE) Blends

Figures 4.3 (a)-(f) show typical micrographs obtained from the rapidly quenched 10, 30, 50, 70, 90 and 100% MViPP blend sheets. In the 10 and 30% blends, circular inclusions of polypropylene (1-3μm diameter) in a matrix of polyethylene can be seen. The 40, 50 and 60% blends show co-continuous tendencies with large elongated regions of polypropylene (>10μm long) containing small droplets of polyethylene and vice-versa; the 50% blend is shown as an example of this type of morphology. The 70 and 90% blends contain both elongated inclusions (>10μm long) and
circular inclusions (≤0.5 μm diameter) of polyethylene. The circular inclusions may either be elongated inclusions that have broken apart or elongated inclusions viewed end on. Again, the polypropylene is shown at a higher magnification than the rest of the samples. Unlike the LViPP/HDPE blends, phase orientation is only seen in the iPP rich blends.

4.5.3 Rapidly Quenched High-Viscosity Isotactic Polypropylene/High-Density Polyethylene (HViPP/HDPE) Blends

Figure 4.4 shows typical micrographs of the rapidly quenched (a) 10%, (b) 30%, (c) 40%, (d) 50%, (e) 60%, (f) 70%, (g) 90%, (h) 99.5% HViPP/HDPE blends. The 10% blend appears similar to the 10% LViPP and 10% MViPP blends. The 30% blend contains some highly elongated inclusions of polypropylene (>10μm) and some elliptical inclusions. The elliptical inclusions appear to be elongated inclusions which have broken apart, rather than elongated inclusions viewed end-on. The 40% blend is similar to the 30% with elongated inclusions of polypropylene; some of the inclusions appear to have been relaxing into circles at the time of the quench (5 seconds after the pressure was released). The 50% blend has co-continuous tendencies and looks similar to the 50% MViPP blend. The 60, 70, and 90 and 99.5% blends contain small circular droplets of polyethylene in a matrix of polypropylene. The 100% HViPP appears very similar to the matrix phase of the 99.5% blend and is therefore not shown. Phase orientation can only be seen in the HDPE rich blends; this is similar to the behaviour of the LViPP/HDPE blends, but opposite to the behaviour of the MViPP/HDPE blends.

4.5.4 Slowly Cooled Blend Sheets

Figure 4.5 shows typical micrographs of (a) 0%, (b) 10%, (c) 30%, (d) 30% from a different area of the sample, (e) 40%, (f) 50%, (g) 60%, (h) 70%, (i) 90% and (j) 100% MViPP blends cooled slowly at 1°C/minute. The blends cooled at 3°C/minute appear very similar to those cooled at 1°C/minute; figure 4.6 shows the 30 and 50% blends cooled at 3°C/minute to illustrate this. After the pressure in the hot press is released, the sheets cooled at 1°C and 3°C/minute spend roughly 80 and 30 minutes respectively in the melt before crystallizing. As expected, the slowly cooled blends have thicker crystalline lamellae than the rapidly quenched blends and, unlike the rapidly quenched blends, no phase orientation effects are seen, indicating that complete morphological relaxation has occurred. The slowly cooled blends show much larger scale phase separation than the rapidly quenched blends, proving that phase ripening has occurred. The observation of small droplets (smaller than the rapidly quenched blends) alongside very large droplets indicates that Ostwald ripening has occurred; see for example the 30, 70 and 90% slowly cooled MViPP blends. Whether Brownian coagulation has also occurred is difficult to tell from this study alone.
In the pure polyethylene the spherulites are much larger than in the rapidly quenched samples. Figure 4.5(a) shows only one spherulite with a central sheaf-like region and radiating lamellae. The 10, 30, 40, 70 and 90% blends contain inclusions of the minority material in a matrix of the majority. In the 40% blend, the inclusions are very large and asymmetric (>20μm across). The 50 and 60% blends show co-continuous tendencies with very large areas of both components extending over 50μm and containing small droplets of the other component. The morphological features of the polypropylene are clearer in these slowly cooled blends because the crystals are thicker. The large-scale spherulitic structure of the polypropylene is especially evident in the 90% blend, where lamellae appear to radiate from a central point far to the left of the picture.

In most of the blends the boundaries between the polyethylene and polypropylene phases is smooth, however, in the 10% blend several polyethylene lamellae penetrate into the polypropylene regions. This is a very interesting and significant observation. This observation provides a clue as to how the components in the slowly cooled blends crystallize. Studies on polymer crystallization have shown that when a polymer crystallizes there is a reduction of volume in the material leading to transport of molten polymer near the growth front, with some lamellae protruding into the melt. As the growing lamellae approach the boundary between the two liquid phases, the transport of molten polymer will start to involve both phases; once all the crystallizable material has been exhausted, the interface between the two phases resembles the overall interface between the growing lamellae and their own melt. A recent in situ AFM study by Hobbs and Miles (2001) on the crystallization of polyethylene revealed that the interface between growing polyethylene lamellae and polyethylene melt closely resembles the shape of the interface between the polyethylene and polypropylene phases in my 10% blend. In general, the boundary between two phases reflects the shape of the interface between the crystals and the melt of the phase that crystallizes first. It therefore seems reasonable to infer that in the 10% slowly cooled blend the polyethylene crystallizes before the polypropylene. If polypropylene crystallizes first, one might expect to see polypropylene lamellae protruding into the polyethylene regions. As polypropylene has much finer lamellae, the scale of such fluctuations along the growth front may be too small to observe, resulting in a seemingly smooth phase boundary. As smooth phase boundaries are observed in the rest of the slowly cooled blends, it seems reasonable to infer that the polypropylene crystallizes first in these blends. Differential scanning calorimetry (DSC) was employed to study the crystallization behaviour further. The results of this study are presented in the following chapter. Briefly, the DSC results support the TEM results by indicating that the polyethylene starts to crystallize first in the 10% slowly cooled blend, whereas the polypropylene starts to crystallize first in the rest of the slowly cooled blends.

Using the same logic as above, it might be concluded (from the TEM results alone) that polypropylene crystallizes first in the rapidly quenched blends, as the phase boundaries are smooth.
However because of the very short time allowed for crystallization and the fact that the lamellae of both components are much finer in the rapidly quenched blends, determining which component crystallizes first is impossible by TEM alone. DSC was used to determine which components crystallize first. In fact it revealed that the polyethylene starts to crystallize at higher temperatures than polypropylene in all three sets of rapidly quenched blends. The detailed results of this study are reported in Chapter 5. The significance of the crystallization behaviour is discussed in the following chapters.

4.6 DISCUSSION

The TEM micrographs reveal that the blend components are always phase separated at the time of crystallization. By rapidly quenching the samples, the melt phase structure is ‘frozen-in’ and preserved, indicating that the components are already phase separated in the melt at 200°C, rather than becoming phase separated on cooling from the melt. Figures 4.2-4.5 show that a range of morphologies can be obtained depending on crystallization conditions and the viscosities of the different components. Table 4.1 gives a summary of the different morphologies obtained for each blend system. Although the morphologies obtained are fairly typical of other iPP/HDPE blend systems, there are several interesting points to discuss. For instance, what determines the size of the inclusions, why do the HViPP/HDPE and MViPP/HDPE blends form co-continuous-like morphologies at certain compositions when the LViPP/HDPE blends do not and why is the degree of phase orientation different in the three sets of blends? For simplicity the following discussion deals with the rapidly quenched blends first, and then moves on to the slowly cooled blends.

4.6.1 Rapidly Quenched Blend Sheets

By looking at the three sets of blends it is clear that by varying the grade of the polypropylene, different morphologies can be obtained. It must be noted that although the viscosities of the polypropylenes are different, many other factors differ between the different grades, such as the tacticity, polydispersity, molecular weight etc. The observed differences in morphology may therefore be due to any of these factors. The following discussion assumes that the differences in morphology are due solely to the differences in viscosity.

It was demonstrated in Chapter 3 that when the blends are extruded in the twin-screw extruder, the HDPE has the highest viscosity followed by the HViPP, MViPP and LViPP respectively. When the blends are prepared in the extruder they are pelletized. For many of the tests, such as tensile testing, pellets are not suitable. The pellets are therefore melted, held in the melt for 10 minutes and pressed into sheets in a hot press. The shear rate in the hot press is much lower than that in the extruder. At such low shear rates, the HViPP has the highest viscosity followed by the MViPP,
LViPP and HDPE respectively. There are therefore several processes involved in determining the final morphology of the sheets (note that it is the final sheet morphologies that are shown in figure 5.1-5.6). These processes are: firstly, mixing and extrusion at a very high shear rate; secondly, storage in the melt for 10 minutes (during which time phase ripening may occur) and thirdly, compression in the hot press at a very low shear rate. For the rapidly quenched blends, the time between being released from the hot press and being quenched is roughly 5 seconds. During this time morphological relaxation will occur.

Clearly, the original mixing conditions in the extruder are important in determining the final morphology of the sheets. It was stated in Chapter 3 that the closer the viscosity ratio of the components is to unity, the finer the dispersion of one phase in the other is expected be. Based on this assumption, when first extruded, the HViPP/HDPE blends should have the largest number of inclusions with the smallest size, followed by the MViPP/HDPE blends and finally the LViPP/HDPE blends. In order to determine whether this is true, the morphologies of the original pellets need to be studied. However, even after subsequent processing in the hot press, the blends seem to follow this pattern with the HViPP/HDPE blends containing many small inclusions and the LViPP/HDPE blends containing the fewest, largest inclusions.

The effect of holding the pellets in the melt for 10 minutes in the hot press introduces the complication of phase ripening. Although unlikely, the blends could all have the same sized inclusions after the initial extrusion. If this were true, the observed differences in morphology would be solely due to the components having different ripening rates. Ripening can occur via Brownian coalescence and/or Ostwald ripening. During Ostwald ripening, large inclusions grow at the expense of small inclusions. By examining the LViPP/HDPE blend micrographs, it is clear that in many of the samples there are small inclusions of HDPE alongside very large inclusions of HDPE. The small and large droplets are not seen in the other rapidly quenched blend systems, suggesting that a larger amount of Ostwald ripening may have occurred in the LViPP/HDPE blends than in the MViPP/HDPE or HViPP/HDPE blends. When considering the blends, two ripening rates can be defined: ripening of polypropylene inclusions in the polyethylene matrix and vice versa. Because different grades of polypropylene are used, it seems fairly obvious that they will have different ripening rates in polyethylene. Which grade of polypropylene has the fastest ripening rate is not clear from this study alone and a lot more work needs to be done in this area. As Ostwald ripening involves diffusion of molecules from small droplets across the matrix to larger droplets, it seems reasonable to assume that the viscosity of the matrix will affect the rate of diffusion. Therefore, although the same grade of polyethylene is used throughout, its ripening rate in polypropylene is probably different in each set of blends. Intuitively, it seems likely that the diffusion of polyethylene molecules through the polypropylene matrix is fastest in the LViPP and slowest in the HViPP. Indeed this may explain why there are several small inclusions alongside
very large inclusions of HDPE in the rapidly quenched LViPP/HDPE blends, but not in the other rapidly quenched blends. Of course, the variation in size of the droplets in the LViPP/HDPE blends may well be due to the poorly matching component viscosities in the extruder, rather than to rapid ripening.

The Bristol blends group is currently undertaking a detailed study of the ripening. The initial studies on the 10 and 90% MViPP blends show that droplets of MViPP in a matrix of HDPE ripen much faster than droplets of HDPE in a matrix of MViPP. The MViPP droplets double in diameter after 10-15 minutes, whereas the HDPE droplets double in diameter after 90 minutes. The study also shows that the MViPP droplets are roughly twice the diameter of the HDPE droplets when initially extruded. The detailed results of this study will be reported in a forthcoming paper entitled “Phase Morphology and Ripening in iPP/HDPE Blends” (Hill et al., 2003 in preparation). So far, no work has been done on the ripening rates of the other blend systems.

When the blend sheets are prepared, the samples spend 10 minutes in the melt before quenching. Given that a droplet of MViPP in an HDPE matrix can double in diameter in 10 minutes, it is not unreasonable to assume that the differences in morphologies between the three blend systems are (as mentioned above) due to the different ripening rates of the components. In reality a combination of the initial mixing and subsequent phase ripening are most likely responsible for the final sheet morphologies. From this study alone it is impossible to tell which has the greatest effect. Much more work needs to be done in this area and the Bristol blends group is currently in the process of doing this.

My results also suggest that the mixing conditions in the extruder determine the blends’ ability to exhibit co-continuity. The fact that the LViPP/HDPE blends do not show any co-continuity is most likely due to their components having poorly matching viscosities in the extruder. The observation that the MViPP/HDPE and HViPP/HDPE blends both show co-continuous tendencies suggests that there might be a critical viscosity ratio that determines whether or not co-continuous morphologies are formed during mixing. However, it is impossible to determine a precise value for this viscosity ratio due to the very complex flow behaviour in the extruder (see Chapter 3).

