A study of the miscibility of crystalline polyolefins

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A STUDY OF THE MISCIBILITY OF
CRystalline Polyolefins

by

NABA KUMAR DATTA,
BChE, PGDip (Engg), MSc,
MIE, AMIIChe, Grad PRI

A Doctoral Thesis submitted in partial fulfilment
of the requirements for the award of the
Degree of Doctor of Philosophy
of Loughborough University of Technology

May 1982

INSTITUTE Of POLYMER TECHNOLOGY
LOUGHBOROUGH UNIVERSITY OF TECHNOLOGY
ENGLAND

© By N K DATTA (1982)
This work is dedicated to the memory of
my father who passed away on 22 June 1974
ACKNOWLEDGEMENTS

I would like to express my gratitude to my first supervisor, Professor A W Birley, Director of the Institute of Polymer Technology, Loughborough University of Technology, for his guidance throughout this work. I want to extend my thanks to him for recommending me for the award of a research studentship.

I am grateful to my joint supervisor, Mr D A Hemsley, for his helpful discussions and useful recommendations.

I wish to express my appreciation for the support in this research programme by Alida Reclamers Limited of the Alida Packaging Group and to many helpful discussions with Dr I McDarmaid of that company.

The assistance received from staff and colleagues of IPT, and from numerous friends and others at various stages of the presentation of this thesis is also thankfully acknowledged.

I thank Mrs Janet Smith for her great assistance in transforming the rough draft into this typed manuscript.

Finally, I wish to acknowledge my particular indebtedness to the members of my family for their understanding, support and patience throughout this work.
SUMMARY

Polymer blends is a subject of great importance for academic as well as industrial interest. The objective of this research programme is to study the miscibility of polymer blends. Polymer blends in general are of three types: amorphous-amorphous; amorphous-crystalline; and crystalline-crystalline systems. This work is concerned with crystalline-crystalline type polymer blends and is restricted to polyolefin crystalline polymers only.

Firstly an outline of crystalline-crystalline polymer blends mainly concentrating on polyolefin blends has been given in an introductory chapter. This chapter presents relevant fundamentals rather than being an extensive critical review of the literatures.

In the first phase of the work three polyolefins (low-density polyethylene, high-density polyethylene and linear low-density polyethylene) have been melt mixed to prepare three sets of binary blends covering the entire range of compositions. A variety of experimental techniques were used to assess the miscibility of the blends prepared. The whole experimental programme can be subdivided into three major areas: the first is concerned with structural characterisation; the second area with the melt properties; and the third with the mechanical properties of the polymers in the solid state. Polymers (including their blends) and experimental techniques are detailed in Chapter 2.

Experimental results are discussed and concluded individually in four subsequent chapters. Chapter 3 gives mainly the information of molecular structure of the three polyolefins. Characterisation of crystalline structure of polyolefins and their mixtures has been covered in Chapter 4. Chapter 5 is concerned with melt properties of polyolefins and their blends; whereas Chapter 6 deals with solid state mechanical properties. In these last two chapters an attempt has been made to correlate, where possible, the structures with their properties.
From the experimental investigations it has been found that the system of linear low-density and high-density polyethylene blends is miscible whereas the system of low-density and high-density polyethylene is not. Structural characterisation has shown that the low-density and linear low-density polyethylene blends system is immiscible at all compositions, although some mechanical compatibility has been found from melt property and mechanical property measurements.

The second phase of the work was mainly concerned with the application of polyolefin blends. Film has been manufactured from polyolefin blends (including their components) and evaluated. Linear low-density/high-density and low-density/linear low-density polyethylene systems have been selected for this part of the work (Chapter 7).

Essential to the understanding of the blends involving linear low-density polyethylene, is appreciation of the molecular structure of the homopolymer. A preliminary characterisation of linear low-density polyethylene has revealed that its structure is more complex than might have been foreseen.

Finally in Chapter 8 overall concluding remarks have been made based on the conclusions drawn from all investigations carried out in this research programme and reported in the individual chapters.
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CHAPTER 1

INTRODUCTION

1.1 Polymer Blends in General

1.1.1 Background (1,2)

The field of polymer science and technology has undergone an enormous expansion over the last several decades primarily through chemical diversity. First, there was the development of new polymers from a seemingly endless variety of monomers. Next, random copolymerisation was used as an effective technique for tailoring or modifying polymers. Later, more controlled block- and graft copolymerisation was introduced. The list of new concepts in polymer synthesis has not been exhausted. However, it has become clear that new chemical structures or organisations are not always needed to meet new needs or to solve old problems.

The concept of physically blending two or more existing polymers to obtain new products or for problem solving has not been developed as fully as the chemical approach but is now attracting widespread interest and commercial utilisation. The successful implementation of this concept requires different knowledge and techniques than that used to develop new polymers. Polymer blends have become a very important subject for scientific investigation in recent years because of their growing commercial acceptance. Physical blending is the less expensive and time-consuming method over chemical modification of polymer. Chemical modification is confined to primary producers, of whom there are relatively few compared to the large number of secondary processors. Polymer blending is basically a variation of compounding or formulating in general, and polymer converters are well able to initiate such developments. It is not necessary to learn how to manufacture a particular polymer in order to use it in blends. Thus almost anyone who can compound can develop polymer blends, at least within the limitations of his processing equipment.
1.1.2 Definition (1,3,4)

Polymer blends are often referred to by the contraction "polyblends" and sometimes as "alloys" to borrow a term from metallurgy. When two or more polymers are intimately mixed in a single continuous solid product, the composition is generally referred to as a polymer blend, or polyblend. It may be physical mixture of either homopolymers or structurally different homopolymer and copolymer. Depending upon the degree of miscibility or immiscibility, such a polyblend may resemble a random copolymer or a block or graft copolymer which in themselves are not blends, but form solid arrays that physically resemble mixtures, or it may show micro- or macroheterogeneous separation into a multiphase system. Block and graft copolymers which generally differ from blends by only a few chemical bonds, share many common features and purposes with blends.

1.1.3 Classification

One simple way to classify polyblends is as plastic-plastic, plastic-rubber, and rubber-rubber blends system (3). Olabisi (5) has classified polyblends in terms of their method of preparation as shown in Figure 1.1. A mechanical polyblend is made by melt blending the polymers either on an open roll or in an extruder or any other suitable intensive mixer. Depending on the state of thermal stability of the polymers being mixed, the high shear involved during
processing could initiate polymer degradation reactions resulting
in the generation of free radicals. The free radicals could react
with the other structurally different polymers present resulting
in true chemical grafts and such mixture is referred to as mechano-
chemical polyblends. A chemical polyblend is made by in-situ
polymerisation and crosslinking of the constituent polymers and
the result is an interpenetrating crosslinked polymer network of
structurally different polymers. The three main categories are
interpenetrating polymer networks (IPNs), simultaneous inter-
penetrating polymer networks (SINs), and interpenetrating elasto-
meric networks (IENs) (6). In general, the IENs are made by
mixing and coagulating two different kinds of polymer latices
and crosslinking the coagulant to form a three-dimensional mosaic
structure. If the latex coagulant is not crosslinked, the resul-
ting product is called a latex polyblend. Solution cast polyblends
are prepared by dissolving the constituent polymers in a common
solvent and mixing the solutions thoroughly. The resulting solu-
tion could be film-cast or dried to form the solution cast poly-
blend.

Nishi (7) from his recent investigations on the possible
applications of thermodynamic concepts to experimental studies of
polymer mixtures by using the phase diagram has classified polymer
blend into three categories based on phase separation behaviour as
shown in Figure 1.2. They are amorphous-amorphous; amorphous-
crystalline; and crystalline-crystalline polymer blends systems.
Nishi noted there has been no attempt to study compatible crystalline-

![Phase diagram for polymer blends]

FIGURE 1.2: Classification of phase separation behaviour for polymer
blends (7)
crystalline polymer mixtures and emphasised this kind of research may be of interest in future. The present study is concerned with crystalline-crystalline type polymer blends only. Crystalline polyolefins have been selected for this work as a representative of crystalline-crystalline system.

1.2 Reasons for Blending Polyolefins

1.2.1 General (8)

Polyolefins form the largest group of commercial thermoplastics. It is necessary in this context to mention some of their salient features. They constitute a group of polymers of complex macromolecular structure: wide molecular weight distributions that are diverse in shape, substantial short and long chain branching, and high crystallinity, coupled with a multitude of spherulitic forms and orientability. Their density is the lowest among polymers and strongly influences performance characteristics.

The characteristics pertinent for blending are: excellent dielectric properties, water repellence, non-polarity, high melt viscosities that respond weakly to temperature changes but strongly to shear rate or stress changes coupled with inherently high melt elasticity and melt strength. Polyolefin glass transition temperatures, with the notable exception of polypropylene, are low.

Polyolefin blends display the characteristic features of macromolecular incompatibility with a texture consisting of either spherulites "swollen" with the lower-crystallinity component or droplets-in-a-matrix alternative with fibrils-in-a-matrix "composites". There is evidence that the latter supermolecular structures persist in the molten state, rendering feasible the existence of so-called "rheologically particular" compositions (RPC). (Evidently this term refers to the compositions in which maxima or minima occur when certain rheological or physical properties are plotted versus blend composition). By and large, the properties of polyolefin
blends are nonlinear functions of composition and the component properties.

The melt mixing of polyolefins should be distinguished from blending. Blending in the language of polyethylene manufacturing processes means the granulate or pellet blending operation. Melt mixing is carried out in two stages, dispersive followed by laminar mixing, and it is aimed typically at the production of new grades of polyolefins tailored to specific applications often inaccessible or uneconomic by an adjustment of the polymerisation process and/or chemical modification.

Strong pressure for environmental protection as well as an ever increasing plastics waste accumulation has initiated numerous investigations of blending as a solution to the plastics scrap reclamation problem. Polyolefins are among the major constituents of plastic waste and scrap, and their recycling as a blend is of considerable value.

1.2.2 Review of selected patents (8)

Within the last 2-3 decades, several patents were granted on processes and/or compositions for manufacturing rheologically modified (i.e. melt-blended) polyolefins. A selection of polyolefin blend patents involving only polyethylene-polyethylene systems is presented in Table 1.1. The most important and historically the first group of polyolefin blends consists of low-density and high-density polyethylenes (LDPE and HDPE). Interestingly, the first patent [2] describing blends of LDPEs is apparently the first record of a critical concentration effect (RPC) in blend melt flow - the composition of 1/3-component ratio is claimed to be the best processable mixture. This effect was rediscovered much later for other blends. Technical reasons for the manufacture of polyethylene blends have been to increase the stiffness of LDPE and the toughness and flexibility of HDPE [3-5]. With increasing numbers of HDPE grades, more sophisticated systems were introduced for which the molecular structure parameters: average molecular
**TABLE 1.1: Review of Patents Involving Polyethylene-Polyethylene Systems in Polyolefin Blends (8)**

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<tr>
<th>No.</th>
<th>Patent Number</th>
<th>Country</th>
<th>Year</th>
<th>Patent Assignee</th>
<th>Components</th>
<th>Merits and Applications</th>
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<td>1109864</td>
<td>France</td>
<td>1956</td>
<td>Philips Petroleum</td>
<td>LDPE</td>
<td>Extrusion</td>
<td>9</td>
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<td>2</td>
<td>2662762</td>
<td>USA</td>
<td>1959</td>
<td>C E McCormick</td>
<td>LDPE</td>
<td>Extrusion and moulding grades of excellent processability</td>
<td>10</td>
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<td>3</td>
<td>827363</td>
<td>UK</td>
<td>1960</td>
<td>Distillers Co. Limited</td>
<td>HDPE</td>
<td>“HDPE-like”, high stiffness, impact resistant moulding</td>
<td>11</td>
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<td>4</td>
<td>843697</td>
<td>UK</td>
<td>1960</td>
<td>Imperial Chemical Industries</td>
<td>HDPE</td>
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<td>5</td>
<td>875366</td>
<td>UK</td>
<td>1961</td>
<td>Union Carbide Corporation</td>
<td>LDPE or HDPE</td>
<td>High stiffness moulding</td>
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<td>6</td>
<td>875040</td>
<td>UK</td>
<td>1961</td>
<td>Union Carbide Corporation</td>
<td>HDPE</td>
<td>High environmental stress cracking resistance blow moulding</td>
<td>14</td>
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<td>7</td>
<td>904865</td>
<td>UK</td>
<td>1962</td>
<td>W R Grace &amp; Co.</td>
<td>PE</td>
<td>Moulding, Extrusion</td>
<td>15</td>
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<td>933194</td>
<td>UK</td>
<td>1963</td>
<td>W R Grace &amp; Co.</td>
<td>LDPE</td>
<td>Low haze films</td>
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<td>9</td>
<td>942369</td>
<td>UK</td>
<td>1963</td>
<td>E I du Pont de Nemours &amp; Co.</td>
<td>LDPE or HDPE</td>
<td>Extrusion coating</td>
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<td>1485303</td>
<td>France</td>
<td>1967</td>
<td>Eastman Kodak Co.</td>
<td>LDPE</td>
<td>Extrusion coating, high shrink stability</td>
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<td>11</td>
<td>3379303</td>
<td>USA</td>
<td>1968</td>
<td>J H Jenkins</td>
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<td>Wire insulations</td>
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<td>12</td>
<td>50056448</td>
<td>Japan</td>
<td>1974</td>
<td>Furukawa Electric Co.</td>
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<td>Tough, blow film</td>
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<td>14</td>
<td>3868409</td>
<td>USA</td>
<td>1975</td>
<td>L J Bolduc</td>
<td>LDPE</td>
<td>Cable through filling compositions</td>
<td>22</td>
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<td>15</td>
<td>820876</td>
<td>Belgium</td>
<td>1975</td>
<td>Union Carbide Corporation</td>
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<td>High weld strength, strong weld bags</td>
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<td>75006022</td>
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<td>Poland</td>
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<td>18</td>
<td>2304998</td>
<td>W. Germany</td>
<td>1973</td>
<td>Du Pont of Canada Ltd</td>
<td>HOPE</td>
<td>Transparent, tough films</td>
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</tbody>
</table>
weight [6,8,14] and branching [16] were specified for the components. The applications have progressed from injection moulding to blow moulding [6,17] then to high-processability extrusion grades [11,12], and the present trend is the production of tough, transparent films [13,15,18].

1.3 Preparation of Polyolefin Blends

Polyolefin blends are prepared by mixing polyolefins. The mixing process is aided by high temperature or by diluents. Melt blending and solution blending are the two distinct common available techniques for preparing polyolefin blends.

1.3.1 Melt blending (3,4)

Mixing two polyolefins in the molten state is a straightforward engineering practice. The ingredients are readily available and clearly identified. The process introduces no impurities, requires no removal of extraneous solvents by evaporation which is very essential for solution blending operations. The balance of equipment design and temperature produces the rheological properties and shear required for controlled rate and degree of mixing. On the other hand, the kinetics of mixing large polymer molecules in the molten state predict that mixing will be slow and incomplete and that the degree of mixing will depend very much upon temperature, shear and time. Furthermore, these same factors, temperature, shear and time, may cause degradation of either or both polymers and alter the properties of the blended product significantly. So in melt blending it is necessary to be constantly aware of these variables and to keep them under close control.

1.3.2 Solution blending (3,4)

In solution blending, a diluent is added to lower the temperature and shear-force requirements for satisfactory mixing. At thermodynamic equilibrium, two polymers can be dissolved separately
but in the same solvent, and the two solutions can then be mixed, and brought to equilibrium. This eliminates, or at least minimises, problems of kinetics, incomplete mixing, and degradation caused by heat and shear. On the other hand, the method excludes the use of polymers that are not soluble in a mutual solvent. The isolation of the solid blend product requires removal of the solvent by evaporation which can cause one component to separate before the other, thus producing gross heterogeneity, which could not occur in the much more viscous molten systems in melt blending. Furthermore, the use of solvents in practical systems involves problems of toxicity, flammability, environmental pollution, and economics. So melt blending is preferable to solution blending in the preparation of polyolefin blends.

1.4 Compatibility, Miscibility and Stability (27, 28, 2)

The blending of two polyolefins immediately raises the question of their mutual compatibility. Some confusion has arisen in the polymer field by use of the word "compatibility" which in its most general sense is not synonymous with "miscibility". Prior studies and reviews have generally used the term "compatible" to describe single-phase behaviour. However "compatibility" has been used by many other investigators involving various studies of polymer blends behaviour to describe good adhesion between the components, average of mechanical properties, behaviour of two-phase block and graft copolymers, and ease of blending. The term "solubility" which is more descriptive and exact than "compatibility", may be another choice for describing molecular mixing in polymer blends. For single-phase, solvent-solvent and polymer-solvent mixtures, solubility is the accepted term. With polymer-polymer-mixtures, ideal or random molecular mixing may not adequately describe the true nature of the blend even though the physical parameters of the blend would suggest true solubility. The term "miscibility" has been chosen to describe in the case of polyolefin blends with behaviour similar to that expected of a single-phase system. The term "misci-
"Stability" used here does not imply ideal molecular mixing but suggests that the level of molecular mixing is adequate to yield macroscopic properties expected of a single-phase material. So a miscible polyolefin blend is defined as a stable homogeneous mixture which exhibits macroscopic properties expected of a single-phase polyolefin.

It may happen that good results are obtained when two immiscible polyolefins are mixed together. In that case it is necessary to define them as "compatible" in the common usage of this term from their particular property point of view, although they do not show single-phase behaviour in miscibility tests.

In the definition of miscibility of polyolefin blends "stability" is one of the very important requirements. Here a stable polyolefin blend is defined as one whose initially favourable properties do not change significantly over a period equivalent to the reasonable lifetime of the mixture under expected usage conditions. To designate such mixtures as stable needs characterisation. The characterisation of a polyolefin blend as stable or unstable is not an easy task by any means. It will involve the use of accelerated ageing tests followed by various appropriate measurements of the properties of the mixture. For polyolefin blends it is likely that a melting and slow cooling cycle will suffice to indicate whether serious demixing can be expected during extended usage. So appropriate experimental techniques will have to be developed for characterisation of polyolefin blends.

1.5 Methods of Miscibility Determination

1.5.1 Criteria for establishing miscibility

For crystalline-crystalline polymer blends perhaps the most unambiguous criterion of miscibility is the detection of crystalline melting point of the blend and the comparison of the measured value to those of the individual components. The crystalline melting
point which reflects the three-dimensional order of main chain segments in crystalline regions, can be determined easily from calorimetric measurement. Regardless of the method of determination, the location of the crystalline melting point is influenced by its heat history, experimental time-scale and condition, any factor which affects the intra- and/or inter-molecular forces of the material. Although crystalline melting temperature which is a first-order thermodynamic entity, and could be referred to as a first order transition, is influenced by local environment interactions at chain segments levels. Because of the sensitivity of the crystalline melting temperature to the disruption in the local structure that results from mixing two crystalline polymers, the existence of a single and sharp, or, single and broad, or, double and depressed, or, double and non-depressed crystalline melting point for a polymer blend reveals the particular macroscopic characteristic of such a blend. A miscible polymer blend exhibits a single crystalline melting temperature intermediate between those of the components, whereas two separate crystalline melting temperatures appear in cases of immiscibility. When strong specific interactions are involved, the observed crystalline melting temperature may go through a maximum as a function of composition. A polyblend with a single crystalline melting point is indicative of a homogeneous system. A blend with two separate crystalline melting points is indicative of a heterogeneous system. Therefore, if an intimately mixed crystalline polymer pair (A and B) exhibits on thermal analysis a single crystalline melting endotherm it can be assumed to be a one-phase alloy system. This has been taken to imply that within the limits of detection of the technique used to measure the crystalline melting temperature, the blend is molecularly homogeneous. The melting behaviour for both miscible and immiscible systems are shown schematically in Figure 1.3.

At the other extreme, blends of immiscible polymers that segregate into distinct phases may exhibit crystalline melting endotherms not corresponding to temperature and width to those of the unblended components. In intermediate cases where there is partial mixing
FIGURE 1.3: Melting Behaviour when Components A and B are combined. ($T_m$ = Crystalline Melting Point)
between the components, the crystalline melting temperature of the individual components may be identical. In addition depression of crystalline melting point can be expected in case of immiscible blends and as well as in partially miscible blends.

1.5.2 Melting point depression

The general equation for melting point depression is given by (27):

\[
\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{RV_2}{\Delta H_2 V_1} \left[ \frac{\ln \phi_2}{\Delta P_2} + \frac{1}{\Delta P_1} \right] \frac{1}{1 - \frac{\Delta P_1}{\Delta P_2}} (1 - \phi_2)^2 + \chi_{12} (1 - \phi_2)^2
\]

(1.1)

The addition of low molecular weight soluble compounds to crystalline polymers results in a melting point depression. In this case if one assumes \(\Delta P_1 = 1\) and \(\Delta P_2 = \omega\) (\(\Delta P_1\) and \(\Delta P_2\) are the degree of polymerisation for components 1 and 2), the equation (1.1) reduces to equation (1.2) and allows one to determine melting point depression by the following expression:

\[
\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{RV_2}{\Delta H_2 V_1} \left[ (1 - \phi_2) - \chi_{12} (1 - \phi_2)^2 \right]
\]

(1.2)

where \(\chi_{12}\) is the interaction parameter

\(T_m\) the experimental melting point

\(T_m^0\) the equilibrium melting point

\(\Delta H_2\) the heat of fusion of 100% crystalline polymer per mole of repeat unit

\(V_1\) the molar volume of diluent

\(V_2\) the molar volume of polymer repeat unit

and \(\phi_2\) the volume fraction of crystalline polymer.

Melting point depression data for solute-polymer blends is an accepted method for the determination of the heat of fusion (\(\Delta H_f\)) for the
crystalline portion of semicrystalline polymers. Calorimetric data of the polymer yield $\Delta H_f$; thus, with the $\Delta H_2$ data of the solute-polymer blend from equation (1.2), the degree of crystallinity can be determined.

The utility of the melting point depression to calculate the interaction parameter was demonstrated by Nishi et al (29,30). This method which provides for calculation of $\chi_{12}$, has definite importance and will be summarised here.

For polymer mixtures, $\Delta P_1$ and $\Delta P_2$ are very large (i.e. $\Delta P_1 \approx \alpha$ and $\Delta P_2 \approx \alpha$), thus equation (1.1) reduces to

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{RV_2}{\Delta H_2 V_1} \chi_{12} (1 - \phi_2)^2$$

(1.3)

Equation (1.3) indicates that a negative $\chi_{12}$ will yield melting point depression. With a positive interaction parameter, the theory predicts that a melting point elevation would result, as pointed out by Nishi and Wang (29). It should be noted that a positive $\chi_{12}$ will most probably result in phase separation due to the unfavourable thermodynamic situation for high molecular weight polymer mixtures.

In equation (1.3), $\chi_{12}$ and $\Delta H_2$, present as a ratio, cannot be determined simultaneously from calorimetric measurements. In order to alleviate this experimental problem, Nishi and Wang suggested the following approach: The interaction parameter $\chi_{12}$ was assumed to be of the form

$$\chi_{12} = \frac{BV_1}{RT}$$

(1.4)

where $\beta$ is the polymer-polymer interaction energy density. Equation (1.3) then reduces to

$$\frac{1}{\phi_1} \left[ \frac{1}{T_m} - \frac{1}{T_m^0} \right] = -\frac{BV_2 \phi_1}{\Delta H_2 V_1}$$

(1.5)
Recasting the data in the form of variable equal to \((1/T_m - 1/T_m^0)/\phi_1\) and \(\phi_1/T_m\) allows \(B\) to be calculated from the slope of a plot of these variables; then \(\chi_{12}\) can be determined. This procedure allows one to average experimental data graphically. The calculation of \(\chi_{12}\) from data on a single blend is possible (with \(T_m^0\) and \(\Delta H_2\) predetermined), but not as accurate.

This analysis indicates that a melting point depression of a crystalline polymer in a polymer blend implies miscibility of the diluent with the non-crystalline part of the system and allows for the calculation of the interaction parameter. In using the analysis for melting point depression to predict \(\chi_{12}\), it must be recognised that a polymeric diluent in a crystalline polymer can alter the spherulite dimensions. As the melting point is influenced by the spherulite size, corrections for this variable will be necessary to obtain more accurate \(\chi_{12}\) values.

If two different crystalline polymers are miscible at a high temperature they will crystallise upon cooling. The melting temperature of each crystalline polymer will be expressed (7) as equation (1.6) and (1.7) using the form of equation (1.3):

\[
\frac{1}{T_m^1} - \frac{1}{T_m^0} = -\frac{R V_1}{\Delta H_1 V_2} \chi_{12} \phi_2^2
\]  
(1.6)

\[
\frac{1}{T_m^2} - \frac{1}{T_m^0} = -\frac{R V_2}{\Delta H_2 V_1} \chi_{12} \phi_1^2
\]  
(1.7)

The melting temperature of each polymer will coincide at a certain volume fraction \(\phi_{1,e}\) and the eutectic temperature \(T_{m,e}\) will be observed:

When \(T_m^1 = T_m^2 = T_{m,e}\) \(\phi_1 = \phi_{1,e}\) and \(\phi_2 = \phi_{2,e} = 1 - \phi_{1,e}\)

then subtraction of equation (1.7) from equation (1.6) gives
\[
\frac{1}{T_{m,2}^0} - \frac{1}{T_{m,1}^0} = \frac{R \, V_1 \, X_{12}}{\Delta H_1 \, V_2} \left[ \frac{\Delta H_1}{\Delta H_2} \left( \frac{V_2}{V_1} \right)^2 \phi_{1,e}^2 - \phi_{2,e}^2 \right]
\]

or,
\[
\frac{\Delta H_1}{\Delta H_2} \frac{V_2}{V_1} \left( \frac{1}{T_{m,2}^0} - \frac{1}{T_{m,1}^0} \right) = \phi_{1,e}^2 \left[ \frac{\Delta H_1}{\Delta H_2} \left( \frac{V_2}{V_1} \right)^2 - 1 \right] + 2\phi_{1,e} - 1
\]

If \( \frac{\Delta H_1}{\Delta H_2} = \left( \frac{V_1}{V_2} \right)^2 \), then
\[
\phi_{1,e} = \frac{1}{2} \left[ 1 + \frac{\Delta H_1}{R \, V_1 \, X_{12}} \left( \frac{1}{T_{m,2}^0} - \frac{1}{T_{m,1}^0} \right) \right]
\]

Figure (1.4) shows model calculations for a crystalline-crystalline polymer mixtures with eutectic points \( T_{m,e} \) and \( \phi_e \) for two different conditions (7).
polymer mixture with eutectic points. The possibility of eutectic crystallisation has been realised for ordered alloys structure.

