Dispersion of additive masterbatches in polyolefin plastics

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DISPERSION OF ADDITIVE MASTERBATCHES

IN POLYOLEFIN PLASTICS

by

OKORO OGBOBE, BSc (Hons), MSc

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

May 1985

Supervisor: D A Hemsley, BSc, Dip.RMS
Institute of Polymer Technology
Loughborough University of Technology

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DEDICATION

Chiny, Uche and Uko
ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to Mr D A Hemsley who I am privileged to have had as my research supervisor. His enthusiasm in the field of microscopy has been a strong source of encouragement to me. His expert guidance and valuable criticism have been of great help. I am also thankful to Professor A W Birley who supervised my research work when Mr Hemsley was away in South Africa. My thanks are also extended to Dr N S Allen of Manchester Polytechnic for advice on Simulated Sunlight exposure experiments.

I also wish to thank the Federal Government of Nigeria for providing the financial support for this research. I wish to thank my senior brother engineer Aka Ogbobe for visits on my behalf to the Federal Ministry of Education Lagos, when I was seeking extension of my financial support.

My sincere thanks to my wife, Uchechukwu and Madubuko for their patience, support and understanding during the process of this work.

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I am grateful to Professor Brandon of Leicester Royal Infirmary for concern when my wife was poorly. The encouragement and support offered my family by Mr and Mrs Samuel Cowley, the Vicars and Congregation of All Saints Church, Thorpe Acre, Loughborough, is very much appreciated. I am grateful to our Social Worker, Mr Tim Skinner, and our Health Visitor for their frequent visits to my family.

Thanks also to S/Lt u.c. Ezeorah of INS Shivaji, India for financial support.
SYNOPSIS

There has been a growing trend in recent years for polymer product manufacturers to use natural polymer and additive masterbatches instead of premixed compounds.

For both polymer converters and polymer manufacturers, masterbatching makes economic sense. For the converter, the advantage is in the ability to buy and store in bulk a small number of base polymers which may be modified according to the dictates of the order book. This prevents the need to maintain an inventory of a large number of special compounds.

Masterbatch base is very often low molecular weight polyethylene or some suitable low molecular weight compound. They are usually used with a wide range of polymer compounds. Manufacturers assume good additive dispersion in the products with use of masterbatch.

This study investigates the quality of dispersion in masterbatches and the extent they can be used with varying polyolefin polymers. Also investigated is how additive particles are transferred from the masterbatch to another polymer during mixing and any morphological features that might relate to the degree of dispersion. A quantitative dispersion procedure in polyolefin products is also sought.

X-ray microradiography, light microscopy and ultraviolet microscopy have enabled pigment and ultraviolet absorber dispersion in masterbatches and products to be studied. Pigment dispersion in low density polyethylene masterbatch is almost invariably bad. Iron oxide particularly was found to be the most poorly dispersed compared to other inorganics such as zinc sulphide, titanium dioxide and cadmium sulphide. On the other hand, the distribution of Cyasorb 531 in LDPE masterbatch is uniform. The degree of dispersion of UV absorber in polyethylene products depends on the difference between the melt flow index between the masterbatch base and the base polymer. Simulated sunlight exposure experiments have shown that increased absorber distribution significantly
increases photostability of a high MFI HDPE/LDPE UV masterbatch blend. A semi-automatic procedure for quantifying pigment dispersion in polyolefin products has been developed. It involves a motorised-stage scanning of a microtomed section of a polyolefin product with measurements being made with a photometer operating in a dark-field illumination and interfaced to a microcomputer. The procedure has enabled the point of significant agglomeration as well as the effect of shear rate and temperature on degree of dispersion in extruded products to be determined.
# Table of Contents

<table>
<thead>
<tr>
<th>Synopsis</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th>ii</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CHAPTER 1:</strong></td>
<td><strong>GENERAL INTRODUCTION</strong></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>1.1</td>
<td>Historical Developments of Additive Dispersion</td>
<td></td>
<td></td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>Background of Dispersion and Distribution Studies</td>
<td></td>
<td></td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>1.3</td>
<td>Additives Used in Polyolefin Plastics</td>
<td></td>
<td></td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>1.3.1</td>
<td>Pigments</td>
<td></td>
<td></td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>1.3.1.1</td>
<td>Morphology of pigment particles</td>
<td></td>
<td></td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>1.3.2</td>
<td>Stabilisers</td>
<td></td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>1.3.3</td>
<td>Surface Additives</td>
<td></td>
<td></td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td>Forms of Additive Materials for Polyolefins</td>
<td></td>
<td></td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>Theory of Dispersion</td>
<td></td>
<td></td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>1.5.1</td>
<td>Factors Affecting Degree of Dispersion</td>
<td></td>
<td></td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>1.5.2</td>
<td>Dispersion Quality</td>
<td></td>
<td></td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>1.6</td>
<td>Dispersion Methods</td>
<td></td>
<td></td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>1.7</td>
<td>Evaluation of Degree of Dispersion</td>
<td></td>
<td></td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>1.7.1</td>
<td>Measurement of Dispersion in the Masterbatch</td>
<td></td>
<td></td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>1.7.2</td>
<td>Pigment Dispersion in Products</td>
<td></td>
<td></td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>1.8</td>
<td>Objectives</td>
<td></td>
<td></td>
<td>48</td>
<td></td>
</tr>
</tbody>
</table>

| **CHAPTER 2:** | **CHARACTERISATION OF DISPERSION IN MASTERBATCHES** |  |  | 51 |
| 2.1 | Introduction |  |  | 51 |
| 2.1.1 | Quantitative Measurement of Dispersion in Masterbatches |  |  | 53 |
| 2.2 | Experimental |  |  | 54 |
| 2.2.1 | Materials |  |  | 54 |
| 2.2.2 | Sample Preparation |  |  | 54 |
| 2.2.2.1 | Melt pressing |  |  | 54 |
| 2.2.3 | Sample examination |  |  | 57 |
| 2.2.3.1 | X-ray microradiography |  |  | 57 |
| 2.2.3.2 | Transmitted light microscopy |  |  | 62 |
| 2.2.3.3 | Image analysis |  |  | 63 |
2.2.3.4 Ultraviolet light microscopy  
2.2.3.5 Determination of amount of undispersed pigment  
2.2.3.6 Intercept length measurements  
2.3 Results and Discussion ....  
2.3.1 Pigment Masterbatches ....  
2.3.2 Ultraviolet Masterbatch ....  
2.4 Conclusions ....  

CHAPTER 3: CHARACTERISATION OF ULTRAVIOLET ABSORBER DISTRIBUTION INCORPORATED BY MASTERBATCH TECHNIQUE INTO POLYOLEFINS  
3.1 Introduction ....  
3.2 History of UV Microscopy ....  
3.3 Equipments ....  
3.3.1 Features ....  
3.3.2 Ray Paths Through the System ....  
3.3.3 Light Sources ....  
3.3.4 Ultraviolet Optical Systems ....  
3.3.5 Illumination ....  
3.3.6 Observation ....  
3.4 Experimental ....  
3.4.1 Materials ....  
3.4.2 Melt Mixing ....  
3.4.3 Sample Preparation ....  
3.4.4 Calibration of Monochromator ....  
3.4.5 UV Microscopy ....  
3.4.6 Recording of Image ....  
3.4.7 Diffraction Effects ....  
3.5 Results and Discussion ....  
3.5.1 Absorber Distribution in a High MFI HDPE ....  
3.5.2 Absorber Distribution in a Low MFI HDPE ....  
3.5.3 Distribution of Ultraviolet Absorber in Polypropylene ....  
3.6 Conclusions ....  

Page No  
63  
63  
65  
66  
66  
84  
84  
87  
87  
88  
90  
90  
92  
94  
95  
95  
97  
97  
97  
98  
101  
102  
106  
106  
107  
107  
111  
114  
115
<table>
<thead>
<tr>
<th>CHAPTER 4: SIMULATED SUNLIGHT EXPOSURE</th>
<th>Page No</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 Introduction</td>
<td>118</td>
</tr>
<tr>
<td>4.2 Experimental</td>
<td>119</td>
</tr>
<tr>
<td>4.2.1 Materials</td>
<td>119</td>
</tr>
<tr>
<td>4.2.2 Compression Moulding</td>
<td>119</td>
</tr>
<tr>
<td>4.2.3 Photooxidation</td>
<td>119</td>
</tr>
<tr>
<td>4.2.4 Failure Assessment</td>
<td>120</td>
</tr>
<tr>
<td>4.2.4.1 Brief review of failure assess-</td>
<td>120</td>
</tr>
<tr>
<td>ment methods</td>
<td></td>
</tr>
<tr>
<td>4.2.4.2 Carbonyl index method of failure assessment</td>
<td>121</td>
</tr>
<tr>
<td>4.3 Results and Discussion</td>
<td>126</td>
</tr>
<tr>
<td>4.3.1 Criteria for Failure</td>
<td>126</td>
</tr>
<tr>
<td>4.3.2 Effect of Dispersion of Ultraviolet Absorber on Stability</td>
<td>126</td>
</tr>
<tr>
<td>4.3.2.1 6.0 MFI HDPE/LDPE UV master-</td>
<td>126</td>
</tr>
<tr>
<td>batch</td>
<td></td>
</tr>
<tr>
<td>4.3.2.2 0.2 MFI HDPE/LDPE/ UV master-</td>
<td>134</td>
</tr>
<tr>
<td>batch</td>
<td></td>
</tr>
<tr>
<td>4.4 Conclusions</td>
<td>141</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHAPTER 5: A SEMI-AUTOMATIC PROCEDURE FOR MEASURING PIGMENT DISPERSION IN POLYOLEFINS USING A PHOTOMETER AND TRANSMITTED DARK FIELD ILLUMINATION</th>
<th>Page No</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1 Introduction</td>
<td>143</td>
</tr>
<tr>
<td>5.2 Measurement of Pigment Dispersion</td>
<td>143</td>
</tr>
<tr>
<td>5.3 Theoretical Concepts</td>
<td>146</td>
</tr>
<tr>
<td>5.3.1 Notation</td>
<td>146</td>
</tr>
<tr>
<td>5.3.2 Assumptions</td>
<td>146</td>
</tr>
<tr>
<td>5.3.3 Measurable Quantities</td>
<td>147</td>
</tr>
<tr>
<td>5.3.4 Number of Primaries per Unit Area for Varying Degrees of Dispersion</td>
<td>149</td>
</tr>
<tr>
<td>5.4 Model Experiment</td>
<td>149</td>
</tr>
<tr>
<td>5.5 Equipment and Hardware</td>
<td>153</td>
</tr>
<tr>
<td>5.5.1 Software and Data Acquisition</td>
<td>153</td>
</tr>
<tr>
<td>5.6 Experimental</td>
<td>156</td>
</tr>
<tr>
<td>5.6.1 Sample Preparation</td>
<td>158</td>
</tr>
<tr>
<td>5.6.2 Dark Field Optics</td>
<td>158</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

To achieve a good dispersion of additives in plastics, two criteria must be satisfied: the additives must be evenly blended throughout the plastic medium and secondly they must be dispersed adequately. Dispersion in this context refers to methods for wetting out and reducing size of agglomerates and aggregates of the additive either in the dry form or within a masterbatch. Blending on the other hand refers to the process of uniformly distributing additives in the polymer system after dispersion. The two terms are not synonymous, although they are mistakenly very often used interchangeably in the plastics industry in a confused form. Occasions may arise when additives are well dispersed but unevenly distributed in the plastic, thus resulting in speckles and flow lines (in the case of pigments) in the product or even the other way round (evenly distributed but not dispersed).

Normally it is not as difficult to achieve even distribution than it is to achieve good dispersion. In fact the problem is more often a dispersion problem than one of distribution. It is therefore to this problem that plastics technologists have devoted most of their attention in additives incorporation.

Pigments constitute the largest group of additives used in the plastics industry and their dispersion is therefore discussed exclusively in this background discussion. The ability of pigments to impart colour and opacity to plastic objects depends not only on their inherent ability to scatter or absorb light, but also on their particle size. Pigment manufacturing processes are generally designed to produce sizes that will yield optimum spectral characteristics.

The so-called primary particle size may range from a few hundredths of a micron for most organic pigments to one micron or more for some inorganics. However, these primary particles tend to stick to each other
during manufacture, resulting in aggregates or agglomerates which are many times the desired particle size.

For pigments precipitated from aqueous solutions, the individual pigment crystals become cemented together to varying degrees due to surface forces, particle growth, residual salts etc, during the filtering and drying operations forming aggregates. In calcined materials, some sintering or interparticle growth may occur, again producing aggregates. Although the pigment manufacturer grinds his product to fine powders, the powder inevitably still contains residual aggregates of varying sizes. In addition to these processes, the primary particles and aggregates may cluster in loose bound agglomerates which may be as much as several thousand microns in diameter. Practically, any pigment which has a size of about 0.2 \mu m will show appreciable agglomeration so that even if we start off with primary particles of this order we still will be faced with the problem of agglomeration.

Generally, the plastics industry is not too worried about aggregates in most products since aggregates are very often too small to impair mechanical properties. Plastics films may be an exception to this as manufacturers are becoming more concerned about the degree of dispersion of additives in films. Dispersion problems arise when aggregates/particles interact to produce agglomerates. If converters are therefore going to obtain full value from additives in terms of say photo-stability in the case of ultraviolet absorbers and strength development, opacity, depth of colour etc, for pigments, the agglomerates must have to be broken down to sizes approaching the primary particle sizes. The process of breaking down these large agglomerates during conversion is referred to as dispersion. Pigments differ considerably in their dispersibility. Titanium dioxide pigments and cadmium pigments are among the easiest to disperse while carbon blacks and iron oxide pigments are among the most difficult\(^2\). The differences in dispersibility arise from the variation in the methods used to manufacture the pigment.

The favouring of masterbatching in recent times by converters to the traditional predispersed compounds has added a pertinent feature not
only to dispersibility but to the entire problem of additives dispersion. This is because masterbatches very often have a low molecular weight base which are arbitrarily used in polymers of varying molecular weights.

Although additives represent only a small part of the mix, their addition may bring with it many varied problems that make poor dispersion unacceptable. It is a waste of an expensive raw material if more additive must be used to achieve the required result; the presence of large particles can lead to electrical or mechanical failure, and later fabrication stages can lead to specks and streaks; and finally irreproducible dispersion, which results in uncontrolled (for pigment additives) colour development making colour matching very difficult. These difficulties can be avoided if routine procedures for the measurement of dispersion are available.

At present, the understanding of the problem of additives dispersion in plastics is still largely qualitative. There is not a sufficient understanding of dispersion in a way that attaches numbers to its description. In striving to develop quantitative methods for describing degree of additive dispersion, it has to be noted that it cannot be described by a single number such as the mean. Having said this, a single number description of dispersion along the line adopted by Vegvari et al.\(^3\) can be a valuable guide when variations in dispersion are considerable. In other words, for the good and the very bad, mean particle sizes for instance can give a useful guide. Standard deviation is a more acceptable statistical quantity for describing dispersion.

1.1 HISTORICAL DEVELOPMENTS OF ADDITIVES DISPERSION

In the United States, pigments were first dispersed in paints early in the 1800s and the first ready mixed paints were marketed in 1867\(^4\). As crude as the early methods were, they showed the basic theory of additives dispersion as it is today.
The turning point in the use of additives particularly in plastics, came as a result of the startling expansion of the plastics industry throughout the world thus resulting in an enormous increase in the use of plastics. This increase consequently resulted in fresh fields of application and the finding of additional outlets in established markets. The new outlets moved the plastic industry from a market of toy goods and decorative kitchen ware to those of functional applications requiring a high degree of performance. From the viewpoint of the plastics additive technologists, a brief examination of the markets that resulted in the upsurge in the use of additives which the plastics industry has now penetrated on a large scale will be useful.

The building industry with a minimum service life of about 20 years poses the problem of good light stability and for this to be realized, plastic materials used in building must have good dispersion of ultraviolet light absorbing additives. Similarly, the plastics film industry requires a high degree of additive dispersion in outdoor films to prevent impairment of their mechanical properties. Markets such as the car industry require precise colour matching in a variety of plastics with differing surface finishes and for this to be achieved, a high degree of pigment dispersion is required. The electric cables industry requires good pigment dispersion to avoid electrical faults arising from agglomerates. Finally, most of the polyethylene plastics being used in outdoor jacketing applications contain a dispersion of ultraviolet absorbers for protection against ultraviolet radiation. Maximum protection from this is governed by the degree of dispersion of the absorbers. Thus the plastic technologist inherited a demanding task. Although the markets mentioned above are apparently secured, there is an ever increasing pressure to find a solution to the problem of achieving good dispersion and also the problem of describing the dispersion quantitatively.
1.2 BACKGROUND OF DISPERSION AND DISTRIBUTION STUDIES

Several studies have been carried out on the dispersion of pigment additives in polymers. Most of these have centred on the dispersion of carbon blacks\(^5\)-\(^8\) in rubbers. Quantitative dispersion measurements of pigments in polymers other than rubbers were reported by Best et al\(^9\), Berenson\(^10\), Smith\(^11,12\) and Reeve et al\(^13,14\). These studies gave suggestions on how dispersion can be described with numbers and also point out the importance of good dispersion of additives in polymer products.

There also has been several studies on the dispersion of non-pigment additives\(^15\)-\(^17\) such as ultraviolet absorbers. The studies indicate that ultraviolet absorber dispersion is more dependent on morphology of crystalline polymers than pigments. Additive dispersion studies in non-pigments is therefore bound to be different from that of pigments where hitherto dispersion of pigments has not been reported to be significantly dependent on morphology. In the case of UV absorbers, it is apparently logical that dispersion can be controlled by choosing appropriate processing variables in addition to paying attention to blending and dispersion. However, ultraviolet absorbers are currently being incorporated into polymers in amounts far in excess of theoretically determined amounts before adequate protection against the ultraviolet light is guaranteed. This of course implies extra material and therefore extra cost.

Additive incorporation into polymers is undergoing a revolution with ultraviolet absorbers now being added by masterbatching\(^18\). Also, there is a movement from dry blending powders with Chemical Blowing Agents (CBA) to the use of concentrates according to concentrates suppliers, Thermofil Inc\(^19\). Many reasons are given for the upsurge in the use of masterbatches but the main reason lies in the cost saving capability of the technique.

The employment of masterbatches, which as already mentioned, has a low molecular weight base in incorporating additives to polymers has given
a whole new aspect to the problem of dispersion. This is because in addition to worrying about dispersion itself, we now have to separately consider how well the low molecular weight masterbatch base mixes with the base polymer and consequently the effect of this new dimension on the degree of dispersion.

1.3 ADDITIVES USED IN POLYOLEFIN PLASTICS

A polyolefin plastic compound consists of a resin and a series of minor ingredients that give the compound some special end use properties. These minor ingredients referred to in this project as additives can be broadly classified into two:

1. Those that confer colour, opacity or reduce production cost such as pigments and extender pigments (non-opaque)

2. Those that prevent undesirable developments that otherwise would reduce the useful life of the polymer such as UV absorbers and antioxidants as heat stabilisers.

1.3.1 Pigments

Pigments by definition are finely divided solids used in plastics, coatings and fibres. They are substantially insoluble in the vehicle as opposed to dyes which are soluble. Both colour and opacity are imparted by pigments but it has to be noted that in view of another class of non-opaque pigments traditionally called extender pigments used originally to reduce production cost, pigments are therefore not necessarily required to have colour or impart opacity.4 Tables 1.1 and 1.2 (respectively referred to later) are included to show the large tonnage of pigments used in the plastics industry in recent years.

The nature and types of pigments used in plastics is discussed in many books and publications20-22. Pigments can be wholly organic or wholly
inorganic or more usually a mixture of organics and inorganics. All organic pigments are synthetic in nature. Several types of organic pigments have been developed but only a few are suited for use in plastics. Although organic pigments are very costly commercially, they occupy a significant place in plastics products manufacture as pointed out in Table 1.1 which shows the United States consumption of organic pigments between 1981 and 1983. Organic pigments available commercially for the plastic industry are:

a) Phthalocyanine pigments
b) Vat pigments (these are compounds based on thioindigo, anthraquinone, perinone and perylene structures)
c) Azo pigments
d) Dioxazine pigments
e) Quinacridone pigments
f) Isoindolinone pigments (a new class of pigment)
g) Carbon blacks.