Whilst it seems that the size and dispersion of the inclusions are due, at least in part, to the mixing conditions in the extruder, I believe that the phase orientation (seen in some blends) is due to the flow experienced by the molten samples in the hot press. The reason why some blends are phase oriented while others are not, is probably due to the viscosity of their components. Phase orientation is a result of two processes. The inclusions are firstly stretched under pressure and subsequently relaxed on removal of the pressure; the viscosity of both components will affect these factors. At the low shear rates encountered in the hot press, the LViPP and HDPE have the most
closely matching viscosities. Blends of these materials show the least amount of phase orientation. When the viscosities of the components do not match so well, as in the MViPP/HDPE and HViPP/HDPE blends, more phase orientation is seen. The MViPP/HDPE blends only show phase orientation in the MViPP rich blends. The LViPP/HDPE and HViPP/HDPE only show phase orientation in the HDPE rich blends.

4.6.2 Slowly Cooled Blend Sheets
Only MViPP/HDPE blends were studied after slow cooling. Essentially, the slowly cooled MViPP/HDPE blends have similar morphologies to the rapidly quenched MViPP/HDPE blends but on a larger scale, indicating that phase ripening has occurred. The observation of small droplets (smaller than in the rapidly quenched samples) near to very large droplets indicates that Ostwald ripening has occurred; it is not possible from this study to determine whether Brownian coalescence has also occurred. If the other blends, i.e. the LViPP/HDPE and HViPP/HDPE were to be slowly cooled, one might expect the same type of relationship between rapidly quenched and slow cooled samples. Of course, the ripening rates of the various components will be different in each blend set, for the reasons discussed above.

The morphologies of the slowly cooled MViPP/HDPE blends also provide a clue as to how the components crystallize. From the unusual morphology observed in the 10% blend, it is possible to infer which component crystallizes first in all of the slowly cooled blends. The micrographs suggest that the polyethylene crystallizes before the polypropylene in the 10% blend, whereas the polypropylene crystallizes before the polyethylene in the rest of the slowly cooled blends. These suggestions are backed up by the DSC study on crystallization behaviour detailed in Chapter 5.

4.7 CONCLUSIONS

Studies of the morphologies of rapidly quenched sheets of LViPP/HDPE, MViPP/HDPE and HViPP/HDPE blends reveal that the components are phase separated over the entire blend composition range. The results show that under the same processing conditions, different morphologies can be obtained by varying the grade of the polypropylene.

The rapidly quenched LViPP/HDPE blend sheets, whose components have the least closely matching viscosities in the extruder, have the fewest, largest inclusions and exhibit no co-continuity. The rapidly quenched MViPP/HDPE blend sheets have more, larger inclusions than the LViPP/HDPE blend sheets. These blends exhibit co-continuous tendencies at central compositions. The rapidly quenched HViPP/HDPE blend sheets, whose component viscosities are the closest in the extruder, have the most, smallest inclusions and exhibit co-continuous tendencies at central
compositions. I suggest that the dispersion of inclusions is partly determined during mixing in the extruder and that phase ripening occurs during subsequent processing in the hot press.

The morphologies of slowly cooled sheets of MViPP/HDPE blends reveal that these samples have larger, thicker crystals and larger scale phase separation than the rapidly quenched samples. The micrographs indicate that Ostwald ripening has occurred in these samples.

Studying the morphologies of the slowly cooled MViPP/HDPE blends also provides a clue as to how the components in the blends crystallize. In the 10% MViPP blend I suggest that the polyethylene crystallizes at a higher temperature than the polypropylene, whereas in the rest of the blends the polypropylene crystallizes first. This work is supported by the DSC results, reported in Chapter 5.
Table 4.1 Morphologies obtained for each blend composition in each blend system. When the size of an inclusion is given in microns it refers to diameter, if the inclusion is elliptical or elongated, it refers to the long axis. A co-continuous morphology has regions of one material containing droplets of the other and vice-versa.

<table>
<thead>
<tr>
<th></th>
<th>Rapidly Quenched LViPP/HDPE blends (fig 4.2)</th>
<th>Rapidly Quenched MViPP/HDPE blends (fig 4.3)</th>
<th>Rapidly Quenched HViPP/HDPE blend (fig 4.4)</th>
<th>Slowly Cooled MViPP/HDPE blend (figs 4.5-4.6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>banded spherulites (5µm)</td>
<td>banded spherulites (5µm)</td>
<td>banded spherulites (5µm)</td>
<td>large scale spherulites (&gt;10µm)</td>
</tr>
<tr>
<td>10%</td>
<td>circular inclusions of LViPP (1µm)</td>
<td>circular inclusions of MViPP (1µm)</td>
<td>circular inclusions of HViPP (1µm)</td>
<td>circular inclusions of MViPP (2-4µm)</td>
</tr>
<tr>
<td>30%</td>
<td>elliptical inclusions of LViPP (2-4µm)</td>
<td>circular inclusions of MViPP (3µm)</td>
<td>elongated inclusions of HViPP (&gt;10µm)</td>
<td>circular inclusions of MViPP (some large, &gt;10µm; some small, 1µm)</td>
</tr>
<tr>
<td></td>
<td>+ elongated inclusions with ragged boundaries (&gt;10µm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40%</td>
<td>large asymmetric inclusions of LViPP (8µm)</td>
<td>co-continuous</td>
<td>elongated inclusions of HViPP (&gt;10µm) + elliptical inclusions of HDPE (3µm)</td>
<td>large asymmetric inclusions of MViPP (&gt;20µm)</td>
</tr>
<tr>
<td>50%</td>
<td>large circular inclusions of HDPE (5-6µm) containing smaller inclusions of LViPP (1-2µm) + small inclusions of HDPE (&lt;1µm) in LViPP</td>
<td>co-continuous</td>
<td>co-continuous</td>
<td>large scale co-continuity</td>
</tr>
<tr>
<td>60%</td>
<td>circular inclusions of HDPE (some large, 5µm; some small, &lt;0.5µm)</td>
<td>co-continuous</td>
<td>circular inclusions of HDPE (1-2µm)</td>
<td>large scale co-continuity</td>
</tr>
<tr>
<td>70%</td>
<td>circular inclusions of HDPE (0.5-5µm)</td>
<td>elongated inclusions of HDPE (&gt;10µm) + circular inclusions of HDPE (≤0.5µm)</td>
<td>circular inclusions of HDPE (1-2µm)</td>
<td>elliptical inclusions of HDPE (some large, &gt;10µm; some small, &lt; 1µm)</td>
</tr>
<tr>
<td>90%</td>
<td>circular inclusions of HDPE (1-5µm)</td>
<td>elongated inclusions of HDPE (&gt;10µm) + circular inclusions of HDPE (≤0.5µm)</td>
<td>circular inclusions of HDPE (0.5-1µm)</td>
<td>circular inclusions of HDPE (1-3µm)</td>
</tr>
<tr>
<td>99.5%</td>
<td>N/A</td>
<td>N/A</td>
<td>circular inclusions of HDPE (0.2µm)</td>
<td>N/A</td>
</tr>
<tr>
<td>100%</td>
<td>too fine to resolve well</td>
<td>too fine to resolve well</td>
<td>too fine to resolve well</td>
<td>large scale spherulites</td>
</tr>
</tbody>
</table>
Figure 4.1 Micrographs taken from the (a) outside and (b) inside of a 10%MViPP blend sheet. The scale bars represent one micron. Pictures courtesy of Mary Hill.
Figure 4.2 (above) (a) 0%, (b) 10%, (c) 30%, (d) 30% from a different area of the sample, (e) 40%, (f) 50%, (g) 60%, (h) 70%, (i) 90% and (j) 100% LViPP rapidly quenched blends. The HDPE has coarser crystals and a characteristic spherulitic structure. The 100% LViPP is shown at a slightly higher magnification due to its finer structure. The scale bars represent one micron.
Figure 4.3 (a) 10%, (b) 30%, (c) 50%, (d) 70%, (e) 90% and (f) 100% MViPP rapidly quenched blends. The 100% MViPP is shown at a larger scale due to its finer morphological details. Dark areas in micrographs (several in figure (a)) are the result of detached polymer adhering to the replicas. The scale bars represent one micron.
Figure 4.4 (a) 10%, (b) 30%, (c) 40%, (d) 50%, (e) 60%, (f) 70%, (g) 90% and (h) 100% HViPP rapidly quenched blends. The scale bar represents one micron.
Figure 4.5 (a) 0%, (b) 10%, (c) 30%, (d) 30% from a different area of the sample, (e) 40%, (f) 50%, (g) 60%, (h) 70%, (i) 90% and (j) 100% MViPP blends cooled at 1°C/minute. Note the higher magnification of the 100% blend. The scale bars represent one micron.

Figure 4.6 (a) 30% and (b) 50% MViPP blends cooled at 3°C/minute. The scale bars represent one micron.
CHAPTER 5: DIFFERENTIAL SCANNING CALORIMETRY (DSC)

5.1 INTRODUCTION

This chapter details the results of the DSC study. Differential scanning calorimetry is an experimental technique that measures heat flow to or from a sample as a function of temperature. It is commonly used to study polymer blends as it provides information about phase behaviour, thermodynamic transitions (i.e. glass transition, crystallization and melting), enthalpies of fusion and the degree of crystallinity of the samples - all of which are important factors in determining the end-uses of a polymer blend. This chapter deals mainly with the practical aspects of phase behaviour and crystallization as the relevant background theories were discussed in Chapter 2. In the following section a brief description of the DSC is given along with a description of the various measurements that can be made from a typical DSC trace. Sections 5.3 to 5.5 present the methods, results, discussion and conclusions of my work.

5.2 DSC OVERVIEW

The DSC instrument consists of two sample holders containing aluminium pans: one pan holds the sample and the other, known as the reference pan, is left empty. Below each pan is a heater and thermocouple; a temperature program heats or cools the pans at a set rate and the electrical power supplied to each heater is adjusted so that the temperatures of both pans remain equal, even during a thermal event in the sample. The difference in the power supplied (heat flow) to each pan is plotted as a function of temperature or time. The DSC is calibrated using a material of known melting point and enthalpy of fusion (usually Indium).

Before discussing polymer blends, consider a single-phase polymer. Figure 5.1(a) shows a typical DSC trace from a heating run of a supercooled polymer (quenched into a non-crystalline glassy state) plotted as a function of temperature. At all temperatures, the sample and the reference pan are kept at the same temperature. As the sample is heated through the glass transition, an increase in heat flow (endothermal) to the sample is needed in order to maintain the temperature balance between the two pans. Further heating causes the sample to crystallize. During crystallization, heat is given out (exothermal), the heat flow to the sample must therefore be reduced in order to keep
the pan temperatures balanced. The area under the exothermal peak is equal to the enthalpy of crystallization, $\Delta H_c$. On further heating, the sample will undergo melting (which is an endothermic process); heat must be supplied to the sample pan to in order to maintain the temperature balance between the pans. The area under the melting endotherm is equal to the enthalpy of fusion, $\Delta H_f$. (N.B. $\Delta H_f$ is equivalent to -$\Delta H_c$) It is sometimes useful to measure the onset and end temperatures of a thermal event. These can be determined by extrapolation of the melting or crystallization curves to the baseline, as illustrated in figure 5.1 (b). The degree of crystallinity of the sample can be determined by comparing the measured enthalpy of fusion to the enthalpy of fusion of the fully crystalline material (which can be found in the literature).

To summarize, using the method described above, DSC can be used to measure the glass transition temperature, $T_g$; the onset, peak and end melting temperatures, $T_m$; the onset, peak and end crystallization temperatures, $T_c$; enthalpy of fusion, $\Delta H_f$, enthalpy of crystallization, $\Delta H_c$, and the degree of crystallinity of the sample. It must be noted that DSC traces can also be recorded for isothermal events, such as isothermal crystallization. In this case, the samples are held at a constant temperature and the DSC plots the heat flow as a function of time, rather than temperature. (N.B. only the first method was employed in my work.)

As well as measuring the properties mentioned above, DSC is frequently used to study polymer blends' miscibility. This can be achieved by rapidly quenching a blend sample from the melt and measuring its glass transition temperature, $T_g$, upon reheating. By rapidly quenching, the melt structure is 'frozen-in' and preserved, allowing it to be observed indirectly. The DSC's sensitivity is considered to be between 2-15nm (Olabisi et al, 1979; Utracki, 1989), thus a blend exhibiting a single $T_g$, is mixed at least down to this level. In this case the blend's $T_g$ will lie between the $T_g$'s of the component polymers and will depend on the composition. If, however, two $T_g$'s are observed which are independent of composition (in the case of a binary blend), the blend is phase separated, with the scale of the domains being at least 15nm in size. These two examples are limiting cases. Partial mixing may result in two $T_g$'s, which are broader than the components' $T_g$'s, and closer together. Since the glass transition occurs over a broad temperature range, the $T_g$'s of the original components must be at least 20°C apart for miscibility to be determined. By varying the composition of the samples, and the temperatures from which they are quenched, a polymer blend phase diagram can be mapped out-see Chapter 2.