1.5.3 Crystallinity (31)

On the basis that crystalline polymers are a mixture of crystalline and amorphous regions, the fraction of the material which is crystalline, is called the degree of crystallinity. In this simple concept, the degree of crystallinity or simply crystallinity, is readily determined from a measured property. Therefore, the crystallinity uniquely specifies the physical composition, i.e. the relative amounts of crystalline and amorphous regions of a sample. In other words crystallinity indicates the fraction of the total material considered to be in crystals.

Since the structure of a sample may be affected by details of the crystallisation process, it is necessary to distinguish carefully between crystallinity and crystallisability. The crystallinity of a sample is the degree of order (either defined by a particular measurement or in terms of a specific model) at a given temperature actually attained under the conditions of crystallisation. The crystallisability is the maximum crystallinity that a sample could attain at the same temperature irrespective of crystallisation conditions. For example, chemically and sterically pure, straight-chain homopolymers are highly crystallisable although their crystallinity is rarely so high. Crystallisability, therefore, is equilibrium crystallinity. For a given sample, it is a function of temperature only. Crystallisability is determined by the chemical structure of a polymer, crystallinity by the physical conditions of crystallisation.

The problem in crystallinity determinations is two fold: (a) specification of experimental techniques capable of responding to differences in crystallinity and (b) relation of an experimentally determined crystallinity with the physical structure of the sample studied. The first step is relatively straightforward: for a variety
of techniques, experimental crystallinity may be defined as if the sample consisted solely of a mixture of amorphous and crystalline regions. An experimental crystallinity thus defined is valid as a parameter characterising a polymer sample even though its interpretation in terms of solid-state structure is invalid. An absolute definition of crystallinity as the single parameter characterising the solid-state structure is rarely justified. The second problem in crystallinity determinations, that of the relation of experimentally determined crystallinity to structure, is much more complicated. There are a number of chemical factors which affect crystallisability. Chemical factors are amenable to theoretical evaluation. The theories are concerned mainly with crystallisability, not crystallinity. They are applicable to real systems only insofar as the environmental factors do not seriously limit the crystallinity attained.

In the past crystallinity was used mainly to characterise crystalline-crystalline polymer blends rather than as a single parameter to assess the miscibility of the blends, because it was observed that miscible as well as immiscible blends showed linear relationship of crystallinity with composition. Practically, one is usually less interested in an absolute crystallinity than in a comparative measurement which indicates changes with compositions for correlation with other properties with the same thermal and mechanical treatments. Hence, any method sensitive to the presence of order, if used systematically, is valid. No single crystallinity method may claim superiority over others with regard to the degree of crystallinity, although some methods have obvious experimental advantages. For example, density measurements may be made rapidly and routinely. Conversion of density to crystallinity is rapid. This is probably the simplest and most applicable method for estimations of crystallinity.
1.5.4 Co-crystallisation (2,5,27)

The phenomenon of co-crystallisation or isomorphism is a rare situation in the case of crystalline-crystalline polymer blends. This involves the ability of the components of a mixture to co-crystallise. These components cannot then demix since portions of each are anchored in the ordered regions in which they both participate. The co-crystallisation phenomenon is exhibited by different species which crystallise over a range of concentration with a common crystal lattice. The conditions (which need not be simultaneously satisfied) for isomorphism for crystalline-crystalline polymer blend systems are:

i) chemical similarity of the macromolecules,
ii) physical similarity (size) of the macromolecules,
iii) physical similarity of the backbone chains,
iv) practically equal cross-sectional dimensions,
v) similarity of the forces of attraction
vi) similarity of conformation and configuration.

Two different types of isomorphism in macromolecules have been experimentally observed. One of them is repeating chain unit isomorphism common in crystalline copolymers. This is a trivial situation where isomorphism obviously occurs with chemically identical polymers containing different isotopes. Substitution of deuterium for hydrogen in polyolefins results in isomorphic behaviour. The simplest repeating chain unit isomorphous polyblends are the mixture of polyethylene with deuto-polyethylene and the mixture of polypropylene with deuto-polypropylene. The other type is polymeric chain molecular isomorphism. This is believed to be possible when the polymer chains (blend) or monomer units (copolymer) are similar in conformation and size in the crystalline state. Only isomorphism of different polymer chains will be reviewed here.

Poly (vinyl fluoride)-poly (vinylidene fluoride) exhibits isomorphic characteristics at all compositions. The crystalline phase structure of the blend is identical with that of poly (vinyl fluoride) and one of the crystalline structures of poly (vinylidene
fluoride) (32). The melting point curve as a function of composition shows no minimum.

Isomorphism of poly (isopropyl vinyl ether) with poly (sec-butyl vinyl ether) was observed at all concentrations by Natta et al (33). Mixtures of isotactic poly (4-methylpentene) with isotactic poly (4-methylhexane) were isomorphic only in the range of 0-25 wt% of either component (33). The unit cells of isotactic poly (4-methyl-1-pentene) and isotactic poly (4-methyl-1-hexene) are tetragonal, and the chains have a helix conformation with 3.5 monomer units per pitch. The poly (vinyl alkyl ethers) cited above likewise have tetragonal unit cells with identical pitch of the helices (3.4 monomer units). Therefore, for both of these isomorphic systems, the chain axes and chain symmetries are identical, as expected for isomorphic behaviour.

Tordella and Dunion (34) studied blends of ethylene/vinyl acetate copolymers and paraffin wax. They concluded from the low-angle X-ray diffraction data that cocrystallisation of paraffin wax with the ethylene sequences of the copolymer occurred.

Table 1.2 gives the list of polymers exhibiting miscibility with isomorphic polymer blends.

### TABLE 1.2

<table>
<thead>
<tr>
<th>Miscible Polyblends</th>
<th>Method of Miscibility Determination</th>
<th>Comments</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Poly(vinyl fluoride)-poly (vinylidene fluoride)</td>
<td>Crystal phase structure</td>
<td>True isomorphism; melting point curve shows no minimum. Lattice constants intermediate between those of PVF and PVF₂</td>
<td>32</td>
</tr>
<tr>
<td>2. Poly(isopropyl vinyl ether)-poly(sec-butyl vinyl ether)</td>
<td>Crystal phase structure</td>
<td>True isomorphism; like the above, the crystal phase structure is homogeneous</td>
<td>33</td>
</tr>
<tr>
<td>3. Poly(4-methylpentene)-poly (4-methylhexene)</td>
<td>Crystal phase structure</td>
<td>Isomorphic only at 0-25 wt% of each component</td>
<td>33</td>
</tr>
<tr>
<td>4. Ethylene/vinyl acetate copolymer-paraffin wax</td>
<td>X-ray diffraction</td>
<td>Isomorphism confirmed by X-ray diffraction; the ethylene sequences of the copolymer crystallise if the ethylene content ≥60 wt%</td>
<td>34</td>
</tr>
</tbody>
</table>
1.5.5 Crystallisation (27)

Earlier the potential of achieving miscible polymer blends in which both the components were crystalline was believed to be quite low due to the heat of fusion which would have to be overcome to achieve the necessary thermodynamic criteria for mixing. Later it is found that in a miscible blend the crystalline components will generally retain the ability to crystallise. The crystallisation behaviour, including crystallisation kinetics of immiscible polymer blends is expected to be different from their individual components. The primary change may be observed with the crystallisation kinetics and a secondary change with the lowering of the crystalline melting point as with polymer and low molecular weight diluent mixtures. However in the cases of miscible polymer mixtures, blends may display certain characteristics similar to its unblended crystalline components; for example, blends may show similarity in crystalline state (i.e. crystal lattice) with its crystalline components. Homogeneous crystallisation can be expected in case of miscible polymer blends whereas heterogeneous crystallisation is obvious in case of immiscible polymer blends. It is believed that crystallisation kinetics is mainly responsible for this kind of crystallisation behaviour. So crystallisation behaviour is quite important for the determination of miscibility.

Crystallisation kinetics can be studied by utilising the spherulitic growth rate equation to predict the effect of a miscible polymer diluent on the crystallisation rate of another component. The spherulitic growth rate equation is:

\[ G = G_0 \exp \left( -\Delta F^*/RT \right) \exp \left( -4 b_o \sigma_e T_m^0/\Delta H_f (\Delta T) k_b T \right) \]  \hspace{1cm} (1.9)

where \( \Delta F^* \) is representative of the barrier restricting polymer diffusion to the crystallising surface and has been suggested by Hoffman and Weeks (35) to be satisfied by the Williams, Landel, and Ferry equation:
\[ \Delta F^* = \frac{4120T}{51.6 + T - T_g} \]

The other variables are

- \( b_0 \): monolayer thickness,
- \( \sigma \): lateral interfacial free energy,
- \( \sigma_e \): interfacial free energy of the chain-folded surface,
- \( T_m^0 \): equilibrium melting temperature
- \( \Delta H_f \): heat of fusion
- \( T \): crystallisation temperature
- \( k_B \): Boltzmann constant

and \( \Delta T = (T - T_m) \)

\( G \) is equal to the radial growth of the spherulite and, thus, is \( \frac{dr}{dt} \).

One further modification of the spherulitic growth rate equation must be made to correct for concentration changes. Equation (1.9) must be multiplied by \((1 - w_d)\), where \( w_d \) is the concentration of the diluent in the weight fraction.

To apply the spherulitic growth rate equation in case of crystalline-crystalline system for projecting the crystallisation kinetics an assumption which would require correction is that the glass transition temperature, \( T_g \) remains constant in equation (1.10)

1.6 Rheology and Processing of Polyolefin Blends

1.6.1 Rheological characteristics (8)

The main rheological characteristics of molten polyolefin blends consist of shear rate- or stress-dependent viscosity. Little is known about the tensile melt viscosity of polyolefin blends in spite of the importance this characteristic has in the development of blow moulding and film extrusion grades of blends.
The viscosity of molten polyolefins and their blends has been studied extensively, including a comprehensive interlaboratory programme of investigation, using routine capillary or rotational viscometers and laboratory mixers. However, the form of presentation of the results, with few exceptions, does not render them applicable for engineering use. The most appropriate form for this application seems to be the logarithmic parabola approximation for the viscosity curve:

\[ \log n = B_0 + B_1 \log \dot{\gamma} + B_2 \log^2 \dot{\gamma} \]  \hspace{1cm} (1.11)

where \( n \) is melt viscosity in poises and \( \dot{\gamma} \) is shear rate in reciprocal seconds. The term \( B_0 \) is related to a standardised viscosity at \( \dot{\gamma} = 1 \text{ sec}^{-1} \), that is, \( n^0 = 10^0 \), and \( B_1 \) is a measure of the shear rate dependence of the viscosity corresponding to the power law exponent when \( B_2 = 0 \). The approximation is usually carried out by applying the least-squares regression technique to the experimental data on any engineering calculator. One may easily extend the approximation to include the effects of temperature, hydrostatic pressure, and even composition by introduction of additional terms accounting for these effects and their interactions. From the viewpoint of engineering applications (both composition selection and scale up of melt-mixing processes) the literature data suffer from two drawbacks: 1. they are in the form of graphs, which show the magnitude and the shape of the \( n(\dot{\gamma}) \) function but these depend nonlinearly on the composition of a blend; 2. the data published thus far do not account for the melt flow behaviour of some polyolefin blends characterised by two or more flow mechanisms. The solution to the problem, in part, appears to be with the use of the logarithmic parabola approximation parameters, for example, \( B_0, B_1 \) which represent the melt viscosity, \( n^0 \) and its rate dependence, \( n \) respectively (i.e. \( B_1 = n-1 \)). Since the confidence limits for the parameters can be readily estimated, an unambiguous comparison of the 'rheology' (that is, melt viscoelasticity within the engineering applications range) of polyolefins and their
blends is feasible therewith. Also the composition-dependence evaluation executed with the approximation parameters is consistent for different viscometers and various viscosity measurements employed. The treatment suggested here for the composition dependence of shear viscosity, might also be applied to that of the tensile melt viscosity.

The experimental values for shear stress ($\sigma_s$) and apparent viscosity ($\eta$) have allowed the calculation of the following equations parameters:

$$\log \eta = A_0 + A_1 \log \sigma_s + A_2 \log^2 \sigma_s + A_3 \log^3 \sigma_s$$  (1.12)

This model has proved to hold for $\eta = f (\sigma_s)$ curves of polyolefins and their blends (36). This is a very similar form of equation as equation (1.11).

1.6.2 Blending laws

The standardised measures of melt viscosity are obviously convenient for predicting the rheological characteristics of a blend of selected composition from known characteristics of the components. In order to perform such a feat some reliable blending law has to be available.

In spite of many publications on blending rules for polyethylenes and polyethylene-wax blends only simple linear or logarithmic mixing rules are available for use with polyolefin blends over the range of viscoelastic characteristics of interest to process and product engineers. The logarithmic mixing rule, introduced for guidance in blending low-density polyethylenes differing in melt flow index (MFI), is illustrated in Figure 1.5 (37).

Apparently, the only 'engineering' type blending law available is that developed by Dobrescu (38) for polyethylene blends. On the
basis of the analysis of viscosity-composition dependence for polyethylene blends the following equation has been proposed to describe the dependence of blend viscosity on the viscosities of components and composition:

\[ \log \eta = \phi_1 \log \eta_1 + \tau \phi_1 \phi_2 + \phi_2 \log \eta_2 \]  

(1.13)

where \( \eta, \eta_1 \) and \( \eta_2 \), are the viscosities of the blends and their components respectively at constant shear stress, \( \phi_1 \) and \( \phi_2 \) are the volume fractions of components, \( \tau \) is a parameter which stands for 'packing coefficient' \( \tau = 0 \) for HDPE/HDPE blends and \( \tau \geq 0 \) for HDPE/LDPE blends, depending on component viscosities and their ratio. The value of parameter \( \tau \) may be calculated from experimental flow curves for pure components and for the blend consisting of equal volume fractions of both components. This value allows then calculation of viscosity for blends of other compositions.
Recently Dobrescu (39) has proposed another equation which is in the following form:

\[ \log \eta = \phi_1^2 \log \eta_1 + 2T \phi_1 \phi_2 \left( \log \eta_1 \log \eta_2 \right)^{\frac{1}{2}} + \phi_2^2 \log \eta_2 \quad (1.14) \]

Identical results can be obtained using this equation. According to Dobrescu the utilisation of this equation is much more correct. Besides, for the first model (equation 1.13) the parameter \( T \) can be positive or negative and the sign change is not correlated with the nature of the blend components. The second model (equation 1.14) ensures positive values of \( T \) for all blends investigated. For HDPE/LDPE blends, the parameter \( T \) in the equation (1.14) may be correlated with component viscosities using an equation of the form:

\[ T = 0.53613 + 0.72537S - 0.21682S^2 \quad (1.15) \]

where \( S = \log \eta_{\text{HDPE}} / \log \eta_{\text{LDPE}} \)

The agreement between calculated and experimental values is satisfactory. Good results have been obtained for HDPE/HDPE, HDPE/LDPE and LDPE/LDPE blends.

1.6.3 Behaviour of polyolefin blends in processing (8,2,40)

The large scale production of polyolefin blends is carried out in two stages: dispersive mixing (typically involving melting and kneading) followed by laminar mixing. The spatial distribution and the initial component grain size depend on the dispersive mixing efficiency. Hence, the effectiveness of laminar mixing in the production of a blend depends to a large degree on the dispersive mixing stage. Laminar mixing is typically carried out in extruders or intensive mixers. Here the interfacial area between components of the mixture is increased in proportion to the total amount of shear strain which is imparted to the fluid substrate. Better laminar mixing is realised if the viscosities of the components of
the blend are reasonably well matched. Such mixers operate by moving their inner metal surfaces relative to each other. Shear strain is imparted to the polymer mixture if it adheres to the moving walls of the mixer. If the components of the mixture have different viscosities, the more fluid component will take up most or all of the imparted strain, particularly if it is the major component of the mixture. Thus it is easy to melt blend a minor fluid component with a major, more viscous component, but a minor viscous component may swim in a more fluid sea of the major component without being dispersed. Similar considerations apply if there are serious mismatches in the melt elasticities of the components of a mixture.

The processibility of the polyolefin blends is influenced by some factors. Processibility is a result of blend structure, which in turn, depends on the microstructure (average molecular weight), molecular weight distribution, and branching and as well as macrostructure (uniformity or dispersion) of the components.

The miscible blend will have a transparent melt and will rheologically behave as if it were a pure material. Its viscosity is expected to change monotonically with composition and to exhibit composition average dependencies on shear rate and temperature. Because of favourable thermodynamics, miscible mixtures are easily formed by simple melt blending such as occurs in a laboratory size single screw extruder, and once formed these single melt phase materials behave like homopolymer materials.

Immiscible mixtures, however, always have multiple melt phases regardless of the intensity of mixing. The presence of multiple phases in the melt can lead to some unexpected blend viscosity behaviour since the phases are comprised of essentially pure components, and each phase, therefore, retains the rheological characteristics of the pure component. Both viscosity minima and viscosity maxima with composition have been expected, and the viscosities of immiscible mixtures are generally found to be functions of both shear stress and composition. This latter observation has been
suggested to be an indicator of immiscibility.

The behaviour of a blend during processing and the properties of its products are obviously influenced by mechanochemical processes and the melt shearing in the processing equipment. The shearing history effects are obscured by an interaction with the thermorheological phenomena, while the former might be reasonably controlled with adequate stabilisers.

In attempts to evaluate structure-property relationships and their dependence on processing, one should realise that blends manufactured from commercial polyolefins pose additional obstacles. Property-molecular weight relationships depend significantly on the polyolefin type: linear polyethylenes that are nominally the same but originate from different polymerisation processes when blended with an LDPE, yield two families of blends.

On the other hand, LDPEs used in the manufacture of blends are usually delivered in granulate form, which is prepared (not via melt mixing followed by granulation) by mixing granulates from various batches. Gross nonuniformity of such granulates may result. A polyolefin blend manufactured from LDPE similar to that would display, during processing, excessively high extrudate swelling and low critical shear rate.

Processing leads to transformations in the supermolecular structure of the blends. These transformations might be divided into three main types:

1. Structure changes due to orientation effects, which may be further influenced by the thermal history of the melt. The differences in product performance characteristics due to orientation effects may result for injection and blow moulded samples from the same blend.

2. Structural changes due to generation of fibrillar and/or lamellar forms.
3. Redistribution of the blend components due to shearing flow. This type of structural change leads to difficulties in processing by weakening the weld lines in mouldings.

Obviously these transformations often act in parallel and are accompanied by a homogenisation effect, leading to a narrowing of blend molecular weight distribution and generation of branched structure.

1.7 Properties of Polyolefin Blends (28)

All new materials attract interest on the basis of their property-processing-cost performance. With regard to properties, polyolefin blends may be expected to exhibit any of the three possibilities shown in Figure (1.6):

![Diagram showing possible patterns of property dependence on blend composition. The classification termed "additive" includes a range of values but does not exhibit maxima or minima.](image-url)
Perhaps the most commonly anticipated property versus composition relationship is the concept of "additivity". It means that when component A is mixed with component B, the blend has a property which is some weighted average of that property for component A and component B. In a general sense, there is no need to be concerned here with the exact form of the weighting function involved. Such averaging of properties has many potential benefits for formulating a new material. For example, component A may have a modulus which is too high for a particular application whereas component B may have a modulus which is too low for this application. Thus if blends of A and B have moduli which are intermediate to those of component A and B, then the possibility exists for formulating a blend which meets the precise modulus requirements of the particular application. Modulus is a property that depends on the degree of crystallinity and can be expected to obey some additivity relationship for blends where the weighting functions of composition will be sensitive to phase morphology.

In many cases, important properties like tensile strength and elongation at break may not follow an additive relationship. Sometimes it is found that these properties exhibit a minimum when plotted versus blend composition such that many mid-range blends have tensile strength or elongation at break that are less than either pure component. This situation usually arises from a poor degree of interfacial adhesion between components that provides a multiplicity of defects for early failure. This situation is the real dilemma that prohibits a more general use of blending two components. Such behaviour is often the reason for terming two components "incompatible".

A very intriguing possibility, although less frequently observed, is when blends of component A and B show "synergism" with respect to some property. Here it is referred to the situation where some property, such as tensile strength and elongation at break, for the blend is larger than that for either pure component A or B. Clearly, such a maximum in the plot of property versus composition is not predicted by any additivity relationship. This kind of behaviour is known to be a rare occurrence and offers unique possibilities when it exists.
The above discussion was concerned with how a single property depends upon blend composition. However, the success of a new material depends on more than one such factor. In this context it is better to identify two general situations which provide a boost for blending two components for commercial applications. The first of these is an advantageous 'combination' of properties. For example, component C may have a very desirable high mechanical property but its processing characteristics may be very poor. On the other hand, component D may have very good processability but poor mechanical property. Therefore it may be of interest to attempt to combine the high mechanical property of component C with the good processability of component D, although there will generally be a compromise involved. Specifically, the blend may be expected to have poorer mechanical property than that from component C and not process as easily as component D, but nevertheless the blend may have adequate combination of the desirable attributes for certain applications that neither pure component C nor pure component D alone could meet. Clearly, the exact relationship between properties - in this example, mechanical property and processability - will be critical to the success of the blend.

A second general reason for interest in blending for commercial products is 'cost dilution'. In this situation, component E may have excellent properties and, in fact, greater levels of some properties than are needed for certain applications. However, the price of component E with a cheaper component F may reduce the properties to a level still acceptable for the particular application but may bring the price of the blend to within a range where it can be competitive in this market. Thus, in these situations, blending can be an attractive means to engineer a material so that the user does not have to pay for more than he needs. This is one of the most strong driving forces for developing blend products.
1.8 Usefulness of Miscible Polyolefin Blends (27)

1.8.1 Specific advantages of one-phase behaviour

The primary advantage with miscible blends compared to the immiscible blend counterparts will be the assurance of mechanical compatibility. The simplified average of ultimate mechanical properties is not always the observed or expected case; the blend can indeed attain ultimate mechanical properties higher than the components.

In fabrication, miscible blends will also offer advantage over immiscible blends in regard to surface characteristics and weld-line strength. These processing variables are more commonly encountered in injection moulding (due to the higher shear rates), as opposed to extrusion or compression moulding. During the injection moulding process, very high shear rates are present during the mould-injection step. This can result in migration of the lower viscosity phase to the surface, thus altering both the surface appearance (i.e. uniformity) and the overall properties. Also, in the moulding process, the use of multiple gating or complex shapes can result in cooled surfaces meeting in the mould to form what is commonly referred to as a weld-line. In blends exhibiting two-phase behaviour, the weld line strengths are generally inferior to single-phase blends.

Generally, two-phase blends have utility only when one phase is the major continuous phase. With miscible blends, useful and commercially viable properties are often possible over the entire composition range. The versatility of matching the price/performance requirements of specific applications allows for a myriad of different products from combinations of the two miscible polymers.

1.8.2 Importance of the interface

For two-phase blends systems, the interfacial adhesion between the respective phases governs the ultimate mechanical properties. For polymer components having limited affinity for each other, the interface represents a flaw yielding ultimate properties significantly
lower than that expected from component values.

Precise physicochemical characterisation of solid surfaces and interfaces is an extremely difficult task, and interpretations are generally not straightforward. There is no appreciable amount of surface-active species in the case of pure materials. The molecular forces pertaining to surface molecules are similar in nature to those pertaining to the molecules in the bulk of the system.

In the field of polymer-polymer miscibility, the existence of a finite interfacial tension is usually taken as an indication of immiscibility. If the interfacial tension is large and the system is highly immiscible, no adhesion, and hence no reinforcement, is achieved between the two polymers. That is immiscibility goes hand to hand with finite interfacial tension and is accompanied by diminished adhesion.

For phase-separated systems, the characteristics of the interfacial regions generally govern the ultimate mechanical properties (e.g. strength and toughness) attainable with the blend. As is generally the case with two-phase blends, poor adhesion leads to a myriad of flaws located at the interfacial regions, resulting in much lower ultimate properties than expected from averaged properties. If indeed the polymers are miscible, excellent adhesion is expected, providing sufficient temperature and pressure are employed to allow for molecular mixing at the interface.