Inorganic pigments on the other hand are either naturally occurring or synthetic. They are generally superior to organics in heat and light stability. Except for lead salts, chrome yellows and some molybdates, they are stable at all plastics processing temperatures. They are comparatively easier to disperse than organics and yield bright colours at high concentrations although never matching the organics in this aspect. Inorganics particularly titanium dioxide carry a very important market in the plastics industry as illustrated by Table 1.2. The inorganic pigments usually employed by the plastics industry include:

a) Metallic oxides - viz, iron oxide, chrome oxides, red lead oxide and more importantly titanium dioxide. See Table 1.2b
b) Sulphides, and
c) Chromates, molybdates, aluminates and titanates.
TABLE 1.1: Total Weight of Organic Pigments in Plastics

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<tr>
<th>Pigment</th>
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<tr>
<td></td>
<td>1981</td>
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<tr>
<td>Carbon blacks</td>
<td>40,500</td>
</tr>
<tr>
<td>Phthalocyanine blues</td>
<td>1,750</td>
</tr>
<tr>
<td>Phthalocyanine greens</td>
<td>950</td>
</tr>
<tr>
<td>Organic reds</td>
<td>1,300</td>
</tr>
<tr>
<td>Organic yellows</td>
<td>250</td>
</tr>
<tr>
<td>Others</td>
<td>600</td>
</tr>
<tr>
<td><strong>TOTAL:</strong></td>
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TABLE 1.2(a): Total Weight of Inorganic Pigments in Plastics

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<tr>
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<tr>
<td></td>
<td>1981</td>
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<tr>
<td>Titanium dioxide</td>
<td>120,000</td>
</tr>
<tr>
<td>Iron oxides</td>
<td>4,000</td>
</tr>
<tr>
<td>Cadmiums</td>
<td>2,500</td>
</tr>
<tr>
<td>Chrome yellows</td>
<td>2,400</td>
</tr>
<tr>
<td>Molybdate oranges</td>
<td>1,700</td>
</tr>
<tr>
<td>Others</td>
<td>1,500</td>
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<tr>
<td><strong>TOTAL:</strong></td>
<td>132,100</td>
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</table>

*Some figures revised in the light of new data*
TABLE 1.2(b): Pigment and Dye Consumption in Plastics
USA and UK 1981

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<tr>
<td></td>
<td>USA</td>
<td>UK</td>
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</tr>
<tr>
<td><strong>Inorganics</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>102,000</td>
<td>16,000 /</td>
<td></td>
</tr>
<tr>
<td>Iron oxide</td>
<td>3,500</td>
<td>675</td>
<td></td>
</tr>
<tr>
<td>Others</td>
<td>3,500</td>
<td>1,500</td>
<td></td>
</tr>
<tr>
<td><strong>Organics</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon black</td>
<td>30,000</td>
<td>5,000</td>
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</tr>
<tr>
<td>Others</td>
<td>5,000</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>Dye</td>
<td>2,500</td>
<td>275</td>
<td></td>
</tr>
</tbody>
</table>

1.3.1.1 Morphology of Pigment Particles

The morphology of pigment particles depends on the type of pigment. The morphology of carbon black pigment particles is the most understood. Briscoe and Warren\(^23\) have showed that carbon black particles were composed of small graphitic crystals using X-ray diffraction studies. It is thought that these crystals have sizes in the range 0.005 - 1.00 µm according to Todd\(^24\) who also noted that directly above pigment crystals are particles of size range 0.5 - 5 µm which he called pigment particles. The usage of crystals and particles may be qualified in the sense that most of them (crystals and particles) are known to be fused into aggregates but are known to have previously existed as single crystals and particles. Aggregates, therefore, are actually the smallest basic units in most pigments under well dispersed conditions. Pigment aggregates can have sizes of up to about 50 µm in diameter.
Secondary association of pigments aggregates give rise to particles called agglomerates. Pigment agglomerates can have sizes of up to several millimetres. Particles which are loosely bound by air or moisture to form flocculates are also known to exist. A schematic representation of morphology of pigment particles is shown in Figure 1.1. These characteristics of carbon black and the idea of structure and substructure is typical of most pigments. Figure 1.1 therefore shows the general concept of the microstructure of pigment particles.

1.3.2 Stabilisers

Degradation problems in polymers can arise when they are exposed to light, heat and micro-organisms. It is generally noticed as a change in colour and/or a deterioration in physical properties, such as surface cracking, loss in mechanical properties and poorer electrical properties. The ultraviolet light reaching the earth from the sun generally has a minimum wavelength of 290 nm (depending on season and location) and extends to approximately 400 nm and accounts for up to 5% of the total radiation falling on the earth's surface. This radiation as well as the heat used during processing in conjunction with oxygen of the air are respectively capable of causing a change in the chemical structure of the polymer. This change can occur in the form of chain scission, crosslinking, or the splitting of labile groups. The constructional applications (e.g. roof lighting and guttering) which plastics have now penetrated require resistance against UV light as well as heat initiated oxidation thus prompting the use of certain stabilising additives to forestall this problem. Although in many cases, the mechanism of breakdown is ill understood, it has been found possible to retard the rate of breakdown by the incorporation of small amounts of certain additives into the polymer either during manufacture or at the processing stage. Additives used for this purpose are known as stabilisers. The stabilisation of polyolefins against the breakdown due to the factors mentioned above are usually dealt with under the headings:
a) Pigment Crystals

Size Range: 0.005 - 1.00 µm

b) Pigment Particles

Particle Size Range: 0.50 - 5 µm

c) Theoretical dispersed state of pigment Crystals/Particles

d) (up to 50 µm)

crystal/Particles

Polymer
matrix

Crystal/Particles

Polymer matrix

Pigment aggregates

3 or 4 thousand microns

f) Matrix

Pigment Agglomerate

Air or moisture

Flocculate

FIGURE 1.1 MORPHOLOGY OF PIGMENT PARTICLES
a) **UV Stabilising Additives**

As already mentioned, the UV reaching the earth's surface is in the range 290 nm - 400 nm. Table 1.3 shows the bond energies/minimum wavelength required for the dissociation of the carbon-carbon single bond in different functional groups while Table 1.4 shows the wavelengths at which maximum degradation occurs in some polymers. It can be seen from these tables that the energy of UV light in the range 300 nm - 400 nm is capable of splitting most chemical bonds. Consequently, it is important for additives which can absorb this radiation and therefore act as a screen to be incorporated into plastics to prevent degradation. Many compounds are known to absorb ultraviolet radiation\(^{25}\) and they operate in various ways. However it has become increasingly clear that UV stabilising additives now fall into four general categories\(^{26}\). Their nature and possible modes of action are described below:

i) **Ultraviolet screeners**

This class of stabilising additives which are opaque additives operate by preventing the ultraviolet light from being absorbed by the photoactive chromophoric species in the polymer. Examples of this type of stabiliser include titanium dioxide (rutile), zinc oxide (ZnO), magnesium oxide (MgO), calcium carbonate (CaCO\(_3\)), iron oxide and carbon black. The effects these types of additives have on photostability have been described in detail by Allen and McKellar\(^{26}\).

ii) **Ultraviolet absorbers**

This class of UV absorbers are believed to operate by a mechanism in which, rather like the screeners, the stabiliser prevents the light from reaching the photoactive chromophoric species in the polymer. The harmful radiation is directly absorbed by the stabiliser and then harmlessly dissipated. Of the known UV absorbers, 2-hydroxybenzophenones, 2-hydroxybenzotriazoles and derivatives of phenyl salicylate are the most widely used in practice\(^{28-33}\). When photoexcited, the 2-hydroxybenzophenones, 2-hydroxybenzotriazoles both dissipate their absorbed energy by a
### TABLE 1.3: Bond Energies and Minimum Wavelengths Required for Dissociation of Some Molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Bond Energies (K/cal)</th>
<th>Minimum Wave Length for Dissociation (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃⁻CH₃→2CH₃⁻</td>
<td>84.2</td>
<td>340</td>
</tr>
<tr>
<td>CH₂=CH⁻CH₃→CH₂=CH⁺⁺CH₃⁻</td>
<td>109.0</td>
<td>264</td>
</tr>
<tr>
<td>CH₂=CH⁻CH₂⁻CH₃⁻CH₂⁻CH₂⁻CH⁻CH₂⁻⁺⁺CH₃⁻</td>
<td>61.5</td>
<td>465</td>
</tr>
<tr>
<td>Ph⁻CH₃⁺Ph⁺⁺CH₃⁻</td>
<td>88.6</td>
<td>323</td>
</tr>
<tr>
<td>PhCH₂⁻CH₃⁻PhCH₂⁻⁺⁺CH₃⁻</td>
<td>63.0</td>
<td>454</td>
</tr>
<tr>
<td>CH₃CO⁻CH₃⁻CH₃CO⁻⁺⁺CH₃⁻</td>
<td>72.0</td>
<td>397</td>
</tr>
<tr>
<td>Ph₃C⁻CPh₃⁻Ph₃C⁺⁺CPh₃⁻</td>
<td>11.3</td>
<td>2530</td>
</tr>
<tr>
<td>H⁻H⁻H⁺⁺H⁺⁻</td>
<td>104.2</td>
<td>274</td>
</tr>
<tr>
<td>H⁻Cl⁻H⁺⁺Cl⁺⁻</td>
<td>103.2</td>
<td>277</td>
</tr>
</tbody>
</table>

### TABLE 1.4: Wavelength for Maximum Degradation for Some Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>300</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>370</td>
</tr>
<tr>
<td>PVC</td>
<td>310</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>318.5</td>
</tr>
<tr>
<td>Polyesters</td>
<td>325</td>
</tr>
<tr>
<td>VC/VA copolymer</td>
<td>322 and 364</td>
</tr>
</tbody>
</table>
mechanism that involves the reversible formation of a six-membered hydrogen bonded ring. For example, for 2-hydroxybenzophenone the following two tautomeric forms in equilibrium provide a facile pathway for deactivation of the excited state induced by absorption of UV light:

The result of this mechanism of light absorption and dissipation thus leaves the stabiliser chemically unchanged and still able to undergo a large number of these activation-deactivation cycles. Direct evidence for such a mechanism is hard to obtain because the stabiliser has a role which is essentially 'passive' in nature. However, the fact that the more effective of these stabilisers exhibits a correspondingly stronger intramolecular hydrogen bond with the carbonyl group, serves as an indirect evidence for the mechanism.

The protection mechanism of aromatic salicylates is slightly different from those of benzophenones in that they are photolysed by the incident light into products with high absorbance in the near ultraviolet. For example, phenyl salicylate is photolysed via a photo-Fries type rearrangement to give derivatives of dihydroxybenzophenone as shown below:
iii) *Excited state quenchers*

The mode of action of this class of UV light stabiliser is to deactivate the photoactive chromophoric species in the polymer before it undergoes chemical reactions that result in polymer dehydration. In general, these stabilisers are complex chelates of the transition metals, usually nickel. Despite their relatively lower light absorption in the region 300 - 400 nm, a number of these chelates are said to be much more effective as light stabilisers in polypropylene than the 2-hydroxybenzophenones\textsuperscript{37}. Deactivation of the photoactive chromophoric species can be achieved in a number of ways, for example, the photoexcited state of the photoactive chromophoric species may be either the singlet or the triplet state or may even initiate degradation by being quenched in its triplet state by oxygen to form excited singlet-oxygen:

\[ ^3\text{PCS} \text{(photoactive chromophoric species)} + ^3\text{O}_2 \rightarrow ^1\text{PCS} + ^1\text{O}_2 \]

which may proceed to attack the polymer matrix\textsuperscript{38}, therefore this class of stabilising additive is both effective light stabiliser for polypropylene and also efficient triplet deactivator as reported by Briggs and McKellar\textsuperscript{37}.

iv) *Ultraviolet stable anti-oxidants*

Here the mode of action of the stabiliser is to inhibit the chain propagation processes by radical scavenging or decomposing hydroperoxides. The mechanisms are believed to be essentially similar to those that operate under thermal processing conditions\textsuperscript{32}, except that the stabiliser molecules must be stable to near ultraviolet light. For example, many primary and secondary anti-oxidants themselves are only weak photostabilisers in commercial polyolefins\textsuperscript{32} since they photodecompose rapidly before they have a chance to inhibit the chain propagation processes. On the other hand, carbon black\textsuperscript{28-31} is an outstanding ultraviolet stable anti-oxidant. Recently, Carlson and
Wiles\textsuperscript{39} have shown that certain nickel (II) chelates operate by collisional quenching and radical scavenging processes and not by long range energy transfer mechanisms. Some phenolic chelates of nickel which do not absorb ultraviolet radiation but still protect the plastic from photodegradation have been reported\textsuperscript{19} but are not very popular because they colour the plastic. However apart from the above mentioned light stabilisers, some of which are structurally shown in Table 1.5, a new class of hindered amines\textsuperscript{40} such as that shown in the structure below

\[
\begin{align*}
R' &= \text{CH}_3 \\
R'' &= \text{O, H, CH}_3
\end{align*}
\]

are currently of interest. These hindered amines certainly do not operate by mechanisms of UV absorption or by quenching of photoactive impurities\textsuperscript{40,41}. Although the precise mechanism is uncertain, model system studies\textsuperscript{41} suggest they could be effective UV stable antioxidants. It is not clear if this new hindered amine is the same that is recently reported\textsuperscript{19} as low/load high efficiency hindered amine (HALS) which is claimed to be effective in polypropylene/polyethylene moulding extension materials, ABS and impact PS.

Many compounds belonging to one of the four classes of stabilisers described above are known to absorb ultraviolet radiation but most have certain drawbacks which preclude their use in plastics. An effective ultraviolet absorber for instance should have high absorbance in the wavelength range which is most harmful to the polymer. The percentage light transmission of an ideal ultraviolet absorber
### TABLE 1.5: Typical UV Absorbing Compounds

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzotriazoles - e.g. 2-(2'-hydroxyphenyl) benzotriazoles</td>
<td><img src="image1" alt="Structure" /></td>
<td>211</td>
</tr>
<tr>
<td>Benzophenones - e.g. O-hydroxybenzophenone</td>
<td><img src="image2" alt="Structure" /></td>
<td>198</td>
</tr>
<tr>
<td>Substituted acrylonitrates - e.g. ethyl-2-cyano-3,3-diaphenylacrylate</td>
<td><img src="image3" alt="Structure" /></td>
<td>277</td>
</tr>
<tr>
<td>Salicylates - e.g. phenyl Salicylate</td>
<td><img src="image4" alt="Structure" /></td>
<td>214</td>
</tr>
</tbody>
</table>
at varying wavelengths of light gives a transmission curve which has a vertical line at 380 nm. In addition to this, an ideal UV absorber should have the following characteristics:

i) It must have high absorption characteristics at the wavelengths harmful to the material in which it is incorporated and be capable of dissipating the energy harmlessly

ii) It should not impart colour to the system - i.e. must not absorb significantly in the visible spectrum

iii) It should be compatible with the system over the range of concentrations to be employed

iv) It must itself have good stability to ultraviolet light

v) It should be non-toxic.

Although this work concerns just one class of the typically used ultraviolet absorbers mentioned in Table 1.5, it can be seen from the same table that these absorbers usually have related structures. We therefore anticipate that any conclusions reached with Cyasorb 531 that is used in this study will be mirrored with any member of the other benzophenones and indeed any member of the other three classes. Table 1.6 shows the plastics use of ultraviolet absorbers in the USA in the last three years. It is easily seen that over 50% of the UV stabiliser consumption in each of these three years went to polyolefins hence the need for their economical use.

However, the performance and economical use of ultraviolet stabilisers (regardless of the possession of ideal requirements) is above all dictated by their dispersion and distribution and it is the characterisation of this that forms one of the important aspects of this thesis.
b) **Anti-oxidants**

A wide variety of anti-oxidants are used for different polyolefins and for different end uses. Formulations that are used in contact with food for instance employ 2,6-Di-tert-butyl-para-cresol (BHT). Typical anti-oxidants employed in polyolefins are shown in Table 1.7(a) while their consumption in some plastics over the last three years in the USA is shown in Table 1.7(b).

Again the performance of these anti-oxidants is dependent on good dispersion and distribution in a similar way with UV stabilising additives. The importance of this cannot be over-emphasised as clearly demonstrated from Tables 1.1, 1.2, 1.6 and 1.7 which indicate the enormous amounts of these additives which are being consumed by the plastics industry. Since these additives particularly UV absorbers are much more costly than the polymers themselves, there is a great need that they be used economically in polymers. This objective is only achievable through good additive dispersion and distribution. The advantages of good additive dispersion are the prevention of impairment of certain properties and possible reduction in the cost of fabricated polymer products containing these additives.

### 1.3.3 Surface Additives

In many cases, dispersion and distribution of additives is not required through the bulk of the material. Such additives operate on the surface of a fabricated product and include among others:

a) **Slip additives:**

In many polyolefin applications such as film and coatings and to some extent injection moulded and extruded parts, it is desirable to have the surface coefficient of friction lower than the one that would result from the use of unmodified resin. This is achieved by the use of slip additives. This class of additive belongs to surface active agents in that they have a polar and a non-polar end. The polar end
TABLE 1.6: Plastics Use of UV Stabilisers

<table>
<thead>
<tr>
<th>Materials</th>
<th>Consumption, Metric Tons</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1981</td>
</tr>
<tr>
<td>Acrylic</td>
<td>69</td>
</tr>
<tr>
<td>Cellulosics</td>
<td>19</td>
</tr>
<tr>
<td>Polycarbonates</td>
<td>148</td>
</tr>
<tr>
<td>Polyester</td>
<td>69</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>1740</td>
</tr>
<tr>
<td>Polyolefins</td>
<td>63</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>71</td>
</tr>
<tr>
<td>Coatings</td>
<td>63</td>
</tr>
<tr>
<td>Others</td>
<td>35</td>
</tr>
</tbody>
</table>

TABLE 1.7(a): Anti-oxidants for Polyolefins

- 2,2-Methylene-bis-(4,6-methyl-tert-butylphenol)
- 2,6-Di-tert-butyl-para-cresol
- Aryl phosphites
- Aryl-alkyl phosphites
- Dilauryl thiodipropionate (DLTDP)
- Diestearyl thiodipropionate (DSTDP)
TABLE 1.7(b): Anti-oxidants Consumption by Plastics

<table>
<thead>
<tr>
<th>Plastic</th>
<th>Consumption, Metric Tons</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1981</td>
</tr>
<tr>
<td>ABS</td>
<td>4,600</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>3,200</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>4,400</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>2,200</td>
</tr>
<tr>
<td>Others</td>
<td>1,500</td>
</tr>
<tr>
<td>TOTAL:</td>
<td>15,900</td>
</tr>
</tbody>
</table>

causes them to be rejected from the plastic mass, while the non-polar end remains firmly attached. This means that although they start mixed into the polymer mass they soon bloom to the surface forming a surface layer which has to have a low coefficient of friction. The importance of the distribution of this is similar to that required for additives which operate in the bulk, the difference being that the distribution is required on the surface.

The materials used for this purpose are commercial products manufactured from natural oil and fats. They have stringent use limitations. They must be odourless, colourless and non-toxic. In the case of polyolefin films, such additives are expected not to affect the optical properties of the film and should not also interfere with printing.

b) Anti-block Additives

Anti-block additives have the function of keeping two polyolefin surfaces from sticking together without making the surface slippery. In many cases, slip additives perform this function adequately. The problem area is in the films because polyolefin films are often so very smooth
and glossy that they exclude air from between them. In cases like this, anti-block additives generally used in films are some very fine grades of diatomaceous earth.

c) Anti-Static Agents

Polyolefin plastic objects, have a very great tendency to accumulate static charge which attracts dust causing clinging of film to conversion equipment which is otherwise detrimental. Although this problem can be solved by surface treatment, it is only temporary. Best results are obtained by additives incorporated into the compound. Like slip additives, antistatic agents have to have limited compatibility with the resin causing them to form an adherent film on the surface. The materials used for the purposes of removing this problem are ethoxylated aliphatic amines and amides, ethylene oxide adducts of aliphatic hydrocarbons, phosphate esters, quarternary ammonium salts and glycol esters.

Optimal performances of the additives mentioned in Section 1.3.3 like pigments and stabilisers all depend on good dispersion of the additives.

1.4 FORMS OF ADDITIVE MATERIALS FOR POLYOLEFINS

The type of additive needed in a polymer for whatever purpose and the way it is incorporated into the polymer can have a very significant effect on the overall performance of the polymer both in service and in production. Many additive systems are now available in the market in the following physical forms:

1. Coloured forms: To meet the needs of colouring, additive manufacturers offer polyolefins in the following forms:
a) **Colour compound:**

These are granules of the polyolefin in which the pigments and any special additives are incorporated into the polymer and can therefore be moulded or extruded directly into coloured items.

b) **Colour powder premix:**

Colour powder premix is available in the form of a physical blend of a polymer powder, pigments and additives which can again be processed directly to coloured items. They are cheap, comparatively, but less clean and less convenient to handle than coloured compounds.

c) **Colour masterbatch:**

These are granules of a particular polyolefin containing a high loading of pigment additive. They are intended to blend with natural granules before processing into finished items.

2. **Other methods of incorporating additives:** Other methods of imparting colour or modifying performance of a polyolefin plastic include:

a) **Low molecular weight masterbatching:**

A masterbatch, is a polyolefin compound containing a high concentration of colour or additive, which is mixed with natural resin in the proper proportions before use to give the final mix the desired additive concentration.

In addition to colours, masterbatches may be used in both injection moulding and extrusion to add slip and anti-block to film resins, ultraviolet absorbers to film and monofilament resins, carbon black to pipe resins, butyl rubber or other elastomers to improve the impact strength of the resin, and glass fibres to improve the strength and heat resistance of mouldings as well as other materials for special uses.
Masterbatches are more often low density polyethylene based. Additive loading in a masterbatch is varied and can range from about 2% to as high as 60%. When the carrier system is the base polymer, the masterbatch is referred to as a dilute masterbatch and such masterbatches may contain up to 20% of the additive. Very much more concentrated masterbatches (which can contain up to 60% colouring system) can be made using carrier systems which are based on low molecular weight resins; such resins have a low melting point of about 60°C and are compatible with a wide range of polymers. Such universal compatibility is a tremendous advantage, although at the same addition level, the same masterbatch may produce slightly different colours in two different polymers. Concentrated masterbatches may be supplied in a range of granule sizes so that if, for instance, powdered polymer is being run, then a fine grain masterbatch could be selected.