However, this method of determining phase behaviour will not work for iPP/HDPE blends as they cannot be quenched into a glassy state. A variation of this technique, employed extensively at Bristol with semi-crystalline blends (Hill et al., 1994b) was therefore used in this project. It involves quenching the samples rapidly from the melt and recording the melting transition on reheating. This technique follows the same principle as above, i.e. if two melting peak are
observed, the components are considered to be immiscible etc. Care must be taken when interpreting the results obtained from this method. Other factors, such as crystal thickening (which will depend on heating rate) and synergistic crystallization effects between the components when blended, will affect the position, shape and number of melting peaks.

In this project, the phase behaviour of the blends was studied by measuring the melting peaks of the samples after rapid quenching from the melt. The phase behaviour was only studied at 200°C as this was the temperature at which the blends were processed throughout the project. DSC was also used to study the crystallization behaviour of the blends and their components, cooled at various rates from the melt. Different cooling rates were employed in order to mimic the conditions under which the compression-moulded sheets were prepared. Recall from Chapter 1 that the sheets were cooled in three ways: by rapidly quenching into cold water, by leaving the sheets to cool outside the hot press and by leaving the sheets to cool inside the hot press with the power switched off. The average rates of cooling between 140°C and 100°C (the temperature region in which the crystallization took place) were found to be approximately 100°C, 3°C and 1°C/minute respectively. However, the fastest cooling rate possible in our DSC was 80°C/minute meaning that at fast cooling rates only a qualitative comparison could be made to the rapidly quenched sheets. Some samples were also cooled at intermediate rates. The aim of this study was to determine whether blending affects the crystallization behaviour of the components, and to see the effect that cooling rate has on the samples' crystallization behaviour. Although these are interesting subjects in their own right, my primary interest lies in how these factors relate to the mechanical properties of the blends.

5.3 EXPERIMENTAL METHODS

The instrument used in this project was a Perkin-Elmer DSC 7 operating with a nitrogen chiller. 1mg samples were cut from the raw pellets and were sealed into aluminium DSC pans. For each blend composition tested at least three samples were taken from different parts of the pellet. DSC traces were recorded for every sample tested. The DSC was capable of achieving heating/cooling rates of 1°C to 80°C/minute. The instrument was calibrated using Indium. Heating at fast rates caused the sample temperature to lag behind the recorded temperature; it was therefore necessary to calibrate for each different heating/cooling rate used.

In order to indirectly study the phase behaviour of the blends in the melt, the samples (in the DSC pans) were heated to 200°C on a Kofler hot bench for 10 minutes and rapidly quenched into freezing acetone. DSC endotherms were then recorded at a heating rate of 10°C/minute. Melting endotherms were recorded for all three sets of blends, i.e.: low-viscosity isotactic
polypropylene/high-density polyethylene (LViPP/HDPE), medium-viscosity isotactic polypropylene/high-density polyethylene (MViPP/HDPE) and high-viscosity isotactic polypropylene/high-density polyethylene (HViPP/HDPE).

In order to study crystallization behaviour, the samples were heated in the DSC to 200°C and held in the melt for 10 minutes (in order to come as close as possible to the conditions in the hot press). DSC exotherms were then recorded at a cooling rate of 80°C/minute for all three sets of blends. The MViPP/HDPE blends were subjected to further cooling rates of 70°C, 50°C, 30°C, 20°C, 10°C, 3°C and 1°C/minute (N.B. fresh samples were used for each run). Enthalpies of crystallization could not be determined for the individual components in the blends as the crystallization curves of the components overlapped. In order to determine the degree of crystallinity, the samples were re-melted and their enthalpies of fusion were recorded. The enthalpies of fusion of the 100% crystalline materials were found in the "Polymer Handbook", 1989. The values were 290J/g for HDPE and 209J/g for iPP.

5.4 RESULTS AND DISCUSSION

This section is divided into two parts with the first being dedicated to the phase behaviour of the blends and the second to the crystallization behaviour of the blends and their components. As most of the work in this chapter concentrates on the MViPP/HDPE blends, these results are presented first, followed by the LViPP/HDPE blends and the HViPP/HDPE blends respectively.

5.4.1 Phase Behaviour

Figure 5.2 shows DSC melting endotherms of the rapidly quenched MViPP/HDPE homopolymers and blends. It is clear that all the traces show two well separated melting peaks, with the higher melting peak (160°C) corresponding to the melting of polypropylene and the lower (130°C) to the melting temperature of the polyethylene. The melting curves of the rapidly quenched LViPP/HDPE and HViPP/HDPE blends are very similar to those in figure 5.2 and to be concise are not shown.

Figure 5.3 shows the peak melting temperature of each component as a function of blend composition for the (a) LViPP/HDPE blends, (b) MViPP/HDPE blends and (c) HViPP/HDPE blends. In the LViPP/HDPE blends, the components in the blends melt at approximately the same temperatures as the pure components indicating that the components are completely immiscible in the melt at 200°C over the entire composition range. In the MViPP/HDPE blends, the polypropylene melts at slightly lower temperatures in the blends than it does on its own, and the polyethylene tends to melt at slightly higher temperatures in the blends than it does on its own. The maximum difference between the melting temperature of the components in the blends and the
melting temperature of the pure components is \( 3^\circ C \). In the HViPP/HDPE blends, both the polypropylene and the polyethylene melt at slightly higher temperatures in the blends than they do on their own. Again the maximum difference between the melting temperature of the components in the blends and the melting temperature of the pure components is \( 3^\circ C \).

Although melting peaks which are closer together in the blends than they are in the pure components can indicate a certain degree of miscibility, other factors such as crystal thickening and synergistic crystallization effects between the components when blended can also result in shifted melting peaks. By looking at the crystallization behaviour described below in section 5.4.2, one can see that the presence of one component influences the crystallization behaviour of the other and vice versa. This means that the components in the blends crystallize differently from the pure components. It therefore seems likely that synergistic crystallization effects, rather than partial mixing, are responsible for the shifted melting peaks in the rapidly quenched blends.

5.4.2 Crystallization Behaviour

5.4.2.1 Medium-Viscosity Isotactic Polypropylene/High-Density Polyethylene Blends (MViPP/HDPE)

Figure 5.4 shows DSC crystallization exotherms of the MViPP/HDPE homopolymers and blends cooled from the melt at 80°C/minute. At this cooling rate, the polyethylene and polypropylene in the blends crystallize at very similar temperatures, resulting in a single, broad crystallization peak. The exotherms indicate that the components in the blends crystallize differently from the pure components. This is well illustrated in figure 5.5, which shows a measured 50% MViPP blend exotherm and an exotherm obtained using unblended pellets of MViPP and HDPE in proportions of 50:50. Clearly the onset temperature of crystallization is higher in the 50% blend than in the unblended sample. In the unblended sample two peaks can be resolved, but in the blended sample only one can be resolved.

Apart from some of the samples cooled at 1°C/minute, only one crystallization peak can be resolved for the blends cooled at other rates. Figure 5.6 shows the DSC exotherms of the samples cooled at 1°C/minute. At this cooling rate the 60, 70 and 90% MViPP blends display two resolvable crystallization peaks. For concision the DSC traces obtained at other cooling rates are not shown.

As the crystallization curves of polyethylene and polypropylene nearly always overlap, it is difficult to define peak crystallization temperatures, \( T_c \). It is therefore more constructive to look at the onset crystallization temperatures. Onset \( T_c \)'s are shown as a function of blend composition and cooling rate in figure 5.7(a). Figure 5.7(b) depicts the general trends of the data given in figure (a).
The figure demonstrates that cooling rate has a significant effect on the samples' crystallization behaviour and that this effect is greatest for the polypropylene rich samples. At cooling rates of 20°C/minute and above, the pure polyethylene crystallizes at higher temperatures than the pure polypropylene. Despite its higher melting point, polypropylene only begins to crystallize first at cooling rates of 10°C/minute or lower.

It can also be seen that at cooling rates of 50°C/minute and above, the components crystallize at higher temperatures in the blends than they do on their own. Taking the samples cooled at 80°C/minute as an example, one can see that polyethylene crystallizes at an onset temperature of 101°C, but as soon as 10% MViPP is added, the onset crystallization temperature rises by about 1°C. At the other extreme, the pure MViPP begins to crystallize at about 90°C; as soon as 10% HDPE is added, the onset crystallization temperature rises by some 7°C. This is a very interesting and significant result. It proves that at fast cooling rates, the crystallization temperatures of the components in the blends are somehow raised in each other's presence.

At intermediate cooling rates, i.e. 20-30°C/minute, the effect disappears and the components in the blends crystallize at similar temperatures to the pure components. At cooling rates of 10°C/minute i.e. when the polypropylene begins to crystallize at higher temperatures than polyethylene, the effect is reversed. The components appear to crystallize at slightly lower temperatures in the blends than they do on their own. At the slowest cooling rates studied, i.e. 3°C and 1°C/minute, the 10% MViPP blend crystallizes at the same temperature as the pure polyethylene. The rest of the blends (i.e. those containing 30% MViPP or more) begin to crystallize at a higher temperature than the pure polyethylene but at a lower temperature than the pure polypropylene. From this, it is possible to infer that at in the 10% MViPP blend the polyethylene crystallizes before the polypropylene, whereas in the blends containing 30% MViPP or more it is the polypropylene that crystallizes first. This supports the TEM results that were reported in Chapter 4, section 4.5.4.

The crystallization behaviour can be explained by considering the possibility of nucleating agents migrating from one phase to the other during melt mixing in the extruder. At fast cooling rates, when polyethylene crystallizes before polypropylene (>50°C/minute), the polyethylene crystallizes at higher temperatures in the blends than it does on its own. I suggest that nucleating agents migrate from the polypropylene regions to the polyethylene regions during melt mixing in the twin-screw extruder and then act as effective nucleating agents for polyethylene. In turn, the polyethylene crystals themselves act as nuclei for the polypropylene making it crystallize at higher temperatures in the blends than it does on its own.

At slower cooling rates (20-30 °C/min), the onset crystallization temperatures of the homopolymers and the blends increase, and the effects that I attributed to enhanced nucleation are
no longer seen. If the behaviour at fast cooling rates is a result of nucleating agents accelerating the crystallization process, I propose that there must be a certain temperature below which these nucleating agents effectively nucleate the polyethylene and above which they do not. From figure 5.7, I estimate this temperature to be roughly 110°C. At higher temperatures the nucleating agents from the polypropylene no longer nucleate the polyethylene; therefore, at slower cooling rates the enhanced onset of crystallization for polyethylene is not observed.

At very slow rates of cooling (<10°C/minute), the polypropylene crystallizes at higher temperatures than the polyethylene (apart from in the 10% MViPP blend). At these cooling rates the components in the polypropylene rich blends crystallize at lower temperatures than they do on their own, indicating that the presence of the polyethylene inhibits the crystallization of the polypropylene. If nucleating agents from the polypropylene migrate into the polyethylene during melt mixing in the extruder, the polypropylene in the blends will contain fewer nucleation sites than the pure polypropylene. Therefore when the blends are re-melted and cooled slowly (so that the polypropylene crystallizes before polyethylene) the lack of nucleation sites will inhibit the polypropylenes' crystallization, causing it to crystallize at lower temperatures in the blends than it does on its own.

The suggestion that nucleating agents can migrate from the polypropylene phase into the polyethylene phase in agreement with a paper by Bartczak et al. (1986). By experimenting with nucleating agents they found that heterogeneous nuclei migrated across the interface boundaries from the iPP melt to the HDPE melt during melt mixing. As further support for the ideas postulated above, it has been reported (Olley et al., 1979) that polypropylene crystals can be nucleated on the surface of polyethylene crystals.

5.4.2.2 Other Blend Systems (LViPP/HDPE and HViPP/HDPE)

Figure 5.8 and 5.9 depict the crystallization exotherms obtained from the LViPP/HDPE and HViPP/HDPE blends cooled at 80°C/minute. They appear similar to the curves obtained for the MViPP/HDPE blends, shown in figure 5.4. In all three sets of blends, the pure polyethylene crystallizes at a higher temperature than the pure polypropylene, and the components begin to crystallize at higher temperatures in the blends than they do on their own. One of the most striking results is the 99.5% HViPP blend. Adding 0.5% HDPE to iPP, raises iPP's onset crystallization temperature by some 12°C.

Given that the same nucleating agent was used in all three polypropylenes (i.e. talc-see Chapter 1) it is not unexpected that all three sets of blends display enhanced nucleation behaviour. The reason why the effect is most pronounced in the HViPP/HDPE blends could be due to a number of factors. It is possible that the nucleating agent migrates more effectively from iPP to HDPE in the
HVIPP/HDPE blends than it does in the others. Or it could be that HVIPP contains more of the nucleating agent than the other iPPs. More work needs to be done in this area to determine the exact role that these factors have in determining the crystallization behaviour.