1.8.3 Compatibility in two-phase behaviour

In theory, for two-phase blends systems, some intermixing of the blend components at the interfacial regions should occur; however, in extreme cases of immiscibility, the degree predicted by phase diagrams would be negligible. For cases where partial or limited miscibility occurs, interpenetration of one molecular species into and beyond the interfacial region would be expected to yield improved mechanical compatibility. These cases present a gradient of composition across the interfacial regions and reduces the magnitude of structural flaws imposed by the interface.
1.9 The Present Work

Currently it is appreciated that there is a need for the study of the miscibility of crystalline polyolefins; thus the present work has been developed into a research programme to understand the basic concept of miscibility of crystalline polyolefins. Low-density polyethylene, high-density polyethylene and linear low-density polyethylene have been used in this study. An approach has been made for better understanding of these crystalline polyolefins and their mixtures via a newly developed thermal analysis technique.

There has been an attempt to understand the behaviour and structure of the new polymer, linear low-density polyethylene by its partial characterisation.

Finally films have been produced from polyolefins and their mixtures to obtain modified properties suitable for film exploitation.
CHAPTER 2
MATERIALS AND EXPERIMENTAL TECHNIQUES

2.1 Polymers and their Blends

2.1.1 Polymers

The low-density polyethylene (LDPE) was Shell 25-010F (Shell Chemicals, UK Ltd); the high-density polyethylene (HDPE), Unifos DMDS-0905 (Unifos Kemi AB, Sweden); and the linear low-density polyethylene (LLDPE), Dowlex Resin 2045 (Dow Chemical Company, USA).

2.1.2 Melt blending of polymers

Three sets of binary blends were prepared by the following methods; composition and sample codes are given in Table 2.1.

TABLE 2.1
Sample Codes and Composition of Polyethylene Blends

<table>
<thead>
<tr>
<th>Set No</th>
<th>Composition (Wt%)</th>
<th>100/0</th>
<th>70/30</th>
<th>50/50</th>
<th>30/70</th>
<th>0/100</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LDPE/HDPE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sample code</td>
<td>LD</td>
<td>LD/HD-70/30</td>
<td>LD/HD-50/50</td>
<td>LD/HD-30/70</td>
<td>HD</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Set No</th>
<th>Composition (Wt%)</th>
<th>100/0</th>
<th>70/30</th>
<th>50/50</th>
<th>30/70</th>
<th>0/100</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>LLDPE/HDPE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sample code</td>
<td>LLD</td>
<td>LLD/HD-70/30</td>
<td>LLD/HD-50/50</td>
<td>LLD/HD-30/70</td>
<td>HD</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Set No</th>
<th>Composition (Wt%)</th>
<th>100/0</th>
<th>70/30</th>
<th>50/50</th>
<th>30/70</th>
<th>0/100</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>LDPE/LLDPE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sample code</td>
<td>LD</td>
<td>LD/LLD-70/30</td>
<td>LD/LLD-50/50</td>
<td>LD/LLD-30/70</td>
<td>LLD</td>
</tr>
</tbody>
</table>
2.1.2.1 Two-roll mixing

Pellets of the two polymers were mixed thoroughly and then blended on a laboratory size two roll mill (300 mm x 150 mm) at 170°C for 15 minutes. In order to give the same thermal and shear history, the pure polymers were also subjected to the same treatment. The milled samples were then compression moulded at 150°C in a Moore hydraulic press to a dimension of 225 mm x 225 mm x 2 mm.

2.1.2.2 Extruder mixing

Pellets of the two polymers were mixed thoroughly and then blended on a laboratory size single screw extruder (35 mm Bone extruder) at 220°C. The extrudate was hauled-off through a water cooling bath and pelletised in a granulator. The pure polymers were also given the same treatment as blends.

2.2 Molecular Structure Characterisation

2.2.1 Molecular weight and molecular weight distribution

Gel permeation chromatography (GPC) technique is used to measure the molecular weight and the molecular weight distribution of the polyethylene sample. This work has been performed in the Polymer Supply and Characterisation Centre (PSCC) at Rubber and Plastics Research Association of Great Britain (RAPRA).

The Gel Permeation Chromatography technique is a method of fractionation based solely on molecular size of polymer molecules, not on chemical constituents. The GPC analysis consists of two steps; firstly the fractionation and secondly the isolation of fractions. In the GPC separation a solution of the polymer is passed through a column or a series of columns containing beads of a porous crosslinked polystyrene gel (StyrageL). Three columns connected in series packed with the gel containing pores of diameter $10^6$ Å, $10^4$ Å and 500 Å respectively were used in this work. This gel is completely immersed in the solvent with the exclusion of
any gases. As the solvent surrounding the gel and filling the column is replaced by the polymer solution, the polymer molecules are free to move into and out of the volume contained within these pores. With the passage of the polymer solution through the column a separation with size of the constituent polymer species takes place. The very large molecules will only have a small pore volume available to them and will hence be eluted from the column first. The very small molecules will enter most of the gel pores and will be eluted last, because they have a longer effective path length. The concentration of the species eluting from the column is measured using a differential refractometer. A schematic diagram of a typical commercially available gel-permeation chromatograph is shown in Figure 2.1 (41).

FIGURE 2.1 Apparatus for gel-permeation chromatography (41)
The final product from the GPC analysis is the chromatogram. This trace shows the difference in refractive index of the eluant from the sample columns to that from the reference columns. The reading is a function of the concentration and refractive index of the dissolved species eluting. The chart marker pulses on the trace give a measure of the elution volume, each mark representing 0.5 ml. The 'elution volume' is the quantity of solvent that has passed through the sample columns from the point of sample solution injection. The species eluting first in the column would be the highest molecular weight material in the sample. Subsequent eluant carries material of progressively lower molecular weight. With suitable calibration the elution volume scale is transposed to a molecular weight scale. The species eluting after the main material are the impurities present in the sample.

Before a chromatogram may be successfully interpreted, a suitable baseline must be constructed. Normally this consists of joining the portions of the chromatogram occurring prior to the sample output and after the impurity peak has eluted.

Once the baseline is fixed the ordinate values for the chromatogram may be interpolated. These chromatogram 'heights' are proportional to the weight concentration of solute. By taking the chromatogram height for equal increments of elution volume and dividing by the sum of all such heights, the resulting values will be weight fraction of the species eluting at that elution volume, dw/dv. This procedure is termed normalisation; the total weight of species in the chromatogram being equated to unity.

Since the elution volume gives a measure of the size of the dissolved molecule, the exact correlation is readily achieved through use of a standard narrow molecular weight distribution sample having a known molecular weight at its peak elution volume. Polystyrene is used as calibration standard. Now a method of indirect calibration is required i.e. to convert the polystyrene calibration to one applicable to the measured polymer. The GPC
separation is determined by the size and shape of the polymer molecule in solution, its hydrodynamic volume. Different polymers of the same molecular weight will have different conformations in the same solvent. The hydrodynamic volume of a polymer is measured as \([\eta_i]M\), where \([\eta_i]\) = intrinsic viscosity and \(M\) = molecular weight. This parameter forms the basis of the "universal" calibration.

The calibration plot is then best considered as \(\log[\eta_i]M\) versus elution volume. The conversion from one polymer to another involves the use of the empirical relationship between \([\eta_i]\) and \(M\), the Mark-Houwink-Sakurada (M-H-S) equation,

\[
[\eta_i] = KM^a
\]  

(2.1)

It is apparent from this equation that the hydrodynamic volumes of polymers 1 and 2 are given by:

\[
[\eta_i]_1M_1 = K_1 M_1^{\alpha_1+1}
\]  

(2.2)

\[
[\eta_i]_2M_2 = K_2 M_2^{\alpha_2+1}
\]  

(2.3)

Hence by equating hydrodynamic volumes of polymers 1 and 2 from equations (2.2) and (2.3), the molecular weight of polymer 2 is obtained in terms of polymer 1 from the relationship

\[
\log M_2 = \left(\frac{1 + \alpha_1}{1 + \alpha_2}\right) \log M_1 + \frac{1}{1 + \alpha_2} \log \left(\frac{K_1}{K_2}\right)
\]  

(2.4)

Mark-Houwink constants used for polymer-solvent systems at 140°C for the solvent 1,2 Dichlorobenzene stabilized with 2,6-di-tert-butyl-p-Cresol are as follows:
After transposing the elution volume scale to the molecular weight scale, to give the true relationship the ordinate has to be changed from the weight fraction per elution volume $dw/dv$ to weight fraction per log molecular weight increment, $dw/d \log M$. This is accomplished by multiplying the normalized chromatogram ordinate by the reciprocal of the gradient of the calibration curve corresponding to the appropriate elution volume i.e.

$$
\frac{dw}{d(\log M)} = \frac{dw}{dv} \left[ \frac{dv}{d(\log M)} \right]
$$

A plot of $dw/d \log M$ versus $\log M$ then gives the true differential molecular weight distribution curve, which is the end product of the GPC analysis. From this curve the molecular weight parameters $M_n$ (number average molecular weight), $M_w$ (weight average molecular weight), $M_z$ (z average molecular weight) and $M_v$ (viscosity average molecular weight) and hence the dispersity indices $M_w/M_n$ and $M_z/M_n$ are calculated. As an example of their calculation $M_n$ and $M_w$ are defined as follows:

$$
M_n = \sum(dw/d \log M)/ \sum [(dw/d \log M)/M]
$$

$$
M_w = \sum[(dw/d \log M)M]/\sum(dw/d \log M)
$$

All measurements whether calibration or otherwise are carried out using solutions of concentration 0.38% wt/vol of solute which are

<table>
<thead>
<tr>
<th>Material</th>
<th>$K$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>$1.38 \times 10^{-5}$ m$^3$/Kg,</td>
<td>0.70</td>
</tr>
<tr>
<td>LDPE and LLDPE</td>
<td>$5.06 \times 10^{-5}$ m$^3$/Kg,</td>
<td>0.70</td>
</tr>
<tr>
<td>HDPE</td>
<td>$5.05 \times 10^{-5}$ m$^3$/Kg,</td>
<td>0.693</td>
</tr>
</tbody>
</table>
injected for two minutes with a flow rate of 1 ml per minute. Data in the form of potential differences are recorded on a chart recorder and also on punched tape. Data points are taken every one count (0.5 ml). The chromatogram is abstracted from the tape with a computer program. All the data are then analysed using a high speed digital computer.

2.2.2 Branching

Various levels of branching are encountered in commercial polyethylenes. Since branches are normally terminated by methyl (CH₃) groups, the number of CH₃ groups per 1000 carbon atoms is frequently used as an index of the degree of branching.

Absorptions within the infrared region are due to vibrations occurring in particular structural groups in a molecule. Thus the intensity of a particular absorption may be used to obtain information about the concentration of a selected group, by application of the Beer-Lambert Law:

\[ A = k \cdot C \cdot h \]  

(2.8)

where

- \( A \) = measured absorbance
- \( C \) = concentration of the absorbing species
- \( h \) = path length of radiation through the sample
- \( k \) = a constant

The Pye Unicam SP3-200 infrared spectrophotometer was used for the determination of methyl group concentration in polyethylene. It is a double beam instrument operating in the infrared region of the spectrum. Infrared radiation from a source is divided into two beams (sample beam and reference beam) which, after passing through the sample compartment, are recombined by a rotating sector mirror. The resulting beam is directed, via the order sorting interference filters, into the entrance slit of the monochromator.
As the monochromator grating is rotated, a narrow band of wave-numbers (which are dependent upon the angle of the grating to the radiation) will be transmitted through the exit slit of the monochromator and on to the detector. The 'ratio recording' principle of photometric measurement is employed, whereby the components of the detector signal corresponding to the energies passing in the sample and reference beams are electronically ratioed, thus defining the amount of radiation which has been absorbed by the sample. A simple schematic diagram of the instrument is shown in Figure 2.2 (43).
An absorption due to \( \text{CH}_3 \) groups occurs in the infrared region at 1380 cm\(^{-1}\). However, direct accurate measurement of this absorption is not possible due to strong absorption maxima at 1370 cm\(^{-1}\) and 1350 cm\(^{-1}\). It is possible to compensate the unwanted absorption by placing a sample of a polymethylene (containing negligible \( \text{CH}_3 \) group concentration) in the reference beam. Since the thickness of the sample and reference films must match, the reference film is prepared in the form of a wedge of varying thickness.

Using a sample of polymethylene having a negligible amount of branching a film as a wedge varying from 0.07 to 0.4 mm in thickness, about 100 mm in length (tapering edge) and about 40 mm in width is prepared by the technique of Harvey and Peters (44). Uniform cross section samples in the form of melt pressed films of approximately 0.1 mm thickness are prepared from a series of samples of known methyl group concentration and from the polyethylene sample of unknown methyl group concentration.

One of the uniform films of measured thickness is placed in the sample beam of the infrared spectrophotometer and the infrared spectrum is recorded from 1250 - 1750 cm\(^{-1}\). To compensate for unwanted absorption the wedge shaped reference film is placed in the reference beam and its position is adjusted until the transmittance at 1360 cm\(^{-1}\) and 1400 cm\(^{-1}\) are approximately equal giving only a single peak at 1380 cm\(^{-1}\) when the infrared spectrum is again recorded from 1250 - 1750 cm\(^{-1}\). The same procedure is repeated for all the samples to be examined. Absorbance values for the methyl group absorptions are obtained directly in each case from the peak height using a standard chart which gives the correlation of absorbance with peak height. A calibration curve is plotted relating absorbance and concentration of the sample of known methyl group concentration, then the unknown methyl group concentration of the polyethylene sample is determined directly from the curve.
Throughout the work the infrared spectrophotometer was used in the "Spectraset" mode; as a result the double beam auto smooth mode is permanently selected. In this mode the transmittance signal response (and therefore the pen response) is controlled by the reference beam energy such that the noise level on the signal remains approximately constant while the reference energy varies. Scan time used was 7 minutes which is recommended for qualitative and quantitative work for this instrument.

There has been a good deal of controversy as to the most satisfactory method of determining the methyl group content of polyethylene. According to Haslam, Willis and Squirrell (45), this method is the most straightforward and simple method of performing this analysis. Besides methyl groups, branches may terminate by ethyl or butyl groups. More refined studies have indicated that the methyl groups are probably part of ethyl or butyl groups. In addition to the short chain branches there is some evidence for the presence of long chain branches which are very long alkyl groups probably several tens of carbon atoms long. This method has a great limitation that it is not available for estimating independently the relative amounts of the different alkyl groups which contribute to the infrared region of 1380 cm$^{-1}$. On the other hand the amount represented in the infrared region at 1380 cm$^{-1}$, is a compound contribution arising from all types of methyl group present in polyethylene.

2.3.3 Fractionation

It is not possible to distinguish between block copolymers and mixtures of homopolymers by their thermal behaviour. A rough fractionation technique was used to find out whether linear low-density polyethylene is a copolymer or mixture of homopolymers.

1 gm of polymer was dissolved in 100 ml of xylene (Fisons SLR grade, supplied by Fisons Scientific Apparatus, Loughborough, Leics) at 100°C. To ensure that the polymer has dissolved completely
the solution was heated up to 120°C and then allowed to cool. During crystallisation from solution two fractions were obtained. The first fraction was precipitated as large crystals at 90°C. The second fraction which appeared at 80°C, remained as a dispersion. The first fraction was separated easily. The second fraction was obtained from the dispersion after centrifugation. Two fractions were dried and weighed to calculate their relative compositions.

2.3 Crystalline Structure Characterisation

2.3.1 Crystallinity

There are many methods of assessing crystallinity. X-ray diffraction, infrared absorption, nuclear magnetic resonance, specific volume and heat of fusion are the well known techniques. In X-ray diffraction, the three-dimensionally ordered structure gives rise to discrete X-ray diffraction patterns. Quantitative estimation of crystallinity involves assumptions concerning the contribution of amorphous scattering to the recorded diffraction pattern. The method requires elaborate equipment and preparation. In the infrared absorption, certain bands can sometimes be related to configurational states, giving a measure of crystallinity, if, and only if, it can be safely assumed that the same configurations do not occur in the noncrystalline regions. Nuclear magnetic resonance is a method of lesser use. The two commonly used techniques are used in the estimation of degree of crystallinity:

a) Specific volume
b) Heat of fusion.

a) Specific Volume:

The weight percent degree of crystallinity, $x$, is given by

$\omega = \frac{V_a - V_s}{V_a - V_c} \times 100 \quad (2.9)$
where $v_a = \text{specific volume of completely amorphous polymer}$

$v_c = \text{specific volume of completely crystalline polymer}$

$v_s = \text{specific volume of sample}$

The derivation of the above equation assumes volume additivity of crystalline and amorphous phases. This, in turn, implies that interfacial effects are negligible and voids are absent.

The above equation can be easily transformed into density terms and hence the weight percent degree of crystallinity at constant temperature is given by (47)

$$x_w = \frac{d_c (d_s - d_a)}{d_s (d_c - d_a)} \times 100$$

(2.10)

where $d_a = \text{density of completely amorphous polymer}$

$d_c = \text{density of completely crystalline polymer}$

$d_s = \text{density of sample}$

Since density can be determined very rapidly and accurately in a density-gradient column and the densities of completely amorphous and completely crystalline polyethylene are known from the literature, the degree of crystallinity can be estimated. The density of the sample is measured by the same method as will be described in Section 2.3.5. The density of completely amorphous and completely crystalline polyethylene are used 0.855 g/ml and 1.014 g/ml respectively in the work to calculate weight percent degree of crystallinity (48).

This is probably the simplest and most convenient method of measuring crystallinity of polyethylene. Direct evidence for or against the assumption that there are no voids present in polyethylene samples, so that their densities may be used to estimate crystallinity, is difficult to obtain on the basis of density measurement alone. So other techniques to estimate crystallinity are necessary to justify the basic assumption.
b) **Heat of Fusion:**

The heat of fusion is the amount of energy necessary to overcome the intermolecular forces in transforming polyethylene from a partially-crystalline state to a completely-disordered amorphous state. Valid heat effects of a reaction can be estimated, according to theoretical considerations (49), with fair reliability by measuring the area under a well defined thermogram peak (50). If the heat of fusion, \( \Delta H_f \) of a perfectly-crystalline polyethylene is known and actual heat of fusion, \( \Delta H_{f_S} \) for a polyethylene sample is measured from the thermogram area, the percentage crystallinity \( x \) can be derived from the following equation (51):

\[
x = \frac{\Delta H_{f_S}}{\Delta H_f} \times 100
\]  

(2.11)

The Du Pont 910 Differential Scanning Calorimeter (DSC) System was used in this work with the Du Pont 990 Thermal Analyser (Programmer/Recorder) and the 990 Mechanical Cooling Accessory (MCA) for programmed cooling. The details of the instrument will be given in Section 2.3.2.

To measure the heat of fusion of the polyethylene samples from the area under a melting endotherm, the instrument is first calibrated with indium which has a heat of fusion of 28.4 J/g and crystalline melting point of 156.6°C (52). Polyethylene sample size used was 6 mg throughout. The thermograms were obtained at a constant heating rate of 10°C/min with a sensitivity of 5 mV/cm. All the measurements were done under a nitrogen atmosphere at a flow rate of 50 ml/min. The sample was sealed into an aluminium pan and an empty aluminium pan is used as a reference. Before being analysed, all samples were given the same thermal pretreatment by heating to 150°C and cooling to 25°C at a constant rate of 1°C/min in the apparatus.

2.3.2 **Thermal analysis**

It is emphasised in Section 1.4 of Chapter 1 that an appropriate experimental technique has to be developed for the characterisation
of polyolefin blends. In the present work a thermal analysis tech­
nique has been developed for the characterisation of polyethylenes and their blends. This technique has been used for the determination of miscibility of polyethylene blends, as well as to characterise the blends as stable or unstable.

The Du Pont 910 Differential Scanning Calorimeter (DSC) system was used in the thermal analysis with the Du Pont 990 Thermal Analyser (Programmer/Recorder) and the 990 Mechanical Cooling Accessory (MCA). The simplified block diagram of the thermal analysis apparatus is shown in Figure 2.3.

![FIGURE 2.3: Block diagram of the thermal analysis apparatus](image)

The Du Pont 910 DSC system includes a Cell Base Module and a DSC cell. The cell base module provides an operating base for the DSC cell. The DSC cell is the system measuring unit shown in Figure 2.4 (52). It uses a constantan disc as the primary heat transfer element, which is enclosed in a silver heating block with a silver lid. The sample of interest and an inert reference are placed in pans which sit on raised platforms on the disc. Heat is transferred through the disc into the sample and reference and is monitored by
chromel-constantan area thermocouples formed by the junction of the constantan disc and a chromel wafer covering the underside of each platform. Chromel and alumel wires connect to the chromel wafers. This thermocouple junction under the sample platform is used to measure the sample temperature. An alumel wire welded to the reference platform is a dummy for thermal balance. Purge gas can be admitted to the sample chamber through an orifice in the block wall on the left between the two raised platforms. The purge gas enters the cell, and is preheated by circulation through the block before entering the sample chamber at block temperature. The VACUUM and COOL ports on the cell base lead to openings in the cell, although not directly into the sample chamber. A bell jar over the cell protects the user from any gas that might be generated and permits cell evacuation.

The Du Pont 990 Thermal Analyser has two complete and independent functions. It controls the DSC cell that perform the thermal analysis and it records the results of the analysis. The two functional units are a temperature programmer-controller and a X-Y-Y' recorder. Temperature of the sample under analysis is controlled by
the programmer-controller. Variance in the sample property is read on the Y or Y' axis as a function of sample temperature on the X axis of the recorder.

The Du Pont 990 Mechanical Cooling Accessory (MCA) is used for programmed cooling. MCA consists of a dual stage refrigerator-compressor attached to a jacketed remote probe by a flexible cable. The probe is placed over the DSC heating block. A cap in the jacket centre provides direct and easy access to the cell for loading and unloading of samples while exposing only a small area of the cell to the atmosphere.

If a sample and an inert reference material are heated at a known rate in a controlled environment, the increase in sample and reference temperature will be about the same (depending on specific heat differences), unless a heat related change takes place in the sample. If this change does take place, the sample temperature either leads (evolves heat) or lags (absorbs heat) the reference temperature. In DSC, the temperature difference between sample and reference from such a heat change is directly related to the differential heat flow. The measured variable in DSC is differential heat flow (Δq) which is plotted against actual sample temperature.

In a systematic classification of different types of differential thermal analysis (DTA) and differential scanning calorimetry (DSC) equipments, Mackenzie (53) has placed Du Pont DSC cell in such a position where it overlaps both the DTA and DSC field. He has suggested that there is certainly justification for considering Du Pont DSC cell (Heat-flux DSC or Boersma-type DTA) within the DSC field in view of Boersma's theory (54).

Before thermal analysis, temperature calibration of the apparatus was made with indium which has a crystalline melting point of 156.6°C. DSC samples were prepared from compression moulded sheets and sealed in an aluminium pan. An empty aluminium pan was used as the reference; the sample weight was 6 mg throughout. The first crystalline melting thermograms were obtained by heating the samples
from 25°C to 200°C at a programmed heating rate of 10°C/min with a sensitivity of 5 mV/cm. The samples were then cooled from 200°C to 25°C to obtain the crystallisation thermograms. Two different programmed cooling rates were used. For fast-cooled samples the thermograms were obtained at a cooling rate of 20°C/min with a sensitivity of 10 mV/cm and for slow-cooled samples the thermograms were obtained at a slower cooling rate of 10°C/min with a sensitivity of 1 mV/cm. The second crystalline melting thermograms were obtained using the same heating conditions as the first, viz 10°C/min. All measurements were made under a nitrogen atmosphere. The crystalline melting point and crystallisation temperature were read from the position of the peak in the thermogram.

2.3.3 X-ray diffraction

The wide-angle X-ray scattering (WAXS) technique is used to measure the spacings between ordered planes in the material and hence to determine the geometry of the regularly repeating unit cell. The packing of the chains is described most completely in terms of the unit cell, and its contents. The volume of the unit cell, and hence the volume occupied in the crystal by a single repeat unit, can be obtained from X-ray diffraction.

When a crystalline material is exposed to a beam of X-rays, the three-dimensional array of atoms in the crystal scatters the electromagnetic radiation in such a way that the scattered waves from different atoms reinforce each other only in certain directions; elsewhere, destructive interference occurs and no radiation is observed. These directions are characteristic of the orientation of the crystal with respect to the beam and of the interatomic separations in the material. They are governed by Bragg's Law (55):

\[ n_0 \lambda = 2d_hk \sin \theta \]  \hspace{1cm} (2.12)

where \( n_0 \) is an integer denoting the order of the diffraction,
\( \lambda \) is the wavelength of the X-rays,
\( \theta \) is the angle of incidence and reflection,
and \( d_{hk\ell} \) is the spacing between planes of atoms causing the reflection, designated by a set of three small integers (Miller indices) \( h, k \) and \( \ell \).

To generate diffraction maxima from the planes with a given spacing \( d \), either \( \lambda \) or \( \theta \) must be varied. It is \( \theta \) that is varied usually. If the sample is properly prepared, the X-ray beam interacts with many tiny crystals, which take up all possible orientations. Now diffraction from a single set of planes takes place at all angles having a fixed relation to the direction of the beam, that is, along the surface of a cone with half angle \( 2\theta \) around the beam direction. A flat film placed normal to the beam cuts this cone in a circle to produce a ring. The locations of the diffracted beams serve primarily to determine the \( d \)-spacings, through the Bragg equation.

The JEOL Model JDX X-ray Diffractometer was used for X-ray diffraction. The general features of the unit are shown in Figure 2.5.