The cost of masterbatch and the blending operation is generally lower than the cost of purchasing premixed compound from the resin manufacturer. The real advantage of on-plant compounding is not cost but ability to buy and store in bulk a small number of base resins which may be modified as needed in accordance with a particular order instead of having to maintain an inventory of a large number of special compounds.

The dispersion of additives in masterbatches is carried out in a heavy duty internal mixer followed by extrusion and chipping so that the final product is available in granular form. The shear rate is such that additive aggregates are broken down in the production of these stiff compounds. Ideally therefore, their let down into polyolefin polymers should involve only distributive action and wetting of particles. The advantage of using masterbatches as opposed to precompounded materials stated above can only be claimed to be truly an advantage if this ideal of obtaining a true dispersion in the masterbatch is achieved. It is claims like this that the present work addresses itself.
b) **Universal masterbatch**

Universal masterbatches are supplied as a mixture of coarse and crumb for use at about 1-2% let downs for injection mouldings. Universal masterbatches are generally of similar colour strength to low density polyethylene based masterbatches. They contain various resins (both polymeric and sometimes non-polymeric) with many other surface active additives included to improve dispersion and render them usable with most plastic materials regardless of structure.

The variety of resins usually employed as carriers, are specially chosen and designed for certain applications. The choice of resin is important as it must melt at a temperature about that of the polymer or be soluble in specific solvents. It must be compatible with the resin and not exude from the system, it must be at least stable to heat and light as the media in which it is being incorporated and should also have toxic clearance. Although the choice of carrier is important, the method of applying the carrier (just like any other type of additive) so that each discrete particle of the additive is coated with the polymer to the exclusion of air is the secret of success or failure.

Whether this elaboration is satisfying the requirement, that necessitated its manufacture, is still not known. The effects of the various resins on product property could be of interest and therefore part of the aims of the present work.

c) **Paste Systems**

These consist of additives dispersed in a viscous liquid carrier and normally injected in pulse quantities by a pump unit fitted to the processing equipment. They may be used by tumble blending with polymer granules. Paste systems tend to work better with granules than with powder because at high dose rates, powders tend to form lumps which obstruct the powder feed around the throat of the hopper.
Generally, the usage rate of liquid pastes is about 1-2%. This method of incorporating additives has become firmly established in many plastic manufacturing processes. The advantages of liquid carriers relate directly to better economics and ability to automate operations. The liquid carrier may be plasticizer, polymer solution, low molecular weight polymer or a combination of these. The principle is to select a carrier which is compatible with a wide range of thermoplastics.

A sizeable industry has grown up around these elaborations of standard pigments, the bulk of them being produced by companies outside the pigment manufacturing industry. In recent years, however, masterbatches have been unable to satisfy the more critical dispersion requirements particularly in the blown polyethylene film, polypropylene fibre and vacuum formed PVC fields. Pressure has therefore been brought to bear on pigment manufacturers to produce pigments free from aggregates and agglomerates, and it is in this area that the greatest strides have been made towards solving the dispersion problem in the plastic industry.

1.5 THEORY OF DISPERSION

A pigment/additive dispersion, by definition, is a heterogeneous mixture of one phase in another. In this case, it is a mixture of the solid phase (pigment) in the liquid phase (vehicle). To obtain a complete dispersion or even approach complete dispersion, the processing must accomplish two basic factors of great importance and interest to the end product manufacturer.

i) Size Reduction

The dispersion must reduce the agglomerated particles to the basic particle size of the pigment powder. This is the most critical and hence the rate determining step to the formation of a good dispersion in the end. It may be achieved by impact, particle-to-particle attrition or by shear transmitted through an intermediate polymer layer.
Whichever route to size reduction is available, enough mechanical energy must be supplied to rupture the aggregates and agglomerates. Since the size reduction process takes place in a polymer melt, the physical characteristics of the vehicle can be very important to the overall dispersion quality. The size, shape, hardness and softening temperature of the resin can influence the extent and efficiency with which size reduction is accomplished. In fluid dispersion processes size reduction is obtained by transmission of shear from grind surfaces through the intermediate fluids to the additive particle. The intermediate vehicle characteristics of importance are therefore:

i) adhesion to the additive particles
ii) adhesion to the grind surface
iii) internal cohesive energy often referred to as tack

The shear force on the additive agglomerate is determined by the strength of the minimum among the above three characteristics.

ii) The Solid/Liquid Interface and Wetting

Reduction of size to the original additive particle size alone is not sufficient to achieve the basic objectives needed for good dispersion. Unless the reduced particles are protected with a complete, stable coating of the vehicle, the additive particles will reagglomerate. This is due to their large surface areas which make them subject to complex physiochemical interactions. The process of protecting additive particles with a stable coating of the liquid vehicle to avoid interfacial forces attraction among particles is referred to as wetting. As a minimum, wetting requires that the additive and vehicle be sufficiently mixed and hence have sufficient affinity for each other to avoid separation when work is applied to the system.

In theory, it is generally felt that the free energy surface of solids is greater than that of liquids, but not strong enough to change the
shape of solid materials. The affinity of solid for liquid is determined largely by the relative polarity and the degree of cohesion in the molecules of the liquid. Obviously, if the cohesion among the liquid molecules is greater than the attraction between them and the solid surface, they will not spread out on the solid. The solid/liquid interface and wetting can be visualised by the simple system of a drop of liquid brought into contact with a flat solid surface. The angle which results from the contact between the liquid and flat solid surface (angle measured within the liquid) represents a balance of the forces of attraction between the molecules of the liquid and vapour, $Y_{LV}$, liquid and solid, $Y_{LS}$ and solid and vapour, $Y_{SV}$. This angle is generally referred to as the contact angle. Liquids which have a high affinity for the solid have a zero contact angle and therefore perfectly wetting. At the other extreme therefore, is a value of $180^\circ$ contact angle for zero adhesion between the solid and liquid (a state not reported to have been observed in practice).

For fine particle solids, the system is more complex. Parfitt has divided the process of wetting into three stages viz: adhesional wetting, spreading wetting and immersional wetting. By considering the changes in the energetics of the above three stages, Parfitt drew the following conclusions:

i) adhesional wetting is positive when the angle of contact ($\theta$) is less than $180^\circ$ and that the process is invariably spontaneous;

ii) immersional wetting is positive and immersion spontaneous only when the angle of contact is less than $90^\circ$; and

iii) spreading wetting is only positive when the angle of contact is zero and work must be done to achieve spreading wetting at all larger values of this angle.

The above conclusions have important implications for the dispersion of solids in liquids. Generally, work must be done to achieve wetting
of solids in liquids, especially if this involves rupturing of agglomerate particles.

It is evident from the above discussion that if an additive of high surface area, or with a surface of opposite polarity from the vehicle is to be properly dispersed, the addition of a surface active agent is necessary. This is because surface active agents concentrate at the interface of the vehicle and the particle. Improvement can therefore be made by the addition of surface active agents which by their nature influence surface forces between vehicle and solid and consequently the contact angle between them. The contact angle ($\theta$) is related to the surface forces by the expression

$$\cos \theta = \frac{Y_{SV} - Y_{SL}}{Y_{LV}}$$

If the contact angle $\theta < 90^\circ$, a decrease in $Y_{LV}$ through the addition of surface active agents for instance decreases the contact angle ($\theta$) between solid and liquid and therefore increases wetting. Singh et al.\(^{44}\) have however shown that a simple reduction in $Y_{LV}$ alone does not always reduce the liquid/solid contact angle. The complex influence of surface active agents and their ultimate effects on the values of $(Y_{SV} - Y_{SL})$, $Y_{LV}$ and wetting has been explained in detail by Newton.\(^{45}\)

1.5.1 Factors Affecting Degree of Dispersion\(^{2,24}\)

As might be expected, the level of dispersion achieved with any mixing process depends upon the energy required to disperse the agglomerates, the capability of the process for supplying that energy, compound type and texture of additive.

The compounding equipment available to the compounder for a compounding operation will, by the nature of its design, determine the maximum level of shear which may be developed within any given polymer at any operating
temperature. It is well established for example, in the paint industry (an industry with mixing requirements similar to that of incorporating additives into plastics), that every mill develops a specific energy, which in turn limits the level of dispersion finally achieved.

Design will also control the residence time (that is the time for which the agglomerates are exposed to shear) as well as the proportion of that time during which the agglomerates are exposed to high rates of shear.

Other variables that limit the shear developed in a compounding equipment include the operating temperature and the mixer speed. High speeds raise the energy input as well as passing material through the zone of maximum intensity more frequently. Thus more agglomerates are dispersed more quickly. The equipment available to the plastic compounder varies considerably and the particular system used by any company will depend upon the quality of additive dispersion required and the economics of the operation. The systems range from the extremely simple to the very complex as illustrated in Table 1.8.

The first two processes are extremely simple, the first being restricted to specific shapes usually very large mouldings. Because not much shear force is brought to bear in the additive particles through this process, not much dispersion can be expected. The second method is popular probably for its simplicity and cheapness. Additionally, the additives and polymer system are subjected to only one heat cycle reducing the risk of break down of either component. Also, flexibility of the process reduces the amount of coloured compound that has to be stocked. It however imposes less work on the coloured system than either of processes 3 and 4 and unless special pigments are used, a very poor dispersion is achieved.

Processes 3 and 4 respectively involve high speed mixing and use of internal mixers before further processing and therefore impose a lot more work on the additive agglomerates and thus generally expected to
TABLE 1.8: *Typical Plastics Additives Compounding Equipments and Types of Products Obtained from the Processes Involved.*

<table>
<thead>
<tr>
<th>No.</th>
<th>Feedstock</th>
<th>Process</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polymer granules + pigment</td>
<td>Tumble blend + Rotational cast</td>
<td>Large mouldings</td>
</tr>
<tr>
<td>2</td>
<td>Polymer granules + pigment</td>
<td>Tumble blend + Injection mould or extrude</td>
<td>Finished mouldings or extrudates</td>
</tr>
<tr>
<td>3</td>
<td>Polymer powder + pigment + other additives</td>
<td>High speed mixer + Extrude and chip + Injection mould or extrude</td>
<td>Compound for subsequent processing + Mouldings or extrudates</td>
</tr>
<tr>
<td>4</td>
<td>Polymer or compound + Colourant</td>
<td>Internal mixer + Extrude and chip</td>
<td>Masterbatch + compound + Coloured compound + Finished product</td>
</tr>
</tbody>
</table>

give better dispersions. This is particularly true if the final product is obtained by extrusion rather than injection after mixing. Process 4 represents the technique likely to give the best dispersion.

The major problem in all these techniques is to attempt to ensure that the energy input is used to break up additive aggregates and not to compact additive particles. This is particularly true when adding large volumes of pigment to an internal mixer or by extending the tumbling time too far when dry tumbling.
b) Compound type

Before a pigment and indeed any additive can be adequately dispersed in a system it is commonly accepted as described in Section 1.5.1 that wetting out of the additive must take place. Wetting out is considered to be the replacement of the air/additive interface by the additive/vehicle interface at minimum liquid/solid contact angle. This change in interface prevents reaggregation of particles after size reduction has been attained through imposed shear forces. Whereas in liquid systems such as paints and inks the presence of solvents facilitates the process of wetting out, plastics systems rarely contain solvent, although certain compositions do contain plasticisers which may act in a similar manner. Polymer systems which are well known for their inability to wet out pigments readily are rigid PVC, ABS and polyolefins. In addition, some of these systems exert little shear on the pigment aggregates due to their low viscosities at processing temperatures. As a result, it is extremely difficult to obtain adequate dispersion in these polymers without modification of the process or the use of special additives as discussed previously.

c) Texture of Additive

A measure of the texture of additives such as pigments would not be simply the size of aggregates present in the powder, but the ease and degree with which they can be broken down to primary particles in a system. The texture of an organic pigment say is very much dependent upon the conditioning applied to it in the final stages of their production. In recent years, the organic pigment manufacturer has become increasingly aware of the vast improvement which can be made, by correct conditioning procedures, in the physical forms of pigments and the great influence these have on their overall dispersion in polymers.

Generally, for a given shear gradient, the smaller the additive particle, the smaller the total shear to which it is exposed. The real
strength of an agglomerate is however determined by the physical characteristic of the material concerned, the cohesive and tensile properties of the additive powder determining the level of agglomeration both before and during powder mixing. As the agglomerates become more compacted, due to handling and mixing, they develop strength and their density increases. The effectiveness of shear developed in the compounding equipment very much relates to the strength (referred to as texture in this sub-heading) of the agglomerates in the bulk material.

1.5.2 Dispersion Quality

Several factors can be affected by dispersion. The factors include:

1. **Appearance:**

   Appearance is characterised by:

   a) **Surface texture:** Some polymers will have surface texture even if unpigmented. These are typified by crystalline polymers. When such polymers contain additives which are poorly dispersed, the surface texture becomes very rough. However, compared to amorphous polymers, the distribution of additives is more critical in the latter as poor dispersion is very easily detectable in them.

   b) **Specks and streaks:** Very poor additive dispersion can be detected as local specks and streaks by the naked eye. The minimum particle size visible by eye is of the order of 40 μm. The appearance of specks and streaks depends on type and colour of pigment (in the case of pigment additive). For example, specks and streaks can be tolerated in TiO₂ even when dispersion is very poor, but not in ferric oxide which is red and therefore very easily detectable in polymers because of their contrasting colours.
c) Gloss: gloss unlike specks and streaks (which appear at aggregate sizes >40 μm) is an overall effect which is affected by aggregate size in a more critical way. Particles as small as 15 μm contribute to gloss problems. Gloss measurement can therefore give an indication of the degree of dispersion in a given plastic/additive system. Gloss is measured by the BS 2782 515B and ASTM D2457 (35) as well as use of the Zeiss GP2 goniophotometer. The gloss measurement obtained is however dependent on test method, therefore relating them to the degree of dispersion has to be done very carefully.

d) Colour: colour like the other appearance traits already mentioned is particle size dependent. Non-uniformity of colour is easily detectable by eye. The colour strength developed in a given system depends on many conditions and varies with pigment type. Phthalocyanine blue for instance has a tremendous colour strength sensitivity to small changes in particle size below 0.4 μm.

e) Transparency: transparency not only depends on particle size but also on degree of wetting obtained during shear mixing. Wetting is very important in colour-pigment applications requiring high transparency or maximum chroma in dark shades. Haze and reduced transparency are produced by light scattering at the plastic/pigment interfaces if wetting is incomplete. Transparency in dark shades can therefore give an indication of the degree of wetting and consequently degree of dispersion obtained in colour-pigment applications.

2. Performance

Performance and processing are affected by the degree of dispersion in a different manner. Performance traits of interest in the consideration of degree of dispersion desired include:
a) Cost: it will be a waste of resources for instance to grind down additive particles to a level less than 5 μm in applications that do not require such high degree of dispersion. The cost of achieving such a level of undesired degree of dispersion can therefore be diverted to another area if the product can tolerate particles of 20 μm say.

b) Processability: processability can be affected by the degree of additive dispersion initially within the additive powder or masterbatch. Processing problems such as plugging of filter packs during extrusion are caused by large additive particles of the order of 30 μm sizes which have not been reduced.

c) Electrical resistivity and weatherability: electrical resistivity is a performance trait which is greatly influenced by additive particles as small as 5 μm in critical applications such as cables. Weatherability refers to the ability of an additive containing product to withstand all forms of weathering, including UV light, atmospheric oxidation etc. The importance of weathering resistance varies appreciably with the product and its application but the effectiveness of the additive in protecting the material from weathering effect depends on the quality of dispersion of the additive.

However, acceptable additive particle size/distribution or degree of dispersion to be attained in any system is determined by the relative importance of the properties outlined above. In other words, the level of surface texture, gloss, colour strength, cost etc, all depend on the degree of dispersion. The level of dispersion eventually to be aimed at has to be weighed against the performance desired of the product. Table 1.9 shows particle size range and associated problems in a given fabricated product containing pigment particles of varying sizes.
TABLE 1.9: PARTICLE SIZE RANGE AND ASSOCIATED PROBLEMS

<table>
<thead>
<tr>
<th>Particle Size (μm)</th>
<th>Associated Problem</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 and over</td>
<td>Stress concentration</td>
</tr>
<tr>
<td>30</td>
<td>Surface imperfections, specking, streaking and processing problems such as pluggage during extrusion</td>
</tr>
<tr>
<td>15-30</td>
<td>Gloss problems</td>
</tr>
<tr>
<td>5</td>
<td>Can influence physical or electrical properties of the product</td>
</tr>
</tbody>
</table>

The level of dispersion and distribution finally attained therefore depend on the application for which the product is designed. However, for optimum performance, less than 5 μm particle sizes are desirable.

1.6 DISPERSION METHODS

Having discussed the theory of dispersion in general in the previous section, the question of how to obtain it is now considered. The dispersion methods in plastic systems are:

1. Dry blending

Dry blending involves low to high intensity mixing of additives with dry resin particles. Dispersion by dry blending alone occurs largely by impact and attrition. Except when followed by other dispersion processes, little opportunity exists in the process to achieve the intimate wetting needed for some critical applications. Nevertheless, techniques and equipment have been developed that permit production of good-quality dispersion by this method. The most important of these are non-fluxing high intensity mixers and the use of particulate resin in pigment-resin co-blending.
The need for the use of equipments that will impart high velocity or impact to the additive particles is obvious, since aggregates and agglomerates can only be fractured by exceeding a threshold energy level holding the particles together. In general, dry-blend dispersion has been more effective at low-pigment loading than at high, mainly because of the caking tendencies of many pigments and additives in general.

The main difficulty or disadvantage of dry-blending dispersion is that very little opportunity exists for an intimate wetting between additive and vehicle. Also, a vigorous dry blending can result in overgrinding. Fracture of the primary particle size as in lead chromates and cadmiums or the compaction of aggregates into larger ones than was started with, as happens in the dry-blending of many organics, are the most frequent results of vigorous dry-blending. These are clear disadvantages in the use of this technique as large and undesired changes in colour and often in performance result. Their main advantage lies in their ability to generate enough shear to rupture aggregates and if they are followed by other processing methods to effect intimate wetting, they can give rise to good additive dispersions.

2. Melt shear dispersion

Melt shear dispersion is the most widely used method of incorporating additives into plastics. The procedure depends on the transmission of high shear through the resin to achieve good dispersion. Melt shear dispersions are usually best at a temperature very close to the softening point of the system because of the high internal shear that develops at this point. At higher temperatures the process becomes one of distribution or mixing rather than one of dispersion because of the greater fluidity. In cases where plasticizers and lubricants are involved the amount of shear available can be increased by adding them only after dispersion is complete.
As already mentioned, the effectiveness of shear transmission to a pigment particle through an intermediate fluid film will depend on: the quality with which the fluid wets the pigment and equipment surfaces; the viscosity of the system under actual dispersion conditions and the internal cohesive strength of the fluid. Each of these therefore suggest the direction that can be taken to improve dispersion through this method. Cohesive strength is an inherent characteristic of the resin and can only be dealt with by modifying the resin or selecting another one or using a compatible carrier as a dispersion medium if cohesive strength is known to limit dispersion very greatly. Since wetting is a function of both fluid and surface to be wetted, surface active agents or carriers can be used to improve wetting characteristics. Although viscosity is more within reach of the compounding to control, he needs some basis of determining what level is desired, and also to recognise that viscosities are likely to fluctuate widely during the processing of thermoplastics.

All melt shear dispersion equipment for plastics depend on the utilization of hydraulic shear to break down pigment or additive aggregates. This shear is directly proportional to the viscosity of the polymer which in turn is directly dependent on the temperature involved.

*Types of equipment used in melt shear dispersion:* Three general types of equipment are in use today:

a) The two-roll-mills - also known as the rubber mill, is an important piece of processing equipment because it is primarily used for solid polymers similar to rubber such as vinyl copolymers and cellulosic polymers. This type of equipment produces the highest amount of shear thus producing extremely fine dispersions. Usually, the temperature of the rolls can be controlled carefully to maintain the viscosity of resin to a level that would give the maximum shear necessary for dispersion and here lies the advantage of this melt dispersion process compared to the other methods to be discussed shortly.
b) Internal mixers - internal mixers are designed to produce intensive mixing at high viscosities. It operates by concentrating a relatively high-power input on a small volume of material resulting in extremely high shear and rapid temperature build-up.

The increase in temperature referred to above is a very serious limitation to a piece of equipment that would otherwise have given very good additive dispersion. The increase in temperature gives rise to a drop in viscosity and consequently a drop in shear force developed. However, since very high shear forces exist in the early stages of this process, it is possible to produce a satisfactory product in the time usually available before temperature build up.

Although this process is capable of obtaining very good dispersions comparable to the two-roll-mill process, it is usually necessary to use the internal mixer in conjunction with the two-roll-mill to give the best additive dispersion obtainable by mechanical means.