In order to be sure that the crystallization effects are due to nucleating agents migrating from the iPP to the HDPE during melt mixing more work must be done. This might include using polymers with different nucleating agents, deliberately adding different amounts of nucleating agent or passing the polymers through the extruder several times and studying the crystallization behaviour after each pass.

5.4.2.3 Degree of Crystallinity
Table 5.1 lists the crystallinities of the MViPP/HDPE homopolymers and the 10% and 50% MViPP blend, as a function of cooling rate. It shows that the crystallinity of the polymer samples decreases as the cooling rate increases. It also shows that the crystallinities of the 10% and 50% blends follow a simple additive mixing rule. As the same is true for the rest of the blends samples, these values are not given. Despite the observation that the components’ crystallization temperatures are significantly affected by each other’s presence, it seems that the crystallinity of the components remains unaffected by the blending process.

5.5 CONCLUSIONS
The DSC crystallization study proves that cooling rate has a significant effect on crystallization behaviour. At cooling rates of >20°C the pure polyethylene crystallizes at a higher temperature than the pure polypropylene; polypropylene only begins to crystallize first at cooling rates of 10°C/minute or slower. From this we can infer that the components follow the same crystallization pattern in the blends, with the HDPE crystallizing before the iPP at fast cooling rates etc.

The results show that blending iPP with HDPE has a dramatic effect on crystallization behaviour. At fast cooling rates, where the polyethylene crystallizes first, the components crystallize at higher temperatures in the blends than they do on their own. At rates where the polypropylene crystallizes first the components crystallize at lower temperatures than expected.

I believe that the crystallization behaviour can be explained by assuming that nucleating agents from the polypropylene migrate into the polyethylene regions during melt mixing in the extruder. The nucleating agents then act as effective nucleating agents for the polyethylene. At fast cooling rates the polyethylene crystallizes at higher temperatures in the blends than it does on its own; the polyethylene crystals then act as nuclei for the polypropylene, making it crystallize at higher
temperatures than it does on its own. At slow rates, where the iPP crystallizes first, the crystallization is inhibited because of the lower nucleation site density caused by migration of nucleating agents. I suggest that the crystallization behaviour may have a significant effect on the mechanical properties of the blends.
Table 5.1 Crystallinities of the MViPP/HDPE homopolymers and the 10% and 50% MViPP blend samples, after cooling at various rates from the melt. The crystallinities were calculated from the enthalpies of fusion upon re-melting (as the crystallization peaks could not be resolved). The values given are accurate to ± 5°C.

<table>
<thead>
<tr>
<th>Cooling rate (°C/minute)</th>
<th>Crystallinity (%)</th>
<th>Crystallinity (%)</th>
<th>Crystallinity (%)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HDPE</td>
<td>10% MViPP</td>
<td>50% MViPP</td>
<td>MViPP</td>
</tr>
<tr>
<td>80</td>
<td>76</td>
<td>72</td>
<td>61</td>
<td>45</td>
</tr>
<tr>
<td>70</td>
<td>80</td>
<td>78</td>
<td>67</td>
<td>52</td>
</tr>
<tr>
<td>50</td>
<td>83</td>
<td>81</td>
<td>69</td>
<td>55</td>
</tr>
<tr>
<td>30</td>
<td>85</td>
<td>84</td>
<td>71</td>
<td>58</td>
</tr>
<tr>
<td>20</td>
<td>88</td>
<td>85</td>
<td>75</td>
<td>59</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>87</td>
<td>76</td>
<td>61</td>
</tr>
<tr>
<td>5</td>
<td>93</td>
<td>89</td>
<td>80</td>
<td>66</td>
</tr>
<tr>
<td>1</td>
<td>94</td>
<td>90</td>
<td>80</td>
<td>67</td>
</tr>
<tr>
<td>Before processing</td>
<td>78</td>
<td>76</td>
<td>65</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 5.2 Crystallinities of the LViPP/HDPE homopolymers and the 10% and 50% LViPP blend samples.

<table>
<thead>
<tr>
<th>Cooling rate (°C/minute)</th>
<th>Crystallinity (%)</th>
<th>Crystallinity (%)</th>
<th>Crystallinity (%)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HDPE</td>
<td>10% LViPP</td>
<td>50% LViPP</td>
<td>LViPP</td>
</tr>
<tr>
<td>80</td>
<td>76</td>
<td>74</td>
<td>60</td>
<td>43</td>
</tr>
<tr>
<td>Before Processing</td>
<td>78</td>
<td>75</td>
<td>62</td>
<td>44</td>
</tr>
</tbody>
</table>

Table 5.3 Crystallinities of the LViPP/HDPE homopolymers and 50% LViPP blend samples.

<table>
<thead>
<tr>
<th>Cooling rate (°C/minute)</th>
<th>Crystallinity (%)</th>
<th>Crystallinity (%)</th>
<th>Crystallinity (%)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HDPE</td>
<td>10% HViPP</td>
<td>50% HViPP</td>
<td>HViPP</td>
</tr>
<tr>
<td>80</td>
<td>76</td>
<td>74</td>
<td>64</td>
<td>50</td>
</tr>
<tr>
<td>Before Processing</td>
<td>78</td>
<td>77</td>
<td>66</td>
<td>53</td>
</tr>
</tbody>
</table>
Figure 5.1 (a) Typical DSC trace showing three thermal transitions. The areas under the peaks are equal to the enthalpies of crystallization and fusion respectively. (b) DSC melting curve illustrating the onset, peak and end melting temperatures. The DSC Perkin-Elmer software calculates the onset and peak melting temperatures by extrapolating the curves towards the baseline. In this project, the true onset (and end) temperatures were considered to be the temperatures at which the curve began to deviate from the baseline.
Figure 5.2 DSC melting endotherms for the rapidly quenched MViPP/HDPE homopolymers and blends. The curves are offset from each other. Tick marks represent 10 W/g.
Figure 5.3 Peak melting temperatures of each component in the rapidly quenched (a) LViPP/HDPE, (b) MViPP/HDPE and (c) HViPP/HDPE blends.
Figure 5.4 DSC crystallization exotherms for the MViPP/HDPE homopolymers and blends cooled at 80°C/minute. Tick marks represent 50 W/g.
Figure 5.5 DSC crystallization exotherms illustrating the effect of blending on the components. The 50% blend curve was measured using a 50% MViPP blend and the 50% comp. curve was measured by placing equal amounts of HDPE and MViPP into the DSC pan.
Figure 5.6 DSC crystallization exotherms for the MViPP/HDPE homopolymers and blends cooled at 1°C/minute. Tick marks represent 2 W/g.
Figure 5.7 (a) Onset crystallization temperatures for MViPP/HDPE blends, cooled at various rates from the melt. Each symbol represents a different cooling rate in °C/minute. (b) General trends of the onset crystallization temperatures shown in figure (b). These results are reproducible to ±1°C (error bars not shown for clarity).
Figure 5.8 DSC crystallization exotherms for the LViPP/HDPE blends cooled at 80°C/minute. Tick marks represent 50 W/g.
Figure 5.9 DSC crystallization exotherms for the HViPP/HDPE blends cooled at 80°C/minute. Tick marks represent 50 W/g.
Figure 5.10 Onset crystallization temperatures for the LViPP/HDPE blends cooled at 80°C/minute.

Figure 5.11 Onset crystallization temperatures for the HViPP/HDPE blends cooled at 80°C/minute.
CHAPTER 6: MECHANICAL PROPERTIES

6.1 INTRODUCTION

This chapter details the mechanical properties of the blends and their components. As polymer blending represents one of the most cost-effective ways of upgrading existing polymers and a possible way of recycling plastic waste, it is desirable to foresee the limits of the blends' mechanical properties, such as modulus, yield strength, tensile strength, extension to break etc. Although the subjects covered in other chapters are interesting in their own right, it is how these properties affected the bulk mechanical behaviour that is of central interest to this project.

In Chapter 3: Capillary Extrusion Rheometry, the properties of polymeric liquids were discussed and it was shown that they deviate from Newton's Law for purely viscous fluids by exhibiting shear-thinning viscoelastic behaviour. It was briefly mentioned that polymeric solids are also termed viscoelastic due to their deviation from purely elastic behaviour. In this chapter (section 6.2), the theoretical models that are used to describe the viscoelastic behaviour of polymeric solids are discussed, along with a description of the various mechanical properties mentioned above. The models used to predict the mechanical properties of composite materials and, more specifically, polymer blends are also discussed. In section 6.3 the work of other researchers in the field is discussed. Sections 6.4 to 6.7 present the methods, results, discussion and conclusions.

6.2 BACKGROUND THEORY

6.2.1 Viscoelasticity
A distinctive feature of the mechanical behaviour of a polymeric solid is the way in which its response to an applied stress or strain depends on the rate or time period of loading. Purely elastic solids obey Hooke's Law which states that for a purely elastic material the stress, $\sigma$, is proportional to the strain, $\varepsilon$, and independent of the strain rate, $\dot{\varepsilon}$:

$$\sigma = G \varepsilon$$  \hspace{1cm} (6.1)

where $G$ is shear modulus (N.B. if the force is applied along one axis, the modulus is known as Young's modulus, $E$)
In Chapter 3, it was shown that purely viscous fluids obey Newton's Law, which states that stress, $\sigma$, is proportional to the strain rate, $\dot{\varepsilon}$, but independent of the strain, $\varepsilon$, itself:

$$\sigma = \eta \dot{\varepsilon} \quad (6.2)$$

where $\eta$ is viscosity.

When an instantaneous load is applied to a polymeric solid, an instantaneous deformation occurs, followed by a time-dependent deformation or creep. For polymers, the delayed response of polymer chains during deformation is the cause of creep behaviour. Deformation stops when the initially folded chains reach a new equilibrium configuration, i.e. slightly stretched. This deformation is recoverable after the load is removed, but recovery takes place slowly, with the chains retracting by folding back to their initial state. A purely elastic material stores all of the energy created by deformation forces so that on removal of the forces (whenever this occurs) it can return to its original dimensions. By definition, an elastic material does not exhibit creep. In a purely viscous fluid, the stress created by external forces relaxes instantaneously to zero because of flow. Polymeric solids are therefore described as viscoelastic because they can display the properties of both elastic solids and viscous fluids depending on the temperature or time scale of the experiment. Stress relaxation is another characteristic of polymeric solids and is a consequence of delayed molecular motions as is creep. However, unlike creep, which is experienced when the load is constant, stress relaxation occurs when deformation (or strain) is constant and is manifested by a reduction in the force (stress) required to maintain a constant deformation.

### 6.2.2 Viscoelastic Mechanical Models

Viscoelasticity is a complex process to model. Most models consider the deformation of a polymeric material to be divided into an elastic component and a viscous component: this is termed linear viscoelasticity. Linear viscoelasticity may be represented by models comprising of massless Hookean springs and Newtonian dashpots (considered as oil-filled cylinders, in which a loosely fitting piston moves at a rate proportional to the viscosity of the oil and the applied stress). One simple possible formulation of the linear viscoelastic behaviour, known as the Kelvin or Voigt model combines a spring and dashpot in parallel. Another system considers the spring and dashpot in series and is known as the Maxwell model. The Voigt model describes creep to a first approximation whereas the Maxwell model similarly describes stress relaxation. The above models do not adequately describe the viscoelastic properties of real materials. More realistic models, known as multi-element models, consider a number of different combinations of the Maxwell and Voigt models. The general equation that describes linear viscoelasticity is (Arridge, 1975):
where $A_i$ and $E_i$ are constants. This is a linear differential equation with constant coefficients with solutions:

$$
\sigma = \sigma_1(t), \quad \sigma = \sigma_2(t), \quad \sigma = \sigma_3(t)
$$
$$
\varepsilon = \varepsilon_1(t), \quad \varepsilon = \varepsilon_2(t), \quad \varepsilon = \varepsilon_3(t)
$$

etc.

Any combination of these solutions will also be a solution.

The general equation can describe all of the models above e.g.:

- Hooke's Law: $A_0 \sigma = E_0 \varepsilon$, or $A_1 \frac{d\sigma}{dt} = E_1 \frac{d\varepsilon}{dt}$

- Newton's viscosity: $A_0 \sigma = E_1 \frac{d\varepsilon}{dt}$

- Maxwell model: $A_0 \sigma + A_1 \frac{d\sigma}{dt} = E_1 \frac{d\varepsilon}{dt}$

- Voigt model: $A_0 \sigma = E_0 \varepsilon + E_1 \frac{d\varepsilon}{dt}$

### 6.2.3 Tensile Testing: Stress-Strain Behaviour

In this section various mechanical properties are described along with a description of how they are calculated from a load-extension curve (produced during tensile testing). In section 6.2.1 it was shown that the Young's modulus, $E$, of a material is the ratio of stress divided by strain. Nominal stress, $\sigma_N$, and nominal strain, $\varepsilon$, can be calculated directly from a load-extension curve using the following equations:

$$
\sigma_N = \frac{F}{A_0} \quad \text{(6.4)} \quad \text{and} \quad \varepsilon = \frac{l-l_0}{l_0} \quad \text{(6.5)}
$$

where $F$ is the load, $A_0$ is the original cross-sectional area of the sample (not to be confused with $A_0$ in equation 6.3), $l$ is the length at a given time and $l_0$ is the original length of the sample.