**FIGURE 2.5:** Essential features of the X-ray diffraction instrument (WAXS) (55)
X-rays are generated by the bombardment of electrons on a metal (copper) target in an evacuated tube; copper provides radiation (at 40 KV and 30 mA) with a good balance of wavelength and penetrating power for polymer materials. A nickel filter is used to isolate the CuKα line, \( \lambda = 1.542 \text{ Å} \). The beam is collimated with suitable pinholes, passes through and is diffracted by the sample, and is captured in photographic film. A flat plate camera is used for the record of the entire diffraction pattern with an exposure time of 30 minutes. The distance between sample and plate is kept constant throughout. To obtain an accurate value for sample to plate distance, using the same condition, a photograph of a sample of graphite powder is obtained. The 002 reflection of graphite at 26.53° 2θ (56) gives the accurate distance between sample and plate through the Bragg equation.

The diffraction pattern of the samples exhibited two strong reflections only, the 110 and 200, making it impossible to calculate the c-dimension of the orthorhombic unit cell of polyethylene. The unit cell a- and b-dimensions were calculated, and since it is these which show any expansion in the lattice they suffice to characterise the unit cell (57). All the compression moulded samples were given the same thermal pretreatment by heating to 150°C and then cooling to 25°C at a controlled rate of 10°C/min.

2.3.4 Light scattering

The small angle light scattering (SALS) technique based on the scattering of visible light by polymer films, is used to provide information about structures having size of the order of the wavelength of visible light. The experimental set-up of a SALS apparatus is shown in Figure 2.6. Polarised light from the He-Ne laser is first passed through the polymer film to be investigated. The scattered light then passes through a polariser (commonly called the analyser) which is oriented perpendicular to the polarisation direction (\( V_H \) scattering). A spatial filter is used in between the laser beam and sample for eliminating non-coherent light coming from the discharge tube.
Instead of recording (the scattered light) on photographic film (58,59), the scattered light is relayed through a standard television system (camera and control) such that it is displayed on a television monitor. The intensity depends upon the scattering angle \( \theta \) between the incident and scattered ray. The range of \( \theta \) that may be recorded depends upon the sample to film distance \( d_{sf} \) since \( \tan \theta = \left( d_{cs} / d_{sf} \right) \), where \( d_{cs} \) is the distance from the centre of the recording device (TV camera) to the point where the intensity is recorded. Since small objects scatter at large angles, the sample to film distance must be kept small for recording these (down to a few mm). The TV signal is also fed into an oscilloscope (Tektronix Type 529 Waveform Monitor) with a single line strobing facility. That is, the instrument has the capability of scanning any one line of a multiline TV signal and of displaying a trace of the intensity distribution across that line on its screen. By virtue of the link
between the oscilloscope and the television monitor, the line manually selected for scan analysis by the oscilloscope appears bright on the monitor. As many lines as required may be analysed separately from a given field of view by the expedient of altering the location of the bright-up line and thus altering the scan region of the oscilloscope.

A camera was used to obtain photographs of traces displayed on the oscilloscope screen and scattering patterns displayed on the TV monitor.

Samples can be quite small and are ordinarily held between glass microscope slides using an immersion fluid to minimise surface contributions to the scattering. All the samples were given the same thermal pretreatment by heating to 150°C and then cooling to 25°C at a controlled rate of 1°C/min.

The SALS technique is well suited to the rapid and qualitative evaluation of the entire scattering pattern. Qualitative observations of the scattering pattern can be used to provide rough approximations to the nature, size, perfection and shape of the polymer superstructure. Light scattering size range of around 100-10000 nm overlaps that of optical microscopy and can be applied to the examination of structures occurring within bulk polymer samples. But it cannot be applied to obtain information about molecular structure where one has to depend on the classical techniques such as X-ray diffraction, infrared and Raman spectroscopy, and NMR.

2.3.5 Density

Density is the mass of a unit volume of material. The density of a polymer may in some cases be critical to the ultimate end-use potential since a polymer with a low density will, obviously, occupy more volume or cover more surface per mass than one of higher density. In any event, density can add to the basic understanding of the material in every instance.
The Davenport Density Measuring Apparatus (Density Gradient Columns) (60) is used to measure the density of the sample at 23 ± 0.5°C according to BS 2782: Part 6: Method 620D: 1980 (61). A density column is prepared from mixtures of two miscible liquids of different densities, or two solutions of different concentration. If a column is prepared carefully and kept at a reasonably constant temperature it is possible to maintain a density gradient ranging from the density of the heavier liquid or solution at the bottom to that of the lighter at the top. Density of a sample may then be determined from the position at which it floats in the column. Compression moulded samples are used for the determination of density of the components and their blends.

2.4 Processibility Tests

2.4.1 Melt flow index and melt memory index

The melt flow index (MFI) is used internationally for the grading of polyethylene. The MFI is the measured gravimetric flow rate of the sample melt extruded from a die of specific length and diameter under prescribed conditions of temperature and pressure. Different standardised combinations of extrusion temperature and pressure are used for different types of polymer but, for purposes of comparison, different samples of the same polymer type should be tested under precisely similar conditions.

The Davenport Melt Indexer (Model III) (62), is used in this work to determine the MFI of the sample. This instrument has been designed to fulfil the apparatus requirements of BS 2782: Part 1: Method 105C: 1965 (63) and of BS 2782: Part 7: Method 720A: 1979 (64). Basically the apparatus is a dead-weight extrusion plasti-meter consisting of a thermostatically controlled heated steel cylinder with a die situated at the lower end and a piston, operating with the cylinder, which can be loaded with suitable weights to give the correct applied load for the material under test.
Throughout this work the die used is of 8.00 mm in length and 2.0955 mm in diameter. Test temperature is maintained at 190°C and dead weight load used is 2.16 kg. Experimental conditions practically used for determining melt flow index is according to test condition number 4 of BS 2782: Part 7: Method 720A: 1979. The melt flow index is calculated from the following equation:

$$\text{MFI} = \frac{10 W_e}{t_e}$$  \hspace{1cm} (2.13)

where  

- MFI = melt flow index (g/10 minutes)
- $W_e$ = average cut-off weight (g)
- $t_e$ = extrusion time per cut-off (minutes)

Extruder mixed samples are used for the determination of MFI of the components and their blends.

Melt memory index or, more precisely, the extrudate swell of the melt flowing out of the die of the melt indexer is widely used in the plastics industry as a quick indication of melt elasticity. Melt memory index is measured with the melt flow index in the Davenport Melt Indexer (Model III) using the same experimental conditions. Melt memory index or extrudate swell ratio is calculated from the following equation (65) and is expressed in percent:

$$\text{Melt memory index} = \frac{d_e - d_d}{d_d} \times 100\%$$  \hspace{1cm} (2.14)

where  

- $d_e$ = extrudate diameter (mm) 
- $d_d$ = die diameter (mm) = 2.0955 mm

All extrudate specimens are cooled in air and average diameter of the uniform extrudate cut offs are measured during MFI determination. However, this practice does not give reasonable physical information.
because (among other reasons) the diameter is determined after cooling the extrudate in air, so that the equilibrium swell is not obtained.

2.4.2 Shear flow behaviour

The Davenport capillary extrusion rheometer (66) is used to provide information about shear flow behaviour of polymer. The polymer sample is placed in a barrel, which is heated and is terminated in a precisely dimensioned extrusion die. When the test sample has reached the desired test temperature, it is extruded through the die at a predetermined shear rate, by a power driven piston, the forward speed of which can be accurately controlled. As the material is forced through the die, the pressure drop in the capillary at the constant piston speed is measured by a calibrated Dynisco pressure transducer (of capacity 10000 psi) whose sensing head is fitted at the end of the barrel and before the entry to the capillary. The pressure drop is recorded on a strip chart recorder. From the piston speed and the pressure drop corresponding thereto, shear rate and shear stress, respectively are calculated. The capacity of the barrel of the machine is such that, on one loading, a number of different piston speeds can be developed and, from these and their corresponding extrusion pressures, a graph of shear stress against shear rate is plotted.

Test temperature used was 190°C throughout. Only one correction - the ends (or Bagley) correction - is applied using the combination of a long die (length/diameter = 20) with an orifice die (length/diameter = 0), such that \( P = P_L - P_o \), where \( P_L \) is the pressure drop through the long die and \( P_o \) is the pressure drop through the orifice die of the same diameter (1 mm) at the same piston speed (67). The entry angle of the dies was 180°. The barrel diameter of the rheometer was 19 mm. Extruder mixed samples were used for the determination of shear stress and shear rate relationship of the components and their blends.
The derivation of the Poiseuille law for capillary flow is available in any standard book (68) and yields

\[ \sigma_s = \frac{P}{2L_c} r_c \]  \hspace{1cm} (2.15)

\[ \dot{\gamma} = \frac{4Q}{\pi r_c^3} \]  \hspace{1cm} (2.16)

where \( \sigma_s \) is the shear stress at the die wall, N/m²
\( \dot{\gamma} \) is the shear rate at the die wall, 1/s
\( P \) is the pressure drop, N/m²
\( Q \) is the volumetric flow rate, m³/s
\( r_c \) is the capillary radius, m
\( L_c \) is the capillary length, m

Shear rate is calculated for each piston speed from the following equation:

\[ \dot{\gamma} = \frac{4}{b} \frac{r_c^2 v_p}{r_c^3} \]  \hspace{1cm} (2.17)

The equation (2.17) results from equation (2.16) and from the relationship given by

\[ Q = \pi r_b^2 v_p \]  \hspace{1cm} (2.18)

where \( r_b \) is the barrel radius, m
\( v_p \) is the piston speed, m/s.

The shear stress corresponding to any given shear rate results from the equation (2.15)

\[ \sigma_s = \frac{(P_L - P_o) r_c}{2L_c} \]  \hspace{1cm} (2.19)
where \((P_L - P_0)\) is the corrected observed pressure drop, N/m².

Interpretation of capillary rheometry data using the Poiseuille equation yields an apparent rather than a true measure of viscosity at the operating temperature. The apparent viscosity \((\eta)\) is given by

\[
\eta = \frac{\sigma_s}{r}, \quad \text{Ns/m}^2
\]  \hspace{1cm} (2.20)

2.4.3 Elongational flow behaviour

In the processing of polymer melts, such as bubble stretching during the manufacture of lay-flat polyethylene film, the melt is subjected to a tensile rather than a shear stress. In this case the flow may be described as elongational. In this work the information on elongational flow behaviour of polymer is provided using Rutherford Elongational Rheometer. The equipment is still in its development stage at IPT and is shown in Figure 2.7. It consists of a constant-temperature silicone oil bath where the polymer sample is placed on two carriage arms, one of which is fixed and the other is movable. The sample is then stretched. The separation of the arms is controlled in either a constant stress or a constant strain rate mode. Both these modes contain electronic circuitry to take account of the decreasing cross-sectional area of the polymer melt as it is stretched. The pulling of the sample is accomplished by a variable speed motor through a selectable gear train via an output drive pulley through a drive cord to the moving carriage. Force imposed on the sample during test is measured by a linearly variable displacement transducer. The length of the sample can be measured so that strain, strain rate and sample dimension may be determined.

Extruder mixed samples were used for the preparation of the specimen for this test using a Fox and Offord Unimoulder (plus transfer mould). The Unimoulder is a horizontal injection moulding machine. The sample was injected into a steam heated mould at 170°C.
FIGURE 2.7: Rutherford Elongation Rheometer Schematic. Top: Front View
Bottom: Top View
The temperature was kept at that level for 3 minutes to allow almost complete stress relaxation. The steam was then turned off and the mould was allowed to free-cool for 10 minutes with the injection pressure holding on. This slow-cool stage avoids cavitation in the specimen. The injection pressure was released and when the specimen was cooled down to below the solidification temperature, the mould was cooled rapidly through circulation of cold water. The specimen obtained by injection moulding was of cylindrical shape of diameter ranging from 5.6 mm to 5.7 mm.

The moulded specimens were cut into 35 mm lengths. The next stage of the specimen preparation was the insertion of two screws at the two ends of the polymer solid cylinder. A thin layer of PTFE tape was laid up on the joints of polymer and screw at the two ends of the specimen. This method helped to form a slightly higher viscosity layer of melt around the screw thread due to heat conduction through the screw root to the carriage arms which were in air at their upper ends.

The specimen was placed into the slotted carriage arms inside the silicone oil bath at 150°C and equilibrated for 10 minutes before the beginning of the experiment. Density-temperature corrections to the cross-sectional area were made. The test was carried out in the constant strain rate mode using a strain rate of 1 s⁻¹. Tensile stress generated in the specimen and length of the specimen during test were recorded continuously on a strip chart recorder. From the length of the specimen at any instant the Hencky strain was calculated. When the deformation is large it is more correct to use Hencky strain rather than engineering strain. Hence a graph of tensile stress corresponding to Hencky strain was plotted, representing the elongational flow behaviour at the selected temperature.

The Hencky strain corresponding to any given tensile stress is calculated from the equation (69):

\[ \varepsilon = \int \frac{\Delta \delta}{\Delta L} = \ln \frac{L_f}{L_i} \]  

(2.21)
where $\varepsilon$ is the Hencky strain

$L_i$ is the initial length of the specimen, m

$L_f$ is the final length of the specimen, m

Transformation of elongational rheometry data yields a measure of elongational viscosity through the following equation (69).

$$\lambda = \frac{\sigma_\varepsilon}{\varepsilon}$$ (2.22)

where $\lambda$ is the elongational viscosity, Ns/m²

$\sigma_\varepsilon$ is the elongational tensile stress, N/m²

$\varepsilon(d\varepsilon/dt)$ is the elongational strain rate, 1/s

2.4.4 Melt rupture characteristics

In the polyethylene-film process a tube of melt is extruded, drawn-down, inflated and simultaneously cooled to achieve a thin biaxially oriented product in a wide range of thicknesses and widths. The thickness to which a polyethylene film can be drawn in the bubble process is limited by rupture. A simple laboratory test method based on the melt flow indexer is used to evaluate comparative melt rupture characteristics of polymers.

The method is based on constant-force extension of the extrudate from a melt flow indexer. The method is to attach a weight to the extrudate and allow it to draw down until the extrudate solidifies. The weight attached is increased until rupture is obtained during the test. This test was carried out using the same Davenport Melt Indexer (with the same die) as described in Section 2.4.1 but at 150°C with 10 Kg load on the piston. Extruder mixed samples were used for this test.
The rupture stress is calculated from the equation (70):

\[ \sigma_R = \frac{W_h D_r}{A_i} \]  \hspace{1cm} (2.23)

where

- \( D_r = \frac{m_i}{m_f} \)
- \( \sigma_R \) is the rupture stress, N/m²
- \( W_h \) is the highest load which the sample can sustain without breaking, N
- \( A_i \) is the initial cross-sectional area of the extrudate, m²
- \( D_r \) is the draw ratio at break
- \( m_i \) is the mass per unit length of the undrawn extrudate, Kg/m
- \( m_f \) is the mass per unit length of the drawn extrudate, Kg/m

This test is very useful for easy qualitative comparison of the drawdown behaviour of different polymers and can be used as a quality control test because of simplicity of operation, convenience of use and ease of interpretation to the practical situation.

2.5 Mechanical Properties

2.5.1 Tensile tests

Tensile properties (tensile stress at yield, tensile strength at break, elongation at yield, elongation at break and secant modulus at predetermined strain) were determined according to BS 2782: Part 3: Method 320A: 1976 (71) using an Instron Model TT-CM tester (72). Tensile specimens were punched out from the compression moulded sheets. Tests were carried out at 100 mm/min, at 21°C and 65% relative humidity. A minimum of 8 specimens was tested, and the average values of the properties are reported. Because the rate of grip separation during testing was fast, the elastic modulus could not be determined accurately from the initial portion of the stress-strain curve. Therefore, the stiffness was evaluated by calculating a secant modulus at a strain of 7 percent (73).
Tensile properties (tensile stress at yield, tensile strength at break and elongation at break) of film samples were measured on a JJ Tensile Testing Machine (Type T5002) at 500 mm/min. For measuring thickness, a dial gauge fitted with flat circular feet was used. A travelling microscope was used for measuring width.

2.5.2 Tear tests

Tear strength of film samples was determined according to BS 2782: Part 3: Method 360B: 1980 using a JJ Tensile Testing Machine (Type T5002). Tests were carried out at 210°C. A dial gauge was used for measuring thickness.

2.5.3 Impact tests

Impact resistance of film samples was determined according to BS 2782: Part 3: Method 352D: 1979 using a Davenport 'Falling Dart' Impact Apparatus. Tests were carried out at 210°C and thickness was measured using a dial gauge. This work has been performed at Britannia Packaging Ltd, Stoke-on-Trent.

2.6 Birefringence

Birefringence is a measure of optical anisotropy. It is defined as the difference between two refractive indices measured in two perpendicular directions. Double refraction by an optically anisotropic medium gives rise to two rays travelling with different speeds and plane polarised at right angles. This is equivalent to stating that the medium presents two refractive indices. If these are \( n_{r1} \) and \( n_{r2} \), then after the beams have passed through a slab of the material of thickness \( h \) of the medium, they will be out of phase by an amount \( hn_{r1} - hn_{r2} \), i.e. \( h(n_{r1} - n_{r2}) \). This quantity is termed the optical path difference or relative retardation. \( \Delta n_r = (n_{r1} - n_{r2}) \) is defined as the birefringence of the section of the medium being...
examined. So the magnitude of the birefringence of the section of a specimen, $\Delta n_r$, is related to the optical path difference (OPD) or relative retardation by the relationship (78)

$$\text{OPD} = h \Delta n_r$$  \hspace{1cm} (2.24)

The thickness, $h$ is readily measurable, so that a knowledge of the OPD will allow the determination of $\Delta n_r$.

The most convenient way of measuring birefrigence is by means of a polarising microscope. It is desirable to describe briefly the principles involved in the polarising microscope.

When a beam of light falls on an anisotropic material it is resolved into two components. A polariser is a device which is designed so that one of these components is totally absorbed. Thus light emerging from the polariser is plane polarised. A similar sheet of polarising material mounted with its plane of polarisation at right angles to the first will absorb all of this light. Only if the two directions of polarisation are parallel will light pass through both filters. This second piece of polarising material is known as the analyser. The two arrangements described above are referred to as 'crossed polars' and 'open polars', respectively.

Now it is considered that a birefringent object is mounted between crossed polars. The simplest case is that where a rectangular object, having its planes of polarisation parallel to its sides, is mounted with one of those planes parallel to the plane of incident light (Figure 2.8(i)) (79). Light from the polariser passes through the birefringent test piece and is absorbed by the analyser, so that the field is dark.

Similarly, if the test piece is rotated through $90^\circ$ the field remains dark (Figure 2.8(ii)). If the test piece is mounted at $45^\circ$ to the plane of polarisation, however, the object stands out brightly on a dark field. To understand this, reference must be made to Figure 2.8 (iii). The original plane-polarised light beam may be
FIGURE 2.8 Interaction of plane polarised light with a birefringent object \((79)\)

Considered to be resolved into two components \(A\) and \(B\) corresponding to the principal planes of the test piece. These two components traverse the test piece at different velocities so that the two emergent beams \(A'\) and \(B'\) are out of phase. On reaching the analyser each of the components \(A'\) and \(B'\) may be resolved into components parallel to and at right angles to the analyser direction. Components parallel to the analyser direction pass through and, since these are out of phase, interference results. Because the phase difference varies with wavelength, brilliant interference colours may be obtained. The effect on these colours of retardation compensator enables an estimate of OPD and hence birefringence. The compensator works on the basis of introducing a further retardation into the optical system of the microscope. This additional retardation is
adjusted to be equal in magnitude to that being measured, but opposite in sign. If the optical characteristics of the compensating device are known then the retardation can be calculated.

To understand the concept of compensation, the test piece is placed between crossed polars using white light and observed. On rotating it through 360° in its own plane it will extinguish four times corresponding to the four occasions on which the vibration direction of the polariser is coincident with a permitted vibration direction of the test piece. These directions may be defined as the 'fast' and 'slow' directions according to the speed of the wave front propagating through the test piece when in an extinction orientation.

If the test piece is turned from extinction through 45° the maximum brightness is observed. If another identical test piece of the material is inserted between the polars and rotated, again in its own plane, in some positions zero light transmission is obtained, while in others 'higher' order interference colours are observed. Here darkness, or exhibition of the zero order polarisation colour, occurs when the slow direction of the test piece is coincident with the fast direction of the other. Higher order colours occur when the slow and fast directions of both test pieces are in the same direction.

In the first case it can be said that the birefringence of the first test piece has been 'compensated' by the second. Obtaining the zero order interference colour is possible only because the path differences of both test pieces are identical for all wavelengths in the white spectrum.

The OPD is estimated in this work by the Senarmont Compensator which consists only of a very accurate λ/4 retardation plate mounted between the specimen and analyser with its slow axis parallel to the direction of vibration of light from the polariser. The analyser is capable of rotation and the amount of rotation is read from an accurately produced angular scale. Monochromatic light is used since
it is necessary that the plate gives a retardation of precisely λ/4. λ, wavelength of light is chosen to be the 546 nm Hg spectral emission line (green).

By insertion of a specimen in the 45° position, plane polarised light is resolved into slow and fast components with an angular phase difference Δψ (related directly to the OPD). These components can be considered in terms of further components obtained by vector resolution on to the fast and slow axes of the λ/4 plate. Passage through this plate increases the phase difference by 90° so that when they emerge these components are 180° out of phase and therefore combine to produce linearly polarised light. This light vibrates at some angle β to the original polarisation direction and can be extinguished by rotating the analyser through this angle. The phase difference Δψ is related to this angle by Δψ = 2β and OPD is calculated from the relationship (78)

\[ \text{OPD} = \frac{\lambda \Delta \psi}{180°} \]  

(2.25)

The Senarmont Compensator is particularly useful for the precise measurement of very low birefringences. It is simple in construction and fits into the diagonal slot of a standard polarising microscope.

Birefringence measurement can give information on molecular orientation and, particularly the magnitude of frozen-in stresses. In turn this can give clues to the processing history of the material.
CHAPTER 3

RESULTS, DISCUSSION AND CONCLUSIONS:

MOLECULAR STRUCTURE OF COMPONENTS AND THEIR BLENDS

3.1 Results and Discussion

3.1.1 Molecular weight and molecular weight distribution

Gel permeation chromatograms of LDPE, HDPE and LLDPE are shown in Figures 3.1, 3.2 and 3.3 respectively. The species eluting after the main material i.e. after count 73 in case of LDPE (Figure 3.1); after count 52 in case of HDPE (Figure 3.2); after count 53 in case of LLDPE (Figure 3.3), are the results of small differences in inhibitor concentration, residual solvents or monomers and air etc. that were present in the sample or acquired during dissolution (42).

Tables 3.1, 3.2 and 3.3 show the respective computed results of LDPE, HDPE and LLDPE from GPC analysis. The format of the computer printout is as follows:

The chromatogram heights in column 2 against the elution volumes in counts (increments of 0.5 ml) from injection in column 1 represent the original chromatogram, the start and finish points of which are shown by arrows in Figures 3.1 to 3.3.

Column 3 shows % heights in terms of elution volume as the abscissa compare column 7.

Column 4 gives the polystyrene molecular weight which would elute at the given elution volume while column 5 gives the corresponding molecular weight of the actual polymer.

Column 7 shows the distribution in terms of a log M abscissa and the differential molecular weight distribution curve can be obtained by plotting these values against the corresponding values in columns 5 or 6.
FIGURE 3.1: Gel Permeation Chromatogram of LDPE
FIGURE 3.2: Gel Permeation Chromatogram of HDPE
FIGURE 3.3: Gel Permeation Chromatogram of LLDPE
TABLE 3.1 Computed results of LDPE from GPC analysis

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<th>Elution Volume (counts)</th>
<th>Polymer M Values</th>
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<th>logM Values</th>
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TABLE 3.2: Computed results of HDPE from GPC analysis

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TABLE 3.3: Computed results of LLDPE from GPC analysis

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<td>0.86</td>
<td>0.7320x10^4</td>
<td>0.2843x10^4</td>
<td>3.4538</td>
<td>0.86</td>
</tr>
<tr>
<td>46</td>
<td>2.50</td>
<td>0.62</td>
<td>0.5100x10^4</td>
<td>0.1972x10^4</td>
<td>3.2949</td>
<td>0.62</td>
</tr>
<tr>
<td>47</td>
<td>1.80</td>
<td>0.44</td>
<td>0.3550x10^4</td>
<td>0.1370x10^4</td>
<td>3.1367</td>
<td>0.44</td>
</tr>
<tr>
<td>48</td>
<td>1.00</td>
<td>0.25</td>
<td>0.2480x10^4</td>
<td>0.9497x10^3</td>
<td>2.9776</td>
<td>0.25</td>
</tr>
<tr>
<td>49</td>
<td>0.80</td>
<td>0.20</td>
<td>0.1720x10^4</td>
<td>0.6581x10^3</td>
<td>2.8183</td>
<td>0.20</td>
</tr>
<tr>
<td>50</td>
<td>0.50</td>
<td>0.12</td>
<td>0.1200x10^4</td>
<td>0.4576x10^3</td>
<td>2.6605</td>
<td>0.12</td>
</tr>
<tr>
<td>51</td>
<td>0.00</td>
<td>0.00</td>
<td>0.8380x10^3</td>
<td>0.3183x10^3</td>
<td>2.5028</td>
<td>0.00</td>
</tr>
</tbody>
</table>

\[ \begin{align*}
M_n &= 0.2011 \times 10^5 \\
M_w &= 0.1332 \times 10^6 \\
M_z &= 0.4824 \times 10^6 \\
M_v &= 0.1048 \times 10^6 \\
M_n/M_z &= 6.22 \\
M_w/M_n &= 6.62 \\
M_z/M_n &= 23.99 \\
M_v/M_n &= 50.83 \\
\end{align*} \]
The number, weight, Z and viscosity average molecular weights are given at the foot of the columns. The tables also include the dispersity indices.