Further improvements in the even distribution of additives during internal mixing and dry blending discussed earlier have been affected in recent years by introducing a low percentage of an oil to the polymer in the mixer before the additive is added. The major effort has been directed towards pigment dispersion and there are now available in the market various modifications to standard pigment additives which have been produced to facilitate incorporation and improve dispersion of pigments into different polymer systems.

c) The compounding extruder: the extruder is the heart of most extrusion, injection and blow moulding operations today. The primary purpose of the extruder is to take room temperature plastic resin in the form of pellets, beads or powders and convert the resin to a molten polymer at sufficiently high pressure to
allow the highly viscous melt to be forced through a nozzle into a mould, in the case of injection-type processes, or through a die, in the case of blow moulding or continuous extrusion. Compounding extruders are very often employed for additive incorporation into plastics. A compounding extruder unit comprises of a motor drive normally with a sizeable torque capacity, a gear train, and a screw keyed into the gear reducing train. The screw is normally allowed to float free at the die end and the fluid layers between the screw flights and the barrel wall keep the screw centred. Figure 1.2(a) shows typical cross-section of a vented barrel extruder design.

Good additive dispersion with compounding extruders depends on the development of suitable shear rates during the compounding process. The accomplishment of this depends on a number of factors such as temperature control in the compounding zone and proper screw design. For example, the principle of screw design for melt shear dispersion allows for fairly close clearance between screw surface and extruder barrel to generate shear that is so necessary for dispersion. The type of screw to be employed depends on resin type and degree of additive dispersion desired in the case of additive containing resins. For example, if the manufacturer has a major mixing problem, a thermally sensitive material, or is dealing with a highly plasticized material, he would probably require a double screw system. On the other hand, a material that requires an intensive mixing to ensure uniform additive dispersion might require a two-stage screw, with a let-down section in the centre of the screw. A typical cross-section of screw design is shown in Figure 1.2(b).

Although great strides have been taken towards solving dispersion problems through proper screw designs, recent studies have shown that adequate screw design alone does not solve additive mixing problems sufficiently. For example, an additive masterbatch in a plastic system can be adequately sheared but not distributed (see reference 47).
In recognition of the above problem, there have been advances in the
design of compounding extrusion processes which are aimed at improving
distribution, through mixing attachments to the conventional compounding
extruder screw. The basis of the modification is to increase turbulence, back
pressure and viscosity thereby creating both greater shear and improved mixing. In extruders, this is usually achieved by incorpo-
rating torpedo-head, water cooled screws, breaker plates and screen
packs. In injection moulding machines, the \textit{ram} machine is being
replaced by the \textit{screw} bringing with it much improved mixing and shear
conditions. Turbulence in the machine can be increased by the inclu-
sion of venturi plates sited just before the nozzle.

The elaborations to the compounding extruder referred to above come
in the following forms:

i) \textit{Barrier mixing element}: extruder screws have been developed with
barriers which hold back unmelted granules whilst allowing fully
melted polymer to continue moving during the extrusion process.
This barrier enables substantially high screw speeds to be used. Reduction in output per screw revolution by the barrier is minimised by having the polymer melt cross the barrier in an approximately circumferential direction. Not only does this allow the use of a long barrier, but the unmelted or semi-melted materials are sheared by the barrier. This barrier attachment is classified as dispersive but some distributive mixing will inevitably occur with their use.

ii) **Roller bearing mixer:** Not all mixer attachments are able to give economic advantages when additives are being incorporated by masterbatch. Mixing accessories specifically added as mixing devices must have to:

a) give adequate masterbatch distribution
b) be easily and cheaply fitted to existing extruders
c) not restrict extruder output rate
d) produce minimal melt temperature rise from generated shear, and
e) not give operating difficulties under factory conditions to be economic in the end.

Existing mixing devices that are designed to satisfy the above requirements fall into four groups:

1. Torpedoes - plain, knurled, fluted, slotted
2. Pins - either confined to screw or intermeshing with pins on barrel
3. Static mixers, and
4. Rotating rollers.

Not all of these mixing devices have satisfied the expectations of their design. Widespread application of pins for instance is retarded in the converting industry because of a number of difficulties experienced with them. These difficulties include: damage due to fouling of rotating pins following either differential thermal expansion between screw and barrel or careless
positioning, problems of purging and cleaning and restriction of output rate.

The effectiveness of roller bearing mixers in mixing carbon black into liquid rubbers and for mixing carbon black masterbatch into polyethylene applying a cascade and in-line arrangements respectively have shown that in comparison with the other mixing screws available, greater overall output rates were obtained with the roller bearing mixer. The report stated that this class of mixers gave substantial improvement of carbon black distribution in polyolefins.

Mixing elements in compounding extruders have therefore become essential in melt shear dispersion processing when using compounding extruders.

3. Liquid Dispersion on Triple-Roll-Mill

Although liquid-additive addition into plastics during processing is the least used of the expanding additive incorporation technology, the process has become firmly established in many resin fabricating operations. This is illustrated by the growth rate of direct feed liquid colours between 1981 and 1983 which showed a pick up of about 15% between 1982 and 1983 (having dropped by the same amount between 1981 and 1982) thus indicating that it is still a popular additive incorporation method.

In liquid additives, the dispersion of additives is made in a liquid carrier, which may be a plasticizer, polymer solution, low molecular weight polymer, or a combination of these. Carriers for liquid additives are selected for compatibility with a wide range of thermoplastic resins. Liquid additives are now said to be available whose carrier systems are compatible with virtually all widely used thermoplastics including some engineering resins such as polycarbonates, nylons etc. This degree of compatibility results from several specific properties of the carrier system, whereby there is a small degree of
chemical compatibility that allows the system to bond to the polymer chain. The major degree of compatibility being obtained by an emulsification process that produces a high degree of syntactic abilities in the resin matrix. The total effect is to provide a carrier system with a high degree of stability for carrying additives with a resin without significant effect on the resin's physical properties.

These products are prepared by dispersing additives into plasticizer or any suitable carrier on a triple-roll-mill or by a flushing technique. The action of the triple-roll-mill wets out the additive in the carrier breaking down any aggregates that may be present. The additive particle size in the flushed pastes is smaller than that produced by a triple-roll-mill and this results in a stronger product, the mode of energy transfer (impact, attrition or shear) dictates the level of fluidity. Generally, liquid dispersion technology has borrowed a lot from paint technology viz - shear processes are common as both perform better at high viscosity. Additive percentages vary according to type. For pigments, loadings of between 10% to 70% are usual depending on viscosity requirements of the dispersion.

The advantages of liquid additives relate directly to better economics and the ability to automate operations. Technological advancements relate to improved product quality. More importantly, the concept of liquid dispersion which originated with colour has been expanded to include the simultaneous feeding of many other plastics additives such as UV stabilizers, blowing agents, antioxidants and lubricants all in a single operation.

A greater variety of dispersion processes are also available for liquid systems because they are easier to handle and offer greater latitude in formulation. The quality of initial wetting and hence an indication of the degree of dispersion in liquid dispersion is easily measured by its mix-in time (i.e. time required to form a coherent mass) as opposed
to other concentrates and hence presents the manufacturer a definite advantage in ability to assess degree of dispersion quantitatively. Also, progress in particle-size reduction is generally followed by fineness or texture measurement on a grindometer scale.

1.7 **EVALUATION OF DEGREE OF DISPERSION**

1.7.1 **Measurement of Dispersion in the Masterbatch**

The determination of the quality of dispersion in the additive masterbatch itself is largely unattempted. Gale\(^47\) has however reported a capillary rheometer screen pack test for the determination of the dispersion of carbon black in a black masterbatch. The viscometer consisted of a vertical heated barrel with a piston operated from a variable speed motor with a range of preset speeds. Melt pressures were recorded by a melt pressure transducer fitted at the entrance to the capillary at the bottom of the cylinder. A 30/60/60/30 mesh (per cm) screen pack was placed on top of a 4.5 mm diameter die at the barrel temperature set at 170°C. The chamber was filled with masterbatch and 5 minutes allowed to warm up. The piston was run at a speed of 2.5 mm per minute until it reached half the total possible travel. It was then returned, refilled and the procedure repeated to give 3 or 4 runs, allowing 5 minutes each time for heating. The pressure readings were recorded on a chart recorder and the "pressure increase rate" calculated.

1.7.2 **Pigment Dispersion in Products**

Several attempts have already been made to devise methods of measuring the degree of dispersion in plastics. Most of the earliest methods in evaluating quality of pigment\(^49-51\) dispersion in plastics have centred on visual assessment and tinting strength test\(^52\). The tinting strength of phthalocyanine blue in a white paint base has been shown to be directly related to its particle size. This provides a technique which may be applied to a plastic media, in which a standard white base is mixed with the pigment being examined. The resulting depth of shade,
or tinting strength, is proportional to the degree of dispersion. A comparison is usually made between the sample in question and one or more controls which were made under conditions especially chosen to give high or low dispersion. For an exact comparison of shades, spectrographic curves are used, but direct colorimetric measurements are usually sufficiently precise to be used on most occasions. There are, however, a number of associated problems. The level of dispersion can have a pronounced effect upon the shade of the final colour and upon the transparency of a coloured pigment, since the amount of white pigment is always used so that the total amount of scattering should remain almost constant. It is assumed that this pigment remains unaltered during subsequent processing.

One convenient and accurate method of measuring the degree of dispersion of pigments in plastics is to prepare a melt pressed section of the coloured plastics and mounting it for viewing in a regular optical microscope at about 400x magnification. A superimposed graduated scale on the field of view of the microscope helps in the estimation of aggregate size. The problem with this procedure is that it is very tedious and subjective, otherwise it is very accurate.

The recent appearance of semi-automatic and automatic particle counters has largely removed the subjectivity usually associated with the microscope method. A semi-automatic device for pigment particle size measurements developed by Endter and Gebaur in 1956 is used to study particle size distribution in the microscope photomicrograph of the sample. The instrument utilizes a manually controlled circular light spot which is adjusted to match the size of the particle whose diameter is then recorded automatically. A commercial version of the Endter-Gebaur instrument (Zeiss particle size analyzer) was subsequently employed by ASTM Committee D-24 for laboratory measurement of particle sizes. Automated versions of the above type of equipment have been introduced by Burgess and co-workers. Hess and McDonald have also reported the availability of more practical image analyzers based on feature specific image analysis utilizing a Quantiment 720 system with television camera linked to a TEM by fibre optic coupling.
Indirect procedures that give qualitative estimates of the degree of dispersion are also available. They measure those properties of the coloured plastics which are dependent on the presence or absence of large particles of pigments. Some of these properties are:

a) Flow of melt through extremely small apertures
b) Electric faults in a wire coating
c) Clogging time of a filter, and
d) Physical strength and integrity of fibres and their films.

There are other quantitative dispersion measurements that are not based on particle counting equipment. Notable among these is the work of Best and Tomfohrde\(^9\) who used a microdensitometric technique to measure black dispersion in polyethylene. They mounted a microdensitometer on an optical bench and using a finely focused beam of white light 10 \(\mu\text{m}\) in diameter to scan the specimen. This spot of light is then viewed by a sensing microscope at a 100x magnification. Variations in the black dispersion result in variations in the optical density of the transmitted beam which falls on a photomultiplier. The output of the photomultiplier is amplified and then fed to a chart recorder and results analysed statistically.

The disadvantages of these methods are discussed later in greater detail.

Surface roughness measurement is another quantitative dispersion measurement which has been reported by Vegvari et al\(^3\). They obtained markedly different traces of cut surface roughness at various black dispersion levels in different polymers. They found that the frequency and size of the roughness peaks diminish as the degree of black agglomeration is reduced. They also reported that the average height of the roughness peaks also diminishes at higher dispersion levels but the order of magnitude of the peak height range is generally well below the size of the black agglomerate as determined by light microscopy.
1.8 OBJECTIVES

The principal aims of this research can be categorised into eight parts:

1. To examine the quality of dispersion of additives in polyethylene masterbatch. The idea being to make sure that the inherent dispersion problems in additive-containing plastics is not due to poor dispersion in the masterbatch in the first place.

2. Ultraviolet absorbers are incorporated into plastics in amounts far in excess of theoretically determined amounts before they are adequately protected. The effect of quality of absorber distribution on use life will be studied to find out if it is because of poor absorber distribution that necessitates using excess material.

3. The effect on degree of dispersion of using a given masterbatch with resins of varying melt flow indices is also investigated.

4. Also investigated are any morphological features (such as the squeezing out of pigment particles by spherulites in a slowly cooled extrude) that might affect the degree of dispersion or product properties.

5. There are a limited number of pigment masterbatches, in fact two types (low load and high load) which are being made at the moment. This means that there are effectively only two melt flow indices available in masterbatch form as opposed to the large range of MFIs available in polyolefins. It should be appreciated that the MFI of a masterbatch is greatly influenced by the pigment type and concentration and is not an indication of the MFI of the carrying polymer. Naturally, when either of these masterbatches is used with a polymer whose MFI differs widely, they would not mix. One of the aims of the present study
therefore is to establish a reasonable masterbatch/polymer mix in terms of their molecular structure that will not give rise to a deterioration of properties and at the same time give rise to adequate dispersion. In other words, what range of polymer MFI can be used with a given additive masterbatch and retain good properties and good additive dispersion?

6. Related to the above is the practice of using a polyethylene masterbatch with polypropylene. This study intends to find out the extent this can be done to expect no deterioration in property.

7. Also of interest is how additives in a masterbatch are transferred to the polymer. Must the masterbatch be broken down into the polymer to achieve good dispersion and distribution or do the particles settle on the big particles of the polymer within the blend or do the particles of the masterbatch coalesce after mixing to leave large additive particles as stress concentrators?

8. We also aimed to develop a procedure for measuring dispersion quantitatively. It was anticipated that such a procedure should be less costly than existing quantitative dispersion equipment.

With these objectives in mind it can be seen that their multiplicity calls for a limited number of specimens. Not only are the objectives numerous, their nature also calls for the use of a large number of different experimental techniques. For example, the need to develop a technique for measuring pigment dispersion quantitatively has been one of the factors that dictated the number of samples to be studied. The technique (as will be seen later) will be involving simulated modelling of dispersion which is time consuming.

Although as many as eight LDPE based masterbatches have been examined, only one of the pigment types and one UV absorber type have been compounded with polyolefin resins for further studies. There was no
particular reason to favour the choice of any of the eight available pigment types except that it was anticipated that since the carrier was the same in all cases, any conclusions reached with the chosen masterbatches would have been true for all.
CHAPTER 2
CHARACTERISATION OF DISPERSION IN MASTERBATCHES

2.1 INTRODUCTION

Homogeneously dispersing additives into polymers at a concentration of about 0.5% to 2% by masterbatch technique has become one of the most preferred ways of incorporating additives into polymers for whatever reason, be it imparting of colour, protection against ultraviolet light or prevention of block in films etc.

The ultraviolet protective action, or colour strength given to the base resin is realised to the full only if the dispersion quality conforms to some reasonable standard. The fine particle additive dispersion which gives the product the best use property readily form aggregates and agglomerates which once formed are difficult to break up and blend. Recently there has been some concern over the dispersibility and degree of dispersion of masterbatches in some polyolefins. Despite the potential danger in further erosion of dispersion quality in the product because of masterbatch/resin miscibility considerations, the practice of incorporating additives into plastics, via masterbatching is on the increase and in fact is now generally preferred by product manufacturers. This is probably because of the lower cost of masterbatch and resin blending operations in comparison with the purchasing of premixed compounds from the resin manufacturers. As already mentioned in Chapter 1, acceptability of the masterbatching process by plastic processors is mirrored in their extension from colour masterbatching to the addition of slip and antiblock additives to film resins, ultraviolet absorbers to films and monofilament resins, carbon black to pipe resins, butyl rubber or other elastomers to improve the strength of resins, glass fibres to improve the strength and heat resistance of mouldings in injection and extrusion mouldings and calcium carbonate fillers for cost reduction. In fact, the ability to buy and store in bulk a small number of base resins which may be modified in accordance
with the dictates of the order book, thus preventing the maintenance of an inventory of a large number of special compounds, is the real advantage of masterbatching. The advantages of masterbatch use are therefore very tempting indeed. However the overall effect of masterbatching on the quality of additive dispersion is largely unattempted and therefore unknown. It may well be that good dispersion is being sacrificed for convenience of product manufacture and economic sense.

The principle of masterbatch manufacture lies in enveloping the primary particles in a carrier system (usually emulsifiable low and high molecular weight polyethylenes, polyvinyl chloride copolymers and emulsion derivatives) during manufacture using heavy duty internal mixers so that by so doing subsequent aggregation and agglomeration of additive particles would have been prevented from source. Based on the good intentioned ideas above, it is reasonable for manufacturers to think that the use of a masterbatch will in fact give better pigment dispersion than the traditional use of precompounded polymers. Unfortunately, the quality of additive dispersion obtained in let downs of some additive masterbatches in the base resin are often very disappointing and worrying particularly in some products requiring critical dispersion levels.

Although the inadequacy of some masterbatching in satisfying the more critical dispersion requirements, particularly in blown polyethylene film, polypropylene fibre and vacuum formed polyvinyl chloride was recognised in the introduction of easily dispersible or predispersed pigment masterbatches, there has not been a real concerted effort to solve the problem of poor pigment dispersion in products by, for instance, asking the question - what does additive dispersion in the masterbatch look like? Not until we address ourselves to such questions as how actually the pigment is dispersed in the masterbatch itself will we find solutions to adequate use of masterbatches in polymers. Put differently, could not poor dispersion in the plastic products be because of an inherent poor additive dispersion in the masterbatch? Answers to such other questions as to what extent should low molecular weight additive carriers be used with varying plastics resins must be found before masterbatch use can be satisfactory.
Because of these uncertainties and the fact that critical products with small tolerance for poor additive dispersion are now in great demand and of course because more and more manufacturers are becoming critical of the quality of additive dispersion in their products, it is advisable to first ascertain the degree of dispersion of additives in the masterbatch before dilution. This is because the outcome might well turn out to be a crucial factor in the overall quality of the dispersion that is finally obtained in the let down.

2.1.1 Quantitative Measurement of Dispersion in Masterbatches

Not very much has been reported in the literature on the measurement of degree of dispersion of additives in masterbatches. Visual assessment procedures involving simply melting a thin slice of masterbatch on a hot glass slide and using a sharp edged instrument to smear the fluxed slice across the surface of the slide and finally examined microscopically in transmitted light illumination at 100x or 200x magnification has been reported \(^1_{4,47}\). Gale \(^47\), as already mentioned, used a capillary rheometer screen pack test to measure dispersion indirectly in carbon black masterbatch.

The studies presented in this chapter are directed at developing a practical procedure for a quantitative understanding of additives dispersion in masterbatches along the following lines:

a) X-ray microradiography
b) Determination of volume of undispersed pigment
c) Image analysis, and
d) Linear intercept length distribution of particles.
2.2 EXPERIMENTAL

2.2.1 Materials

The masterbatches used in our experiments are those of Cole Plastics and Hoechst UK and supplied by RB Moulders. A total of eight low density polyethylene (LDPE) pigment masterbatches and one LDPE ultra-violet absorber masterbatch (Cyasorb 531 masterbatch) were studied. Table 2.1 shows the masterbatches used reported alongside colour type and the percentage composition of the inorganic and organic components for some of them. All the pigment masterbatches have a 3% pigment loading while the ultraviolet (UV) absorber masterbatch has a 1.5% absorber loading.

2.2.2 Sample Preparation

2.2.2.1 Melt Pressing

Although thin sectioning followed by transmitted light microscopical observation is a well established and widely used method for examining the internal morphology of additive containing plastic material or rubber compounds, the technique does not always apply in compounds with very unfavourable sectioning characteristics. These compounds are very often the materials in which the amounts of additives are so high that specially cut thin sections are required. This situation is typified by the study of the internal structure of additive masterbatches, rubber and plasticised PVC compounds containing high loadings of carbon black. The sectioning problems posed by such materials can be solved by melt pressing techniques though.

The melt pressed samples used for X-ray microradiography work were prepared by melt pressing a small sample of the masterbatch at 160°C between a glass slide and coverslip on a hot plate. Sample specimens of the order of 50 μm were pressed out for microradiographic examination. For samples examined in transmitted light microscopical examination, masterbatch samples of the size of a pin head were used before specimens thin enough to allow light through were obtained. With some
### TABLE 2.1: ADDITIVE MASTERBATCHES EXAMINED

<table>
<thead>
<tr>
<th>Technical Name</th>
<th>Colour</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Remafin black (100/100468/11)</td>
<td>Black</td>
<td>Unknown</td>
</tr>
<tr>
<td>VBM 301-22380</td>
<td>Drab green</td>
<td>$\beta$-copper phthalocyanine 1.645%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cadmium sulphide</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Barium sulphate 6.292%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zinc sulphide</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Carbon black 0.189%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ferric oxide 5.511%</td>
</tr>
<tr>
<td>VBM 301-22360</td>
<td>Pantanone green</td>
<td>Titanium dioxide 2.915%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cadmium sulphide</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Barium sulphate 3.130%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zinc sulphide</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Halogenate copper phthalocyanine 0.309%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ultramarine blue 1.800%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Carbon black 0.017%</td>
</tr>
<tr>
<td>VBM 301-22381</td>
<td>Brown</td>
<td>Unknown</td>
</tr>
<tr>
<td>VBM 301-22363</td>
<td>Dark blue</td>
<td>Ultramarine blue 23.837%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Carbon black 0.047%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Calcium salt 0.285%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\beta$-copper phthalocyanine 0.751%</td>
</tr>
<tr>
<td>VBM 301-16751</td>
<td>Grey</td>
<td>Unknown</td>
</tr>
<tr>
<td>VBM 301-2000</td>
<td>White</td>
<td>Unknown</td>
</tr>
<tr>
<td>BXL 190</td>
<td>Yellow</td>
<td>Benzidine Yellow $\text{CH}_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{C}=\text{O}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{C}=\text{O}$</td>
</tr>
<tr>
<td>Cyasorb 531</td>
<td>Natural</td>
<td>Unknown</td>
</tr>
</tbody>
</table>
care, it was possible to get respectable specimens of about 5 \( \mu \text{m} \) thick. However, melt pressing method of sample preparation has some serious limitations:

i) the distribution of the phases in a composite material will probably be changed

ii) degradation may occur, giving rise to non-representative crystalline texture, particularly round the edges of the specimen

iii) the crystalline texture developed will not necessarily be that which would develop in bulk under equivalent thermal conditions due, mainly to surface nucleation and melt orientation. The distribution of additives for which we are concerned here does not change significantly as melt pressing is a low shear process and therefore does not worry us very much.