Nominal stress and strain are often referred to as engineering stress and strain. However, when a sample is stretched, its cross-sectional area decreases. True stress, $\sigma_T$, is defined as:
where $A$ is the instantaneous cross-section at any given time.

True stress may therefore be increasing while the nominal stress is constant or decreasing (Nadai, 1950; Orowan, 1949). If it is assumed that deformation takes place at approximately constant volume, $A$ can be related to $A_0$ through the equation:

$$Al = A_0l_0 \tag{6.7}$$

Combining equations 6.4-6.7 gives the relationship between the nominal stress and true stress to be:

$$\sigma_T = (1+\varepsilon)\sigma_N \tag{6.8}$$

Figure 6.1 shows the idealised nominal stress-strain behaviour of a ductile polymer subjected to tensile testing at a constant strain rate. The change in cross-sectional area of the sample is also shown. Although the curve has some similarities to the stress-strain curves of other materials, such as metals and ceramics, there are several differences. As discussed in section 6.2.1 the stress is strain rate dependent. It is also dependent on temperature. Generally, increasing the temperature has a similar effect to decreasing the strain rate. Figure 6.2 shows the effect that strain rate and temperature can have on the nominal stress-strain behaviour. The mechanical properties of polymers also depend strongly on their sample history i.e. preparation conditions, deformation history etc.

In figures 6.1 the initial gradient of the curve is linear and obeys Hooke's law. This linear elastic region only holds for very small strains. Young's modulus, $E$, which is a measure of the stiffness of a material, can be obtained from the initial gradient. As the strain is increased (assuming fracture does not occur first) the curve decreases in slope and yielding occurs. In simple terms, the yield point, which corresponds to the yield stress, $\sigma_y$, and yield strain, $\varepsilon_y$, can be regarded as the point at which permanent plastic deformation occurs. Whilst this is an adequate description for other materials, such as metals, where there is a clear distinction between elastic recoverable deformation and plastic irrecoverable deformation, it is not so useful for polymers, where the distinction is less clear. A clear definition of the yield stress, often used when describing polymers, corresponds to the value of stress at the maximum observed load. The value of true stress at maximum load is often termed yield strength, however, as yielding occurs at comparatively low strains, it is often
adequate to describe yield strength as the nominal stress at maximum load. The yield strength is an important property of many plastics, and defines the practical limit of its uses much more than the ultimate fracture, unless, of course, the plastic fails by brittle fracture before the yield point is reached, as for some of the curves in figure 6.2

Once the yield point has been reached, the cross-sectional area of the sample may rapidly decrease to form a neck; this is accompanied by a drop in the nominal stress. A second turning point may then be observed, which corresponds to the formation of a stable neck. After this point, the nominal stress and cross-sectional area remain constant and the neck travels along the sample in a process called cold drawing. Once all the material has been drawn into the neck, the polymer molecules are highly oriented and aligned parallel to the stretching direction. Further stretching results in strain hardening, where the nominal stress rises until fracture occurs. The maximum value of true stress that can be obtained before fracture is often termed the tensile strength. Polymers differ in their ability to form a stable neck; some form an unstable neck, whereby the sample reaches a first yield point (but not a second) and thins until fracture. Some polymers do not neck at all. Cold drawing only occurs if a stable neck is formed.

The phenomenon of necking and cold drawing can be represented mathematically by the Considère construction. When a neck starts to form, the load on the specimen ceases to rise as the strain is increased. This corresponds to the condition that $\frac{d\sigma_N}{d\varepsilon} = 0$. Applying this to equation 6.8 gives the condition to form a neck to be:

$$\frac{d\sigma_N}{d\varepsilon} = 0 = \frac{1}{(1+\varepsilon)} \frac{d\sigma_T}{d\varepsilon} - \frac{\sigma_T}{(1+\varepsilon)^2}$$

(6.9)

or

$$\frac{d\sigma_T}{d\varepsilon} = \frac{\sigma}{(1+\varepsilon)}$$

(6.10)

The use of this equation is illustrated in figure 6.3. The point at which necking occurs, often called the ultimate stress, can be determined by drawing a tangent to the curve of the true stress against nominal strain from the point $\varepsilon = -1$. Equation 6.10 will then be satisfied at the point at which the tangent meets the curve. The construction can also be used to determine whether or not the neck will be stable. In figure 6.3(a) only one tangent can be drawn and after the neck forms the sample continues to thin down in the necked region until fracture occurs. A stable neck can only be formed if a second tangent can be drawn as in figure 6.3(b).
The ability of polymers to neck and cold draw has been recognised for many years (Capaccio and Ward, 1973 and 1974; Geil, 1964; Hay and Kellar, 1965; Peterlin, 1965 and 1979; Sadler and Barham, 1990). Necking and cold drawing involves the change of an isotropic unoriented material into one consisting of highly oriented molecules. In a semi-crystalline polymer, the spherulitic structure is first deformed and then transformed into a fibrillar structure. Plastic deformation of this fibrillar structure then occurs. The exact way in which the spherulitic structure is deformed has been the subject of much debate. For instance, Peterlin (1979) described the drawing of a polymer through a neck by proposing that small blocks of crystals break away from their lamellar stacks in the unoriented material and then re-stack in an oriented fashion to form microfibrils, which together form the fibrillar structure mentioned above. Others, such as Sadler and Barham (1990) supported this model but proposed that thin lamellae do not break up, rather they are simply rotated and aligned. Once all the material available has been aligned and incorporated into the neck, the load required for further extension increases, as further extension requires deformation of the chain bonds (strain hardening). Failure of a sample requires sufficient stress to break the bonds within the material.

In the discussion above, deformation is assumed to take place at constant volume, however certain polymers can undergo a localised form of plastic deformation known as crazing. The crazes appear as small crack-like entities, which are usually initiated on the specimen surface and are oriented perpendicular to the tensile axis. The formation of crazes results in an increase in volume. Close examination of crazes reveals that they are regions of cavitated polymer and not true cracks, however the cracks that lead to fracture are often nucleated within the crazes (Kambour, 1973).

6.2.4 Semi-Crystalline Polymers
In semi-crystalline polymers the mode of crystallisation has a profound effect on the morphology (as seen in Chapter 4) and the mechanical properties. Slow crystallisation near the melting point results in thicker, more perfect crystals; faster crystallisation produces smaller spherulites with many more tie molecules. Semi-crystalline polymers can be thought of as two-phase materials, where the crystalline and amorphous regions contribute separately to the overall modulus. The degree of crystallinity is therefore important: crystalline regions are generally stiffer than amorphous regions (McCrum, 1988). The exact way in which this combination of moduli can be represented mathematically is a complicated problem. For example, polymers with a spherulitic morphology have elastically isotropic properties in bulk, but the individual crystals within the spherulites are highly anisotropic. In polyethylene the modulus parallel to the chain direction is roughly one hundred times greater than the modulus perpendicular to the chain axis. (Gray, 1969; Krigbaum, 1964; Ward, 1975).
In many applications molecular orientation is induced in order to improve mechanical properties along a certain axis. Amorphous polymers can be drawn or stretched at temperatures above, but close to, the glass transition temperature, in order to impose increased order on the chains. The polymer must be rapidly quenched to ensure that the orientation does not relax out. In semi-crystalline polymers the process is complicated by the presence of the crystallites which themselves are already locally oriented. When highly drawn, both crystalline and amorphous regions can achieve a high degree of orientation. Electron micrographs of drawn polymers with a fibrous structure (Ward, 1975) reveal the basic structural unit to be highly aligned microfibrils, of the order of tens of microns in length and with lateral dimensions of 10 - 20nm. The fibres are laterally very weak but a high percentage of taut tie molecules can impart great axial tensile strength. It is therefore the orientation of the amorphous regions, in addition to the crystallites, which is responsible for the increased longitudinal strength. The modulus of the material parallel to the drawing axis increases as the molecules are oriented, while the modulus in a direction perpendicular to the drawing axis decreases. Again taking polyethylene as an example, orientation can increase the bulk longitudinal modulus by a factor of 10, depending on the degree of crystallinity and orientation (Ward, 1975). Under industrial processing conditions polymers may crystallize in the oriented state. The most well known resulting architecture is the shish kebab (Pennings and Keil, 1965) or row-nucleated structure (Keller and Machin, 1967). The characteristics of this morphology are influenced by the degree of orientation and hence depend heavily on processing conditions such as shear rate and temperature.

By considering all the factors mentioned above it is clear that the mechanical properties of semi-crystalline polymers are dependent on many different elements. The prediction of mechanical properties is further complicated when dealing polyolefin blends, as there are two semi-crystalline components to consider. Not only are the individual properties of the components important, but how the components interact with each other. The following section discusses some of the models used to predict the mechanical properties of polymer blends.

6.2.5 Polymer Blends

The mechanical properties of polymer blends depend not only on the volume fraction of the components but also on the respective properties of the components, as stated above. They may also depend on the phase structure, morphology, interfacial adhesion, presence of additives etc. The models used to calculate the mechanical properties of binary immiscible polymer blends are largely based on models used in other types of composite materials. The simplest models are those of parallel and series coupling which provide upper and lower bounds for various mechanical properties such as modulus (Bucknall, 1977; Flaris, 1992; Hashin, 1970; Nielson, 1974 Takayagi, 1963), yield strength (Chuang, 1985; Kolarik, 1992, 1993) and tensile strength (Nielson, 1974a, 1974b).
Taking modulus, $E$, as an example, the parallel (also known as Voigt) model yields:

$$E_B = \phi_1 E_1 + \phi_2 E_2$$  \hspace{1cm} (6.11)

where the two blend components have moduli $E_1$ and $E_2$ and volume compositions $\phi_1$ and $\phi_2$ ($\phi_1 + \phi_2 = 1$); the blend has a modulus $E_B$. N.B this model can also be referred to as a simple additive rule of mixtures or a linear additive rule.

The series (also known as Reuss) model yields:

$$\frac{1}{E_B} = \frac{\phi_1}{E_1} + \frac{\phi_2}{E_2}$$  \hspace{1cm} (6.12)

Parallel and series coupling are illustrated in figure 6.4. In practice, the complete stress transfer required to satisfy either of these extreme models is rarely, if ever, realised and the modulus of the mixture lies somewhere between the two limits. In the case of composite materials, where the moduli of the two components are often very different (e.g. carbon fibre reinforced polymers), the difference between these simple bounds is very great. As a result, a good deal of effort has gone into finding alternative and closer bounds; see for example the work of Arridge (1972) and Hashin, (1963). The bounds on the composite modulus depend on the morphology of the composite - so they differ widely between, for example, a composite of parallel fibres in a matrix and a random placement of spheres of reinforcing material in a similar matrix.

The approach of finding bounds is very useful in the case of composite materials where the morphologies are known a priori, and the compositions are not normally varied over a particularly large range. It is not so useful in the case of polymer blends where the full composition range is available and where the morphology depends on the composition, viscosity ratio of the components, processing conditions, etc. (see Chapter 4). To date no models have been proposed that accurately describe the mechanical properties over the whole range of compositions and morphologies. It is common for models to describe the mechanical properties of blends with specific morphologies, (such as the disperse droplet morphology) with particular, and carefully chosen, boundary conditions to determine the mechanisms of stress transfer between the phases. A type of morphology that is often focussed on is the co-continuous network morphology that often occurs in blends with proportions close to 50:50. There have been a number of attempts to estimate the moduli of such blends, see, for example, the work of Coran, 1976; Davies, 1971; Kolarik, 1997, Lees, 1968; Lyngaae-Jorgensen, 1993. Details of these models are given in a paper by Willemse (1999b) which shows that although each model yields different equations, they all
provide remarkably similar results, with the blends' moduli lying between the upper and lower bounds, given by the parallel and series model. However, these models are only of interest if the moduli of the blend components are very different in value. If the blends' moduli are very close in value, (as is the case for my blends-see section 6.5 below) the upper and lower bounds are so close together that any attempts to better the model are not very useful. Similar models have been proposed to more accurately predict other mechanical properties, such as the yield strength, (see Kolarik, 1993). Again, these models are only of interest if the mechanical measurements of the pure components are very different in value.