The differential molecular weight distribution curve was obtained by plotting \( \frac{Dw}{D\log M} \% \) values from column 7 against the corresponding \( \log M \) values from column 6. The molecular weight distributions of LDPE, HDPE and LLDPE thus obtained are represented in Figures 3.4, 3.5 and 3.6 respectively. All of them showed normal unimodal distribution. It is necessary to provide full description of molecular weight distribution, since dispersity index as a measure of molecular weight distribution provides no information about any unusual high or low molecular weight tail which might have profound significance (80).
FIGURE 3.5: Molecular Weight Distribution of HDPE

\[ \log M \]

\[ \frac{Dw}{D\log M} \% \]
FIGURE 3.6: Molecular Weight Distribution of LDL

![Diagram showing molecular weight distribution of LDL](image-url)
3.1.2 Molecular Weight and Molecular Weight Distribution of Blends

Considering that ideal molecular mixing was achieved during the blending operation and there was no degradation during blending, the number average molecular weights of the blends are calculated from the simple classical relation (81):

\[
\frac{1}{M_{n2}} = \frac{w_1}{M_{n1}} + \frac{w_2}{M_{n2}}
\]

(3.1)

where:
- \(M_{n2}\) = Number average molecular weight of the blend
- \(M_{n1}\) = Number average molecular weight of component 1
- \(M_{n2}\) = Number average molecular weight of component 2
- \(w_1\) = Weight fraction of component 1
- \(w_2\) = Weight fraction of component 2

The weight, Z and viscosity average molecular weights of the blends are calculated on the same assumption from the simple additive rule (81):

\[
P_{12} = w_1 P_1 + w_2 P_2
\]

(3.2)

where:
- \(P_{12}\) = Property of the blend
- \(P_1\) = Property of component 1
- \(P_2\) = Property of component 2
- \(w_1\) = Weight fraction of component 1
- \(w_2\) = Weight fraction of component 2

The experimental values of \(M_n\) of the components and calculated values of \(M_n\) of their blends from equation (3.1) are summarised in Tables 3.4 to 3.6. The experimental values of \(M_w\), \(M_z\) and \(M_v\) of the components and calculated values of \(M_w\), \(M_z\) and \(M_v\) of their blends from equation (3.2) are summarised in Tables 3.7 to 3.9, Tables 3.10 to 3.12 and Tables 3.13 to 3.15 respectively. Jacovic and co-workers (82) calculated the values of molecular weights of the blends in similar manner.
### TABLE 3.4: $M_n$ of LOPE and HOPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental</th>
<th>Calculated for blends from equation (3.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>17,890</td>
<td>15,640</td>
</tr>
<tr>
<td>LD/HD-70/30</td>
<td></td>
<td>14,430</td>
</tr>
<tr>
<td>LD/HD-50/50</td>
<td></td>
<td>13,390</td>
</tr>
<tr>
<td>LD/HD-30/70</td>
<td>12,090</td>
<td></td>
</tr>
<tr>
<td>HD</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 3.5: $M_n$ of LLDPE and HDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental</th>
<th>Calculated for blends from equation (3.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLD</td>
<td>20,110</td>
<td>16,770</td>
</tr>
<tr>
<td>LLD/HD-70/30</td>
<td></td>
<td>15,100</td>
</tr>
<tr>
<td>LLD/HD-50/50</td>
<td></td>
<td>13,730</td>
</tr>
<tr>
<td>LLD/HD-30/70</td>
<td>12,090</td>
<td></td>
</tr>
<tr>
<td>HD</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 3.6: $M_n$ of LDPE and LLDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental</th>
<th>Calculated for blends from equation (3.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>17,890</td>
<td>18,500</td>
</tr>
<tr>
<td>LD/LLD-70/30</td>
<td></td>
<td>18,940</td>
</tr>
<tr>
<td>LD/LLD-50/50</td>
<td></td>
<td>19,390</td>
</tr>
<tr>
<td>LD/LLD-30/70</td>
<td>20,110</td>
<td></td>
</tr>
<tr>
<td>LLD</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 3.7: $M_w$ of LDPE and HDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental</th>
<th>Calculated for blends from equation (3.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>129,800</td>
<td>160,580</td>
</tr>
<tr>
<td>LD/HD-70/30</td>
<td></td>
<td>181,100</td>
</tr>
<tr>
<td>LD/HD-50/50</td>
<td></td>
<td>201,620</td>
</tr>
<tr>
<td>LD/HD-30/70</td>
<td>232,400</td>
<td></td>
</tr>
<tr>
<td>HD</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 3.8: $M_w$ of LLDPE and HDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental</th>
<th>Calculated for blends from equation (3.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLD</td>
<td>133,200</td>
<td>162,960</td>
</tr>
<tr>
<td>LLD/HD-70/30</td>
<td></td>
<td>182,800</td>
</tr>
<tr>
<td>LLD/HD-50/50</td>
<td></td>
<td>202,640</td>
</tr>
<tr>
<td>LLD/HD-30/70</td>
<td>232,400</td>
<td></td>
</tr>
<tr>
<td>HD</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 3.9: $M_w$ of LDPE and LLDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental</th>
<th>Calculated for blends from equation (3.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>129,800</td>
<td>130,820</td>
</tr>
<tr>
<td>LD/LLD-70/30</td>
<td></td>
<td>131,500</td>
</tr>
<tr>
<td>LD/LLD-50/50</td>
<td></td>
<td>132,180</td>
</tr>
<tr>
<td>LD/LLD-30/70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LLD</td>
<td>133,200</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 3.10: $M_z$ of LDPE and HDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental</th>
<th>Calculated for blends from equation (3.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>387,200</td>
<td>557,390</td>
</tr>
<tr>
<td>LD/HD-70/30</td>
<td>557,390</td>
<td>670,850</td>
</tr>
<tr>
<td>LD/HD-50/50</td>
<td>670,850</td>
<td>784,310</td>
</tr>
<tr>
<td>LD/HD-30/70</td>
<td>784,310</td>
<td></td>
</tr>
<tr>
<td>HD</td>
<td>954,500</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 3.11: $M_z$ of LLDPE and HDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental</th>
<th>Calculated for blends from equation (3.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLD</td>
<td>482,400</td>
<td>624,030</td>
</tr>
<tr>
<td>LLD/HD-70/30</td>
<td>624,030</td>
<td>718,450</td>
</tr>
<tr>
<td>LLD/HD-50/50</td>
<td>718,450</td>
<td>812,870</td>
</tr>
<tr>
<td>LLD/HD-30/70</td>
<td>812,870</td>
<td></td>
</tr>
<tr>
<td>HD</td>
<td>954,500</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 3.12: $M_z$ of LDPE and LLDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental</th>
<th>Calculated for blends from equation (3.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>387,200</td>
<td>415,760</td>
</tr>
<tr>
<td>LD/LLD-70/30</td>
<td>415,760</td>
<td>434,800</td>
</tr>
<tr>
<td>LD/LLD-50/50</td>
<td>434,800</td>
<td>453,840</td>
</tr>
<tr>
<td>LD/LLD-30/70</td>
<td>453,840</td>
<td></td>
</tr>
<tr>
<td>LLD</td>
<td>482,400</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 3.13: $M_v$ of LDPE and HDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental</th>
<th>Calculated for blends from equation (3.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>104,100</td>
<td>123,960</td>
</tr>
<tr>
<td>LD/HD-70/30</td>
<td></td>
<td>137,200</td>
</tr>
<tr>
<td>LD/HD-50/50</td>
<td></td>
<td>150,440</td>
</tr>
<tr>
<td>LD/HD-30/70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HD</td>
<td>170,300</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 3.14: $M_v$ of LLDPE and HDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental</th>
<th>Calculated for blends from equation (3.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLD</td>
<td>104,800</td>
<td>124,450</td>
</tr>
<tr>
<td>LLD/HD-70/30</td>
<td></td>
<td>137,550</td>
</tr>
<tr>
<td>LLD/HD-50/50</td>
<td></td>
<td>150,650</td>
</tr>
<tr>
<td>LLD/HD-30/70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HD</td>
<td>170,300</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 3.15: $M_v$ of LDPE and LLDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental</th>
<th>Calculated for blends from equation (3.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>104,100</td>
<td>104,310</td>
</tr>
<tr>
<td>LD/LLD-70/30</td>
<td></td>
<td>104,450</td>
</tr>
<tr>
<td>LD/LLD-50/50</td>
<td></td>
<td>104,590</td>
</tr>
<tr>
<td>LD/LLD-30/70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LLD</td>
<td>104,800</td>
<td></td>
</tr>
</tbody>
</table>
Dispersity indices are important parameters to describe molecular weight distribution. Dispersity indices \( (M_w/M_n \text{ and } M_z/M_n) \) of the blends are obtained from the calculated values of molecular weights. The values of dispersity indices \( (M_w/M_n) \) of components obtained from experimental values of molecular weights and of their blends obtained from calculated values of molecular weights are summarised in Tables 3.16 to 3.18. The values of dispersity indices \( (M_z/M_n) \) of components obtained from experimental values of molecular weights and of their blends obtained from calculated values of molecular weights are summarised in Tables 3.19 to 3.21.
TABLE 3.16: $\frac{M_n}{M_w}$ of LDPE and HDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental</th>
<th>Calculated for blends from Tables 3.7 and 3.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>7.26</td>
<td></td>
</tr>
<tr>
<td>LD/HD-70/30</td>
<td></td>
<td>10.27</td>
</tr>
<tr>
<td>LD/HD-50/50</td>
<td></td>
<td>12.55</td>
</tr>
<tr>
<td>LD/HD-30/70</td>
<td></td>
<td>15.06</td>
</tr>
<tr>
<td>HD</td>
<td>19.22</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 3.17: $\frac{M_n}{M_w}$ of LLDPE and HDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental</th>
<th>Calculated for blends from Tables 3.8 and 3.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLD</td>
<td>6.62</td>
<td></td>
</tr>
<tr>
<td>LLD/HD-70/30</td>
<td></td>
<td>9.72</td>
</tr>
<tr>
<td>LLD/HD-50/50</td>
<td></td>
<td>12.11</td>
</tr>
<tr>
<td>LLD/HD-30/70</td>
<td></td>
<td>14.76</td>
</tr>
<tr>
<td>HD</td>
<td>19.22</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 3.18: $\frac{M_n}{M_w}$ of LDPE and LLDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental</th>
<th>Calculated for blends from Tables 3.9 and 3.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>7.26</td>
<td></td>
</tr>
<tr>
<td>LD/LLD-70/30</td>
<td></td>
<td>7.07</td>
</tr>
<tr>
<td>LD/LLD-50/50</td>
<td></td>
<td>6.94</td>
</tr>
<tr>
<td>LD/LLD-30/70</td>
<td></td>
<td>6.82</td>
</tr>
<tr>
<td>LLD</td>
<td>6.62</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 3.19: $M_z/M_n$ of LDPE and HDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental</th>
<th>Calculated for blends from Tables 3.10 and 3.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>21.64</td>
<td></td>
</tr>
<tr>
<td>LD/HD-70/30</td>
<td>35.64</td>
<td></td>
</tr>
<tr>
<td>LD/HD-50/50</td>
<td>46.49</td>
<td></td>
</tr>
<tr>
<td>LD/HD-30/70</td>
<td>58.57</td>
<td></td>
</tr>
<tr>
<td>HD</td>
<td>78.92</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 3.20: $M_z/M_n$ of LLDPE and HDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental</th>
<th>Calculated for blends from Tables 3.11 and 3.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLD</td>
<td>23.99</td>
<td></td>
</tr>
<tr>
<td>LLD/HD-70/30</td>
<td>37.21</td>
<td></td>
</tr>
<tr>
<td>LLD/HD-50/50</td>
<td>47.58</td>
<td></td>
</tr>
<tr>
<td>LLD/HD-30/70</td>
<td>59.20</td>
<td></td>
</tr>
<tr>
<td>HD</td>
<td>78.92</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 3.21: $M_z/M_n$ of LDPE and LLDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental</th>
<th>Calculated for blends from Tables 3.12 and 3.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>21.64</td>
<td></td>
</tr>
<tr>
<td>LD/LLD-70/30</td>
<td>22.47</td>
<td></td>
</tr>
<tr>
<td>LD/LLD-50/50</td>
<td>22.96</td>
<td></td>
</tr>
<tr>
<td>LD/LLD-30/70</td>
<td>23.41</td>
<td></td>
</tr>
<tr>
<td>LLD</td>
<td>23.99</td>
<td></td>
</tr>
</tbody>
</table>
3.1.3 **Intrinsic Viscosity**

The intrinsic viscosity gives the comparative measure of molecular weight from the behaviour of the polymer in a very dilute solution and is related to viscosity average molecular weight, $M_v$, by the Mark-Houwink-Sakurada (M-H-S) equation. (Section 2.2.1 of Chapter 2):

$$[\eta] = K M_v^\alpha \quad (2.1)$$

and $K$ and $\alpha$ are Mark-Houwink constants for a given polymer, solvent and temperature.

Since $M_v$ was obtained at $140^\circ C$ in O-dichlorobenzene and Mark-Houwink constants are known at that condition, the intrinsic viscosities of the components are calculated from M-H-S equation using

- $K = 5.06 \times 10^{-5}$ m$^3$/Kg, $\alpha = 0.70$ for LDPE and LLDPE
- $K = 5.05 \times 10^{-5}$ m$^3$/Kg, $\alpha = 0.693$ for HDPE

The intrinsic viscosities of the blends are then calculated from the equation (3.2) as calculated by Jacovic and co-workers (82). The intrinsic viscosity values of the components and their blends are summarised in Tables 3.22 to 3.24.
TABLE 3.22: Intrinsic Viscosity of LDPE and HDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\eta_i$ (m³/Kg) at 140°C in O-dichlorobenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated from M-H-S equation (2.1)</td>
</tr>
<tr>
<td>LD</td>
<td>0.1646</td>
</tr>
<tr>
<td>LD/HD-70/30</td>
<td>0.1792</td>
</tr>
<tr>
<td>LD/HD-50/50</td>
<td>0.1889</td>
</tr>
<tr>
<td>LD/HD-30/70</td>
<td>0.1986</td>
</tr>
<tr>
<td>HD</td>
<td>0.2131</td>
</tr>
</tbody>
</table>

TABLE 3.23: Intrinsic Viscosity of LLDPE and HDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\eta_i$ (m³/Kg) at 140°C in O-dichlorobenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated from M-H-S equation (2.1)</td>
</tr>
<tr>
<td>LLD</td>
<td>0.1654</td>
</tr>
<tr>
<td>LLD/HD-70/30</td>
<td>0.1797</td>
</tr>
<tr>
<td>LLD/HD-50/50</td>
<td>0.1893</td>
</tr>
<tr>
<td>LLD/HD-30/70</td>
<td>0.1988</td>
</tr>
<tr>
<td>HD</td>
<td>0.2131</td>
</tr>
</tbody>
</table>

TABLE 3.24: Intrinsic Viscosity of LDPE and LLDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\eta_i$ (m³/Kg) at 140°C in O-dichlorobenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated from M-H-S equation (2.1)</td>
</tr>
<tr>
<td>LD</td>
<td>0.1646</td>
</tr>
<tr>
<td>LD/LLD-70/30</td>
<td>0.16484</td>
</tr>
<tr>
<td>LD/LLD-50/50</td>
<td>0.1650</td>
</tr>
<tr>
<td>LD/LLD-30/70</td>
<td>0.16516</td>
</tr>
<tr>
<td>LLD</td>
<td>0.1654</td>
</tr>
</tbody>
</table>
3.1.4 Degree of Branching

The results of branching measurements of the components are shown in Tables 3.25 to 3.27; these also include the calculated values of branching of the blends using the equation (3.2). Branching was calculated for blends by Jacovic and co-workers (82) by the same method.

The degree of branching of HDPE suggests that it is linear in structure and has negligible structural irregularity, whereas the degree of branching obtained for LDPE is normal and very common for this type of polyethylene. It is highly branched. The value of LLDPE is intermediate between LDPE and HDPE. It indicates that it is modestly branched.
### TABLE 3.25: Branching of LDPE and HDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>CH$_3$ groups/1000 carbon atoms</th>
<th>Experimental</th>
<th>Calculated for blends from equation (3.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td></td>
<td>27.50</td>
<td>19.40</td>
</tr>
<tr>
<td>LD/HD-70/30</td>
<td></td>
<td></td>
<td>14.00</td>
</tr>
<tr>
<td>LD/HD-50/50</td>
<td></td>
<td></td>
<td>8.60</td>
</tr>
<tr>
<td>LD/HD-30/70</td>
<td></td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>HD</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 3.26: Branching of LLDPE and HDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>CH$_3$ groups/1000 carbon atoms</th>
<th>Experimental</th>
<th>Calculated for blends from equation (3.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLD</td>
<td></td>
<td>13.00</td>
<td>9.25</td>
</tr>
<tr>
<td>LLD/HD-70/30</td>
<td></td>
<td></td>
<td>6.75</td>
</tr>
<tr>
<td>LLD/HD-50/50</td>
<td></td>
<td></td>
<td>4.25</td>
</tr>
<tr>
<td>LLD/HD-30/70</td>
<td></td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>HD</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 3.27: Branching of LDPE and LLDPE and their blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>CH$_3$ groups/1000 carbon atoms</th>
<th>Experimental</th>
<th>Calculated for blends from equation (3.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td></td>
<td>27.50</td>
<td>23.15</td>
</tr>
<tr>
<td>LD/LLD-70/30</td>
<td></td>
<td></td>
<td>20.25</td>
</tr>
<tr>
<td>LD/LLD-50/50</td>
<td></td>
<td></td>
<td>17.35</td>
</tr>
<tr>
<td>LD/LLD-30/70</td>
<td></td>
<td>13.00</td>
<td></td>
</tr>
<tr>
<td>LLD</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.1.5 Fractionated Linear Low-Density Polyethylene

Two fractions obtained from the fractionation have the following composition in weight percent: first fraction - 67% and second fraction 33%. Degrees of branching of the two fractions were measured and are represented in Table 3.28.

TABLE 3.28: Branching of LLDPE and its Fractions

<table>
<thead>
<tr>
<th>Sample</th>
<th>CH₃ groups/1000 carbon atoms</th>
<th>Experimental</th>
<th>Calculated from fractions by equation (3.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First Fraction</td>
<td></td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>(67% LLDPE)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Second Fraction</td>
<td></td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>(33% LLDPE)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LLDPE</td>
<td></td>
<td>13</td>
<td>13</td>
</tr>
</tbody>
</table>

The first fraction has lower branching than that from the second. The branching of LLDPE is calculated from the two fractions using the equation (3.2). The value obtained from this calculation gave the same value as obtained from experimental measurement of degree of branching of LLDPE whole polymer.

The two fractions were then subjected to thermal analysis as described in Section 2.3.2 of Chapter 2. After giving slow-cooled sample treatment, melting thermograms of the two fractions were obtained and are shown in Figure 3.7. Thermograms show similar melting behaviour to that obtained in the melting behaviour of slow-cooled LLDPE (Figure 4.18 in Section 4.1.2 of Chapter 4) indicating the existence of two crystal species - one is responsible for low temperature melting peak and the other for the high temperature
FIGURE 3.7: Melting Behaviour of two Fractions of LLDPE
melting peak. The values of melting points of low temperature melting species and high temperature melting species were found to be the same for the two fractions and for LLDPE. They are 108.5°C and 124.5°C respectively.

To find out the composition of the two crystal species in the two fractions and in LLDPE, from the two endothermic peaks of the melting thermograms, the method used by Inoue (83) was applied. Since the two endothermic peaks are not distinctly separated, and some overlapping portions occur, the evaluation of the peak areas of the two species was carried out by dividing the overlapping regions into areas belonging to each species graphically. Since the peak areas are almost proportional to the amount of each crystal species present, the contributions due to two crystal species were estimated and are represented in Table 3.29. The first fraction which was crystallised from solution

<table>
<thead>
<tr>
<th>Sample</th>
<th>DSC estimated composition (wt %)</th>
<th>Calculated composition (wt %) from fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low temperature melting species</td>
<td>High temperature melting species</td>
</tr>
<tr>
<td>First Fraction</td>
<td>54.5</td>
<td>45.5</td>
</tr>
<tr>
<td>(67% LLDPE)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Second Fraction</td>
<td>66.0</td>
<td>33.0</td>
</tr>
<tr>
<td>(33% LLDPE)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LLDPE</td>
<td>59.0</td>
<td>41.0</td>
</tr>
</tbody>
</table>

TABLE 3.29: Composition of two crystal species in LLDPE and its fractions
at 90°C, contains a lower amount of low temperature melting species and a higher quantity of high temperature melting species than that of LLDPE. The second fraction which was crystallised from solution at 80°C, contains a higher concentration of low temperature melting species and a lower amount of high temperature melting species than LLDPE. The material balance of low temperature melting species and high temperature melting species from the two fractions gave approximately the same value as that obtained from DSC measurement of LLDPE.

Polarised light microscopy confirmed that the two fractions form the same spherulitic structure which is very similar to that formed by LLDPE.

3.2 Conclusions

The components have the following ordering among themselves in:

1. Number average molecular weight, $M_n$
   
   $$\text{LLDPE} > \text{LDPE} > \text{HDPE}$$

2. Weight average molecular weight, $M_w$
   
   $$\text{HDPE} > \text{LLDPE} \sim \text{LDPE}$$

3. Z average molecular weight, $M_z$
   
   $$\text{HDPE} > \text{LLDPE} > \text{LDPE}$$

4. Viscosity average molecular weight, $M_v$
   
   $$\text{HDPE} > \text{LLDPE} \sim \text{LDPE}$$
5. Dispersity index, $M_w/M_n$

$$\text{HDPE} > \text{LDPE} \sim \text{LLDPE}$$

6. Dispersity index, $M_z/M_n$

$$\text{HDPE} > \text{LLDPE} \sim \text{LDPE}$$

7. Intrinsic viscosity, $\eta_i$

$$\text{HDPE} > \text{LLDPE} \sim \text{LDPE}$$

8. Branching

$$\text{LDPE} > \text{LLDPE} > \text{HDPE}$$

9. Linear low-density polyethylene consists of two species which are chemically linked. It is not a physical mixture.
CHAPTER 4

RESULTS, DISCUSSION AND CONCLUSIONS:
CRYSTALLINE STRUCTURE OF COMPONENTS AND THEIR BLENDS

4.1 Results and Discussion

4.1.1 Density and crystallinity

The structure of a polyethylene can be described in terms of three factors: (a) the molecular weight and its distribution; (b) the various structural heterogeneities which can occur on or within the chain, particularly chain branches; (c) their distribution within a given chain and between chains of the given sample which influences the degree of crystallinity. These structural factors determine and control the properties of the polymer. Density is a solid state property which gives the overall combined information of the structure of a polyethylene.

The results of density measurements of the components and their blends are shown in Figures 4.1 to 4.3. It is normal that the density of LDPE obtained (0.9215 g/ml) is lower than the value of HDPE (0.9485 g/ml). The values of all the LD/HD blends showed that they follow the volume additive rule given by (84):

\[
\frac{1}{d_{12}} = \frac{w_1}{d_1} + \frac{w_2}{d_2}
\]  

(4.1)

where \( d_{12} \) = density of the blend  
\( d_1 \) = density of component 1  
\( d_2 \) = density of component 2  
\( w_1 \) = weight fraction of component 1  
\( w_2 \) = weight fraction of component 2

The similar results were reported by Stafford (84) for LDPE and HDPE and their blends. But surprisingly the density value of LLDPE (0.9185 g/ml) is in the region of LDPE or more precisely its value is marginally lower than the LDPE value. The density results of LLD/HD blends and LD/LLD blends are also in accord with the volume additive rule.
FIGURE 4.1: Density of LDPE and HDPE and their Blends
FIGURE 4.2: Density of LLDPE and HDPE and their Blends
FIGURE 4.3: Density of LDPE and LLDPE and their Blends
Crystallinity data, estimated by the specific volume method, of the components and their blends are shown in Figures 4.4 to 4.6. The LDPE has a lower crystallinity than HDPE; the presence of a high degree of branching interferes with the crystallisation in LDPE. The higher the degree of branching and the lower the crystallinity - is the expected rule in the case of polyethylene. But the crystallinity result of LLDPE contradicts this behaviour. Though it has appreciably lower degree of branching than LDPE, its overall crystallinity is marginally lower than that of LDPE.

The crystallinity of both LD/HD blends (Figure 4.4) and LLD/HD blends (Figure 4.5) show a gradual increase with increase in HDPE content and there is a gradual decrease in crystallinity with increase in LLDPE content in LD/LLD blends (Figure 4.6). All the sets show a linear relationship between crystallinity and composition. These results indicate that the crystallinity of the blends appears to follow the simple additive rule given by the equation (3.2) (Section 3.1.2 of Chapter 3). The similar observation was reported by Donatelli (85) in the case of low-density/high-density polyethylene blends.