2.2.2.2 Cold Sectioning

Masterbatch samples for examination in transmitted light microscopical observation were obtained by thin sectioning on a freezing stage microtome fitted with a liquid carbon dioxide stage. Freezing the masterbatch allows one to approach the glass transition temperature of the low density polyethylene masterbatch base thus making the sectioning simpler. Despite the cooling, the high additive loading still made sectioning difficult. The procedure involves freezing a masterbatch pellet on the freezing stage with liquid carbon dioxide and using a steel or glass knife to cut sections. Good sections can be obtained by a careful freeze mounting process coupled with smooth planing of the stage surface.

It was necessary in the first place to do low temperature sectioning. Low density polyethylene is very difficult to section at room temperature because of the strain induced on the specimen. This strain manifests itself when such a section is examined between crossed polars. In order to microtome LDPE fairly easily, it is necessary therefore to reduce its temperature to around the glass transition temperature
of the amorphous region of the material (-120°C). Practically, it is inconvenient to take the temperature this low. However, considerable improvement in sectioning quality is usually obtained at temperatures ~-50°C.

Sections were mounted between microscope slides and coverslips using the methods established for biological studies. Sections of the masterbatch were mounted in Canada balsam. The choice of mounting medium was dictated by the polymer (in this case LDPE) since care must be taken to avoid solvent attack and the refractive index should be at least roughly matched.

2.2.3 Sample Examination

2.2.3.1 X-ray Microradiography

The technique of X-ray microradiography is well established\(^{58,59}\) for the examination of internal structures of materials. A wide range of materials including metals, biological specimens, short glass fibre orientation in thermoplastics and in particular plastics and rubbers\(^{60}\) can be examined.

The basis of the method of adapting scanning electron microscopes for X-ray microradiography has been described by Pugh and West\(^{61}\), an improved version of which was described by Hemsley and Hayles\(^{62}\). The power of the technique lies in its ability to distinguish inorganic pigment components from organics in the polymer matrix through the relative difference between the X-ray absorption coefficients of these components which show variations of X-ray absorption on exposure. The image contrast which depends on the atomic number of the elements present in the specimen is defined by:

\[
C = \frac{B_1 - B_2}{B_1 + B_2}
\]
PLATE 2.1: X-RAY_MICRORADIOGRAPHY_EQUIPMENT_READY_FOR_INSERTION
INTO_AN_S2A_STEREOSCAN
FIGURE 2.1(a): X-ray Projection Measure

\[ I_1 = I_0 e^{-u_1 t} \]

\[ I_2 = I_0 e^{-u_1(t-x) - u_2 x} \]

\( I_0 \) = Initial X-ray intensity
\( t \) = Thickness of element
\( I_t \) = Transmitted X-ray intensity
\( u \) = Extinction coefficient dependent on atomic structure

FIGURE 2.1(b): Absorption of X-rays in a Specimen
copper foil bombarded by electrons. X-rays generated in the target and passing through the specimen are recorded by a 1 cm square silicon solar cell. The carrier for the cell also acts as a shutter which is normally interposed between specimen and recording film. The movements of both target and the shutter are controlled from outside the specimen chamber by adaptation of the normal tilt and rotation controls.

The X-ray film used is contained in a sachet constructed as a sandwich of black opaque polyethylene film, the photographic film and an opaque adhesive coated PVC tape (Advance tape type AT/47). Therefore once assembled, the sachet becomes light tight as schematically shown in Figure 2.2.

The X-ray exposure takes place through the thin (65 μm) polyethylene film which has been specially chosen in that it contains no X-ray absorbing fillers i.e. it contains only carbon black and contains no fillers, such as silica. A minimum thickness for light opacity was also chosen specially.

The adhesive on the PVC tape again was specially chosen to allow removal from photographic film without damage to the film surface.

The photographic film is a Kodak Industrex MX which was chosen because it has a very fine grain texture coupled with reasonable speed. The design of the equipment ensured that the film was not affected by fluorescence and reflection effects.

Film development was done by first taking off the polyethylene film and then developing in Kodak DX80 developer for 4 mins with the PVC tape still adhering to the reverse side of the film (development time may be used to adjust contrast). Thus only the top emulsion is developed. The tape is removed prior to fixing so that the image is then visible on only one side of this two-sided emulsion film. The film may then be enlarged either microscopically or photographically to achieve a higher useful magnification of up to 150x.
2.2.3.2 Transmitted Light Microscopy

The optical microscopical observation of the distribution of pigment particles in masterbatches was done by means of a Zeiss light microscope. The quality of pigment dispersion was observed in transmitted light illumination for each of the masterbatches studied. Important observations were recorded photographically in order to allow comparison of the same specimen previously studied by X-ray microradiography technique.

This method of examination became necessary because it showed both the inorganic and organic pigment components in the masterbatch as opposed to X-ray microradiography in which high atomic number elements only were observed. Although the procedure—probably relates more to the main interest (showing all particles organic and inorganic in the field of view), examination of a sample of a pigment masterbatch in a light microscope is accompanied by a lot of difficulties. Because of the high additive content in the masterbatch, too many particles are usually in the field of view. Inevitably there is an overlap of pigment particles which gives rise to a very poor image contrast.

Another limitation of the use of the light microscope is that its resolution limits compares very poorly with the X-ray microradiography technique.
2.2.3.3 Image Analysis

Pigment particle sizes were determined in 100x photomicrographs by using a Zeiss semi-automatic device for particle size measurements. The instrument utilizes a manually controlled circular spot light, the diameter of which is adjusted to match equal areas of pigment particles in the magnified photomicrograph. The instrument can also be fitted for minimum or maximum diameter measurements but a fit for equal area was chosen because this mode relates more to the number of primary particles than say a fit for maximum and minimum diameters, both of which would have been appropriate if shape had been of interest. The diameters of the fits for equal area were then recorded on the appropriate channel counters of the instrument. Between 1000 and 1066 pigment particles were fitted for equal area in each case. Although this has been tedious, it is much more accurate than the use of image analysers. This is because whereas particles boundaries can be precisely fitted on this instrument, the contrast of pigment particles on micrographs is not as good on the image analyser. This is a fundamental problem of this type of fully automated image analyser.

2.2.3.4 Ultraviolet Light Microscopy

The study of the distribution of ultraviolet absorber in low density polyethylene masterbatch containing 1.5% Cyasorb 531 was done by means of an ultraviolet microscope (details given in the next chapter). The degree of absorber distribution in the masterbatch was observed at the peak absorption wavelength of 285 nm and photographically recorded as described (see later).

2.2.3.5 Determination of Amount of Undispersed Pigment

X-ray microradiography and light microscopy suggest that pigment dispersion in the pigment masterbatches is invariably poor. This raises the important question of how much of the pigment in the master-
batch is undispersed. This is an important question to answer because it will give some idea of what improvement can be made in pigment masterbatch manufacture. An improvement that gives rise to better dispersion in the masterbatch should be of great interest to the plastic manufacturing industry since this inevitably would help in bringing down the production cost of coloured plastics through potential savings that can be made from such expensive additives, for example, the extra cost of breaking down the pigment aggregates/agglomerates during moulding would have been largely eliminated in the masterbatch production line, thus saving energy and material.

Generally, the level of degree of dispersion required is determined by the relative importance of properties such as surface texture, gloss, streaks, cost and processability in the end product. In view of associated problems to aggregation/agglomeration in relation to aggregate/agglomerate size (see Table 1.8) the level at which an agglomerate is regarded as being large has been arbitrarily chosen to be that greater than 20 \( \mu \text{m} \).

Assuming that all aggregates/agglomerates are spherically shaped and that the diameter of aggregate/agglomerate \( i \) is \( d_i \).

The mean diameter (\( d_m \)) is therefore given by the arithmetic mean diameter, i.e. the sum of the diameters of all particles divided by the total number of particles

\[
d_m = \frac{\sum_i f_i d_i}{\sum_i f_i}
\]

where
- \( d_m \) = mean diameter of particles
- \( d_i \) = diameter of aggregate/agglomerate \( i \)
- \( f_i \) = frequency of occurrence
The volume of a pigment aggregate according to ASTM D3849 states that the volume of a pigment agglomerate is given by

\[ V = \frac{8A^2}{3P} \]

where \( A \) = the two dimensional area
\( P \) = total boundary length of an aggregate.

The amount of aggregation in percent is the ratio of the volume of all aggregates with diameter >20 \( \mu \)m to total volume of all particles multiplied by 100.

2.2.3.6 Intercept Lengths Measurement

In order to assess the degree of dispersion in the masterbatches, we have studied the spatial distribution of pigment particles by semi-automatically measuring the linear intercept lengths in the polymer matrix between successive particles along straight line profiles. The frequency of occurrence \( f(\xi) \) of linear intercepts in the matrix between successive particles will correspond roughly to the distribution of random points on a line which is given by

\[ f(\xi) = \left( \frac{1}{\bar{\xi}} \right) \exp \left( -\frac{\xi}{\bar{\xi}} \right) \]  \hspace{1cm} (1)

where \( \xi \) = linear intercept length, and
\( \bar{\xi} \) = mean linear intercept length.

From (1)

\[ \log_e f(\xi) = \log_e \left( \frac{1}{\bar{\xi}} \right) - \frac{\xi}{\bar{\xi}} \]  \hspace{1cm} (2)
Alternatively, the cumulative frequency of the intercept length is given by

\[ F(\lambda) = 1 - \exp \left( \frac{\lambda}{\bar{\lambda}} \right) \]  

(3)

which can be expressed as

\[ \log_e [1 - F(\lambda)] = \frac{\lambda}{\bar{\lambda}} \]  

(4)

A graph of \( \log_e f(\lambda) \) or \( \log_e [1 - F(\lambda)] \) against \( \lambda \) (microns) is linear in case of a random distribution of pigment particles.

Linear intercept length measurements were carried out with the Zeiss particle size analyzer. A particle boundary along a straight line profile was focused with the light spot and opened up until the next particle boundary on the line profile was reached. The distance covered was then signalled to the instrument using the foot control and the instrument slots the distance to the appropriate channel. The traverse was continued until all measurements along the line profile were completed. Other lines were scanned in a similar way with the operation continuing until enough data was collected. A graph of \( \log_e f(\lambda) \) against \( \lambda \) was plotted in each case.

2.3 RESULTS AND DISCUSSION

2.3.1 Pigment Masterbatches

The main objective has been to understand the distribution of additives in masterbatches before let down. The idea being that knowledge of this would to a great extent, help in the interpretation of the degree of additive dispersion in the product and hence the effectiveness of the use of masterbatches for additive incorporation.

A great deal of information towards this goal has been gained. Visual assessment of photomicrographs of the dispersion and distribution of
pigments in masterbatches shows that dispersion in the masterbatches is very poor and that the degree of dispersion depends on the types of pigments therein.

a) Visual assessment of dispersion and distribution

Photomicrographs of the series of masterbatches studied using X-ray microradiography and light microscopy techniques are shown in Plates 2.2 to 2.10. These photomicrographs show that dispersion in the masterbatches is generally bad, for example, Remafin black shown in Plate 2.2, although distributed, contains a large number of undispersed agglomerates with size range of about 20-85 μm. Drab green masterbatch (VBM 301-22380) shown in Plate 2.3 and containing salts of copper, cadmium and barium, ferric oxide as well as carbon black is even more atrociously dispersed than Remafin black (Plate 2.2). Of particular interest in this masterbatch is a single agglomerate sitting at the bottom right-hand side of Plate 2.3(a) which has a size of the order of 300 μm maximum diameter and minimum diameter of about 200 μm. This single agglomerate constitutes a large proportion of the particles in the field of view and represent a serious dispersion problem indeed. However, it is known that carbon black (which constitutes only 0.189%) of the total additive content in this masterbatch is very difficult to disperse but since this is excluded by the technique, either or all of the heavy metal (copper, zinc, iron and barium) salt components must have been by nature difficult to disperse assuming adequate production process.

The same specimen viewed in transmitted light microscopy shows an additional feature in the form of white agglomerates and particles which is believed to be the organo metallic component (β-copper phthalo-cyanine) seen as greenish-orange colour down the microscope. Bearing in mine that the particular component is only 1.645% of the total additive content in this masterbatch, it is safe to conclude that β-copper phthalocyanine is not well dispersed in view of the roughly 80 μm agglomerate sitting at the bottom left of Plate 2.3(b).
PLATE 2.2: X-RAY MICRORADIOGRAPH OF MELT PRESSED SAMPLE OF REMAFIN BLACK MASTERBATCH
A: X-ray microradiograph of a melt pressed drab green masterbatch

B: Bright-field micrograph of melt pressed drab green masterbatch

PLATE 2.3: X-RAY MICRORADIOGRAPH AND BRIGHT-FIELD MICROGRAPH OF DRAB GREEN MASTERBATCH
PLATE 2.4: X-RAY MICRORADIOGRAPH AND BRIGHT-FIELD MICROGRAPH OF PANTANONE GREEN MASTERBATCH
A: X-ray microradiograph of a melt pressed VBM 301-22381 masterbatch

B: Bright-field micrograph of melt pressed VBM 301-22381 masterbatch

PLATE 2.5: X-RAY MICRORADIOGRAPH AND BRIGHT-FIELD MICROGRAPH OF VBM 301-22381 MASTERBATCH
PLATE 2.6: TRANSMITTED LIGHT MICROSCOPY OF VBM 301-22363 MASTERBATCH

PLATE 2.7: X-RAY MICRORADIOGRAPH OF VBM 301-16751 MASTERBATCH
PLATE 2.8: TRANSMITTED LIGHT MICROSCOPY OF BXL 190 MASTERBATCH

PLATE 2.9: X-RAY MICORADIOGRAPH OF VBM 301-2000 MASTERBATCH
Pantanone green masterbatch (VBM 301-22360) shown in Plate 2.4 has a composition rather like the drab green, discussed previously. The major difference being that the ferric oxide component (in drab green) is being replaced by titanium dioxide. A comparison of Plates 2.3 and 2.4 reveals that although dispersion is bad in pantanone green, it is nothing like was seen for drab green. Since the only difference in component is the replacement of ferric oxide in drab green by titanium dioxide, it is reasonable to point an accusing finger on ferric oxide as the main cause for the poor dispersion in the drab green masterbatch. An additional feature of Plate 2.4A reveals that not only are additives not dispersed, they are not distributed in the carrier. This however is not a serious defect as there will be another chance during let-down or compounding to distribute the additive. Again, the main organic component (constituting 1.80% of total additive content) in the form of ultramarine blue is shown not to be dispersed as seen from Plate 2.4B.

Plate 2.6 again highlights the greater difficulty in dispersing organic additives in LDPE carriers. Organic additives (ultramarine blue and carbon black) which constitute the major components of the masterbatch are shown to be very poorly dispersed indeed. An organometallic calcium salt and β-copper phthalocyanine constituting less than 1% of the total additive content among them were not picked up by X-ray microradiography to allow comparison with the light microscope sample. They may have been very finely dispersed or the elements involved show very low absorption at the wavelength used.

Plates 2.5, 2.7 and 2.9 show similar trends of gross poor pigment dispersion as discussed above. Plate 2.8 however deserves to be specifically mentioned. This is because this masterbatch which is purely organic, is known to make it impossible for yellow polythene bags to be made by heat sealing. Plate 2.8 shows that this additive is not at all dispersed in the masterbatch. Although it is not for a moment being suggested that this is the route of the problem in heat sealed polythene bags, it has to be recognised that the dispersion of benzidine yellow in a LDPE carrier is very poor.
TABLE 2.2: PARTICLE SIZE DISTRIBUTION OF PIGMENT PARTICLES IN A NUMBER OF MASTERBATCHES IN SIZE RANGES

<table>
<thead>
<tr>
<th>Size Range (µm)</th>
<th>Agglomerate Count per 230 mm² Area of Photomicrograph</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Remafin Black</td>
</tr>
<tr>
<td>10.00-11.67</td>
<td>381</td>
</tr>
<tr>
<td>11.67-13.33</td>
<td>11</td>
</tr>
<tr>
<td>13.33-15.00</td>
<td>31</td>
</tr>
<tr>
<td>15.00-16.67</td>
<td>91</td>
</tr>
<tr>
<td>16.67-18.34</td>
<td>101</td>
</tr>
<tr>
<td>18.34-20.00</td>
<td>130</td>
</tr>
<tr>
<td>20.00-21.66</td>
<td>96</td>
</tr>
<tr>
<td>21.66-23.33</td>
<td>65</td>
</tr>
<tr>
<td>23.33-25.00</td>
<td>26</td>
</tr>
<tr>
<td>25.00-26.66</td>
<td>26</td>
</tr>
<tr>
<td>26.66-28.33</td>
<td>9</td>
</tr>
<tr>
<td>28.33-30.00</td>
<td>10</td>
</tr>
<tr>
<td>30.00-31.66</td>
<td>2</td>
</tr>
<tr>
<td>31.66-33.33</td>
<td>5</td>
</tr>
<tr>
<td>33.33-35.00</td>
<td>5</td>
</tr>
<tr>
<td>35.00-36.67</td>
<td>1</td>
</tr>
<tr>
<td>36.67-38.33</td>
<td>2</td>
</tr>
<tr>
<td>38.33-40.00</td>
<td>-</td>
</tr>
<tr>
<td>40.00-41.67</td>
<td>1</td>
</tr>
<tr>
<td>41.67-43.33</td>
<td>4</td>
</tr>
<tr>
<td>43.33-45.00</td>
<td>1</td>
</tr>
<tr>
<td>45.00-46.67</td>
<td>1</td>
</tr>
<tr>
<td>46.67-48.33</td>
<td>-</td>
</tr>
<tr>
<td>48.33-50.00</td>
<td>-</td>
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<tr>
<td>66.67-68.34</td>
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</tr>
<tr>
<td>76.67-78.34</td>
<td>-</td>
</tr>
<tr>
<td>88.34-90.01</td>
<td>-</td>
</tr>
</tbody>
</table>
b) **Volume of undispersed pigment**

The distribution of particle sizes in each of the masterbatches is shown in Table 2.2. The volume of the amount of undispersed pigment (> 20 μm) compared to the total volume of pigment particles is given in Table 2.3. Evidently, the volume of undispersed pigment is very significant in most of the masterbatches with percentage agglomeration being as high as 65% for drab green. This suggests that ferric oxide, barium sulphate, zinc sulphide, cadmium sulphide and β-copper phthalocyanine which are the main components (carbon black being only 0.189%) of the additive contents are very poorly dispersed in a LDPE carrier. The results shown in this table show a generally poor pigment dispersion in LDPE carrier. The best dispersed is VBM 301-22381 with percent volume of aggregation of less than 30%.

Table 2.4 shows the cumulative frequency of particles above size for each of the masterbatches studied. Figure 2.2 shows graphically on a log-scale the cumulative frequency distribution above size. It can be seen that there is not a great deal of difference in size distribution among the masterbatch particles as suggested by the results in Table 2.3.