6.3 PREVIOUS/OTHER RESEARCH

Over the past few decades there has been a great deal of interest in the mechanical properties of polymer blends. Since this project deals with polyethylene/polypropylene blends, the following discussion will be mostly limited these blends. In the literature many reports have been made on the morphology and mechanical properties of isotactic polypropylene blended with different polyethylenes, such as high-density polyethylene, HDPE, (Deanin and Sansone, 1978; Greco et al., 1980; Gupta et al., 1982; Lee et al., 1994; Lovingier and Williams, 1980; Noel III and Carley, 1975), low-density polyethylene, LDPE, (Nolly at al., 1980; Teh, 1983), linear low-density polyethylene (Dumoulin, 1987; Yeh, 1985), very low density polyethylene, VLDPE, (Lee at al., 1991), ultralow density polyethylene, ULDPE, (Lee at al., 1991) and ultrahigh molecular weight HDPE, UHMWHDPE, (Sawatari, 1990; Zhu, 1996).

Most of these polymer pairs are found to be immiscible due to an unfavourable free energy of mixing (see Chapter 2) however, conflicting conclusions have been drawn about their mechanical properties when blended. For instance, Robertson and Paul (1973) found that the yield strengths and moduli of iPP/HDPE blends obeyed a linear additive rule. Others, such as Greco et al. (1980), reported that adding small amounts of HDPE to iPP decreased the iPP matrix plasticity, resulting in a delay in neck formation - as a consequence of this delay, yield strength showed positive deviation from linearity. Authors, such as Lovingier and Williams (1980) and Noel III and Carley (1975), found that adding small amounts of HDPE to iPP significantly increased iPP's modulus. They found that the crystallinity of iPP was higher when HDPE was present and believed that HDPE acted as a nucleating agent for iPP. They thought that the increased crystallinity was the cause of the improved modulus behaviour. In contrast, authors such as Wenig and Meyer (1980) found that iPP nucleation was unaffected by the presence of HDPE.

Conversely, other authors have reported modulus and yield strength values that deviate negatively from linearity (Varin and Djokovic, 1988). They attribute this negative deviation to the poor
cohesion between the immiscible components in the blend. In all of the cases mentioned above, elongation at break was found to be markedly decreased for the blends compared to the homopolymers.

Higher than expected moduli have also been reported in other immiscible blend systems. In a series of papers from Delft (Willemse et al., 1998; Willemse et al., 1999b; Veenstra et al., 2000), it was reported that co-continuous blends of polystyrene and high-density polyethylene (PS/HDPE) had higher moduli than existing co-continuous mechanical models predicted. Loos et al. (2000) reported similar findings to Willemse et al. in blends of syndiotactic polypropylene/high-density polyethylene (sPP/HDPE). Loos et al. suggested that synergistic crystallization effects between the components might have been the cause of the higher than expected moduli.

In a study by Bains et al. (1994) on isotactic polypropylene/linear low-density polyethylene (iPP/LLDPE), the viscosity ratio of the components was found to have a profound effect on blend performance. They showed that when viscosities of iPP and LLDPE were very closely matched, a modulus increase of up to 50% over the additive rule of mixtures could be obtained. They attributed the high modulus behaviour to the diffuse interface formed when the component viscosities were very close in value. When the component viscosities were poorly matched, they found interface boundaries to be less diffuse and the modulus behaviour to deviate negatively from linearity. Lee et al. (1991) reported similar results to Bains et al. (1994) in a study of iPP/ULDPE blends. However Gunderson and Chilcote (1991) found that the melt flow rate of iPP had little effect on the mechanical properties of its blends with HDPE.

N.B. it is important to state here that the authors that found higher than expected blend moduli and yield strengths, only did so over a limited blend composition range. None of them reported this behaviour over the entire blend composition range.

In all of the studies above, the blends were prepared by melt mixing, followed by extrusion. However the authors do not mention many of the processing details, such as shear rate in the extruder, subsequent processing, cooling rate of samples etc. Differences in experimental procedure may well account for the observed differences in mechanical properties of seemingly similar polypropylene/polyethylene blend systems. One of the aims of my study was to see whether viscosity ratio could have an effect on the properties of iPP/HDPE blends. Another aim was to determine the effects that processing conditions can have on the final properties of the blends.
6.4 METHODS

The sheets used for mechanical testing were prepared in a hot press at 200°C as described in Chapter 1. Samples were cut from the sheets using a standard ASTM 'dog bone' cutter whose central section measured 14mm x 2.3mm. Samples were cut with their long axes in different directions within the sheets to check for systematic changes in mechanical properties as a result of phase and molecular orientation in the sheets. Wide-angle X-ray diffraction was also used to check for molecular orientation. This work was done in collaboration with a fellow PhD student - Edgar Cervantes. Diffraction patterns were obtained using Ni-filtered CuKα radiation from a Philips PW2213 sealed beam X-ray generator operating at 35kV and 40mA. The samples were placed in the beam both face-on and side-on in order to check for orientation in all planes. The detailed results of this study are to be reported in Edgar Cervantes' PhD thesis. Briefly the study showed that none of the samples used for mechanical testing displayed any molecular orientation. This is well illustrated in figure 6.5 which shows some of the diffraction patterns obtained for the rapidly quenched MViPP/HDPE blends.

The mechanical testing was carried out using a Hounsfield H5K-W tensile testing machine. The Hounsfield was capable of exerting a load of up to 5KN and extending the samples up to 1m. The samples were fixed into the Hounsfield so that the edges of the clamps came up to the ends of the shank. It was assumed that only the part of the sample that was outside the edges of the clamps (i.e. the central 14mm) was subject to the tensile forces exerted by the machine. Young's modulus was measured from the initial gradient of the resulting force-extension curves. To ensure that a proper comparison could be made between samples, the initial gradient was taken between 0 and 0.5% strain. The yield strength (if reached) was also recorded, as well as the extension to break (breaking strain) and tensile strength. Tensile strength was taken to be the maximum value of true stress before breaking, and was determined by measuring the cross-sectional area of the sample after fracture.

The mechanical properties were measured for all three sets of rapidly quenched blends, i.e. low-viscosity isotactic polypropylene/high-density polyethylene (LViPP/HDPE) blends, medium-viscosity isotactic polypropylene/high-density polyethylene (MViPP/HDPE) blends and high-viscosity isotactic polypropylene/high-density polyethylene (HViPP/HDPE) blends. The mechanical properties of the MViPP/HDPE blends cooled at 3°C and 1°C/minute were also measured. Each blend system was subjected to three different extension rates, in order to check for strain rate dependence. The extension rates were 1, 5 and 10mm/minute at room temperature. These extension rates correspond to strain rates of 1x10⁻³, 6x10⁻³ and 12x10⁻³ s⁻¹. For each composition, at least ten tests were performed.
6.5 RESULTS

When stretching the samples, three different types of load – extension curves were observed, depending on the composition and blend system. These are illustrated in figure 6.6.

Curve (a) is typical of the rapidly quenched homopolymers and some of the rapidly quenched 10 and 90% blends. It shows that the samples extend elastically at first, then reach their first, upper yield point, neck, and reach their second, lower, yield point and then cold draw. Prior to fracture the homopolymers exhibit strain hardening. During cold drawing, stress whitening (as a result of crazing) is observed in the form of zigzag lines across many of the samples. The extension to break values for the homopolymers range from 700 to 1000%. Although many of the 10 and 90% samples have similar shaped load – extension curves to the homopolymers, their extension to break values are generally lower, ranging from 500 to 800%.

Curve (b) is typical of the rapidly quenched blends with central compositions, i.e. 40, 50 and 60%. For the rapidly quenched MViPP/HDPE and HViPP/HDPE blends, these compositions correspond to co-continuous-like morphologies, however, for the rapidly quenched LViPP/HDPE blends, these compositions correspond to disperse droplet morphologies (see Chapter 4). The curve shows that the samples are very brittle and fail quickly, fracturing in the region of the first yield point. These samples show no sign of necking or cold drawing. The slowly cooled MViPP/HDPE homopolymers and blends behave in a similar way but are even more brittle, failing well before the first yield point is reached.

Curve (c) is fairly typical of the rapidly quenched 30 and 70% blends. These compositions correspond to disperse droplet morphologies. In these cases, the samples extend elastically at first before reaching their first yield point. The samples then form an unstable neck and thin until fracture. Typical extension to break values for these samples are 400 to 600%.

Load-extension curves were recorded for all the blend compositions at three different extension rates (1, 5 and 10 mm/min). Despite the fact that mechanical behaviour in polymers is known to be strain rate dependant, the mechanical behaviour of these blends does not appear to vary noticeably at these different rates. In order to see strain rate dependence, it is possible that a larger range of extension rates must be employed.

It must be noted that the testing of the samples took place over several months; during this time the temperature of the room varied by as much as 10°C. Unsurprisingly, the samples were more ductile when the temperature was higher, resulting in a considerable amount of scatter in the mechanical data. It must also be noted that phase orientation did not seem to have an effect on the mechanical
properties, as samples cut with their long axes in different directions displayed the same mechanical behaviour.

In the following sections various mechanical properties such as modulus, yield strength, extension to break and tensile strength are reported for each blend system.

6.5.1 Rapidly Quenched Low-Viscosity Isotactic Polypropylene/High-Density Polyethylene (LViPP/HDPE) Blends

6.5.1.1 Young's Modulus as a Function of Composition

Figure 6.7 shows the scatter of Young's modulus as a function of blend composition, measured at extension rates of (a) 1mm/min, (b) 5mm/min and (c) 10mm/min. The figure clearly shows that Young's modulus does not vary much with these different extension rates. As the same is true of the rest of the measurements, subsequent figures only show the results obtained at an extension rate of 1mm/min. When quoting the composition of the blends so far, the mass fraction has been used (since the blends were prepared by weighing out the components). However, the mechanical models (such as the parallel and series model) use volume fractions. Accordingly the data in the figures have been converted to volume fractions using the density measurements given in Chapter 1. In fact, the numerical values are very similar and for simplicity the text will continue to refer to the mass, rather than volume, fractions.

The data in figure 6.7 displays a large degree of scatter, partly as a result of temperature fluctuations throughout the course of the experiments. Due to the scatter, there are several ways in which to calculate the upper and lower bounds of the parallel and series models. It is not appropriate to calculate bounds based on other models, as the moduli of the HDPE and the LViPP are very similar in value. One way to calculate upper and lower bounds is to take the average moduli of the homopolymers and use these values to calculate average upper and lower bounds. The average upper and lower bounds are shown in figure 6.7 (a). Because the average moduli of the components are very similar, the difference between the upper and lower bounds is very small. Another way to calculate the bounds is to use the maximum and minimum moduli of the homopolymers to calculate extreme upper and lower bounds; these bounds are illustrated in figure 6.7 (b). Showing extreme upper and lower bounds has the advantage of highlighting the blends that fall outside these extreme limits.

It is clear from figure 6.7 that the moduli of all the blends lie above the average upper bound. In fact many of the blends' moduli lie above the extreme upper bound. Interestingly, the higher than expected blend moduli are observed over the entire blend composition range. A detailed discussion of these findings can be found in section 6.6.
6.5.1.2 Yield Strength as a Function of Composition
Yield strength was defined earlier as the value of true stress upon yielding. The yield strength as a function of composition is shown in figure 6.8 along with extreme upper and lower bounds. Most of the samples lie between these bounds.

6.5.1.3 Extension to Break as a Function of Composition
In figure 6.9 the extension upon breaking (or breaking strain) is shown as a function of composition. The homopolymers have the highest extension to break values, ranging from 700 to 1000%. The 10% blend samples behave similarly to the homopolymers; i.e. they neck and cold draw, but do not extend as far. The remaining blend samples snap in the region of their first yield point. In this system, all the blends display disperse droplet morphologies.

6.5.1.4 Tensile Strength as a Function of Composition
It was stated earlier that tensile strength is often defined as the maximum value of true stress that can be achieved before fracture. Figure 6.10 shows the tensile strength of the materials as a function of composition. In the case of the homopolymers and the 10% LViPP blend samples, the tensile strength given refers to the maximum value of true stress after cold drawing and immediately before fracture. However the rest of the blend samples fail in the region of their first yield point and do not undergo cold drawing; for these blends, the tensile strength given is approximately equal to the yield strength.

6.5.2 Rapidly Quenched Medium-Viscosity Isotactic Polypropylene/High-Density Polyethylene (MViPP/HDPE) Blends
Figures 6.11 to 6.14 show the variation of modulus, yield strength, extension to break and tensile strength with composition for the rapidly quenched MViPP/HDPE blends. The modulus behaviour of these blends is very similar to the rapidly quenched LViPP/HDPE blends, with many of the blends' moduli lying well above the extreme upper bound.

The yield strengths for these blends are also very similar to the rapidly quenched LViPP/HDPE blends, with the blends' yield strengths lying between the extreme upper and lower bounds. The extension to break values are different from the rapidly quenched LViPP/HDPE blends. The MViPP and HDPE homopolymers and the 10 and 90% blends have load-extension curves similar to curve (a) in figure 6.6. The 30 and 70% have curves similar to (b) and the 40, 50 and 60% have curves similar to (c). In this system the 40, 50 and 60% blends show signs of co-continuity.