4.1.2 Melting and crystallisation behaviour

Thermograms obtained from thermal analysis of LDPE (Figures 4.7 and 4.8) and HDPE (Figures 4.9 and 4.10) both for fast- and slow-cooled samples showed normal melting and crystallisation behaviour with a single peak. LD/HD-70/30 showed two distinct peaks for both fast- and slow-cooled samples during melting as well as during crystallisation as shown in Figures 4.11 and 4.12 respectively. Two peaks are associated with the occurrence of two types of crystalline species. One was associated with LDPE and the other with HDPE. LD/HD-50/50 also showed two distinct melting peaks both for fast- and slow-cooled samples; whereas during crystallisation the slow-cooled specimen showed two distinct peaks, the fast-cooled sample showed mainly the peak due to the HDPE phase though the peak due to the LDPE phase is very poorly resolved - Figures 4.13 and 4.14 -
FIGURE 4.4: Crystallinity of LDPE and HDPE and their Blends
FIGURE 4.5: Crystallinity of LLDPE and HDPE and their Blends
FIGURE 4.6: Crystallinity of LLDPE and LLDPE and their blends.
FIGURE 4.7: Thermograms of fast-cooled LDPE
FIGURE 4.8: Thermograms of slow-cooled LDPE
FIGURE 4.9: Thermograms of fast-cooled HDPE
FIGURE 4.10: Thermograms of slow-cooled HDPE
FIGURE 4.11: Thermograms of fast-cooled LD/HD-70/30 blend
FIGURE 4.12: Thermograms of slow-cooled LD/HD-70/30 blend
indicating that the resolution of two distinct peaks was not possible with the faster cooling rate. The thermograms of LD/HD-30/70 for fast- and slow-cooled samples are shown in Figures 4.15 and 4.16. The peak due to the LDPE phase is only detectable in the melting of the slow-cooled sample, though the contribution is naturally much lower than that in the LD/HD-50/50 slow-cooled sample.

No cocrystallisation phenomenon was observed in the case of LD/HD blends. Similar behaviour was observed by several authors in the case of low- and high-density polyethylene blends (84,85,86) and low- and intermediate density polyethylene blends (84).

Thermograms of linear low-density polyethylene for fast- and slow-cooled samples are shown in Figures 4.17 and 4.18 respectively. Thermal behaviour of LLDPE is quite different from that for LDPE or HDPE. Melting of the fast-cooled sample showed a broad shallow melting curve followed by a high temperature melting peak with a small melting deflection between the two. This multiple peak behaviour is unusual in any type of polyethylene. During crystallisation at the faster cooling rate mainly one crystallisation peak was predominant though a broad shoulder appeared followed by main crystallisation peak, but during crystallisation at the slower cooling rate the thermogram clearly suggested two crystal species. The second melting thermogram showed only two peaks - one broad but shallow and the other narrow but sharp; the peak appearing in between the two in the case of the fast-cooled sample disappeared in the case of the slow-cooled sample.

It is evident that LLDPE consists of two stable crystal species - one is responsible for the low temperature melting peak and the other for the high temperature melting peak. Bubeck and Baker (87) recently commented from the DSC measurements that LLDPE show multiple melting endotherms due to presence of heterogeneous (i.e. "blocky") branching, whereas LDPE shows single melting endotherm due to presence of random branching. The present results support this. The peak appearing in between the two in the case of the fast-cooled LLDPE
FIGURE 4.13: Thermograms of fast-cooled LD/HD-50/50 blend
FIGURE 4.14: Thermograms of slow-cooled LD/HD-50/50 blend
FIGURE 4.15: Thermograms of fast-cooled LD/HD-30/70 blend
FIGURE 4.16: Thermograms of slow-cooled LD/HD-30/70 blend
FIGURE 4.17: Thermograms of fast-cooled Dowlex LLDPE
FIGURE 4.18: Thermograms of slow-cooled Dowlex LLDPE
sample may be due to the cocrystal formation of the two crystal species for their limited miscibility in that heat history.

The thermal behaviour of the other linear low-density polyethylenes (LLDPE), Unifos LPLD-8001 (Unifos Kemi AB, Sweden), and Escorene LPX-1 (Exxon Chemical, USA) are shown in Figures 4.19 to 4.20 and Figures 4.21 to 4.22 respectively. They showed the similar low temperature broad melting peak followed by a sharp high temperature melting peak. This indicates that the presence of low melting point crystal species is usual beside the main high melting point crystal species in LLDPE, although it is reported that these copolymer utilise different comonomer (87).

Thermograms of LLD/HO blends (Figures 4.23 to 4.28) showed only one high temperature peak indicating the existence of one type of crystal species at all compositions for all cooling conditions. It would appear, therefore, that cocrystallisation of the high melting point constituent of LLDPE and HDPE took place in LLD/HO blends, whereas for LD/HD blends each component tended to crystallise separately. However, the low temperature broad peak has appeared in the melting of the sample of LLD/HO blends, though its contribution has decreased with an increase in HDPE content. It is perhaps significant that although there is one high temperature peak in any of the LLD/HO blends the low temperature peak recurred indicating that miscibility of LLD/HO blends does not extend through this low melting point crystal species.

The thermograms of LD/LLD-70/30 for the fast-cooled sample are shown in Figure 4.29. The sample showed multiple melting behaviour representing three peaks. During cooling the crystallisation exotherm mainly showed one peak coupled with a shoulder, but during crystallisation at slower cooling rate this was distinctly resolved into two peaks as shown in Figure 4.30. The melting endotherm of the slow-cooled sample showed only two peaks indicating the existence of two types of crystalline phase. Similar behaviour was observed in the rest of the LD/LLD blends, as is evident from the thermograms of fast- and slow-cooled samples of LD/LLD-50/50 in Figures 4.31 and
FIGURE 4.19: Thermograms of fast-cooled Unifos LLDPE
FIGURE 4.20: Thermograms of slow-cooled Unifos LLDPE
FIGURE 4.21: Thermograms of fast-cooled Escorene LLDPE
FIGURE 4.22: Thermograms of slow-cooled Escorene LLDPE
FIGURE 4.23: Thermograms of fast-cooled LLD/HD-70/30 blend
FIGURE 4.24: Thermograms of slow-cooled LLD/HD-70/30 blend
FIGURE 4.25: Thermograms of fast-cooled LLD/HD-50/50 blend
FIGURE 4.26: Thermograms of slow-cooled LLD/HD-50/50 blend
FIGURE 4.27: Thermograms of fast-cooled LLD/HD-30/70 blend
FIGURE 4.28: Thermograms of slow-cooled LLD/HD-30/70 blend
FIGURE 4.29: Thermograms of fast-cooled LD/LLD-70/30 blend
FIGURE 4.30: Thermograms of slow-cooled LD/LLD-70/30 blend
Thermograms of slow-cooled samples of all LD/LLD blends indicate the presence of two stable crystalline phases. The first low temperature phase is associated with LDPE and the other high temperature phase is the high melting point constituent of LLDPE. It must be noted that there is a possibility of formation of miscible mixture of LDPE and low melting point crystal species of LLDPE. There is a gradual increase in contribution of high melting point crystal species of LLDPE, and decrease in combined contribution of LDPE phase and low melting point crystal species of LLDPE with an increase in LLDPE content in all LD/LLD blends. This is observed from the crystallisation exotherms and as well as from the melting endotherms of the blends.

Melting of the fast-cooled samples of all LD/LLD blends show the presence of the third peak in between the two expected peaks. It is suggested that the third peak is the result of the cocrystal formation of the two crystal species for their limited miscibility in that heat history. It has, however, been previously observed in the fast-cooled sample of LLDPE. Clampitt (88) in a DTA study of blends of HDPE and LDPE was able to resolve the DTA curve into three peaks corresponding to the fusion of the various types of crystals. Two peaks were associated with the fusion of LDPE and HDPE; the third peak was associated with the fusion of cocrystal of the components having only a small range of miscibility for molecules of the two types. On further study over a series of blends he (89) concluded that low branching of LDPE favours cocrystal formation and LDPE's containing higher degree of branching do not appear to possess a cocrystal peak. This is the reason why LD/HD blends in the present work do not possess any cocrystal peak, because LDPE used was of high degree of branching (27 methyl groups/1000 carbon atoms).

The first crystalline melting endotherm and the second crystalline melting endotherm are very similar in the case of the fast-cooled sample of all sets of blends. Such a result is due to similar thermal
FIGURE 4.31: Thermograms of fast-cooled LD/LLD-50/50 blend
FIGURE 4.32: Thermograms of slow-cooled LD/LLD-50/50 blend
FIGURE 4.33: Thermograms of fast-cooled LD/LLD-30/70 blend
FIGURE 4.34: Thermograms of slow-cooled LD/LLD-30/70 blend
crystallisation history between the first cooling cycle (after compression moulding) and the second one, obtained by DSC. In the case of the slow-cooled sample there was a difference in second crystalline melting endotherm from the first one, due to the different thermal crystallisation history.

4.1.3 Crystalline melting point and crystallisation temperature

To summarise the thermal analysis results, phase diagrams of all the blends were drawn for both cooling conditions using the values of crystalline melting point and crystallisation temperature. The phase diagrams of fast- and slow-cooled samples of LDPE/HDPE blends are shown in Figures 4.35 and 4.36 respectively. Above the melting point curve of the HDPE phase there is only one melt phase. This is based on the assumption that LDPE and HDPE are miscible in their melt condition. The melt phase of LDPE and the crystalline phase of HDPE exist below the melting point curve of HDPE phase and above the melting point curve of LDPE phase. Whereas below the melting point curve of LDPE phase there are two crystalline phases - one for LDPE and the other for HDPE. The same explanation applies in the case of phase diagrams based on crystallisation temperature curve.

The crystalline melting points of both LDPE and HDPE are depressed by the other component, possibly due to the following effects (90):

i) The kinetic effect of one solid phase which may obstruct or make irregular the growth of the lamellar crystallites of the spherulites of the other phase;

ii) Thermal perturbations due to different rates of crystallisation of the two components.

A similar melting point depression was observed by Stafford (84) in case of low- and high-density polyethylene mixtures and by Greco et al (90,91) in the case of polyethylene and polypropylene mixtures.
FIGURE 4.35: Phase diagram of fast-cooled LDPE/HDPE blends

- (□) crystalline melting point;
- (■) crystallisation temperature
FIGURE 4.36: Phase diagram of slow-cooled LDPE/HDPE blends

(□) crystalline melting point; (●) crystallisation temperature
Figures 4.37 and 4.38 show the respective phase diagrams of fast- and slow-cooled samples of LLDPE/HDPE blends based both on crystalline melting point curve and crystallisation temperature curve. If the LLDPE and HDPE are miscible in their melt stage, there is one phase melt above the melting point curve and one LLDPE/HDPE cocrystalline phase below the same curve. The situation is exactly similar in the case of the phase diagram based on the crystallisation temperature.

No melting point depression was observed in this case. On the other hand there is a gradual increase in crystalline melting temperature of LLDPE/HDPE blends with an increase in HDPE content both for fast- and slow-cooled samples. The melting point curves showed no minimum as observed before in the case of isomorphous mixtures of poly(vinyl fluoride) and poly(vinylidene fluoride) (32) already stated in Section 1.5.4 of Chapter 1.

In the case of slow-cooled sample of both LDPE/HDPE and LLDPE/HDPE blends there was an increase in crystalline melting point and crystallisation temperature compared with the fast-cooled sample.

The phase diagram based on melting point curve is quite different from that based on the crystallisation temperature curve in the case of fast-cooled LDPE/LLDPE blends as shown in Figure 4.39. It can be described as follows:

a) Above the melting point curve of LLDPE phase, there is a presence of one phase melt based on the same assumption that LDPE and LLDPE are miscible in their molten condition;

b) Above the melting point curve of LDPE/LLDPE cocrystalline phase and below the melting point curve of LLDPE phase, the melt phase of LDPE/LLDPE cocrystal and the crystalline phase of LLDPE exist;

c) Above the melting point curve of LDPE phase and below the melting point curve of LDPE/LLDPE cocrystalline phase,
FIGURE 4.37: Phase diagram of fast-cooled LLDPE/HDPE blends

(O) crystalline melting point;

(●) crystallisation temperature
FIGURE 4.38: Phase diagram of slow-cooled LLDPE/HDPE blends

(o) crystalline melting point;
(b) crystallisation temperature
FIGURE 4.39: Phase diagram of fast-cooled LDPE/LLDPE blends

(◊)crystalline melting point;
(♦)crystallisation temperature
there are the occurrence of LDPE melt phase, LDPE/LLDPE cocrystalline phase and LLDPE crystalline phase;

d) Below the melting point curve of the LDPE phase, there are three crystalline phases - the first one for LDPE, the second one for LLDPE and the third one for LDPE/LLDPE cocrystal.

The LDPE/LLDPE cocrystalline phase is believed to exist in the interface between the LDPE and LLDPE crystalline phases. The phase diagram based on crystallisation temperature curves suggests the presence of single melt phase above the curve and single crystalline phase below the curve.

The phase diagram of slow-cooled samples of LDPE/LLDPE blends are shown in Figure 4.40. This is very similar to, the phase diagram of LDPE/HDPE blends but quite different from the phase diagram of fast-cooled samples. Above the melting point curve of LLDPE there exists only one phase melt, and below the same curve and above the melting point curve of LDPE phase there are the presence of melt phase of LDPE and crystalline phase of LLDPE. But below the melting point curve of LDPE there are two crystalline phases - one for LDPE and the other for LLDPE. The similar explanation applies in the case of phase diagram based on crystallisation temperature curves.

The similar melting point depression of both LDPE and LLDPE were observed by the other component as observed in both LDPE and HDPE in their blends. This is possibly due to the similar effects as stated before in the case of LDPE/HDPE blends.

4.1.4 Diffraction patterns and unit cell dimensions

Wide-angle X-ray diffraction patterns of LLDPE and HDPE and their blends are shown in Figure 4.41. The diffraction patterns of all blends showed only the two reflections (110 and 200) as shown by the components. This result supports the fact that the blends of
FIGURE 4.40: Phase diagram of slow-cooled LDPE/LLDPE blends

(◊) crystalline melting point;
(♦) crystallisation temperature
FIGURE 4.41: Wide-angle X-ray diffraction patterns of LLDPE and HDPE and their Blends
LLDPE and HDPE behave like a single component system. Greco et al (90,91) when they characterised high-density polyethylene-isotactic polypropylene blends by wide-angle X-ray diffraction found that the diffraction patterns of the blends corresponded to a simple superposition of the reflections of the components and concluded that this was due to the immiscibility of the two components, because they found neither co-crystallisation phenomena nor shifts in the spacing of the reflections. No such behaviour was observed in LLD/HD blends.

To obtain the unit cell dimensions first the spacing between planes of atoms, \( d_{hkl} \) was calculated through Bragg's equation as defined in Section 2.3.3 of Chapter 2, for first order reflections it is given by:

\[
\lambda = 2d_{hkl} \sin \theta
\]  

(2.12)

The angle of incidence and reflection, \( \theta \) was obtained from the simple geometry

\[
\tan 2\theta = \frac{r_p}{d_{sp}}
\]

where \( r_p \) = measured radius of each ring

\( d_{sp} \) = accurate distance between sample and plate.

In a three-dimensional lattice of unit cell sides \( a, b, c \) in the X, Y, Z directions respectively, the Miller Indices are \( h, k, \ell \) and the planes intercept the X, Y, Z axes at intervals of \( a/h, b/k, c/\ell \). These are related to \( d_{h\ell k} \) by the following equation

\[
\frac{1}{d_{h\ell k}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{\ell^2}{c^2}
\]

(4.2)
For the two reflections (110 and 200) the equation (4.2) reduces to equations (4.3) and (4.4) respectively:

\[
\frac{1}{d_{110}^2} = \frac{1}{a^2} + \frac{1}{b^2} \tag{4.3}
\]

\[
\frac{1}{d_{200}^2} = \frac{2^2}{a^2} = \frac{4}{a^2} \tag{4.4}
\]

The "a" dimension was obtained from equation (4.4) and hence "b" dimension from equation (4.3) using the calculated value of \(d_{h,k}\).

The results of unit cell dimensions of LLDPE and HDPE and their blends are shown in Figure 4.42. They behaved in a very regular fashion. The dimensions \((a = 7.486 \, \text{Å} \text{ and } b = 5.020 \, \text{Å})\) are identical for the LLDPE, LLD/HD-70/30 and LLD/HD-50/50 samples. At the other end of the scale the LLD/HD spacing \((a = 7.342 \, \text{Å} \text{ and } b = 4.902 \, \text{Å})\) is identical to that of the HDPE sample. The dimensions of the unit cells of LLD/HD blends are in a linear relationship with composition and are always in between the values of the components. This is the case of true isomorphism as observed in similar manner by X-ray diffraction in the systems of 4-methyl-1-pentene/4-methyl-1-hexene and isopropyl vinyl ether/sec-butyl vinyl ether as homopolymer mechanical mixtures (33) as stated in Section 1.5.4 of Chapter 1.

It is perhaps noteworthy that the volume of the unit cell of HDPE is lower than the LLDPE. This is to imply that the structure of HDPE is more closely packed than LLDPE. HDPE is linear in structure whereas LLDPE is modestly branched. Swan (92) on the basis of a detailed X-ray analysis of linear polyethylene reported that the inclusion of branching causes the expansion of the orthorhombic unit cell dimensions of polyethylene. The present result is in line with the effect of branching on the unit cell of polyethylene.

4.1.5 Morphology

Small angle light scattering (SALS) patterns and oscilloscope traces of LDPE and LLDPE and their blends are shown in Figures 4.43
FIGURE 4.42: Unit Cell Dimensions of LLDPE and HDPE and their Blends: (O) a dimension; (●) b dimension
to 4.47. SALS pattern of LDPE showed the characteristic four distinct equivalent lobes as reported before by several authors (58, 59, 93). It indicates that the superstructure formed was perfect in nature. The pattern of LLDPE gave the similar information as LDPE, but comparison of the two patterns indicates the spherulite size of LLDPE formed was larger than that from LDPE. The pattern of LD/LLD-70/30 blend was quite different from the others. No distinct four equivalent lobes were observed in this case. So there was a disruption in the perfection of the formed spherulitic structure. But the patterns of LD/LLD-50/50 and LD/LLD-30/70 are very similar to the pattern of LDPE in nature as well as in size.

It is apparent from Figures 4.43 to 4.47 that the addition of 30% LLDPE in LDPE causes a deterioration of the initial clearly defined spherulitic morphology of LDPE. But addition of 50% LLDPE helps to regain the original morphology and maintain up to pure LLDPE through the LD/LLD-30/70 blend. There is, therefore, a transition in the morphological form of the mixtures at the LD/LLD-70/30 composition. It is believed due to the influence of voids and other isotropic density fluctuations such as differences in refractive index between the non-spherulitic material (the medium) and each of the indices of the spherulite (radial and tangential) (59). Mandelkern et al (95) on light scattering studies of mixtures and fractions of polyethylene reported the similar deterioration of the initial spherulitic morphology characteristic of the lower molecular weight species on the addition of a higher molecular weight fraction.

In past scattering from anisotropic spheres has been calculated and agrees quite well with observed pattern of undeformed polyethylene (59). From the theory the average size of the scattering sphere can then be calculated by using the following equation (94):

\[ r_s = \frac{1.025\lambda}{\pi n_r \sin(\theta_m/2)} \]  \hspace{1cm} (4.5)
FIGURE 4.43: $V_H$ Light scattering pattern and oscilloscope trace of LDPE
FIGURE 4.44: $V_H$ Light scattering pattern and oscilloscope trace of LD/LLD-70/30 blend
FIGURE 4.45: $V_H$ Light scattering pattern and oscilloscope trace of LD/LLD-50/50 blend
FIGURE 4.46: $V_H$ Light scattering pattern and oscilloscope trace of LD/LLD-30/70 blend
FIGURE 4.47: $V_H$ Light scattering pattern and oscilloscope trace of LLDPE
where $r_s$ = average radius of the scattering sphere,
$\lambda$ = wavelength of incident light,
$n_r$ = average refractive index of the medium,
$\theta_m$ = scattering angle (azimuthal angle $= 45^\circ$) at which
the maximum intensity occurs in the four equivalent
lobes of the pattern.

Since the scattering angle is inversely proportional to the
average radius of the scattering sphere, small spherulites will
have a pattern with maxima at large scattering angles while large
spherulites will have maxima at small scattering angles. This is
observed in the present results.

It is possible to find out the ratio of the spherulite size
of LLDPE and LDPE using the equation (4.5). Since other terms are
constant, for two cases, it yields:

$$\frac{r_{s1}}{r_{s2}} = \frac{\sin (\theta_{m2}/2)}{\sin (\theta_{m1}/2)}$$  (4.6)

Again

$$\tan \theta_m = \frac{d_{cs}}{d_{sf}}$$  (4.7)

where: $d_{cs}$ = distance of the intensity maximum of one of the lobes
from the centre of the whole pattern
$d_{sf}$ = constant sample to film distance.

Since $\theta_m$ is small, it can be assumed safely

$$\sin \theta_m = \tan \theta_m$$

Then equations (4.6) and (4.7) give
The measured value of the right hand term of the equation (4.8) is 2. So the average spherulite size of LLDPE is double the average spherulite size of LDPE.
4.2 Conclusions

1. The components have the ordering among themselves in density and crystallinity:

\[ \text{HDPE} > \text{LDPE} \approx \text{LLDPE} \]

Experimentally measured density and hence crystallinity of the blends obey the additive rule in all three systems.

2. Since LDPE and HDPE can be mixed intimately in the amorphous region in the blends of low-density and high-density polyethylene (96), it is reasonable to assume that LDPE and HDPE are miscible in the amorphous phase, but based on thermal analysis their crystalline phases are immiscible. Whereas LLDPE and HDPE are miscible in the crystalline phase in the blends of linear low-density and high-density polyethylene.

Immiscibility of the crystalline phases of LDPE and LLDPE has been found in the low-density/linear low-density polyethylene system on the basis of stability of the blends. It is believed that partial miscibility has occurred at the interface of the two crystalline phases in the meta stable state of the blends.

3. Isomorphism has been seen in the linear low-density/high-density polyethylene system on the basis of X-ray diffraction.

4. Small angle light scattering has shown that LDPE, LD/LLD-50/50 and LD/LLD-30/70 are very similar in their morphology in the low-density/linear low-density polyethylene system. No perfect structure has been observed in the LD/LLD-70/30 blend. Calculated spherulite size from perfect LLDPE structure has been found twice the spherulite size of LDPE.
CHAPTER 5

RESULTS, DISCUSSION AND CONCLUSIONS:
MELT PROPERTIES OF COMPONENTS AND THEIR BLENDS

5.1 Results and Discussion

5.1.1 Melt flow index

The results of melt flow index (MFI) of components and their blends are shown in Figures 5.1 to 5.3. The MFI of HDPE is lower than that of LDPE, but the MFI of LLDPE is approximately equal to that of LDPE, due to similarity in their molecular weights, since it is known that there is a correlation between MFI and weight average molecular weight - the higher the MFI the lower the molecular weight (97).

In semilogarithmic coordinates MFI data of the LDPE/HDPE blends seemed to vary approximately linearly with composition according to the logarithmic mixing rule (Figure 1.5 of Section 1.6.2 of Chapter 1). So did the LDPE/LLDPE blends, but the data of LLDPE/HDPE blends showed that they are all perfectly on a straight line. It should be noted that in the case of LDPE/LLDPE blends the similar behaviour was observed using a 10 kg load at 150°C in place of the standard test condition, using 2.16 kg load at 190°C.

From measurements of MFI various workers have calculated the apparent viscosity and correlated this with molecular weight. The estimation of apparent viscosity from MFI data is inaccurate since large corrections have to be made. It is preferable to use a high shear viscometer to minimise the sources of error.

5.1.2 Melt memory index

On the assumption that the total deformation occurring during flow is composed of viscous flow and high elastic deformation due to chain uncoiling, melt memory index or extrudate swell can be used as
FIGURE 5.1: Melt flow index of LDPE and HDPE and their blends at 190°C, load 2.16 Kg
FIGURE 5.2: Melt Flow Index of LLDPE and HDPE and their Blends at 190°C, load 2.16 Kg
FIGURE 5.3: Melt Flow Index of LDPE and LLDPE and their Blends
(○) at 190°C, load 2.16 Kg; (♦) at 150°C, load 10 Kg
a measure of the elastic component of the melt.

The results of melt memory index (MMI) of components and their blends are shown in Figures 5.4 to 5.6. The MMI of HDPE is lower than that of LDPE. Since HDPE is linear in structure, the value of MMI is the magnitude of the viscous component only, as its elastic component is very minor (98). It was reported that for polydisperse samples, the weight average molecular weight should correlate more quantitatively with the MMI than would the number average molecular weight (99,100), and it was found that MMI tended to increase with molecular weight (101). The similar behaviour was observed in LLDPE and HDPE. The MMI of HDPE is higher than that of LLDPE, due to its higher molecular weight. So it is seen that the MMI of LDPE is higher than LLDPE. Guillet et al (99,100) from their experimental work concluded that the MMI of polyethylene samples with similar degrees of long-chain branching increases uniformly as the molecular weight distribution broadens. They recommended that MMI can be used as a convenient index of the breadth of molecular weight distribution for polyethylenes of similar degrees of long-chain branching. On the basis of the MMI data it is deduced that the degree of long-chain branching in LDPE is higher than that in LLDPE because their molecular weight distributions are similar; an entirely plausible conclusion.