**TABLE 2.3: VOLUME OF UNDISPERSED PIGMENTS IN MASTERBATCHES**

<table>
<thead>
<tr>
<th>Masterbatch</th>
<th>Total volume x 10⁵ (µm)³</th>
<th>Volume of aggregates x 10⁵ (µm)³</th>
<th>% Volume of aggregates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drab green</td>
<td>32.99</td>
<td>21.62</td>
<td>65.56</td>
</tr>
<tr>
<td>Remafin black</td>
<td>31.55</td>
<td>18.96</td>
<td>60.10</td>
</tr>
<tr>
<td>Pantanone green</td>
<td>14.38</td>
<td>7.88</td>
<td>45.20</td>
</tr>
<tr>
<td>VBM 301-22381</td>
<td>11.23</td>
<td>7.87</td>
<td>29.90</td>
</tr>
<tr>
<td>VBM 301-22363</td>
<td>2.64</td>
<td>0.96</td>
<td>63.75</td>
</tr>
<tr>
<td>VBM 301-16751</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>VBM 301-2000</td>
<td>12.81</td>
<td>5.89</td>
<td>46.00</td>
</tr>
<tr>
<td>BXL 190</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Size (μm)</td>
<td>Remafin Black</td>
<td>Drab Green</td>
<td>Pantone Green</td>
</tr>
<tr>
<td>----------</td>
<td>---------------</td>
<td>------------</td>
<td>---------------</td>
</tr>
<tr>
<td>10.83</td>
<td>920</td>
<td>1066</td>
<td>1030</td>
</tr>
<tr>
<td>12.50</td>
<td>619</td>
<td>548</td>
<td>130</td>
</tr>
<tr>
<td>14.17</td>
<td>608</td>
<td>475</td>
<td>117</td>
</tr>
<tr>
<td>15.83</td>
<td>577</td>
<td>364</td>
<td>103</td>
</tr>
<tr>
<td>17.50</td>
<td>486</td>
<td>235</td>
<td>78</td>
</tr>
<tr>
<td>19.15</td>
<td>385</td>
<td>152</td>
<td>64</td>
</tr>
<tr>
<td>20.83</td>
<td>255</td>
<td>105</td>
<td>46</td>
</tr>
<tr>
<td>22.50</td>
<td>159</td>
<td>69</td>
<td>37</td>
</tr>
<tr>
<td>24.16</td>
<td>94</td>
<td>48</td>
<td>26</td>
</tr>
<tr>
<td>25.83</td>
<td>68</td>
<td>34</td>
<td>24</td>
</tr>
<tr>
<td>27.50</td>
<td>42</td>
<td>29</td>
<td>16</td>
</tr>
<tr>
<td>29.16</td>
<td>33</td>
<td>23</td>
<td>13</td>
</tr>
<tr>
<td>30.83</td>
<td>23</td>
<td>17</td>
<td>12</td>
</tr>
<tr>
<td>32.50</td>
<td>21</td>
<td>11</td>
<td>10</td>
</tr>
<tr>
<td>34.16</td>
<td>16</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>35.83</td>
<td>11</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>37.50</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>39.12</td>
<td>-</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>40.83</td>
<td>8</td>
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<td>42.50</td>
<td>7</td>
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<td>44.17</td>
<td>3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>45.83</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>47.50</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>49.17</td>
<td>-</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>50.83</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>52.51</td>
<td>-</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>54.17</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>67.50</td>
<td>-</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>77.51</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>89.18</td>
<td>-</td>
<td>2</td>
<td>-</td>
</tr>
</tbody>
</table>
FIGURE 2.2: Cumulative Frequency Above Size Vs Particle Size (µm) on a Log-Log Scale
c) Intercept length measurements

A quantitative determination of the degree of distribution in some of the pigment masterbatches has been determined using procedures previously described in Section 2.2.3.6. The results are illustrated in Figures 2.3 to 2.5 and Table 2.5. The graph of $\log_e f(\xi)$ against $\xi$ $\mu$m for VBM 301-22381 shown in Figure 2.4 is linear thus indicating a random distribution of pigment particles. This result compares reasonably well with the qualitative visual result shown in Plate 2.5. There is also a reasonable correlation in the inference made here with the results obtained on the volume of undispersed pigment in this masterbatch shown in Table 2.3. Although this method of intercept length measurement characterises distribution, and does not give any idea about the degree of dispersion, it is known that randomness relates to dispersion in such a way that non-random distribution of particles tend to be aggregated while random distributions tend to be dispersed.

The results shown in Figures 2.3 and 2.5 show that the $\log_e f(\xi)$ against $\xi$ $\mu$m is linear for intercept lengths above 20 $\mu$m for drab green (see Plate 2.3A) and non-linear for pantanone green (Plate 2.4A). This is an interesting outcome because it demonstrates clearly that additives in a polymer system may be distributed without actually being dispersed, as is clearly the case with the drab green masterbatch. The result shown in Figure 2.5 agrees with earlier results from visual assessment that pigment in this masterbatch is neither dispersed nor distributed.

Table 2.5 illustrates the mean intercept length, standard deviation of intercept length and ratio of standard deviation of intercept length distribution of pigment particles to mean intercept length for three masterbatches. For a random distribution, this ratio is unity\textsuperscript{64} and much less than unity for non-random (aggregated) particles. The value of 0.18 and 0.23 for pantanone green and drab green masterbatches respectively, reasonably correlate with their intercept length distribution results but the ratio of 0.47 for VBM 301-22381 contradicts the result and randomness predicted by Figure 2.4. This disagreement may be due to the inclusion of short intercept length values where the model described in Section 2.2.3.6 is said to break down\textsuperscript{64}. 

\textsuperscript{64}
FIGURE 2.3: Graph of Log Intercept Length Distribution Against Intercept Length (μm) for Drag Green Masterbatch
FIGURE 2.4: Log Frequency of Intercept Length Against Intercept Length for VBM 301-22381
FIGURE 2.5: Log Frequency of Intercept Against Intercept Length for Pantanone Green
PLATE 2.10: ULTRAVIOLET MICROSCOPY MICROGRAPH OF CYASORB 531 MASTERBATCH
TABLE 2.5: TABLE OF MEAN INTERCEPT LENGTH (l), STANDARD DEVIATION (σ) AND STANDARD DEVIATION: MEAN RATIO

<table>
<thead>
<tr>
<th>Masterbatch</th>
<th>̄l</th>
<th>σ</th>
<th>Standard Deviation: Mean Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pantanone green</td>
<td>12.74</td>
<td>2.30</td>
<td>0.18</td>
</tr>
<tr>
<td>Drab green</td>
<td>21.80</td>
<td>4.96</td>
<td>0.23</td>
</tr>
<tr>
<td>VBM 301-22381</td>
<td>34.13</td>
<td>16.10</td>
<td>0.47</td>
</tr>
</tbody>
</table>

2.3.2 UV Masterbatch

The distribution of Cyasorb 531 in an LDPE carrier is shown in Plate 2.10. A number of features can be observed in this photomicrograph. The features include black aggregate looking regions which in this case are probably dirt: in the microscope optics, diagonal lines seen running across the section which are cutting marks and black absorbing regions uniformly spread which is the additive. The first two features are artefacts which make interpretation rather difficult. However, these artefacts are unavoidable in cases like this and have to be ignored.

In contrast to the pigment masterbatches examined earlier, the distribution of the UV absorber is apparently uniform. Because only one UV masterbatch has been examined, it is not possible to reach any generalised conclusions on the distribution of UV absorbers in an LDPE carrier.

2.4 CONCLUSIONS

1. The results obtained in this chapter indicate that pigment dispersion in LDPE pigment masterbatches is invariably bad. This is illustrated by Plate 2.3 where aggregates of up to 300 μm maximum diameter are clearly seen. However this particular case is the extreme on the bad side - and represents the worst case (with the
exception of BXL 190 to be referred to later) of all the specimens examined. VBM 301-3238I has the best dispersion and distribution of pigment particles.

2. Pigments containing metals such as iron, cadmium, barium, zinc, copper and titanium as is the case with drab green (Plate 2.3) and pantanone green (Plate 2.4) are very poorly dispersed in the LDPE carrier. Comparison of Plates 2.3 and 2.4 whose formulations only differ by the fact that the ferric oxide is drab green is being replaced by titanium to form pantanone green suggests that ferric oxide has the worst dispersibility of the heavy metal inorganic salts in pigments. This is because the dispersion of pigment in pantanone green (Plate 2.4) is not as bad as it is in drab green (Plate 2.3) and since ferric oxide is the only thing contained in drab green which is not in pantanone green, it is reasonable to conclude that ferric oxide must be responsible for the very poor dispersion in drab green.

3. Organo metallics such as β-copper phthalocyanine are not dispersed as shown by the transmitted light photomicrograph in Plate 2.3B. This ingredient which is only 1.645% of the additive content of drab green but showing an aggregate whose size \( \sim 80 \ \mu m \) makes it reasonable to reach the above conclusion. Related to this is the all organic masterbatch (BXL 190) shown in Plate 2.8 which, as can be seen, has an extreme poor pigment dispersion. These two evidences suggest that organic pigments are very poorly dispersed in an LDPE carrier.

4. It is known that dispersion in masterbatches is carried out in a heavy duty internal mixer followed by extrusion and chipping. The shear rate used is such that pigment aggregates are broken down during production. Evidence from the present study suggests that enough shear forces are not generated to rupture aggregates during masterbatch production. Again this conclusion is ably supported by Plates 2.3, 2.8 and 2.9. The agglomerate in Plate 2.9 with a maximum diameter of \( \sim 450 \ \mu m \) is worth mentioning.
5. The obvious implication of the poor dispersion from the point of view of the plastic product manufacturer is that he will have to pay more to have the aggregates referred to above broken down by investing in the right processing equipment or incorporating mixing accessories to what he has got, either of which contradicts the original idea of adopting masterbatches in preference for premixed compounds.

6. There is a general belief in the plastic manufacturing industry that once a masterbatch of some sort has been used, then dispersion is necessarily uniform. The results presented in this chapter indicate that this assumption is unreasonable and that a manufacturer who is using drab green (Plate 2.3) or VBM 301-2000 (Plate 2.9) has to work hard to obtain a good dispersion in the end.

7. If agglomerates such as those shown in Plates 2.3 and 2.9 escape break down during processing, it will be a complete waste of an expensive material - which the manufacturer can do without.

8. The distribution of intercept length measurements of pigment particles in a masterbatch matrix is a useful tool for monitoring the degree of distribution of pigment in the masterbatch. Its importance is pointed out clearly when Plate 2.3 and Figure 2.3 are compared. The former clearly shows that the pigment is undispersed but the latter (Figure 2.3) shows that (although these pigment particles are undispersed) the particles are randomly distributed. This has the advantage of supplementing information on particle size distribution or degree of dispersion.
CHAPTER 3

CHARACTERISATION OF ULTRAVIOLET ABSORBER DISTRIBUTION INCORPORATED BY MASTERBATCH TECHNIQUE INTO POLYOLEFINS

3.1 INTRODUCTION

There has been a trend in recent years towards incorporating ultraviolet absorbing additives into polymers by masterbatching.

Most use requirements demanding the inclusion of about 0.5% - 5% ultraviolet absorber into polyolefin products to ensure sufficient protection against ultraviolet light. The process of compounding this ingredient and its subsequent degree of dispersion is of great importance because the thoroughness with which this is done has a bearing on the product properties. It has been well known for a long time that satisfactory performance of the finished plastic products depend to some extent on the complete dispersion of the ingredients. Recently, some manufacturers are reported to be using ultraviolet absorbers in amounts far in excess of normal amounts in an attempt to improve stability of products against ultraviolet light. Ultraviolet absorbers are very costly, in fact much more costly than the polymers. If they are adequately used by dispersing them properly in the polymer product, a considerable amount of materials saving can be gained. It is therefore important to study the effect of processing on the degree of dispersion of the absorbers. The importance of good UV absorber distribution has been pointed out by Gilroy\textsuperscript{66}.

Most of the reported work on the dispersion of masterbatch incorporated ultraviolet absorbing additives in polymers is based on carbon black\textsuperscript{47,66}. A lot more non-black ultraviolet absorbers are now in the market\textsuperscript{25} but very limited information on the dispersion of these non-black UV absorbers in polyolefin products is available. Even then, the most important of such reports have centred on the effect of polyolefin morphology\textsuperscript{15,16,67,68} on degree of dispersion. Gale\textsuperscript{47} mentioned in passing some microscopy work on absorber distribution in polyethylene containers. There is hardly any-
thing on direct examination of UV absorber dispersion in extruded products. The new method of incorporating these additives by master-batching makes a greater case for studying the dispersion of additives in products in view of possible miscibility problems between master-batch base and base polymers. The problems of using masterbatch to incorporate carbon black into polymers have been reported by both Boes and Gale.

For a qualitative determination of ultraviolet absorber distribution in extrudates and then compression moulded samples of two different grades of high density polyethylene and polypropylene, ultraviolet photomicrographs of microtomed sections have been assessed. This qualitative assessment was permitted by the characteristic absorption properties of Cyasorb 531 in the ultraviolet region. The procedures employed are similar to those used by previous authors.

3.2 HISTORY OF UV MICROSCOPY

The first microscope optics for use in the ultraviolet radiation were developed by Kohler and Van Rohr about 1900. Several microscope systems soon followed from Zeiss about 1904. The intention of developing optical systems operating in the region 230-280 nm was to take advantage of the potential increased resolution or desire to reveal finer specimen structure than that offered by the visible spectrum. However, the gain in resolution soon became unimportant with the advent of the electron microscope. Very little work was therefore done with the equipment during the first 25 to 30 years of its manufacture. In fact, it was only in 1930 that workers in the biological field exploited the ultraviolet microscope. The fact that various biochemicals show marked absorptions and various wavelengths within the ultraviolet regions (e.g. nucleic acid - purine and pyrimidine - absorb highly at 260 nm while protein absorbs to a much lesser extent at the same wavelength) gave the equipment a significant role in medicine and the biological sciences when it appeared to have been displaced by the electron microscope. Although outstanding work has been done in the medical, biological
fields \(^{74,75}\), and studies in the spatial distribution of lignin in various woods \(^{76-79}\) using the ultraviolet microscope, the application of the equipment to polymer studies is only just beginning to make its mark \(^{16,67,68}\).

One of the earliest contributions to the application of ultraviolet microscopes to synthetic polymeric substances according to Felton et al. \(^{80}\) were made by Dr T G Rahow et al. They used it to study the distribution of melamine-formaldehyde and formaldehyde used as an additive in paper to give it wet strength. Contrast was generated by the characteristic of melamine formaldehyde to absorb at 253.7 nm where paper fibres did not absorb. Most commercially important synthetic polymers have no strong ultraviolet absorption from about 250 nm to 400 nm. Useful application of the ultraviolet microscope will therefore depend on their containing ultraviolet absorbing additives. The main application of the ultraviolet microscope in synthetic polymers has therefore remained largely in the study of the distribution of ultraviolet absorbers.

Finally, it should be emphasised that the UV microscope used here is in no way connected with fluorescence microscopy. Here we are concerned with the distribution of ultraviolet absorbing additive (Cyasorb 531 which absorbs in the range 285-320 nm where polyolefins do not absorb) in polyolefin plastics.

Fluorescence microscopy on the other hand, is a phenomenon displayed when substances are exposed to electromagnetic radiation where they absorb part of that radiation and re-emit it at, usually, a longer wavelength according to Stoke's Law. However the radiation necessary to produce fluorescent light is within the visible spectrum.
3.3 EQUIPMENT

3.3.1 Features

The experimental needs for ultraviolet microscopy differ from those of conventional visible region apparatus in two ways. Firstly, it does not employ a normal optical glass at any point in the system since glass absorbs ultraviolet light. Secondly, it is not possible to form an ultraviolet image on the human retina (see later in Section 3.3.6) so that some means must be provided to make the image visible for examination and subsequent recording on a photographic plate. Ultraviolet microscopes that satisfy both of these needs were originally commercially available from Zeiss.

Figure 3.1 shows schematically the ultraviolet microscope equipment which is in use at the Institute of Polymer Technology, Loughborough. The equipment is custom built from a collection of parts made by a variety of manufacturers. It consists of an Ernst Leitz microscope stand, equipped with Zeiss quartz optics, a 500 watt high pressure mercury vapour lamp (150 atm), a monochromator (Banch) and Lomb) for wavelength selection, an image converter (Zeiss) which receives ultraviolet images and converts them to visual images electronically or by means of a self-contained fluorescent screen and a 35 mm Olympus OM1 camera. A Philips television viewing system was also available. The equipment here can also be adapted for quantitative work with a photometer attached but was not used in the present work which is entirely qualitative.

3.3.2 Ray Paths Through the System

Ultraviolet rays are projected through the specimen and optics specially designed for the transmission of ultraviolet radiation. After passing through the eyepiece, the ultraviolet image is reflected onto the face plate of the image converter tube. The face plate transmits ultraviolet and has a photosensitive material on its inner surface which converts the ultraviolet image into a corresponding pattern of electrons. This pattern is in turn focussed on a fluorescent viewing screen at the
FIGURE 3.1  ULTRAVIOLET MICROSCOPY EQUIPMENT
opposite end of the tube producing a visible image. When photographs are desired, the reflector is swung out of the optical path and the ultraviolet image passes directly into the camera.

3.3.3 Light Sources
Suitable light outputs for ultraviolet microscopy can be obtained from both high pressure xenon and high pressure mercury lamps as far down as 250 nm. As shown in Figure 3.2, the xenon spectrum is continuous approximately but the power output falls markedly below 300 nm making it an inappropriate light source for work below this wavelength. On the other hand, the mercury lamp has high power outputs down to 240 nm and is therefore more suited for work in the far ultraviolet. These lamps operate at up to 2500W and varying atmospheres pressure. A third class of lamp is the quartz halogen lamp whose spectra is also shown in Figure 3.2. This type of lamp, although used in some biological UV work, is totally useless for polymer work because its emission at the wavelength we are interested in is very low.

A 500W mercury arc lamp operating at 150 atmospheres has been used for the present work. We used a mercury arc lamp because:

i) it has a high emission efficiency at certain wavelengths. At these wavelengths, there is greater emission than for equivalent wavelengths in the xenon or quartz halogen lamps;

ii) the arc size is small, i.e. there is high power concentration in a small volume. This is important since the arc is imaged into the specimen plane;

iii) it is equipped with a stabilising transformer which allows for quantitative work if needed.

This high pressure lamp however has the disadvantage of wide spectral lines.
FIGURE 3.2  OUTPUT SPECTRA OF MERCURY, XENON AND QUARTZ HALOGEN LAMPS
(reproduced by permission, Oriel Optics Ltd.)
3.3.4 Ultraviolet Optical Systems

There have been three types of objective lenses for use in ultraviolet microscopy. The earliest of these objectives was the quartz refracting objectives. These are monochromats with limited use and that is in conjunction with narrow line metallic arc sources. The second type of objective lenses is reflecting objectives which are inherently achromatic. This facilitates focusing in that an image in focus in the visible can be viewed in the ultraviolet without loss of focus. This class of lenses almost permits the use of polychromatic radiation without loss of resolution. The reflecting surfaces are cemented between quartz elements to protect them from atmospheric oxidation. Leitz manufacture 300x and 170x ultraviolet achromatic objectives of numerical aperture 0.85. A third type of ultraviolet objective is the fully achromatic refracting quartz-fluorite type with magnification of 10x, 32x and 100x. They have numerical apertures of up to 1.25 with glycerol immersion. They have glycerol immersion for resolution enhancement. Resolution is defined by:

\[ d = \frac{0.61\lambda}{N.A} \]

where N.A = numerical aperture defined by \( n \sin \theta \). Since \( n \) is normally 1 (i.e. the refractive index of air) and smaller \( d \) values give higher resolution, the only way of making the numerical aperture larger so as to get smaller \( d \) is to replace air with a liquid of higher refractive index. Glycerol transmits UV and has a refractive index of 1.5. For this reason, this class of objectives was employed for the present work. They are said to be fully achromatic over the range 230 nm to 700 nm, but in the author's experience, there is a slight focus variation in going from the visible to the ultraviolet.

The equipment has a Carl Zeiss achromatic ultraviolet condenser of numerical aperture 0.8 but this was discarded in favour of a high numerical aperture objective lens which was found more satisfactory in imaging the
arc on to the specimen. The problem with the condenser may have been a lens separation effect giving rise to excess scattering.

3.3.5 Illumination

A monochromator selects the precise wavelength of light, with which the specimen is illuminated. A cylindrical wavelength selector on the equipment with an arbitrary scale ranging from 0-14 units sends light into the monochromator for precise wavelength definition.

The monochromator consists of two slits viz:

a) entry slit which defines the light going into the monochromator and subsequently through the rest of the optical system. The light through the entry slit is reflected by a mirror onto a prism which sends the light to another mirror which in turn reflects the light through

b) an outlet slit - this slit selects the spectrum width. The outlet slit is usually set to contain only one peak from the mercury spectrum. It is wished to keep this slit wide to maximise the amount of light. A schematic diagram of the ray paths through the monochromator is shown in Figure 3.3.

The monochromator employed has the disadvantage of having a poor spectral resolution. It would have been better with a diffraction grating type of monochromator.

3.3.6 Observation

Because the eye is not able to detect light below 400 nm and the fact that the long exposure to ultraviolet light in the range 280-400 nm not only causes problems to the eye, image observation in the ultraviolet cannot be done directly because the retina fluoresces. Commercial ultraviolet image converts which produce an image on a small fluorescent screen
are now available. The image converter consists of a face plate onto which light from the eyepiece falls. This face plate transmits UV and has a photosensitive material on its inner surface which converts UV images into a corresponding pattern of electrons. At the end of the image converter tube is a fluorescent screen which converts the pattern of electrons to a visible image.

In practice, the image of the specimen is initially picked up in visible light as it would be done on a common light microscope after which it becomes easy to illuminate the sample with ultraviolet light using the monochromator to select the appropriate wavelength. An image intensifier is added to improve the sensitivity of images seen in the image converter.

The equipment is equipped with a television system specially chosen with UV optics. The television is also a vidicon type with UV sensitivity. The advantages of a television system lie in the electronic contrast control it offers and in ease of viewing. The camera system uses a specially adapted Olympus OM1.
Although each of these viewing accessories have a major role to play in the system, in practice it is very difficult to get all of them parfocal at the same time.