The tensile strength behaviour of the rapidly quenched MViPP/HDPE blends is different from the rapidly quenched LViPP/HDPE blends, due to the different nature of the stress-strain curves. The tensile strengths of the homopolymers and the 10, 30, 70 and 90% blends, given in figure 6.14,
correspond to the maximum true stress values after necking and drawing (or thinning), whereas the tensile strengths of the 40, 50 and 60% blends correspond roughly to the yield strengths.

6.5.3 Rapidly Quenched High -Viscosity Isotactic Polypropylene/High-Density Polyethylene (HVIPP/HDPE) Blends

Figures 6.15 to 6.18 show the variation of modulus, yield strength, extension to break and tensile strength with composition for the rapidly quenched HVIPP/HDPE blends. The modulus behaviour in these blends is very similar to the other rapidly quenched blends, with many of the blends’ moduli lying well above the upper bound. Of particular interest are the 99.5% HVIPP blend samples; even though these samples contain <0.5% HDPE, every sample tested rises above the extreme upper bound.

The yield strengths for these blends are very similar to the other rapidly quenched blends, with the blends’ yield strengths lying between the extreme upper and lower bounds.

Extension to break values for these blends are similar to the rapidly quenched MViPP/HDPE blends. The rapidly quenched HVIPP and HDPE homopolymers and the 10, 90 and 99.5% have load-extension curves similar to curve (a) in figure 6.6. The 30% and 70% have curves similar to (b) and the 40, 50 and 60% have curves similar to (c). In this system only the 40 and 50% blends show any signs of co-continuity.

The tensile strength behaviour in these blends is similar to the behaviour of the rapidly quenched MViPP/HDPE blends.

6.5.4 Slowly Cooled Medium -Viscosity Isotactic Polypropylene/High-Density Polyethylene (MViPP/HDPE) Blends

The slowly cooled homopolymers and blends are much more brittle than the rapidly quenched MViPP/HDPE samples, with typical extension to break values of 10%. As a consequence, all the samples snap before yielding. In fact, many of the samples snap when being cut or when the jaws of the clamps are tightened, and have to be discarded. Figure 6.19 shows the moduli of the samples cooled at (a) 3°C/minute and (b) 1°C/minute. The figures show extreme upper and lower bounds. The yield strength and extension to break are not shown, for the reasons given above. The tensile strengths are given in figure 6.20.

Overall, the slowly cooled samples have higher moduli than the rapidly quenched ones. However, neither set of data show blends with moduli that lie above the extreme upper bound. The reasons for this are discussed in section 6.6.
For blends cooled at 3°C/minute the moduli of the two homopolymers are very similar. Only the 10% blend samples have moduli that lie on the extreme upper bound. The rest of the blends have moduli that fall below the extreme upper bound and in many cases fall below the extreme lower bound.

The moduli of the MViPP rich samples cooled at 1°C/minute are slightly higher than those cooled at 3°C/minute. The behaviour of the blends is very similar to those cooled at 3°C/minute, where some of the 10% blend samples rise slightly above the extreme upper bound and none fall below the extreme lower bound. The rest of the blend samples have moduli which fall below the extreme upper bound and in some cases fall below the extreme lower bound.

Tensile strength is an important measurement to look at in the slowly cooled MViPP/HDPE blends, as these samples, unlike the rapidly quenched ones, fail before yielding. Figure 6.20 shows that slowly cooled homopolymers are slightly stronger than the slowly cooled blends. However, overall the slowly cooled MViPP/HDPE samples are much weaker than the rapidly quenched MViPP/HDPE samples. This is particularly evident in the pure HDPE, where the rapidly quenched samples are between five and ten times as strong as the slowly cooled samples.

6.6 GENERAL DISCUSSION

6.6.1 Young's Modulus
In all three sets of rapidly quenched blends, the moduli of the blends rise well above the average upper bound, and in many cases, rise above the extreme upper bound. This indicates that the viscosity ratio of the components has little effect on the modulus behaviour. This contradicts the findings of Bains et al. (1994) but is in agreement with the findings of Gunderson and Chilcote (1991).

In each set of rapidly quenched blends, a range of different morphologies is observed. The MViPP/HDPE and HViPP/HDPE blends have co-continuous tendencies at central compositions, whereas the LViPP/HDPE blends do not. The scale of the phase separation is also different in each set of blends, with the LViPP/HDPE blends having the fewest, largest inclusions and the HViPP/HDPE blends having the most, smallest inclusions. The fact that the modulus behaviour is similar in all three sets of blends indicates that morphology does not significantly affect the modulus behaviour. The observation that, in each set, the entire blend composition range has moduli that rise above the extreme upper bound is further evidence that morphology is unrelated to modulus behaviour.
Varying the cooling rate clearly has a pronounced effect on the mechanical properties of the MViPP/HDPE blends. At slower cooling rates, the blends have higher moduli overall, but do not deviate positively from linear additive behaviour. When the samples are rapidly quenched, the cooling rate is >100°C/min (see Chapter 1). The slower cooling rate of the blends cooled at 3°C and 1°C/minute allows the materials to crystallize at higher temperatures (as seen in the DSC, Chapter 5), which in turn leads to thicker, and presumably stiffer, crystalline lamellae (as seen in the TEM, Chapter 4). The combination of the larger crystals and the higher crystallinity of the samples crystallized at higher temperatures are undoubtedly the cause of the overall higher moduli. This simple argument predicts that blends cooled at 1°C/minute should have higher moduli than those cooled at 3°C/minute, and this is in fact seen. Although the cooling rate was not varied in the LViPP/HDPE and HViPP/HDPE blends, it seems reasonable to assume that the same argument would apply.

Studying the moduli of slowly cooled blends provides a clue as to why the rapidly quenched blends have particularly high moduli. In the DSC it was shown that at rapid cooling rates, the components crystallize at higher temperatures in the blends than on their own and I suggested that some synergistic crystallization effects were responsible for this (see Chapter 5 for details). From the study of slowly cooled blends, it is clear that the higher the crystallization temperature of a sample, the higher its modulus value. It therefore seems reasonable to infer that the higher crystallization temperatures of the blend components in the rapidly quenched samples, result in higher component moduli and this explains the observation that the measured moduli of the blends apparently exceed the upper bound.

Perhaps the most convincing argument for the synergistic crystallization theory is the observation that the moduli of the 99.5% LViPP blend samples are considerably higher than the moduli of the pure LViPP samples. At such low concentrations of HDPE, any composite modulus would show only a small deviation from the modulus of the pure LViPP — it therefore seems likely that the modulus of the LViPP in the blends must somehow be increased by the presence of the HDPE. At rapid cooling rates, it was shown in the DSC that adding 0.5% HDPE to LViPP increases the onset temperature of crystallization by 12°C degrees. I suggest that this dramatic increase gives rise to the dramatic increase in modulus, for the reasons given above.

From the DSC measurements in Chapter 5, I inferred that at slow cooling rates MViPP crystallizes at lower temperatures in the blends than on its own (see figure 5.7). On the other hand, HDPE appears to crystallize at the same temperature in the blends as on its own. Given that the crystallization behaviour seems directly responsible for the high moduli in the rapidly quenched blends, one might expect the crystallization behaviour at slow cooling rates to be directly related to
the modulus behaviour of the slowly cooled blends. If so, one would expect the moduli of slowly cooled HDPE rich blends to have similar modulus values to the pure HDPE. When the MViPP content is increased, the modulus values should begin to deviate negatively from linearity, due to the MViPP crystallizing at lower temperatures in the blend (resulting in thinner, less stiff crystalline lamellae). Looking at the data in figure 6.19, one can see that this prediction is true - the 10% MViPP samples have similar modulus values to the pure HDPE and the rest of the blends have moduli which deviate negatively from linearity, with many falling below the extreme lower bound.

Another explanation as to why the 10% blend samples have higher moduli than the rest of the blends can be found by looking at the TEM micrographs in figure 4.2. The calculation of the lower bound makes the assumption that stress is transferred from one phase to another across the boundary. In the slowly cooled 10% MViPP blend there is clear evidence for the penetration of polyethylene lamellae into inclusions of polypropylene - thus providing a mechanism for excellent stress transfer from one phase to the other. On the other hand, the rest of the blends show relatively smooth interfaces between the two phases. If there are voids along these boundaries, stress transfer will be less than perfect and islands of polyethylene of polypropylene may bear little or no stress, thus leading to a modulus below the extreme lower bound.

6.6.2 Yield Strength
Given that the rapidly quenched blends' moduli lie well above the average upper bound, it seems reasonable to expect the yield strength to show a similar relationship. However the blends' yield strengths lie between the extreme upper and lower bounds and do not show any positive deviation from linearity. A possible reason for this is that yield strength is not affected by crystallization temperature in the way that modulus is. As the slowly cooled blends snap before yielding, it is not possible to determine how their yield strength behaviour compares to the rapidly quenched samples. More work at intermediate cooling rates must be done in order to determine whether yield strength is related to crystallization temperature.

6.6.3 Extension to Break
The rapidly quenched homopolymers have the greatest extension to break values. None of the blends with central compositions extend past yield. This observation is in agreement with the findings of other workers mentioned in section 6.3. In Chapter 3 it was shown that the blends with central composition have viscosities that deviate negatively from a linear additive rule. From this I inferred that the interfacial adhesion between the blend components is poor at central compositions. The prediction I made in Chapter 3 - i.e. the poor interfacial adhesion at central compositions might result in brittle blends - is therefore correct.
The three sets of rapidly quenched blends have different morphologies at central compositions: the MViPP/HDPE and HViPP/HDPE have co-continuous morphologies, whereas the LViPP/HDPE have disperse droplet morphologies. The fact that the extension to break is very low in all blends with central compositions indicates that type of morphology is not important. Low extension to break values are not limited to blends with central compositions in the rapidly quenched LViPP/HDPE blends; the 30, 70 and 90% blends also have very low extension to break values. There are two possible explanations for this. Because the viscosities of the LViPP and the HDPE are poorly matched when mixing in the extruder, the interfacial tension may be poor over a wider range of compositions than the other blend sets, resulting in more brittle blends. However, the observation that the 30, 70 and 90% LViPP blends do not have viscosities that deviate negatively from linearity does not support this hypothesis. Another explanation is the scale of phase separation. Apart from the 10% LViPP blend, the inclusions are much larger in the rapidly quenched LViPP/HDPE blends than in the rapidly quenched MViPP/HDPE and HViPP/HDPE blends. It is possible that any small faults in the material propagate more quickly in the LViPP/HDPE blends than the others, due to the larger size of the phase separated components.

6.6.4 Tensile Strength

In all three sets of rapidly quenched blends, the tensile strength is highest for the homopolymers and lowest for the blends with central compositions. However, given the different nature of the load-extension curves, a comparison is not entirely meaningful.

Although stiffer, the slowly cooled MViPP/HDPE homopolymers and blends are much weaker than the rapidly quenched samples. Although interesting from a scientific point of view these blends would have no practical applications.
6.7 CONCLUSIONS

The measured moduli of many rapidly quenched iPP/HDPE blends are found to exceed the extreme upper bound calculated from the parallel (Voigt) model, using the maximum moduli of the quenched homopolymers as those of the two components. From this observation it can be concluded that neither viscosity ratio nor morphology type have a significant effect on the modulus behaviour of rapidly quenched iPP/HDPE blends.

In Chapter 5 it was reported that the crystallization temperatures of the components are higher in the quenched blend samples than in the homopolymers quenched under the same conditions. I believe that the higher crystallization temperatures in the blends lead to thicker, stiffer crystals and this explains why the rapidly quenched blends components have higher moduli than the pure homopolymers.

Overall, the slowly cooled blends have higher moduli than the rapidly quenched blends due to the higher crystallinity and thicker crystals. However, unlike the rapidly quenched blends, the slowly cooled blends containing >10% MViPP have moduli which fall below the extreme upper bound and in many cases fall below the extreme lower bound (calculated from the series or Reuss model). Again these effects can be attributed to the crystallization behaviour. In Chapter 5 it was shown that the MViPP crystallizes at lower temperatures in the blend than on its own. I believe that the lower crystallization temperatures of the MViPP rich blends lead to thinner, more flexible crystals, and this explains why the moduli of the slowly cooled blends containing >10% MViPP are lower than the parallel and series model predict.

In all three sets of blends, the extension to break values are lower for the blends than for the pure homopolymers. I conclude that this is due to the poor interfacial adhesion between the components; this is supported by the viscosity measurements reported in Chapter 3. The slowly cooled MViPP/HDPE blend samples are far more brittle than the rapidly quenched samples; this can be attributed to the higher crystallinity of these samples.
Figure 6.1 Idealised stress-strain behaviour of a ductile polymer subjected to tensile testing. The change in specimen dimensions is also depicted.