In the blends of LDPE and HDPE, firstly there is an increase in MMI over LDPE level up to 50% HDPE content, then MMI of the blends is decreased on further addition of HDPE. In the blends of LLDPE and HDPE there is a sharp increase in MMI initially but it is maintained roughly at the HDPE level throughout. The LDPE/LLDPE blends behaved in very regular fashion: there is a gradual decrease in MMI with increase in LLDPE. They behaved in similar manner even after changing the standard test condition.
FIGURE 5.4: Melt Memory Index of LDPE and HDPE and their Blends at 190°C, load 2.16 Kg
FIGURE 5.5: Melt Memory Index of LLDPE and HDPE and their Blends at 190°C, load, 2.16 Kg
FIGURE 5.6: Melt Memory Index of LDPE and LLDPE and their Blends
(◊) at 190°C, load 2.16 Kg; (◊) at 150°C, load 10 Kg
5.1.3 Shear flow behaviour

The plots of shear stress against shear rate of LDPE and HDPE and their blends are shown in Figure 5.7; apparent viscosity vs shear rate data are plotted in Figure 5.8. At low shear rate the apparent viscosity of LDPE is lower than that of HDPE, due to the higher molecular weight of HDPE, since low-shear melt viscosity is directly related to Z average molecular weight (102). The change in apparent viscosity with increasing shear rate (non-Newtonian behaviour) is more pronounced in HDPE than LDPE, because HDPE has higher dispersity index than LDPE. This is in accordance with the work of Guillet et al (99,100) who reported that the degree of non-Newtonian behaviour increases with breadth of distribution, so that among polyethylenes having similar low-shear melt viscosity the ones with broad distributions have lower viscosities at high shear rates.

The flow behaviour of LD/HD-70/30 blend is very similar to that of LDPE, but at high-shear rates the melt viscosity decreases with increase in HDPE content as evident from the flow curves of the LD/HD-50/50 and LD/HD-30/70 blend. It should be noted that the flow curve of the LD/HD-30/70 blend surprisingly lay outside the boundaries determined by the pure components. This is not the expected behaviour of the blend, whereas the LD/HD-50/50 and LD/HD-70/30 blends remained in between the two components at low-shear rate.

Figure 5.9 shows the flow curves of LLDPE and HDPE and their blends. The plot of apparent viscosity vs shear rate obtained from it is shown in Figure 5.10. At low shear rate the apparent viscosity of LLDPE is lower than that of HDPE, due to its lower molecular weight. All the blends of LLDPE and HDPE remained in between these of the two components keeping the right order, although there is a cross over roughly at a particular shear rate. This is due to increase in molecular weight distribution from LLDPE to HDPE as explained previously, leading to more non-Newtonian behaviour.

The plot of shear stress vs shear rate and that of apparent viscosity vs shear rate of LDPE and LLDPE and their blends are shown
FIGURE 5.7: Shear Stress-Shear Rate Behaviour of LDPE and HDPE and their Blends at 190°C
FIGURE 5.8: Shear Rate Dependent Apparent Viscosity of LDPE and HDPE and their Blends at 190°C
FIGURE 5.9: Shear Stress-Shear Rate Behaviour of LLDPE and HDPE and their Blends at 190°C
FIGURE 5.10: Shear Rate Dependent Apparent Viscosity of LLDPE and HDPE and their Blends at 190°C
in Figures 5.11 and 5.12 respectively. The flow behaviour of LLDPE is very similar to the behaviour of LDPE, at both low and high shear rate. In the case of branched polyethylenes, the dependence of melt viscosity on short-chain branching is quite minor compared to that on long-chain branching (103). This would be expected that unbranched polymers have higher melt viscosities than long-branched polymers of similar weight average molecular weight, since the long-branched molecules would be more compact and be expected to entangle less with other molecules (80). LDPE and LLDPE are similar in their weight average molecular weight and molecular weight distribution, although LLDPE has slightly higher $Z$ average molecular weight than that of LDPE. The higher melt viscosity of LLDPE over LDPE in the present result again suggests that LLDPE has a smaller degree of long-chain branching than LDPE.

All the blends of LDPE and LLDPE behaved in a very regular fashion which was not found for either of the two earlier sets of blends. No sign of increase in non-Newtonian behaviour was observed in this case, due to similarity of the molecular weight distribution of the two components.

Graphs of apparent viscosity vs composition are obtained by cross-plotting the flow curves at a particular shear rate and are represented in Figure 5.13. This shows a regular trend of viscosity as a function of composition. There is a gradual increase in viscosity with increase in LLDPE content in LDPE.

5.1.4 Elongational flow behaviour

The plots of elongational tensile stress vs Hencky strain (Hencky measure of strain = $\ln$ (draw ratio) = $\ln$ (final length/initial length) as defined in Section 2.4.3 of Chapter 2) of LLDPE and HDPE and their blends are shown in Figure 5.14. The same plots show the curves of elongational viscosity as a function of Hencky strain. The flow behaviour of LLDPE in elongation is completely
FIGURE 5.11: Shear Stress-Shear Rate Behaviour of LDPE and LLDPE and their Blends at 190°C
FIGURE 5.12: Shear Rate Dependent Apparent Viscosity of LDPE and LLDPE and their Blends at 190°C
FIGURE 5.13: Apparent Viscosity of LDPE and LLDPE and their Blends at 190°C at a Series of Constant Shear Rates
FIGURE 5.14: Tensile Stress-Strain Behaviour in Elongation and Strain Dependent Elongational Viscosity of LLDPE and HDPE and their Blends at 150°C at a Constant Elongational Strain rate of 1 s⁻¹.
different from that of HDPE: pronounced strain-hardening behaviour was observed in the case of HDPE, whereas LLDPE shows no such behaviour. All the blends showed elongational flow behaviour very similar to that of HDPE; they are more influenced by HDPE than LLDPE even at low concentration of HDPE, although there is a gradual decrease in elongational viscosity with increase in LLDPE content. The higher viscosity value of HDPE over LLDPE is believed to be due to higher weight average molecular weight and molecular weight distribution of HDPE than those of LLDPE. The present results support the work of Attalla et al (104) who reported that the elongational viscosity of polyethylene increases linearly with increase in the weight average molecular weight and molecular weight distribution product having approximately the similar degree of branching. Similar behaviour has been found by Munstedt (105) in low-density polyethylenes of similar weight average molecular weight, but different molecular weight distributions and as well as by Munstedt and Laun (106) in LDPE samples of different weight average molecular weight.

The plot of elongational tensile stress vs Hencky strain of LDPE and LLDPE and their blends are shown in Figure 5.15. The same plot shows the curves of elongational viscosity as a function of Hencky strain. The flow behaviour of LDPE is quite different from that of LLDPE, but similar to that of HDPE. Strain-hardening behaviour was observed in the case of LDPE and as well as in the case of all the blends. All the blends of LDPE and LLDPE showed a very regular behaviour; there is a uniform increase in elongation viscosity with increase in LDPE content in LLDPE.

It should be noted that both LDPE and LLDPE are similar in their weight-average molecular weight and molecular weight distribution but they differ in elongational viscosity values. This is suggested from the present results that LDPE has higher degree of long-chain branching than that of LLDPE. This is in line with the conclusion drawn by Munstedt and Laun (106) that elongational viscosity of polyethylene increases with degree of branching.
FIGURE 5.15: Tensile Stress-Strain Behaviour in Elongation and Strain Dependent Elongational Viscosity of LDPE and LLDPE and their Blends at 150°C at a Constant Elongational Strain rate of 1 s⁻¹.
besides molecular weight distribution. They further stated that
the shear viscosities compared at the same weight average mole­
cular weights are the higher, the smaller the degree of branching.
The shear viscosity results of the LDPE/LLDPE system (Figure
5.12) confirmed this statement, but the present results do not
agree with the conclusion of Attalla et al (104) who stated that
long-chain branching lowers the elongational viscosity for the
same weight average molecular weight and molecular weight dis­
tribution product. They further noted that the influence of long­
chain branching on elongational viscosity is the same as on shear
viscosity.

Graphs of elongational viscosity vs composition are obtained
by cross-plotting the flow curves at a particular Hencky strain
and are represented in Figure 5.16 at a series of constant Hencky
strains. This shows a regular trend of viscosity as a function
of composition. There is an appreciable decrease in elongational
viscosity in the blends of LDPE and LLDPE with increase in the
amount of LLDPE.

Most of the specimens showed strain-hardening characteristics
indicating the homogeneity of the sample deformation, Since strain-
hardening behaviour has a distinct effect (105). This fact can
easily be understood as a self-healing mechanism following from
the existence of strain hardening, i.e. a locally occurring higher
strain results in an increase of the tensile stress necessary for
elongation.

In a stress-strain diagram, the point at which melt ruptures,
gives the value of melt strength and as well as maximum viscosity
attained (Figures 5.14 and 5.15). So there is a linear relation­
ship between melt strength and elongational viscosity. Attalla
et al (104) reported the similar findings on elongational visco­
sity vs melt strength relationship. It must be noted that in the
case of LDPE/LLDPE system, the LDPE, LD/LLD-70/30 and LD/LLD-50/50
sample did not rupture at the highest strain applied.
FIGURE 5.16: Elongational Viscosity of LDPE and LLDPE and their Blends at 150°C at a Series of Constant Hencky Strains
During the test, recovery in length of the stretched samples was estimated by allowing them to recover in the silicone oil bath at 150°C. The results of LLDPE and HDPE and their blends are given in Table 6.1. There is an increase in recovery up to 50% of HDPE in LLDPE and then it remains more or less constant. This is due to increase in weight average molecular weight and molecular weight distribution from LLDPE to HDPE (105).

Table 6.2 represents the recovery results of LDPE and LLDPE and their blends. There is a gradual decrease in recovery from

### Table 6.1: Recovery of LLDPE and HDPE and their Blends at 150°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Length $L_i$ (mm)</th>
<th>Final Length $L_f$ (mm)</th>
<th>Recovered Length $L_i - L_f$ (mm)</th>
<th>Recovery $\frac{L_i - L_f}{L_i} \times 100$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLD</td>
<td>250</td>
<td>150</td>
<td>100</td>
<td>40.0</td>
</tr>
<tr>
<td>LLD/HD-70/30</td>
<td>260</td>
<td>110</td>
<td>150</td>
<td>58.0</td>
</tr>
<tr>
<td>LLD/HD-50/50</td>
<td>225</td>
<td>75</td>
<td>150</td>
<td>67.0</td>
</tr>
<tr>
<td>LLD/HD-30/70</td>
<td>270</td>
<td>90</td>
<td>160</td>
<td>67.0</td>
</tr>
<tr>
<td>HD</td>
<td>190</td>
<td>65</td>
<td>125</td>
<td>66.0</td>
</tr>
</tbody>
</table>

### Table 6.2: Recovery of LDPE and LLDPE and their Blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Length $L_i$ (mm)</th>
<th>Final Length $L_f$ (mm)</th>
<th>Recovered Length $L_i - L_f$ (mm)</th>
<th>Recovery $\frac{L_i - L_f}{L_i} \times 100$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>500</td>
<td>190</td>
<td>310</td>
<td>62.0</td>
</tr>
<tr>
<td>LD/LLD-70/30</td>
<td>500</td>
<td>290</td>
<td>210</td>
<td>42.0</td>
</tr>
<tr>
<td>LD/LLD-50/50</td>
<td>500</td>
<td>340</td>
<td>160</td>
<td>32.0</td>
</tr>
<tr>
<td>LD/LLD-30/70</td>
<td>390</td>
<td>230</td>
<td>160</td>
<td>41.0</td>
</tr>
<tr>
<td>LLD</td>
<td>250</td>
<td>150</td>
<td>100</td>
<td>40.0</td>
</tr>
</tbody>
</table>
LDPE to LD/LLD-50/50 through the LD/LLD-70/30 sample. This is due to the higher degree of long-chain branching in LDPE than in LLDPE, since LDPE and LLDPE are similar in their weight average molecular weight and molecular weight distributions. The recovery value of LD/LLD-30/70 and the LLDPE sample is higher than that of LD/LLD-50/50 sample, but it must be pointed out that the initial lengths were different from those samples which did not fail at the highest applied strain: a constant test condition was not maintained throughout the five samples.

5.1.5 Melt rupture characteristics

Melt rupture characteristics of LDPE and LLDPE and their blends are summarised in Table 6.3. Rupture stress of LDPE showed a marginally higher value than that of LLDPE. There is an appreciable increase in rupture stress with 30% LLDPE level in LDPE. On further addition of LLDPE in LDPE, further increase in rupture stress was observed as evident from the values for LD/LLD-50/50 and LD/LLD-30/70 blends. Thus there is a regular rise in rupture stress in all three blends with increase in LLDPE content.

Draw ratio at break data of LDPE and LLDPE and their blends showed a very regular trend. Draw ratio increases as the LLDPE content increases in the blends. Swerdlow et al (70) in a study of biaxial extensional flow found an inverse relationship between the draw ratio at break and the minimum running thickness of polyethylene film. It is suggested from the present results that minimum running thickness of polyethylene film will decrease with increase in LLDPE content in the blends of LDPE and LLDPE.

During the test, recovery in length of the stretched samples was estimated by allowing them to recover in air at 21°C. The results of LDPE and LLDPE and their blends are represented in Table 6.4. The trend observed was similar to that obtained during elongational flow behaviour. There is a gradual decrease in recovery
TABLE 6.3: Melt Rupture Characteristics of LDPE and LLDPE and their Blends at 150°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Highest Load $W_h$ (N)</th>
<th>Initial diameter of the extrudate (mm)</th>
<th>Initial cross-sectional area of the extrudate $A_i$ (m$^2$)</th>
<th>Mass per unit length of the undrawn extrudate $m_i$ (Kg/m)</th>
<th>Mass per unit length of the drawn extrudate $m_f$ (Kg/m)</th>
<th>Draw ratio at break $D_r = \frac{m_i}{m_f}$</th>
<th>Rupture stress $\sigma_R = \frac{W_h D_r}{A_i}$ (N/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>0.2747</td>
<td>3.8</td>
<td>11.34 x 10^{-6}</td>
<td>0.093</td>
<td>0.040</td>
<td>2.33</td>
<td>5.65 x 10^{4}</td>
</tr>
<tr>
<td>LD/LLD-70/30</td>
<td>0.3139</td>
<td>3.7</td>
<td>10.75 x 10^{-6}</td>
<td>0.096</td>
<td>0.025</td>
<td>3.84</td>
<td>11.21 x 10^{4}</td>
</tr>
<tr>
<td>LD/LLD-50/50</td>
<td>0.3434</td>
<td>3.6</td>
<td>10.18 x 10^{-6}</td>
<td>0.101</td>
<td>0.023</td>
<td>4.39</td>
<td>14.81 x 10^{4}</td>
</tr>
<tr>
<td>LD/LLD-30/70</td>
<td>0.2747</td>
<td>3.5</td>
<td>9.62 x 10^{-6}</td>
<td>0.088</td>
<td>0.015</td>
<td>5.87</td>
<td>16.76 x 10^{4}</td>
</tr>
<tr>
<td>LLD</td>
<td>0.0589</td>
<td>3.1</td>
<td>7.55 x 10^{-6}</td>
<td>0.061</td>
<td>0.010</td>
<td>6.10</td>
<td>4.76 x 10^{4}</td>
</tr>
</tbody>
</table>
TABLE 6.4: Recovery of LDPE and LLDPE and their Blends at 21°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Length $L_i$ (mm)</th>
<th>Final Length $L_f$ (mm)</th>
<th>Recovered Length $L_i - L_f$ (mm)</th>
<th>Recovery $\frac{L_i - L_f}{L_i} \times 100$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>200</td>
<td>85</td>
<td>115</td>
<td>57.5</td>
</tr>
<tr>
<td>LD/LLD-70/30</td>
<td>200</td>
<td>120</td>
<td>80</td>
<td>40.0</td>
</tr>
<tr>
<td>LD/LLD-50/50</td>
<td>200</td>
<td>150</td>
<td>50</td>
<td>25.0</td>
</tr>
<tr>
<td>LD/LLD-30/70</td>
<td>200</td>
<td>190</td>
<td>10</td>
<td>5.0</td>
</tr>
<tr>
<td>LLD</td>
<td>200</td>
<td>200</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

with increase in LLDPE, although the level of recovery is lower here than those obtained before (Table 6.2). This is due to the difference in temperature at which recovery was measured. The equilibrium recovery was not obtained since the samples were cooled in air which brought the crystallisation factor into the picture. However, on the basis of comparative study it is suggested that elasticity of the melt decreases from LDPE to LLDPE in the LDPE/LLDPE system, again in confirmation that LDPE has a higher degree of long-chain branching than LLDPE.
5.2 Conclusions

1. The pure components have the following ordering among themselves in:

   i) Melt Flow Index
      LLDPE ~ LDPE > HDPE

   ii) Melt Memory Index
       LDPE > HDPE > LLDPE

2. In melt flow index, the blends of LLDPE and HDPE follow the logarithmic mixing rule more accurately than either of the blends of LDPE and HDPE or LDPE and LLDPE.

3. Melt memory index of the blends of LDPE and HDPE has been found to be higher compared to the blends of LLDPE and HDPE at the same level of HDPE content. There is approximately a linear relationship between melt memory index and composition in the blends of LDPE and LLDPE.

4. Shear flow behaviour of the blends of LLDPE and HDPE was affected by each component differently but regularly at low- and high-shear rates. No such behaviour was found in the blends of LDPE and HDPE. For blends of LDPE with LLDPE all the shear flow curves were uniformly throughout between those of the pure components.

5. Elongational flow behaviour of the blends of LDPE and LLDPE was affected uniformly by each component. Although all the elongational flow curves of the blends of LLDPE and HDPE were between those of pure components, they were not uniformly spaced.

6. Based on melt rupture characteristics, the rupture stress of all the blends of LDPE and LLDPE have been found to be higher than that of either pure component LDPE or LLDPE.
CHAPTER 6

RESULTS, DISCUSSION AND CONCLUSIONS: MECHANICAL PROPERTIES OF COMPONENTS AND THEIR BLENDS

6.1 Results and Discussion

The mechanical properties of polyethylene are best understood and related to each other through a knowledge of its chain structure and its texture, i.e. in terms not only of the sizes and shapes of the molecules, but also of the manner in which they are organised in the amorphous and crystalline regions. The individual crystallites are normally organised in spherulitic aggregates and behave as reinforcing units embedded in a rubber-like amorphous matrix, the whole being tied together by the long molecules which meander from crystallite to crystallite through the amorphous regions. If the average molecular length is less than some critical value, the crystallites will be less effectively tied together, and rupture will occur at relatively small deformations; this appears to be the explanation for premature failure which can be introduced in polyethylene by combining high crystallinity with short chain length (107).

Broadly speaking, those mechanical properties (tensile stress at yield, elongation at yield and secant modulus) which involve only small deformations are dependent upon the degree of crystallinity; whereas behaviour at large deformations, and in particular ultimate mechanical properties (tensile strength at break and elongation at break), depend upon molecular chain length and crystallinity together.

6.1.1 Tensile stress at yield

The results of tensile stress at yield of components and their blends are shown in Figures 6.1 to 6.3. The yield stress of HDPE is higher than that of LDPE because it has a higher degree of crystallinity than LDPE, but the value of LLDPE is approximately
FIGURE 6.1: Tensile Stress at Yield of LDPE and HDPE and their Blends
FIGURE 6.2: Tensile Stress at Yield of LLDPE and HDPE and their Blends
FIGURE 6.3: Tensile Stress at Yield of LDPE and LLDPE and their Blends
equal to that of LDPE, due to the similarity in their crystallinity levels.

The tensile stress at yield data of three sets of blends roughly vary linearly with composition, similar to the results of degree of crystallinity in all cases.

6.1.2 Tensile strength at break

Figures 6.4 to 6.6 show the results of the tensile strength at break of the components and their blends. Tensile strength of LDPE is lower than HDPE due to its lower degree of crystallinity which could not provide sufficient quantity of reinforcing units. Tensile strength of LLDPE is higher than that of LDPE because of its higher chain length, since their degree of crystallinity is the same. But LLDPE has higher tensile strength than that of HDPE. The reason may be seen from details of the strain-strain behaviour as shown in Figure 6.7. After the appearance of the yield point when the LLDPE specimen is stretched, the strain is readily accommodated by the amorphous portion of the polymer and the crystalline portion reinforces the total structure leading to higher strength. In the case of HDPE no such behaviour was observed. After the yield point the stress remained more or less constant with increase in strain, indicating no transfer of strain to amorphous portion. This is due to combination of higher degree of crystallinity and shorter chain length which leads to premature failure. It should be noted that the Figure 6.7 also includes the stress-strain behaviour of LDPE. It is very similar to LLDPE.

In the case of LDPE/HDPE system none of the blends showed tensile strength higher than the value of LDPE. There was no beneficial effect in the blends with increase in HDPE content. On the other hand all the tensile strengths in LLDPE/HDPE blends showed higher value than either of the components. Even though there was a gradual increase in tensile strength with increase in LLDPE in the blends of LDPE and LLDPE, no significant increase in tensile strength was found in the LD/LLD-70/30 blend.
FIGURE 6.4: Tensile Strength at Break of LDPE and HDPE and their Blends
FIGURE 6.5: Tensile Strength at Break of LLOPE and HDPE and their Blends
FIGURE 6.6: Tensile Strength at Break of LDPE and LLDPE and their Blends
FIGURE 6.7: Stress-Strain Behaviour of LDPE, HDPE and LLDPE
6.1.3 Elongation at yield

Elongation at yield data of components and their blends are shown in Figures 6.8 to 6.10. The higher the degree of crystallinity the lower the elongation at yield - is the normal rule in the case of polyethylene. There was no exception in the present results. HDPE has lower elongation at yield than that from LDPE. Also the value of LLDPE is higher than LDPE for its marginally lower degree of crystallinity.

All the blends in all sets roughly showed that the elongation at yield tended to vary in a linear manner as a function of composition as observed in crystallinity results, although in the blends containing LLDPE with HDPE, HDPE appeared to exert a greater influence on the elongation at yield. In other words the value of LLDPE is remarkably high in the whole series.

6.1.4 Elongation at break

The results of elongation at break of components and their blends are shown in Figures 6.11 to 6.13. Elongation at break of LDPE is lower than HDPE which is lower than that of LLDPE. This is in line with the results of tensile strength, so it is likely that a similar explanation can be applied.

In the blends of LDPE and HDPE no increase in elongation at break was observed with increase in HDPE content. On the other hand the blends containing up to 50% HDPE even showed the values lower than LDPE. All the blends of LLDPE and HDPE showed that they are more or less in the LLDPE class. It appeared that LLDPE affects the elongation at break of the blends to a greater extent. Elongation at break seemed to vary roughly in a linear manner as a function of composition in the blends of LDPE and LLDPE. It should be noted that the value of the blend containing 70% LLDPE is similar to the value of LLDPE, whereas the value of the blend containing 30% LLDPE is lower than the expected value.
FIGURE 6.8: Elongation at Yield of LDPE and HDPE and their Blends.
FIGURE 6.9: Elongation at Yield of LLDPE and HDPE and their Blends
FIGURE 6.10: Elongation at Yield of LDPE and LLDPE and their Blends
FIGURE 6.11: Elongation at Break of LDPE and HDPE and their Blends
FIGURE 6.12: Elongation at Break of LLDPE and HDPE and their Blends
FIGURE 6.13: Elongation at Break of LDPE and LLDPE and their Blends
6.1.5 Secant modulus (at 7% strain)

Figures 6.14 to 6.16 show the results of the secant modulus of the components and their blends. The secant modulus of LDPE is lower than that from HDPE because of its lower crystallinity; the secant modulus of LLDPE is slightly lower than that from LDPE. This is due to its marginally lower crystallinity.

It would appear that secant modulus data of the blends in all three sets tended to vary more or less in a linear manner as a function of composition as did the crystallinity.
FIGURE 6.14: Secant Modulus (at 7% Strain) of LDPE and HDPE and their Blends
FIGURE 6.15: Secant Modulus (at 7% Strain) of LLDPE and HDPE and their Blends
FIGURE 6.16: Secant Modulus (at 7% Strain) of LDPE and LLDPE and their Blends
6.2 Conclusions

1. The components have the following ranking among themselves in:

   i) Tensile stress at yield
      
      \[ \text{HDPE} > \text{LDPE} \sim \text{LLDPE} \]

   ii) Tensile strength at break
        
        \[ \text{LLDPE} > \text{HDPE} > \text{LDPE} \]

   iii) Elongation at yield
        
        \[ \text{LLDPE} \sim \text{LDPE} > \text{HDPE} \]

   iv) Elongation at break
        
        \[ \text{LLDPE} > \text{HDPE} > \text{LDPE} \]

   v) Secant modulus at 7% strain
        
        \[ \text{HDPE} > \text{LDPE} \sim \text{LLDPE} \]

2. Tensile stress at yield, elongation at yield and secant modulus of the blends in all sets follow approximately a linear relationship and correlate directly with degree of crystallinity results.

3. Tensile strength at break and elongation at break of the LLDPE/HDPE blends have shown an optimum effect whereas no such relationship has been found in LDPE/HDPE blends. These properties have shown approximately a linear relationship in the case of LDPE/LLDPE blends.
7.1 Introduction

The manufacture of polyethylene film by the tubular blown film extrusion process is a well-established method and it has been recognised that a wide range of properties are obtainable. The effect of process variables on the film properties and the complexity of the mechanism of film formation have been fully appreciated. It is perhaps worth noting the effect of the relevant processing variables on some of the important properties of polyethylene film.