3.4 EXPERIMENTAL

3.4.1 Materials

In all the experiments performed, low density polyethylene UV absorber masterbatch has been used in incorporating the additive into the base polymer. The ultraviolet masterbatch contained 1.5% of Cyasorb 531 which is a commercial name for an ultraviolet absorber with 2-hydroxy-4-n-octo-benzophenone as the active substance.

The base polymers employed in the present study were supplied by RB Moulders. The polymers and some of their physical properties (obtained from the technical data sheet) are shown in Table 3.1.

3.4.2 Melt Mixing

Dilution of the masterbatch with base polymer to give a 0.5% ultraviolet stabiliser concentration in the blend was carried out by a distributive action in an extruder after a physical tumble mixing of resin and masterbatch.

The polymeric UV stabilised HDPE or polypropylene/LDPE masterbatch blends were obtained by melt mixing the pelletised resins with the masterbatch in a laboratory extruder - Betol Max mixing extruder, model CS-194 manufactured by Instron Scientific Instruments Inc.

The extruder is a 1" type and has a 20:1 ratio polythene screw, three independent barrel heaters, feed hopper cooling and a variable screw drive from 0-100 rpm. The die is a rectangular slit die. The slit dimension is 20 mm ± 0.1 mm x 4 mm ± 0.1 mm. Heating to the die is by an independently controlled heater. The diagram of the design of die used is given in the appendix.
The extrusion procedure consists of switching on the extruder electrical supply and setting the temperature as shown in Table 3.2 for each of the materials studied at the varying screw speeds also shown. When the temperatures were steady, the screw was started, set at 10 rpm. After a few minutes, slow cooled or fast cooled extrudates were collected. The process was repeated for a screw speed of 40 rpm taking care to allow the system to settle down for the new processing condition. This is done by allowing 5 minutes before collecting samples.

3.4.3 Sample Preparation

Sample preparation for work in the ultraviolet region is a very important aspect of ultraviolet microscopy. In a microscope, the sample plane is supposed to be uniformly illuminated by the substage optical system (i.e. using Kholer illumination). A major problem commonly encountered in ultraviolet microscopy is contrast produced by rough sample surfaces because of diffraction effects (more about diffraction effects can be found in Section 3.4.7). These difficulties, capable of making interpretation of results difficult, should be borne in mind during sample preparation in order to ensure that effects arising from them are reduced to a minimum.

Sample preparation procedures employed are:

1(a) Melt pressing

The demerits of melt-pressing techniques for preparing additive containing samples for examination in the microscope for purposes of assessing additive dispersion, have already been highlighted in Section 2.2.2.1. Samples for examination were obtained by melt pressing pinhead size pieces of the extrudates which had been chipped and compression moulded into 200 μm films (see compression moulding in Section 4.2.2) between the slide and coverslip at a temperature at which the polymer flows well (160°C for HDPE and 200°C for polypropylene). With some care, it is possible to press out films as thin as 5 μm. For reasons already stated, melt pressing was only used exploratorily in the initial stages of the work.
### TABLE 3.1: BASE POLYMERS USED AND THEIR PROPERTIES

<table>
<thead>
<tr>
<th>Property</th>
<th>Polymer</th>
<th>Units</th>
<th>Test Method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>HSE 110</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Polypropylene copolymer</td>
<td>BS 3412, 1976</td>
</tr>
<tr>
<td>MFI</td>
<td>0.2</td>
<td>6.0</td>
<td>2.16 kg load</td>
</tr>
<tr>
<td>Density</td>
<td>953</td>
<td>945</td>
<td>BS 3412, 1976 Ab2 B3</td>
</tr>
</tbody>
</table>

### TABLE 3.2: EXTRUDER PROCESSING CONDITIONS

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temperature Setting (°C)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Barrel Temperatures</td>
<td>Head Temperatures</td>
<td>Die Temperature</td>
<td>Screw Speed (rpm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.0 MFI HDPE</td>
<td>140 145 150 160 170</td>
<td>140 150 150 170 180</td>
<td>10 40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0 MFI HDPE</td>
<td>140 145 150 160 170</td>
<td>140 145 150 160 170</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2 MFI HDPE</td>
<td>150 160 170 180 190</td>
<td>160 170 180 190 200</td>
<td>10 40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polypropylene</td>
<td>170 180 190 200 210</td>
<td>180 190 200 210 220</td>
<td>10 40</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
b) **Thin sectioning**

To avoid the problems of changing the distribution of additives as it is after extrusion and compression moulding which is bound to occur to some extent during melt pressing operation, thin sectioning of specimens was done using glass knives. Glass knives are considered as being sharper than steel knives, although less robust and limited in the width of section which can be cut. The main disadvantages of glass knives is that they become blunt after cutting 5 to 10 sections.

For examination of the HDPE/masterbatch blend specimens, thin sections (25 μm thickness) were cut using a Leitz 1400 base sledge microtome. In the case of PP/masterbatch blend, 10 μm thin sections were cut and examined. The factors that influence section thickness to be examined microscopically are:

a) For thinner sections:
   1) there is less overlapping detail - the importance of this factor is a function of additive concentration, spherulite size etc
   2) in some cases, thinner sections are easier to handle e.g. sections with molecular orientation do not roll up so easily so that cutting thin sections in such samples is a clear handling advantage
   3) there is no depth of field problem in thin sections.

b) For thicker sections:
   The thicker the section, the greater the absorption or concentration of absorbing additives and the greater the absorption, the greater the contrast.

The best compromise in this work is the choice of thick sections for HDPE/masterbatch samples and thin sections for PP/masterbatch samples.
2. Slide Preparation

The cut sections were mounted between a quartz slide and coverslip. Quartz-slide and coverslip are necessary to reduce UV absorption otherwise not enough UV reaches the eyepiece. The UV spectra of a glass slide and quartz slide are shown in Figure 3.4 for comparative purposes. It can be seen that glass is highly absorbing in the wavelength region of interest unlike quartz. Figure 3.4 shows that the absorption peak of glass is in the range 200-320 nm and therefore very unsuitable for the present work. A suitable mounting liquid is also necessary. Such a liquid must:

i) be non-UV absorbing
ii) not interact with the polymer, nor extract the additive,
iii) have a refractive index which matches that of the polymer as closely as possible in the UV region,
iv) be non-volatile.

Glycerol was chosen for this purpose because it is the only one available with reasonable refractive index match which did not absorb UV but actually is not adequate, particularly for polyethylene.

However, since this work was completed, we have found that there is a liquid recently developed by the Petrochemicals and Plastics Division, Research and Technology Department of Hoffman-La Roche and Co, AGF, Switzerland which ideally satisfies the above conditions. The immersion liquid is 3-0-benzylglycerol-1,2-carbonate with a refractive index of 1.515 (23°C). The absorbance curve of the liquid within the quartz slide and quartz coverslip is shown in Figure 3.5.

3.3.4 Calibration of Monochromator

The actual wavelength in nanometres corresponding to a given value on the arc lamp wavelength selector drum is given in the calibration curve shown in Figure 3.6. This was obtained by noting the values on the wavelength selector drum corresponding to the wavelengths of green, yellow, blue, purple and red colours whose values are readily available
in the literature. The readings in the wavelength selector can very easily be related to the mercury spectrum shown in Figure 3.2. For example, the peak corresponding to a value of about 7.0 on the lamp wavelength selector corresponds to the 546 nm sharp peak on the mercury spectrum (see Figure 3.2). A graph of wavelength selector reading against wavelengths in the mercury spectrum were plotted to give the calibration curve. Although the wavelength of maximum absorption viewed from the image converter was found to be of the order of 285 nm, the actual wavelength at which results were photographically recorded is 320 nm. This was due to the slight focus variation in the camera. This did pose some problems at the initial stages of the work. The method used to overcome this difficulty is discussed in Section 3.4.6.

3.4.5 UV Microscopy

Images of absorber distribution within sections of the polyolefin extrudates in UV light were obtained with the Leitz UV microscope employing a linear mirror monochromator and quartz optics previously described in Section 3.3. The major problems encountered included:

i) alignment problem: aligning the optical system before viewing samples is very important not only because it saves a lot of time in the end but if the entire optical system is unaligned, it is possible to record nothing on photographic films even when a focused image has been seen on the image converter. Alignment is usually done in sections moving from the mercury lamp to the camera using a cardboard screen to pick up the light from the lamp at each stage;

ii) the UV intensity is low and this usually necessitates operating the image converter at a maximum voltage. This high voltage gives rise to a noisy image;

iii) finally, the system was not achromatic.
FIGURE 3.4: UV Absorption of Quartz and Glass Slides
FIGURE 3.5: UV Absorption Spectra of a New Immersion Fluid (3-O-benzylglycerol-1,2-Carbonate)
FIGURE 3.6: Calibration Curve for Monochromator
3.4.6 Recording of Image

The magnified microscope image was recorded on a 35 mm Ilford FP4 film which possesses an optimum range of spectral sensitivity from 250-440 nm. Each film was developed for 6 minutes at 20°C in Acuto1 developer and fixed for 2 minutes in Hypam fixer.

The major difficulty encountered in recording images initially was the question of the image converter and camera not being perfocal. This difficulty was overcome by taking a through photograph series to establish error in focus variation. The point on the wavelength selector at which an image which is in focus in the image converter becomes focused in the camera, was found to correspond to 320 nm on the mercury spectrum.

3.4.7 Diffraction Effects

A major problem in ultraviolet microscopy is diffraction effects. Diffraction effects occur at the surfaces. Surface roughness produced during cutting of sections can therefore pose serious problems in the interpretation of what we see down the microscope. The problem is much more pronounced for UV than for the visible region, probably because we are dealing with shorter wavelengths in the ultraviolet region of the spectrum.

Diffraction is a function of refractive index difference between specimen and immersion liquid (glycerol in this case). The refractive index difference between specimen and immersion liquid has to be zero for zero diffraction. Additionally, the visibility of diffraction is influenced by focusing. Defocusing increases diffraction and that is why more diffraction is seen in some micrographs than others (see Section 3.5).
3.5 RESULTS AND DISCUSSION

3.5.1 Absorber Distribution in a High MFI HDPE

Examination of the quality of ultraviolet absorber distribution incorporated into polyolefins by the use of LDPE masterbatch reveals a considerable amount of information regarding absorber distribution and dispersion in varying grades of HDPE and polypropylene.

Plates 3.1 and 3.2 show photomicrographs of microtomed sections of extrudates obtained at low temperature/low shear rate (die temperature of 170°C and screw speed of 10 rpm) and low temperature/high shear rate (die temperature of 170°C and screw speed of 40 rpm).

These micrographs reveal a number of features similar to those already mentioned in the discussion of Plate 2.9. For example, Plate 3.1A shows the following features:

a) horizontal lines along sectioning direction which are due to knife marks during cutting

b) ripples running transversely to sectioning direction brought about by knife chatter on specimen surface during sectioning

c) black patches that look like agglomerates or highly absorbing UV regions which are dirt in the microscope optics

d) black regions along the edges of the specimen caused by diffraction effects

e) streaks of highly absorbing regions running along the sectioning direction brought about by the UV absorbing characteristics of the additive.

It is only the feature referred to in (e) above that is of interest here. Features brought about by sectioning difficulties and diffraction effects are at most times unavoidable in ultraviolet microscopy and should be ignored and not confused with absorption brought about by UV absorbers.
For the low magnification UV photomicrograph of low temperature/low shear rate extrudate, streaks of highly absorbing regions are very clearly observable (Plate 3.1A). These streaks are similar to those described by Gale\textsuperscript{47} for carbon black dispersion in HDPE. This non-uniform absorption indicates that the masterbatch is poorly distributed in the HDPE resin.

Plate 3.1B shows the same specimen referred to in Plate 3.1A viewed at higher magnification. Non-uniform absorption of the UV additives is more clearly shown at a higher magnification because diffraction effects are less pronounced at high magnification when a lens of higher numerical aperture is used. Regions of highly absorbing area (dark areas) can be seen as tadpole like features at the top left hand side of Plate 3.1B.

The distribution of UV absorber in the same polymer but extruded at a higher screw speed is shown in Plate 3.2. As indicated in Section 3.4.7, it can be seen from this photomicrograph (Plate 3.2A) that a slight defocus which may have taken place before photographic recording, gave rise to more pronounced diffraction compared to Plate 3.1A. Ignoring this effect, it is clearly seen that there is a substantial improvement in the distribution of the UV absorber. The absence of local regions of highly absorbing materials of the type seen in Plate 3.1A for the low temperature/low shear rate extrudate indicates that a better mixing due to increased distributive forces was attained employing increased screw speed. Again the high magnification micrograph (Plate 3.2B) makes the point clearer. It can be seen that absorption is reasonably uniform compared to the obvious non-uniformity seen in Plate 3.1B for the lower screw speed extrudate. The dark regions at the bottom of Plate 3.2B are artefacts caused by contamination and should be ignored.

Either of two things might have happened in the two cases discussed above. The LDPE masterbatch may not have been sheared sufficiently to distribute it within the bulk, particularly for the low screw speed extrudate in which case there is bound to be differential absorption of
PLATE 3.1: UV MICROGRAPHS OF A SECTION OF 6.0 MEI HDPE/UV MASTERBATCH BLEND EXTRUDED AT LOW TEMPERATURE/LOW SHEAR RATE
A Low magnification micrograph of 6.0 MFI HDPE/masterbatch blend

B High magnification micrograph of A

PLATE 3.2: UV MICROGRAPHS OF 6.0 MFI HDPE/MASTERBATCH BLEND
EXTRUDED AT LOW TEMPERATURE/HIGH SHEAR RATE
additives or the LDPE may have been sheared with the additive not being distributed. Another possibility is that the additive may prefer to remain associated with the LDPE. Further work on this aspect has been discussed in Chapter 6.

3.5.2 Absorber Distribution in a Low MFI HDPE

Plate 3.3 shows a high magnification photomicrograph of a microtomed section of a blend of 0.2 MFI HDPE and the LDPE UV masterbatch extruded at low temperature/low shear rate processing conditions (die temperature of 190°C and screw speed of 10 rpm). The presence of broad streaks of highly absorbing material is clearly visible and shows an even greater effect of poor mixing on absorber distribution than was seen for the high melt flow index HDPE discussed earlier (Section 3.5.1). There is a marked difference in the quality of UV absorber distribution in the low MFI material and the high MFI material. While the high UV absorbing streaks seen in the high MFI HDPE under the same processing condition showed non-uniform dark absorbing regions that looked tadpole like in places (Plate 3.1B), the ultraviolet absorbing regions in the 0.2 MFI HDPE remain continuous and broad (Plate 3.3). Comparatively therefore, it is obvious that the distributive action generated in the extruder and the shear rate generated in the die improved the quality of dispersion in the 6.0 MFI HDPE more than it did for the 0.2 MFI HDPE. In view of the fact that the 0.2 MFI HDPE has a higher melt viscosity, it is expected that greater shearing force was brought to bear on the masterbatch. Since despite this the absorber distribution was obviously poorer, it was reasonable to think that the masterbatch may have been sheared but not distributed, perhaps because of greater rheological difference between the base polymer and the masterbatch base. It is also possible that the distributive action generated in the case of a higher melt viscosity blend is not high enough to distribute the sheared masterbatch. Another possibility may be because the greater difference in structure between masterbatch base and polymer gives rise to an incompatible blend.

Plate 3.4 shows the micrographs of a section of a blend of 0.2 MFI HDPE and the LDPE masterbatch extruded at low temperature/high shear rate
PLATE 3.3: UV PHOTOMICROGRAPH OF A SECTION OF AN EXTRUDUDATE OF 0.2 MFI LDPE/MASTERBATCH BLEND EXTRUDED AT LOW TEMPERATURE AND LOW SHEAR RATE
A Low magnification micrograph of 0.2 MFI HDPE/Masterbatch blend

B High magnification micrograph of A

PLATE 3.4: UV MICROGRAPHS OF A SECTION OF 0.2 MFI HDPE/UV MASTERBATCH BLEND EXTRUDED AT LOW TEMPERATURE/ HIGH SHEAR RATE
(die temperature of 190°C and screw speed of 40 rpm). As was seen earlier in Section 3.5.1, higher shear rate improved the distribution of the UV absorber in the high MFI polyethylene considerably. It can be seen in this case that the improvement at increased shear rate is only marginal. The broad streaks of highly absorbing regions seen previously still remain. It is likely that these streaks originate from the melting of individual masterbatch granules as a result of long stripes due to laminar flow in the extruder screw channel. If this is the case, the point previously raised in Section 3.5.1 regarding the absorber preferring to be associated with the LDPE, must be taken seriously. These results, coupled with the suggestions made earlier in Section 3.5.1, suggest that poor absorber distribution in the low MFI HDPE may have to do with the greater difference in molecular structure between the masterbatch base (LDPE) and the 0.2 MFI HDPE.

3.5.3 Distribution of Ultraviolet Absorber in Polypropylene

Plate 3.5 shows the photomicrograph of a section of polypropylene extruded at low temperature/low shear rate (die temperature of 210°C and screw speed of 10 rpm). Regions of highly absorbing areas and non-absorbing areas are clearly visible. The dark areas show where the UV absorber is positioned, while the light areas indicate parts of the polymer matrix not containing any UV absorber. For this material to be adequately protected, the whole area should have been dark. For some reason, the absorption observed here is much more intense than was seen for the HDPE samples even though both contain the same amount (0.5%) of UV absorber. This is even more surprising when we consider that thinner sections were examined for polypropylene. The factors that influence section thicknesses have already been discussed in Section 3.4.3(b).

The non-uniform distribution of UV absorber could have been caused by either or all of a number of things viz:

i) the shearing force developed in the extruder may have not been enough to disperse the additive adequately
ii) the masterbatch may have been sheared but not distributed
iii) the difference in crystalline texture of polypropylene and polyethylene may have been responsible. The former, for example, has large spherulites which grow slowly. These spherulites reject UV absorber in the crystalline regions as previously known\textsuperscript{67,68}. Polyethylene on the other hand has small but many spherulites which grow fast and may not have a significant effect on the redistribution of UV absorber in the blend.

Plate 3.6 is the ultraviolet photomicrograph of polypropylene extruded at a low temperature/high shear rate condition (die temperature of 210\textdegree C and screw speed of 40 rpm). Visual assessment of dispersion here does not reveal any significant improvement in absorber distribution over the low shear rate extrudate (Plate 3.5). Regions of highly absorbing areas as well as areas devoid of any additive are seen as was the case in Plate 3.5.

3.6 CONCLUSIONS

The overall objective of assessing the dispersion of UV absorber in varying polyolefin polymers and relating the dispersion to polymer structure cannot be said to have been achieved at this stage, although very vital information based on the work discussed above has been gained.

It has been shown that streaks of highly ultraviolet absorbing regions respectively appear in low temperature/low shear rate and low temperature/high shear rate extrudates of both high and low melt flow index grades of HDPE and masterbatch blends. Whereas these streaks reduce significantly in low temperature/high shear rate extrudates of the high melt flow index grade HDPE and masterbatch blend, the streaks persist in the low MFI grade high density polyethylene/masterbatch blend under the same processing conditions. The following conclusions can therefore be drawn:
PLATE 3.5: UV MICROGRAPH OF A SECTION OF POLYPROPYLENE/UV MASTERBATCH BLEND EXTRUDED AT LOW TEMPERATURE/LOW SHEAR RATE

PLATE 3.6: UV MICROGRAPH OF A SECTION OF POLYPROPYLENE/UV MASTERBATCH EXTRUDED AT LOW TEMPERATURE/HIGH SHEAR RATE
1. As already observed in Plate 2.8, Chapter 2, the distribution of ultraviolet absorber in the masterbatch itself is uniform so that the poor absorber distribution which has been shown to exist in most of the extrudates studied as shown in Plates 3.1, 3.3, 3.4, 3.5 and 3.6 could not have been caused by poor absorber distribution in the masterbatch. The poor absorber distribution must have been of processing or polymer rheological origin.

2. Polyolefin products protected from ultraviolet light by the use of LDPE UV masterbatch are unlikely to meet the requirements for technical products as a result of undistributed UV absorber streaks and unprotected areas demonstrated in Plates 3.1 to 3.6.

3. Comparison of Plates 3.1 and 3.2 show that in the case examined, increased shear rate improves UV absorber distribution in 6.0 MFI HDPE, but does not have a similar effect on 0.2 MFI HDPE.

4. Improved absorber distribution with increased shear rate in 6.0 MFI HDPE and the lack of it in 0.2 MFI HDPE under similar processing conditions (see Plates 3.2 and 3.4) shows that the degree of dispersion achieved with a given masterbatch in polymers of varying molecular weight is a function of the molecular weight or melt flow index.

5. Finally, the application of UV microscopy to dispersion studies depends on the ability to prepare good samples. This is important because diffraction effects and artefacts can pose a major problem when it comes to the interpretation of what we see. For example it requires some experience to know that the lump of dark area at the bottom of Plate 3.2B is an artefact and not UV absorber agglomerate.
CHAPTER 4
SIMULATED SUNLIGHT EXPOSURE

4.1 INTRODUCTION

In the previous chapter it was observed that increased shear rate improved ultraviolet absorber distribution in high melt flow index (6.0 MFI) high density polyethylene containing low density polyethylene ultraviolet masterbatch. It was also noted that UV absorber distribution was poor for all processing conditions studied for the low melt index (0.2 MFI) high density polyethylene and the masterbatch. Since the inferences reached in Chapter 3 were based on a qualitative visual examination of ultraviolet photomicrographs, it is important that the practical significance of those observations be investigated using simulated sunlight exposure experiments.