Figure 6.2 Curves illustrating the effect of temperature and/or shear rate on the stress-strain behaviour of a ductile polymer.
Figure 6.3 Schematic curves of true stress, $\sigma_T$, against nominal strain, $\varepsilon_N$, for polymers showing the Considère construction: (a) unstable neck and (b) stable neck.

Figure 6.4 Schematic representations of the parallel (Voigt) and series (Reuss) models.
Figure 6.5 Wide angle x-ray diffraction patterns of the (a) 0%, (b) 50%, (c) 90%, and (d) 100% rapidly quenched MViPP blend sheets, face-on.
Figure 6.6 (above) Load-extension curves for various different blend systems. Curve (a) is typical of the rapidly quenched homopolymers and rapidly quenched 10% and 90% blends. The broken line indicates that the curves are not to scale; the extension to break is very much larger than is indicated in the figure. Curve (b) is typical of the rapidly quenched 40, 50 and 60% blends and curve (c) represents the rapidly quenched 30 and 70% blends. All of the slowly cooled samples break before their first yield point.
Figure 6.7 Scatter of Young's modulus as a function of blend composition for the rapidly quenched LViPP/HDPE blends. Each data point represents a separate tensile test. Tests were performed at extension rates of (a) 1mm/min, (b) 5mm/min and (c) 10mm/min. The average upper and lower bounds are shown in figure (a) whereas the extreme upper and lower bounds are shown in (b).
Figure 6.8 Scatter of yield strength for the rapidly quenched LViPP/HDPE blends. Extreme upper and lower bounds are shown.

Figure 6.9 Extension to break (breaking strain) values for the rapidly quenched LViPP/HDPE blends.
Figure 6.10 Tensile strength for the rapidly quenched LViPP/HDPE blends.

Figure 6.11 Variation of Young’s moduli with composition for the rapidly quenched MViPP/HDPE blends. Extreme upper and lower bounds are shown.
Figure 6.12 Scatter of yield strength for the rapidly quenched MViPP/HDPE blends. Extreme upper and lower bounds are shown.

Figure 6.13 Extension to break (breaking strain) values for the rapidly quenched MViPP/HDPE blends.
Figure 6.14 Tensile strength for the rapidly quenched MViPP/HDPE blends.

Figure 6.15 Variation of Young's moduli with composition for the rapidly quenched HViPP/HDPE blends. Extreme upper and lower bounds are shown.
Figure 6.16 Scatter of yield strength for the rapidly quenched HViPP/HDPE blends. Extreme upper and lower bounds are shown.

Figure 6.17 Extension to break (breaking strain) values for the rapidly quenched HViPP/HDPE blends.
Figure 6.18 Tensile strength for the rapidly quenched HViPP/HDPE blends.
Figure 6.19 Variation of Young's moduli with composition for the MViPP/HDPE blends cooled at (a) 3°C/min and (b) 1°C/min. In both cases the extreme upper and lower bounds are shown.
Figure 6.20 Tensile strength of the slowly cooled MViPP/HDPE blends as a function of composition: (a) samples cooled at 3°C/minute and (b) samples cooled at 1°C/minute.
CHAPTER 7: SUMMARY AND GENERAL DISCUSSION

Studies on the rheological, morphological and crystallization behaviour of polyolefin blends are interesting from a scientific viewpoint and with more detailed investigation could easily be the subject of a thesis in their own right. However, unless blends can be produced which have desirable mechanical properties, these materials will have no practical uses and studies on their behaviour will remain purely academic.

The aim of my project was to determine how a range of physical properties such as viscosity, morphology and crystallization affect the mechanical properties of iPP/HDPE blends. This was achieved by preparing three sets of blends of varying viscosity ratios in a twin-screw extruder. The blended samples were then compression moulded into sheets and cooled at approximately 100°C (rapidly quenched), 3°C and 1°C/minute.

Capillary extrusion rheometry was used to measure the viscosities of the blends and their components over a range of shear rates. At fast rates (similar to those in the extruder) the HViPP and the HDPE were found to have the most closely matched viscosities whereas the LViPP and the HDPE had the least closely matched viscosities. In the extruder the LViPP did not mix well with the HDPE and produced a very poor extrudate. This indicated that matching of viscosities is crucial if a high quality extrudate is to be produced.

Many of the blends were found to have lower viscosities than expected; blends with central compositions had viscosities which were lower than either of the component polymers. From this I inferred that the interfacial adhesion between the components was poor, meaning that the components slipped past each other in the melt. This proved to have a significant effect on the mechanical properties of the blends. Blends with central compositions were particularly brittle and, as a result, weak compared to the pure homopolymers. The poor interfacial adhesion did not, however, affect the modulus behaviour of the blends. Neither did varying the viscosity of the iPP, as all three sets of blends had similar moduli when prepared under the same conditions.

TEM revealed that a range of morphologies could be produced by varying the cooling rate of the samples and the grade of the iPP. In all cases both disperse droplet and co-continuous morphologies were observed, with the size and shape of the domains being different for each set of
blends and cooling rates. I proposed that this was partly due to the differing viscosities of the components during melt mixing and partly due to different ripening rates during storage in the hot press. Like viscosity, morphology had a significant effect on the mechanical properties. Blends with larger phase-separated domains (such as the slowly cooled samples) were more brittle (and hence weaker). Morphology did not appear to influence the modulus behaviour.

DSC showed that cooling rate significantly influenced crystallization behaviour. The effect was most pronounced on the iPP phase. At cooling rates of $>20^\circ$C/minute the polyethylene crystallized at higher temperatures than the polypropylene. Despite its higher melting point, polypropylene only crystallized first at rates of $10^\circ$C/minute or slower. As expected the crystallinity of the samples increased as cooling rate decreased, i.e. the slow cooled blends had the highest degree of crystallinity. As a result the slowly cooled blends had higher moduli than the rapidly quenched blends, but were far more brittle. Many of the slowly cooled samples snapped during cutting and would therefore have no practical uses.

DSC also showed that blending could have a significant effect on crystallization behaviour of the component polymers. At fast cooling rates ($>50^\circ$C/minute) both components crystallized at higher temperatures in the blends than they did on their own. At slow cooling rates ($<10^\circ$C/minute) the iPP crystallized at lower temperatures in the blends than it did on its own. At intermediate cooling rates the components crystallized at roughly similar temperatures in the blends as they did on their own. I proposed that heterogeneous nucleating agents from the polypropylene migrated into the polyethylene regions during melt mixing, thereby enhancing the nucleation site density in the polyethylene phase. I also proposed that there was a certain temperature ($\sim110^\circ$C) above which the nuclei could not effectively nucleate the polyethylene. Hence, at fast cooling rates, (where the components crystallized below $110^\circ$C) polyethylene nucleation was enhanced. The polyethylene crystals then acted as nuclei for the polypropylene thus raising its crystallization temperature. At intermediate cooling rates, where the polyethylene crystallized first (at a temperature of $110^\circ$C or higher) the nuclei could not effectively nucleate the polyethylene and the components behaved as expected. At the slowest cooling rates, where polypropylene crystallized first, polypropylene's crystallization temperature was lowered, due to the nuclei having migrated into the polyethylene during melt mixing.

These unusual crystallization effects had a pronounced effect on the modulus behaviour of the blends. At fast cooling rates the moduli of the blends exceeded the bounds imposed using existing models of composite materials. I proposed that the enhanced crystallization temperatures of the components in the blends produced thicker, stiffer crystals, leading to an overall higher modulus than one would expect. The behaviour of the slowly cooled blends, whose moduli often fell below the bounds imposed by existing models, was explained using the same logic: the lower
crystallization temperatures of the iPP in the blends, led to thinner, more flexible crystals, with an overall lower modulus.

Throughout the thesis, I have reviewed the work of many other authors. Some of them have reported that blends of iPP and HDPE could have moduli which deviate positively from existing models and some have attributed this to crystallization effects. Others report that blending iPP with HDPE has little or no effect on the crystallization behaviour, or on the mechanical properties. Others still, report modulus values that deviate negatively from existing models. In my work, I have shown that for the same set of blends, all of these cases can be true, simply by varying the cooling rate of the samples. It seems possible that previous works contradict each other simply because of the differences in sample preparation conditions (especially cooling rate).

Overall the project has proved that under the right processing conditions, blends can be produced which have particularly advantageous properties. Luckily, these conditions are very similar to those already used in the polymer industry, meaning that producing these blends would not be too time-consuming or expensive.
CHAPTER 8: CONCLUSIONS AND FUTURE WORK

8.1 CONCLUSIONS

The Young's moduli of rapidly quenched iPP/HDPE blends were measured and found to be higher than can be predicted by simple composite theories using the moduli of the two rapidly quenched homopolymers as representing the moduli of the two components in the blends. These findings apply to the whole range of blend compositions and do not appear to be affected by morphology type or viscosity ratio.

DSC has shown that at rapid cooling rates the polyethylene crystallizes at a higher temperature than the polypropylene and that the crystallization temperatures are higher in quenched blend samples than in the homopolymers quenched under the same conditions. I believe that heterogeneous nucleating agents migrate from the polypropylene regions into the polyethylene regions during melt mixing in the twin-screw extruder. The increased crystallization temperatures arise because the materials in the blends are influencing each other via enhanced nucleation. The nucleating agents from the polypropylene act as effective nuclei for the polyethylene, making it crystallize at higher temperatures in the blends than it does on its own. In turn, the polyethylene crystals act as nuclei for the polypropylene, making it crystallize at higher temperatures than it does on its own. The higher crystallization temperatures of the components in the blends lead to thicker, stiffer crystals, with higher moduli. This means that the moduli of the two blend components are themselves higher than those of the quenched pure homopolymers.

The moduli of slowly cooled blends iPP/HDPE blends were also measured. Unlike the rapidly quenched blends, the moduli did not exceed the bounds imposed by theories of composite materials. In many cases the moduli were lower than the theories of composite materials predict. DSC showed that polypropylene is generally the first component to crystallize in the slowly cooled samples and that it crystallizes at lower temperatures in the blends than it does on its own. The lower crystallization temperatures of the components in the slowly cooled blends presumably lead to thinner, more flexible crystals; this can explain why the moduli of these blends are lower than predicted.

Although viscosity ratio and morphology type do not influence the modulus behaviour, they do have an effect on the other mechanical properties such as extension to break and tensile strength.
Overall the blends are weaker and more brittle than the pure homopolymers — especially at central compositions. I believe this to be due to the poor interfacial adhesion between the components when blended. Use of a compatibilizer could help to improve the interfacial adhesion and could produce desirable materials with high modulus values and improved strength.

In summary, predictions of mechanical properties of blends are not as simple as might be expected — the detailed nature of the polymers (including details of the additives), viscosity ratio, scale of phase-separation and detailed crystallization effects due to sample preparation must be taken into account.

8.2 FUTURE WORK

This project has been very fruitful and has opened up many avenues for future research. Many ideas for this work have been mentioned throughout the thesis and are currently being undertaken by the Bristol Blends group. This includes a detailed analysis of the phase-ripening phenomenon mentioned in Chapter 4.

Further research could involve a more in-depth look at the flow behaviour of the blends in order to determine how the blends behave in the complex shear flows which arise in a twin screw extruder. Other experiments could include varying the grade of the HDPE and choosing grades of iPP with different additives (other than talc). It would also be interesting to deliberately add specific additives to each component in order to determine whether migration of nucleating agents from one phase to another really does occur. Addition of compatibilizers in order to improve the interfacial adhesion between the components could also be investigated.

Further X-ray studies using small angle X-ray diffraction are needed in order to determine whether the crystal thickness is different for the components in the blends.
REFERENCES


Faraday Discussions of the Royal Society of Chemistry, (1979), 68


Hay, I. L.; Kellar, A. (1965) *Kolloidzeitschrift*, 204, 43

148


Huggins, M. L. (1942a) *Ann. NY Acad. Sci.* 41, 1


Huggins, M. L. (1942c) *J. Am. Chem. Soc.* 64, 1712


Judges 5:5, Old Testament (c. 550 BC)


Keller, A. (1957) *Phil. Mag.* 2, 1171


Krigbaum, W. R.; Roe, R. J.; Smith, K. J. (1964) *Polymer*, 5, 533


Orowan, E. (1949) *Rept. Prog. Phys.*, 12, 185


152


Willemse, R. C.; Posthuma de Boer, A.; van Dam, J.; Gotsis, A.D. (1999a) Polymer, 40, 827 (interfacial tension)

Willemse, R. C.; Speijer, A.; Langeraar, A. E.; Posthuma de Boer, A. (1999b), Polymer, 40, 6645

Williams, M. L.; Landel, R. F.; Ferry, J. D. (1955) J. Am. Chem. Soc. 77, 3701


Yoon, D. Y.; Flory, P. J. (1977) Polymer, 19, 509