There is little doubt that orientation is the major factor controlling the mechanical properties. There are three sources of stress which may impose orientation during film formation (108):

i) the shear stress causing flow of the visco-elastic melt through the die; this would normally result in swelling or melt elastic recovery of a subsequently unrestrained melt and any orientation imposed will be in the machine or longitudinal direction, and vary from zero at the centre to maximum at the surfaces of the melt;

ii) the transverse or circumferential stress arising from the blowing process after the melt has left the die; this depends upon the air pressure within the bubble and the diameter of the bubble. Any orientation it imposes is in the transverse direction; and

iii) the drawing stress applied by the nip rolls during the longitudinal or machine direction drawing process.

At the same time molecular relaxation occurs continuously throughout the bubble forming and blowing process at a rate depending upon the temperature gradient of the melt from the die to the freeze line. Orientation arising in the die is small compared with
that from melt drawing and does not greatly influence the orientation finally frozen into the film; its importance lies in that it may affect the way in which the melt draws.

It is well known that the effect of decreasing the longitudinal or machine direction orientation by increasing the lateral blow ratio is to increase the impact strength and to alter the ratio of the tear and tensile properties in the machine and transverse directions. The exact relationship between tear strength, impact strength and elongation at break is undoubtedly complex, but all three depend significantly on the way in which polyethylene film draws when strained at different rates.

The effect of increasing the freeze-line distance on the impact strength is generally small and variable. This variability may be explained by the opposing effects of the resultant changes in the density of the film and the melt drawing behaviour in the nascent bubble. An increase in freeze-line-distance will give films of higher density and may be expected therefore to result in a decrease of impact strength.

The main criteria affecting the mechanical properties of tubular film are not only the relative magnitude of the transverse and machine direction drawing between the die and the freeze-line, but also the order in which they occur (109). This is not altogether surprising because the relaxation times of molten polyethylene are comparatively short. The most likely orientation to be frozen and retained in the film as well as the consequential crystallisation behaviour, are determined by the orientation existing in the melt at or just before the freeze line.

7.2 Experimental

7.2.1 Materials

The same polymers as mentioned in Section 2.1.1, of Chapter 2 were used.
7.2.2 Processing

7.2.2.1 Blend preparation

Two sets of binary blends were prepared by mixing the pellets of the two polymers thoroughly; composition and sample codes are given in set No. 2 and set No. 3 of Table 2.1 (Section 2.1.2 of Chapter 2).

7.2.2.2 Film production

LLDPE and HDPE and their blends were processed into 15-30 \( \mu \)m film in a large scale film extruder (90 mm Dolci extruder). The temperature profile in the extruder was 180\(^\circ\)/190\(^\circ\)/200\(^\circ\)/220\(^\circ\)/240\(^\circ\)C. Blow-up ratio used was 2.5-3.00. The production of the film was carried out at Longworth Paper and Plastics Ltd., Manchester.

LDPE and LLDPE and their blends were processed into 45-55 \( \mu \)m film in a small scale film extruder (25 mm Betol extruder). The temperature profile in the extruder was 160\(^\circ\)/170\(^\circ\)/180\(^\circ\)/190\(^\circ\)/200\(^\circ\)C. Blow-up ratio used was 3.0-3.5. The extruder was run at 40 rpm.

7.2.2.3 Film blowing

The film was produced by the most common method nowadays using the film blowing process illustrated in Figure 7.1. The molten polymer from the extruder passes through an annular die and emerges as a thin tube. A supply of air to the inside of the tube prevents it from collapsing and indeed may be used to inflate it to a larger diameter. Initially the bubble consists of molten polymer but a jet of air around the outside of the tube promotes cooling and at a certain distance from the die exit, a freeze line can be identified. Eventually the cooled film passes through collapsing guides and nip rolls before being taken off to a storage roller.

The major advantage of film blowing is the ease with which biaxial orientation can be introduced into the film. The pressure of the air in the bubble determines the blow-up and thus controls the transverse
FIGURE 7.1(a): Film Blowing Process

FIGURE 7.1(b): Film Blowing Die
and longitudinal orientation. In addition, draw-down can be applied by increasing the nip roll speed relative to the linear velocity of the bubble. The nip rolls have a dual function, therefore in that they also seal the air in the polymer bubble.

It is possible to make a simple estimate of the orientation in blown film by considering only the effects due to the inflation of the bubble (110). Since the volume flow rate is the same for the polymer in the die and in the bubble then for unit time

\[ \pi D_d h_d L_d = \pi D_b h_b L_b \] (7.1)

where \( D, h \) and \( L \) refer to diameter, thickness and length respectively and the subscript 'd' is for the die and 'b' is for the bubble.

So the orientation in the longitudinal direction, \( O_{LD} \), is given by:

\[ O_{LD} = \frac{L_b}{L_d} = \frac{D_d h_d}{h_b D_b} = \frac{h_d}{h_b B_R} \] (7.2)

where \( B_R \) = blow-up ratio \( (D_b / D_d) \).

Also the orientation in the transverse direction, \( O_{TD} \), is given by

\[ O_{TD} = \frac{D_b}{D_d} = B_R \] (7.3)

Therefore the ratio of the orientations may be expressed as:

\[ \frac{O_{LD}}{O_{TD}} = \frac{h_d}{h_b (B_R)^2} \] (7.4)
It is desirable to produce balanced property film of thickness 0.05 mm using an annular die with a die gap of 0.5 mm. Assuming that the inflation of the bubble dominates the orientation in the film, determine the blow-up ratio required to give uniform biaxial orientation.

Since $O_{LD} = O_{TD}$ in this case, the equation (7.4) gives the blow-up ratio,

$$B_R = \sqrt{\frac{h_d}{h_D}}$$

$$= \sqrt{\frac{0.5}{0.05}} = 3.16$$

This is a simplified approach in film blowing to show the reason why LDPE and LLDPE and their blends were processed into 45-55 μm film with a blow-up ratio of 3.0-3.5 to obtain balanced property film.

7.2.3 Film Characterisation and Properties Measurement

7.2.3.1 Crystallinity

Crystallinity was measured by the two following methods as described in Section 2.3.1 of Chapter 2, viz. specific volume and heat of fusion.

7.2.3.2 Melting and crystallisation behaviour

The thermal analysis described in Section 2.3.2 of Chapter 2 was used. The first crystalline melting thermograms were obtained by heating the samples from 25°C to 150°C at a programmed heating rate of 10°C/min with a sensitivity of 5 mV/cm. The samples were then cooled from 150°C to 25°C at a slow cooling rate of 1°C/min with a sensitivity of 1 mV/cm to obtain the crystallisation thermograms. The second crystalline melting thermograms were obtained using the same heating conditions as the first, viz 10°C/min.
7.2.3.3 Crystalline melting point and crystallisation temperature

Crystalline melting point and crystallisation temperature were measured with the melting and crystallisation behaviour and read from the position of the peak in the thermogram.

7.2.3.4 Melt flow index

The method described in Section 2.4.1 of Chapter 2 was used to measure melt flow index.

7.2.3.5 Density

Density was measured by the method described in Section 2.3.5 of Chapter 2. Before being measured, all samples were given the same thermal pretreatment by heating to 150°C and cooling to 25°C at a constant rate of 1°C/min.

7.2.3.6 Mechanical properties

Tensile properties (tensile stress at yield, tensile strength at break and elongation at break) were measured in both longitudinal and transverse directions by the method described in Section 2.5.1 of Chapter 2; the tear strength also in both longitudinal and transverse directions by the method described in Section 2.5.2; and the impact resistance by the method described in Section 2.5.3.

7.2.3.7 Orientation

The method described in Section 2.6 of Chapter 2 was used to measure orientation.
7.3 Results and Discussion: Linear Low-Density and High-Density Polyethylene Blends

7.3.1 Crystallinity

Crystallinity data estimated by the specific volume method and by the heat of fusion method are shown in Figures 7.2 and 7.3 respectively. The level of crystallinity obtained is higher than that obtained in compression moulded samples (comparing Figures 7.2 and 4.5 of Chapter 4), due to different thermal history. The nature of the relationship between crystallinity and composition obtained by the two methods is very similar, but the crystallinity levels are quite different. It is better to consider these crystallinity data as a basis for comparison rather than they be taken as absolute values.

7.3.2 Melting and crystallization behaviour

They showed similar melting and crystallization behaviour as obtained before in compression moulded samples (Section 4.1.2 of Chapter 4). Only the crystalline melting thermograms of the slow-cooled samples are shown in Figure 7.4.

7.3.3 Crystalline melting point and crystallization temperature

The crystalline melting points and crystallization temperatures of slow-cooled samples are shown in Figure 7.5. The nature of the phase diagram is very similar to that obtained before for compression moulded samples (Figure 4.38 of Chapter 4). The values of the crystalline melting points and crystallization temperatures were different in the two cases, possibly since orientation can influence the melting point of the samples (111).

7.3.4 Melt flow index

Melt flow index gives quick information about molecular characteristics. It is also very useful for quality control and
FIGURE 7.2: Crystallinity (measured by specific volume method) of LLDPE/HDPE blends
FIGURE 7.3: Crystallinity (measured by heat of fusion method) of LLDPE/HDPE blends
FIGURE 7.4: Melting behaviour of LLDPE/HDPE blends
FIGURE 7.5: Phase diagram of LLDPE/HDPE blends
(○) crystalline melting point;
(●) crystallisation temperature
as a guide to processability. MFI data can be used through the logarithmic mixing rule (Figure 1.5 of Chapter 1) as a measure of degree of mixing of the components in the blends.

MFI results are shown in Figure 7.6, which are quite different from the results obtained before in the case of extruder mixed samples (Figure 5.2 of Chapter 5). Those MFI data lay perfectly on a straight line, whereas no such behaviour was observed in this case. It suggests that the degree of mixing of these polymers is not as perfect as was achieved previously.

7.3.5 Density

The density results are shown in Figure 7.7; they behaved in similar manner to previous results (Figure 4.2 of Chapter 4).

From Figures 7.5 and 7.7 the relationship between melting point and density for LLDPE and HDPE and their blends was obtained and is represented in Figure 7.8. This type of correlation is very useful for practical purposes, because it is very easy to measure the density of the sample and hence from this correlation melting point can be readily obtained.

7.3.6 Tensile properties

The tensile strength is normally adequate in polyethylene film and gives no information about serviceability in most applications; in spite of this it is a property often discussed. Elongation at break, like impact resistance and tear strength, is affected by the way in which a neck develops after yield; it is therefore broadly related to these other mechanical properties. A measurement of yield stress might well provide more useful information about the behaviour of film in service or, for example, in high speed conversion equipment.

The results of tensile stress at yield are shown in Figure 7.9. Yield stress tended to vary approximately in a linear manner with composition. There is a gradual increase in yield stress with
FIGURE 7.6: Melt flow index of LLDPE/HDPE blends
FIGURE 7.7: Density of LLDPE/HDPE blends
FIGURE 7.8: Melting point - density correlation of LLDPE/HDPE blends
FIGURE 7.9: Tensile stress at yield of LLDPE/HDPE blends

(●) longitudinal direction;
(○) transverse direction
increase in HDPE content in LLDPE. The values are very similar in both longitudinal and transverse directions.

The results of tensile strength and elongation at break are shown in Figures 7.10 and 7.11 respectively. Tensile strength of the blends from LLDPE and HDPE passes through a minimum; whereas elongation at break decreases in both longitudinal and transverse directions with increase in HDPE contribution in LLDPE although LLD/HD-70/30 blend has shown comparatively lower value than expected. Both tensile strength and elongation results are very random in nature.

7.3.7 Tear strength

Tear strength (like tensile strength) is measured both in the longitudinal and transverse directions. The tear is initiated with a small slit or cut and the specimen is stretched and cold drawn to the breaking point. The result is a measure of the work done in propagating this tear and depends upon the geometry of the sample and its elongation to break. These two quantities together control the amount of film drawn during the tearing process. The tear is free to run towards or along the weakest line which is generally in the transverse direction. The length of the tear is thus variable particularly if initiated in the longitudinal direction and will affect the energy absorbed, i.e. the measured tear strength. Thus the interpretation of this result is not straightforward, but nevertheless it has some value in assessing the likely durability of film in service.

The results of tear strength are shown in Figure 7.12. Tear strength in both longitudinal and transverse directions passes through a minimum at lower level of HDPE and then increases with increase in HDPE content in LLDPE particularly at higher level. During the test everywhere tear deviated substantially from the original direction of the cut and failed to reach the end of the test piece except in the case of LLD/HD-50/50 sample where only in longitudinal direction the test piece was torn from the original
FIGURE 7.10: Tensile strength at break of LLDPE/HDPE blends

(●) longitudinal direction;
(○) transverse direction
FIGURE 7.11: Elongation at break of LLDPE/HDPE blends

(●) longitudinal direction;
(O) transverse direction
FIGURE 7.12: Tear strength of LLDPE/HDPE blends
   (●) longitudinal direction;
   (○) transverse direction
direction of the cut. This suggests that all the blends have high tear strength, even the lowest value obtained in LLD/HD-50/50 blend (in longitudinal direction) is higher than the minimum acceptable value.

7.3.8 Impact resistance

Measurement of the tensile and tear strengths have always been used as an indication of the mechanical strength of polyethylene film. However, the important factor is the likely durability of film in service and the measurement of impact resistance might well provide useful information to assess this durability.

The results of impact resistance are shown in Figure 7.13. Although the results are of a very random nature, it can be observed that impact resistance decreases with increase in HDPE in LLDPE. This is the expected case because density increases from LLDPE to HDPE. As a result films of higher density will give lower impact strength.

A large variation has been observed in the results of all the mechanical properties of the film. That is why the range of maximum and minimum value has been represented in the figure to demonstrate the variation of results.

7.3.9 Orientation

The results of birefringence measurements of LLDPE and HDPE and their blends are given in Table 7.1. The results appear to be random in nature and no regular trend was found in these blends. Since birefringence measurement can give information on molecular orientation and, particularly the magnitude of frozen-in stresses and in turn this can give clues to the processing history of the material, it is suggested from the present results that the processing conditions were not maintained similar throughout the whole series.
FIGURE 7.13: Impact resistance of LLDPE/HDPE blends
TABLE 7.1: Birefringence of LLDPE and HDPE and their Blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample Thickness (um)</th>
<th>Optical path difference (nm)</th>
<th>Birefringence</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLD</td>
<td>25</td>
<td>65.80</td>
<td>2.6 x 10^{-3}</td>
</tr>
<tr>
<td>LLD/HD-70/30</td>
<td>17</td>
<td>58.70</td>
<td>3.5 x 10^{-3}</td>
</tr>
<tr>
<td>LLD/HD-50/50</td>
<td>30</td>
<td>85.00</td>
<td>2.8 x 10^{-3}</td>
</tr>
<tr>
<td>LLD/HD-30/70</td>
<td>25</td>
<td>107.20</td>
<td>4.3 x 10^{-3}</td>
</tr>
<tr>
<td>HD</td>
<td>25</td>
<td>29.20</td>
<td>1.2 x 10^{-3}</td>
</tr>
</tbody>
</table>

The experimental values of birefringence are found to be lower than the maximum value which is in the region of 30 x 10^{-3}, but the level of birefringence obtained is normal in polyethylene film. So it is most likely to affect the mechanical properties of the film by the molecular orientation in the plane of the film.
7.4 Results and Discussion: Low-density and Linear Low-density Polyethylene Blends

7.4.1 Processing behaviour of film

During the making of the film blow-up ratio maintained was 3.0-3.5 throughout the whole series except in the case of LD/LLD-70/30 blend. Difficulties were encountered to attain that blow-up ratio in this particular blend. The highest obtainable blow-up ratio of 2.00-2.25 was limited by the bubble bursting. It is believed that the deformation instability in melt flow behaviour is the result of low degree of miscibility of LDPE and LLDPE in this composition.

In the film blowing process, within the die there exists an additional superposition of the simple shear flow by a nonuniform biaxial elongational flow, due to the change in the mean melt channel diameter and the width of orifice in the direction of flow, whereas the plastic melt flow in the bubble expansion zone consists of a biaxial elongation (112). So the flow in this case cannot be described ideally either by simple shear or by uniaxial elongation.

No sign of immiscibility has been found in this composition either from shear flow behaviour (Figure 5.13 of Section 5.1.3 of Chapter 5) or from elongational flow behaviour (Figure 5.16 of Section 5.1.4 of Chapter 5). But onset of instability in this experiment has shown immiscibility in biaxial elongational flow. Simple theory (113) states that for a constant stress the strains in simple shear, elongation and equal biaxial extension should be in the ratio 1:1/3:1/6. Cogswell and Moore (114) supported this ratio from their study. The equivalent shear strain can be obtained by multiplying the strain in elongation by 3 and that in biaxial extension by 6. So it is deduced that the stresses necessary to obtain equivalent strain in shear, elongation and equal biaxial extension must be approximately in the ratio 1:3:6. This is perhaps the reason of occurrence of immiscibility in LD/LLD-70/30 blend in biaxial elongational flow, but not in simple shear and in uniaxial elongational flow.
7.4.2 Tensile properties

The results of tensile stress at yield are shown in Figure 7.14. Yield stress tended to vary linearly with composition in longitudinal direction, but no such behaviour was observed in transverse direction. There is an increase in tensile strength and elongation at break with increasing LLDPE content in LDPE as seen from Figures 7.15 and 7.16 respectively. It must be noted that all the tensile properties of both longitudinal and transverse directions are balanced except in the case of LD/LLD-70/30 blend, where unbalanced properties have resulted due to use of lower blow-up ratio which has favoured more molecular orientation in longitudinal direction than in the transverse direction.

7.4.3 Orientation

The results of birefringence of LDPE and LLDPE and their blends are given in Table 7.2. There is an increase in birefringence

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample thickness (µm)</th>
<th>Optical path difference (nm)</th>
<th>Birefringence</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD</td>
<td>55</td>
<td>158.08</td>
<td>2.9 x 10^{-3}</td>
</tr>
<tr>
<td>LD/LLD-70/30</td>
<td>55</td>
<td>183.92</td>
<td>3.3 x 10^{-3}</td>
</tr>
<tr>
<td>LD/LLD-50/50</td>
<td>50</td>
<td>152.00</td>
<td>3.0 x 10^{-3}</td>
</tr>
<tr>
<td>LD/LLD-30/70</td>
<td>45</td>
<td>123.12</td>
<td>2.7 x 10^{-3}</td>
</tr>
<tr>
<td>LLD</td>
<td>50</td>
<td>15.20</td>
<td>0.30 x 10^{-3}</td>
</tr>
</tbody>
</table>

from LDPE to LD/LLD-70/30 blend and then it decreases gradually with increase in LLDPE. There is a maximum value in LD/LLD-70/30 blend in the whole series. This higher birefringence is the result of difference in molecular orientation which is imposed by the use of lower blow-up ratio. The similar information was obtained previously from tensile properties of the blend. It is pointed out that the molecular orientation in LLDPE is exceptionally low.
FIGURE 7.14: Tensile stress at yield of LDPE/LLDPE blends

(*) longitudinal direction;
(%) transverse direction
FIGURE 7.15: Tensile strength at break of LDPE/LLDPE blends
(●) longitudinal direction;
(◇) transverse direction
FIGURE 7.16: Elongation at break of LDPE/LLDPE blends
(◊) longitudinal direction;
(○) transverse direction
7.5 Conclusions

In the blends of low-density and linear low-density polyethylene an improvement in the property of the manufactured LDPE film has been achieved by the addition of LLDPE in LDPE. In this system the LD/LLD-70/30 blend has been found as a "rheologically particular" composition (RPC).

Characterisation and property evaluation of the film manufactured from the LLDPE/HDPE blends have demonstrated the lack of uniformity or dispersion of the components. Gross nonuniformity has resulted in the manufacture of blends which were prepared (not via melt mixing followed by granulation) by mixing granules only. It is suggested that the manufacture of blends should be carried out in two stages: dispersive mixing followed by laminar mixing, particularly in large scale production of blends. Because of the small scale production the LDPE/LLDPE blends did not display any inhomogeneity.

In addition to the blends the large variation in mechanical properties of the pure components, LLDPE and HDPE has shown non-uniformity of processing variables during film production.
CHAPTER 8
GENERAL DISCUSSION AND CONCLUDING COMMENTS

In this study of the miscibility of crystalline polyolefins first of all an attempt will be made to link the observed behaviour of the three sets of binary blends (LDPE/HDPE, LLDPE/HDPE and LDPE/LLDPE) from experimental investigations to reach ultimate conclusions and then comments will be passed on LLDPE.

8.1 Low-density and High-density Polyethylene Blends

The thermal analysis technique has proved that the LDPE/HDPE system is immiscible (Chapter 4). For phase-separated systems, the characteristics of the interfacial regions generally govern the ultimate mechanical properties attainable with the blend. In this two-component system, for the limited affinity of LDPE and HDPE for each other, poor adhesion has resulted at the interfacial regions due to presence of multiplicity of defects, resulting in lower ultimate mechanical properties than expected from averaged properties (Chapter 6). Though early failure has indicated the incompatibility of the blends, their crystallinity results have followed additivity rule (Chapter 4) and all the crystallinity dependent mechanical properties correlate directly with the crystallinity (Chapter 6). Melt properties of the blends of LDPE and HDPE did not show compatibility at all compositions (Chapter 5).

Technical reasons for the manufacture of polyethylene blends have been to increase the stiffness of LDPE and the toughness and flexibility of HDPE. The great limitation of the immiscible LDPE/HDPE system is that two-component blends are useful only when one phase is the major continuous phase.

8.2 Linear Low-density and High-density Polyethylene Blends

Thermal analysis has indicated that the LLDPE/HDPE system is miscible, because of the ability of its components to co-crystallise
in the mixture (Chapter 4). The phenomenon of co-crystallisation or isomorphism which is a rare occurrence in the case of crystalline-crystalline polymer blends, has been supported by X-ray diffraction measurements (Chapter 4). The advantage of the miscible LLDPE/HDPE system over the immiscible LDPE/HDPE system is the assurance of mechanical compatibility at all compositions. The blends of LLDPE and HDPE have obeyed the additivity rule in their crystallinity results (Chapter 4) and as expected all the crystallinity dependent mechanical properties correlate directly with the crystallinity (Chapter 6). The simplified average of ultimate mechanical properties was not observed, the blends having attained ultimate mechanical properties higher than the components (Chapter 6). The synergistic effect is the result of co-crystallisation of LLDPE and HDPE.

Since the system has shown compatibility in melt properties (Chapter 5), the blends must possess advantageous 'combination' of properties; e.g. high stiffness of HDPE coupled with good processability of LLDPE. The main advantage of the miscible LLDPE/HDPE system is that the blends have utility over the entire composition range because they are very similar to a single component system.

In the present work only one type of LLDPE has been blended with HDPE. It would be interesting to study the LLDPE/HDPE system with other types of LLDPE and HDPE. The study can be extended with different molecular weights of the components to investigate the effect of molecular weight on miscibility.

8.3 Low-density and Linear Low-density Polyethylene Blends

In the miscibility test, thermal analysis has concluded from the experimental results (Chapter 4) that the LDPE/LLDPE system is immiscible, because it has shown multi-phase behaviour. Although the blends of LDPE and LLDPE did not show single-phase behaviour in the miscibility test, compatibility has been found in their melt properties (Chapter 5). The ultimate mechanical properties of the LDPE/LLDPE system have shown "additive" effects (Chapter 6). This similar effect was found in the
ultimate mechanical properties of the film sample (Chapter 7), thus giving more evidence of the compatibility of this system.

LDPE/LLDPE is a system where partial miscibility has occurred at the interfacial regions of the two components; as a result mechanical compatibility has been found in spite of the multi-phase behaviour of the blends. The system is a very useful one and highly recommended for film application.

In this system one of the blends particularly has drawn attention from different experimental investigations. Small angle light scattering has revealed the disruption of spherulitic morphology in the LD/LLD-70/30 blend (Chapter 4). Further during the manufacture of film this blend has been found as a "rheologically particular" composition (Chapter 1) supported by the tensile properties of the film (Chapter 7). The ultimate mechanical properties of this composition have shown values lower than the expected additive values (Chapter 6). This composition needs more exploration in future.

8.4 Linear Low-density Polyethylene

Thermal analysis has concluded that Dowlex LLDPE consists of two stable crystal species - one is responsible for the low temperature broad melting peak and the other for the high temperature sharp melting peak (Chapter 4). Similar results were obtained for the melting behaviour of Unifos LLDPE and Escorene LLDPE (Chapter 4). Fractionation of the Dowlex LLDPE has indicated that the chains giving rise to the two crystalline species are probably linked together chemically, with the block length of the two species, but not the degree of branching varying from molecule to molecule (Chapter 3). On the other hand LDPE shows a single melting peak due to presence of random branching. It has been found that the overall degree of branching due to combined contribution of the two species in LLDPE is lower than that in LDPE (Chapter 3) and similarly LLDPE has a lower degree of long-chain branching than LDPE (Chapter 5). So LLDPE as a whole is more linear in structure than LDPE, but not as linear as HDPE.
As a result spherulite size of LLDPE is larger than that of LDPE and unit cell dimension of LLDPE is higher than that of HDPE (Chapter 4). It has been realised that the structure of LLDPE is not as simple as LDPE and HDPE are.

LLDPE is a polymer which can be placed between LDPE and HDPE, because it has shown miscibility of its high melting crystal species with HDPE and the low melting crystal species with LDPE (Chapter 4). With its excellent ultimate mechanical properties (Chapter 6) coupled with good processability (Chapter 5) it will bridge the gap between LDPE and HDPE. The polymer is very useful for film application (Chapter 7).
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