This chapter therefore deals with the accelerated exposure experiments of samples of two grades of high density polyethylene and polypropylene which respectively contain the ultraviolet absorber Cyasorb 531 incorporated by masterbatching as already described in the previous chapter. The effective life of the materials extruded at varying processing conditions at failure are compared. The experiment is not designed to predict long range performances of these polymers, but is designed to indirectly ascertain how degree of dispersion of UV absorber obtained qualitatively from the previous chapter, relates to photostability of these polyolefins. In other words it is purely designed to test the significance of the conclusion reached in Chapter 3. It is also anticipated that the experiment would point out the great need to attach more importance to the problem of obtaining good dispersion. Presently, manufacturers use excess UV masterbatch in base polymers before adequate protection against UV light is achieved. The extra material could be saved by obtaining good UV absorber distribution.
4.2 EXPERIMENTAL

4.2.1 Materials

The materials studied are 200 μm thick films of

a) 6.0 MFI high density polyethylene
b) 2.0 MFI high density polyethylene
c) 0.2 MFI high density polyethylene, and
d) Polypropylene (HSE 110).

respectively containing 0.5% Cyasorb 531 incorporated into the resin using a low density polyethylene ultraviolet masterbatch.

4.2.2 Compression Moulding

The extrudates referred to in Chapter 3 were chipped and compression moulded using a 200 μm thick aluminium sheeting cut to form a (15x20) cm² rectangular shape in the middle. Films of the order of 200 μm thick were obtained by compression moulding the materials between two steel blocks. The high density polyethylenes were compression moulded at 160°C and rapidly cooled under pressure. Polypropylene films were formed at 200°C and also cooled rapidly under pressure. The idea of cooling the compression moulded materials quickly is to maintain the level of additive dispersion as closely as possible to what it was before compression moulding.

4.2.3 Photooxidation

Fluorescent lamps have been used for accelerated testing of light fastness for many years in the manner recommended by the ASTM Committee D-20 on plastics (ASTM Designation D-1501-65T, Exposure of Plastics in Fluorescent Sun Lamps; F.W. Reinhart and M.K. Mutchler, Natl. Bur. Std. Report 2742 1953). Their use without employing a dark cycle is controversial. Allen has noted that current commercial systems do not have a long enough dark cycle to simulate day and night closely enough and has successfully been using the same Sunlight
Simulation System used in the present study and which is described below.

Polymer films ~200 μm thick were photooxidized in a Simulated Sun exposure equipment consisting of a 75 cm high and 48 cm diameter aluminium lined drum mounted on a 2.7 mm thick block board. The whole of the inside surface of the drum was lined with aluminium foil to ensure minimum loss of radiation. At the centre of the drum is a 500 watt high pressure mercury/tungsten fluorescent lamp (MBTF) supplied by Thorn EMI. Air vents were drilled on the wooden block board at the base of the drum to prevent excessive heat build-up. The spectral power distribution of the 500 watt MBTF used is supplied by Thorn and is shown in Figure 4.1 while that of sunlight is shown in Figure 4.2. The lamp plugs directly into the mains and requires no choke to start it. A metal ring was fitted around the drum some 20 cm from the bottom. This ring was used as film holder. A schematic diagram of the set up we employed is shown in Figure 4.3.

4.2.4 Failure Assessment

4.2.4.1 Brief Review of Failure Assessment Methods

A literature search discloses a wide variety of techniques employed as criteria for polyolefin degradation resulting from ultraviolet light exposure. Some of the methods found include the determination of:

a) tensile properties

b) flex tests

c) brittleness temperature

d) ultraviolet absorber concentration

e) flexural strength

f) power factor

g) dielectric constant

h) melt index

i) surface crazing
121

j) ageing of stressed specimens \(^88,93\)
k) carbonyl index determination \(^96-98\).

Although tensile properties are the most commonly used criteria for determining weatherability of plastics, we have employed the carbonyl index determination method to assess failure because of its simplicity with the expenditure of small numbers of specimens. The same specimen is needed throughout the simulation test as opposed to tensile properties method where the test destroys the specimen.

4.2.4.2 Carbonyl Index Method of Failure Assessment

Polymer films of 200 \(\mu\)m thickness were obtained as described in Section 4.2.2. Samples to be photooxidised were prepared by mounting each of them within (5x12) cm\(^2\) aluminium sheeting as film holder. The aluminium sheet is cut to expose the film leaving enough allowance round the sides to be folded into the film so as to hold it. The arrangement is schematically demonstrated in Figure 4.4. After preparation, the film was then hung up in the simulated exposure equipment with films facing the lamp.

Carbonyl formation in each sample was periodically monitored in the region 2000 down to about 1500 cm\(^{-1}\) by means of the expression

\[
\frac{I_0}{\log_{10} \left( \frac{I_0}{I_T} \right) / d} \times 100
\]

where
- \(I_0\) = initial light intensity
- \(I_T\) = transmitted light intensity
- \(d\) = film thickness in microns

by using a Perkin-Elmer Model 521 infra-red spectrophotometer. A growth in the non-volatile carbonylic oxidation product absorption appears at about 1710 cm\(^{-1}\). The point of failure is normally taken
FIGURE 4.1

500W MBTF SPECTRAL POWER DISTRIBUTION

RADIANT FLUX (WATTS/30NMS)

WAVELENGTH (NMS)
FIGURE 4.2  SPECTRAL POWER DISTRIBUTION OF SUNLIGHT
Aluminium sheeting lining

Drum

Air vents

G.E.S. fitting

500 Watt High pressure Mercury/tungsten fluorescent lamp (MBTF)

1"bolts to hold metal ring on which films were hung

FIGURE 4.3  SIMULATED SUNLIGHT EQUIPMENT
FIGURE 4.4  ALUMINIUM SHEETING FILM HOLDER AND SAMPLE
to be at 0.06 carbonyl index. A schematic diagram of the carbonyl absorption and carbonyl index measurement is shown in Figure 4.5.

4.3 RESULTS AND DISCUSSION

4.3.1 Criteria for Failure

As already stated, the progress of deterioration of the polyolefins has been followed by Carbonyl Index content measurement which is defined by

\[
\text{Carbonyl Index (CI)} = \left( \frac{I_0}{I_t} \right) \times 100
\]

The increase in carbonyl units with exposure to ultraviolet radiation is what determines deterioration and failure. The carbonyl index measurement was continued until 0.06 carbonyl index was reached. The time for the various specimens to reach this point were compared. In some cases such as in Figures 4.6, 4.8 and 4.10, it was found unnecessary to photooxidise the specimens until a 0.06 carbonyl index was reached. This is because the time to reach this point for outdoor grade polymers, such as the low MFI resin used here, is too long. It was therefore found more convenient to compare results at 0.03 carbonyl index which represents time to 50% failure.

4.3.2 Effect of Dispersion of Ultraviolet Absorber on Stability

4.3.2.1 6.0 MFI HDPE/LDPE masterbatch blend

In view of the qualitative assessment made in Chapter 3 on the degree of dispersion of ultraviolet absorber in the 6.0 MFI high density polyethylene extruded at low temperature/low shear rate and low temperature/high shear rate processing conditions, it is of interest to compare the ultraviolet stability of the specimen extruded at low temperature/low shear rate and low temperature/high shear rate and see
\( I_0 = \text{initial light intensity} \)

\( I_T = \text{transmitted light intensity} \)

FIGURE 4.5: Typical Infra-red Spectrum of a Degraded Polyolefin Sample
how the results correlate with the microscopic visual assessment. This not only attaches numbers to the description but will probably point out the significance of good absorber distribution in relation to photostability.

Figure 4.6 shows the variation of carbonyl index with time (in hours) of irradiation in the simulated sun lamp exposure equipment for extrudates of 6.0 MFI high density polyethylene and low density polyethylene ultraviolet masterbatch blend at a die temperature/extruder screw speed of $170^\circ C/10$ rpm, $170^\circ C/40$ rpm and $180^\circ C/40$ rpm respectively. The figure indicates that at up to 600 hr in the exposure equipment, the time to failure of all three samples do not vary significantly. However, after 600 hours of simulated sun irradiation, the development of carbonyl units in the sample extruded at a die temperature of $170^\circ C$ and 10 rpm screw speed became rapid while the development in the other two samples extruded at low temperature/high shear rate and high temperature/high shear rate remained slow with the former slower. This indicates that the low temperature/high shear rate extrudate is most stable to ultraviolet light. Basing the point of failure at 0.06 carbonyl index, the low temperature/low shear rate sample failed after 32 days while the high temperature/high shear rate sample failed after about 62 days. Significantly, the low temperature/high shear rate sample stayed stable much longer than 70 days.

Comparing these results with the photomicrographs of Plates 3.1 and 3.2, it can be seen that they are consistent with the qualitative assessment obtained from microscopic examinations.

The significance of the results obtained in Sections 3.4.1 and 4.3.2 can be better appreciated from Figure 4.7 which shows the time to 50% failure (time to the development of 0.03 carbonyl index respectively for the three specimens considered above). For the $170^\circ C/40$ rpm extrudate, the time to 50% failure is $\gg$70 days while for the $180^\circ C/40$ rpm it is 62 days and only 32 days for the low temperature/low...
Resin Melt Index = 6.0 g/10 min

Die temp/screw speed
- 170°C/10 rpm (low temp/low shear)
- 170°C/40 rpm (low temp/high shear)
- 180°C/40 rpm (high temp/high shear)

FIGURE 4.6: Variation of Carbonyl Index (Cl) With Time of Irradiation for 6.0 MFI HDPE
FIGURE 4.7: Time to 50% Failure for 6.0 MFI HDPE/UV Masterbatch Blend Processed Under Three Different Conditions
shear rate extrudate. Looking back on Plate 3.1, we recall that absorber dispersion for the latter sample was very poor compared to the absorber distribution in the low temperature/high shear rate extrudate. It is easily inferred that the service life of a high density density polyethylene protected from ultraviolet light using a low density polyethylene ultraviolet masterbatch can be increased two-fold by dispersing the ultraviolet absorber in the blend properly through increased shear rate.

Figure 4.8 compares the variation of carbonyl index with time of irradiation for slow cooled and rapidly cooled (quickly dropped into an ice mixture at a temperature of 4-10°C) extrudates. The samples are those extruded at low temperature/low shear rate - slow cooled and quenched and also at low temperature/high shear rate - slow cooled and quenched. It is seen from this figure that merely quenching the extrudates slows down the development of carbonyl formation for all the samples on exposure to ultraviolet light. This implies that the degree of dispersion of the ultraviolet absorber is higher for the quenched samples than for the slow cooled samples. This is in line with the works of Billingham and Calvert\textsuperscript{16,17} regarding the distribution of additives in crystalline polymers. Polyethylene being about 60% crystalline is expected to reject Cyasorb 531 additive from within the crystal regions.

Figure 4.9 compares days to 50% failure for the slow cooled and rapidly cooled samples of materials extruded at low temperature/low shear rate and low temperature/high shear rate. The time to 50% failure increases significantly for the rapidly cooled extrudates for both processing conditions referred to above.

It is therefore possible to improve the service life of high density polyethylene protected from ultraviolet light by masterbatch technique by more than three-fold through a careful control of processing conditions.
FIGURE 4.8: Variation of Carbonyl Index (CI) with Time (Hours)
For Slow Cooled and Quenched Samples of 6.0 MFI HDPE
FIGURE 4.9: Time to 50% Failure for Slow Cooled and Quenched Samples of 6.0 MFI HDPE/UV Masterbatch Blend
4.3.2.2 0.2 MFI HDPE/LDPE UV Masterbatch

In Section 3.4.1(c), it was noted that ultraviolet absorber distribution in a low melt flow index high density polyethylene containing a low density polyethylene ultraviolet masterbatch is non-uniformly distributed for all the processing conditions studied (Plates 3.3 and 3.4). Figure 4.10 compares the variation of carbonyl index with time of irradiation for extrudates of a 0.2 MFI high density polyethylene and low density polyethylene ultraviolet masterbatch blend extruded at low temperature/low shear rate, low temperature/high shear rate and high temperature/high shear rate processing conditions. Compared to what was seen earlier in Figure 4.6, the results here are less well correlated. Between 0 and 600 hours of irradiation, the variation of carbonyl index in the low temperature/low shear rate extrudate moved faster for the low temperature/high shear rate extrudate as expected, but thereafter the carbonyl index development became slower in the former. Again, judging by the visual assessment of dispersion of UV absorber as shown in Plates 3.3 and 3.4 this trend may not be surprising as there is very little to choose between the degree of dispersion of UV absorber in Plates 3.3 and 3.4 for instance. The high temperature/high shear rate extrudate carbonyl index content with exposure time is included in Figure 4.10 for comparative purposes. It is a half way house between the two extreme processing conditions discussed above.

The number of days to 50% failure for the three samples is shown in Figure 4.11. The low temperature/low shear rate sample reached 50% failure in about 67 days while the low temperature/high shear rate sample reached an equivalent point at a faster time of about 52 days. Although the low temperature/low shear rate extrudate is apparently more stable than the low temperature/high shear rate extrudate studies in the 6.0 MFI high density polyethylene, the kind of significant difference seen in the 6.0 MFI resin is absent. Additionally, the low temperature/high shear rate sample was doing better until after 600 hours of irradiation. Again this is in agreement with the qualitative assessment made in the previous chapter.
FIGURE 4.10: Variation of Carbonyl Index (CI) with Time in Hours for 0.2 MFI HDPE
FIGURE 4.11: Time to 50% Failure for 0.2 MFI HDPE/UV Masterbatch Blend Processed Under Three Different Conditions
Figure 4.12 compares the carbonyl index for slow cooled samples and rapidly cooled samples for blends of the 0.2 MFI resin with masterbatch at the three processing conditions mentioned above. Again, as was found in Section 4.3.2.1, photostability is further enhanced when samples are rapidly cooled after extrusion. The number of days to 50% failure for the rapidly cooled samples is not very significant in this case as shown in Figure 4.13.

It is not reasonable to compare the results obtained for the 6.0 MFI resin and the 0.2 MFI resin directly since 0.2 MFI resin is an outdoor high density polyethylene grade. There are however, definite indications from the results to suggest that absorber poor distribution in the 0.2 MFI resin might be due to the difference in molecular weight between resin and the low density polyethylene masterbatch base. This is because the expected improvement of the distribution of masterbatch by increased shear rate as pointed out by Gale and as is the case in the present study for the 6.0 MFI resin with the masterbatch is not attained when the same masterbatch is used in a low MFI resin. The persistent broad ultraviolet absorbing areas which remain even at increased shear rate (Plate 3.4) and the subsequent lack of improvement on photostability support the view held in the last chapter that low density polyethylene streaks are even more likely when polymers with widely different molecular weights are blended in this way.

Figure 4.14 shows the growth of carbonyl index with time of irradiation for the two high density polyethylene grades at the processing conditions studied collected together for easy reference. Table 4.1 shows the time in days to 50% failure for the two grades of HDPE at the various processing conditions.
HDPE MFI, Die temperature/screw speed

- 0.2, 190°C/10 rpm (low temp/low shear)
- 0.2, 190°C/10 rpm and quenched @ 4-10°C
- 0.2, 190°C/40 rpm
- 0.2, 190°C/40 rpm and quenched @ 4-10°C

**FIGURE 4.12:** Variation of Carbonyl Index (CI) with Time (Hours) 
For Slow Cooled and Quenched Samples of 0.2 MFI HDPE
FIGURE 4.13: Time to 50% Failure for Rapidly Cooled and Slow Cooled Extrudates of 0.2 MFI HDPE/UV Masterbatch Blend
Resin melt index, die temperature/screw speed

- 6.0 MFI 170°C/10 rpm
- 6.0 MFI 170°C/40 rpm
- 6.0 MFI 180°C/40 rpm
- 0.2 MFI 190°C/10 rpm
- 0.2 MFI 190°C/40 rpm
- 0.2 MFI 200°C/40 rpm

FIGURE 4.14: Variation of Carbonyl Index (CI) with Time (hours) in Different Grades of HDPE Respectively Processed Under Varying Conditions
TABLE 4.1: TIME IN DAYS TO 50% FAILURE FOR 6.0 AND 0.2 MFI HDPE EXTRUDED UNDER DIFFERENT CONDITIONS

<table>
<thead>
<tr>
<th>Processing Condition</th>
<th>Time (days) to 50% failure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6.0 MFI</td>
</tr>
<tr>
<td>Die Temp (°C)</td>
<td>Slow Cooled</td>
</tr>
<tr>
<td>6.0 MFI HDPE</td>
<td></td>
</tr>
<tr>
<td>170</td>
<td>32</td>
</tr>
<tr>
<td>170</td>
<td>70</td>
</tr>
<tr>
<td>180</td>
<td>62</td>
</tr>
<tr>
<td>0.2 MFI HDPE</td>
<td></td>
</tr>
<tr>
<td>170</td>
<td></td>
</tr>
<tr>
<td>170</td>
<td></td>
</tr>
</tbody>
</table>

4.4 CONCLUSIONS

1. Table 4.1 shows the time in days to 50% failure for the two grades of high density polyethylene studied at various processing conditions. It can be seen from this that:

a) the photostability of the 6.0 MFI HDPE is increased by about two-fold for the low temperature/high shear rate extrudate compared to the low temperature/low shear rate extrudate. In view of the results obtained in Chapter 3 where visual assessment of UV photomicrographs showed better dispersion for the low temperature/high shear rate extrudate, the result stated in (a) above leads to the conclusion that photostability of UV absorber containing products is a function of degree of dispersion of the additive.

b) similarly the times to 50% failure for the 0.2 MFI HDPE (67 days for the lower screw speed and 52 days for a screw speed of 40 rpm) under similar conditions do not vary significantly just as UV photomicrographs of the same specimens (Plates 3.3 and 3.4) identically showed poor absorber distribution. Again
leading to the conclusion that photostability is a function of degree of dispersion.

2. Figures 4.8 and 4.9 show that a quenched low temperature/low shear rate extrudate of the 6.0 MFI HDPE is significantly more stable to light than a slow cooled sample of the same specimen. This observation leads to the conclusion that the degree of dispersion of UV absorbers in crystalline polymers is a function of morphology. This conclusion correlates with the observation of Frank and Lehner\textsuperscript{15} on the distribution of ultraviolet stabilisers in crystalline polymers.

3. Figures 4.6 and 4.7 respectively show carbonyl index versus time of irradiation and time in days to 50\% failure for extrudates of 6.0 MFI HDPE obtained at low temperature/high shear rate and high temperature/high shear rate. It is easily seen that increased temperature reduces the photostability of the sample. This implies that reduced melt viscosity affects the degree of dispersion of UV absorber.
CHAPTER 5

A SEMI-AUTOMATIC PROCEDURE FOR MEASURING PIGMENT DISPERSION IN POLYOLEFINS USING A PHOTOMETER AND TRANSMITTED DARK-FIELD ILLUMINATION

5.1 INTRODUCTION

Quantitatively, the state of pigment dispersion in plastics, rubbers or similar systems is a comparison between the actual state of pigment dispersion and the ideal state of dispersion for a given system.

Relevant data on pigment dispersion in plastics are surprisingly scarce and very difficult to extract from the literature. In view of the fact that dispersion of additives in general is of the utmost importance for the behaviour of a technical polymer material, this is an unfortunate trend.

In material science, biology, medicine and some other disciplines, the relationship between geometrical properties of the microstructure and the function, the behaviour or properties of materials or tissue are of great interest. Of the many procedures developed to describe and characterise size, size distribution together with shape and orientation, only some, mostly in biology are well established. The quantitative characterisation of features, that is, their mutual position in a plane or in space has been treated by numerous authors. These studies give detailed consideration of the statistical foundations of the analysis of point distributions. Though some consideration was given to this problem in the field of material science and biology, there are very few examples in which data on plastics were evaluated and conclusions drawn from numerical results.

5.2 MEASUREMENT OF PIGMENT DISPERSION

One of the earliest methods used to measure pigment dispersion was the use of an eyepiece graticule in a microscope to measure aggregate sizes.
and their distribution. This method is now generally unacceptable because it is extremely time consuming. As already mentioned in Chapter 1, there have been a few other methods such as the microdensitometer, surface roughness analysis and particle size measurements since. The microdensitometer which was reported by Best\textsuperscript{9} was based on the measurement of the optical density of thin sections of black filled polyethylene using an optical bench type of set up which restricts the degree of precision obtainable. Dispersion Index (DI) measurements were derived from surface roughness values by Vegvari et al\textsuperscript{3} and defined as follows:

\[
DI = 100 - K f^2 \bar{h}
\]

where \( f \) = frequency of roughness peaks per cm of rubber surface
\( \bar{h} \) = the average peak height
\( K \) = a proportionality constant based on the ASTM D-2 663 light microscope dispersion measurements.

The method therefore defines dispersion essentially by an average value. Defining dispersion by a single average value obtained from surface roughness analysis is not only limited to rubbers but can be misleading.

Image analysis using fully automatic image analysers such as the Quanti- met, and semi-automatic counters such as the Zeiss TGZ3 have been perhaps the only significant advancement in pigment dispersion studies from the very first eyepiece graticules procedure. Even this capital intensive equipment\textsuperscript{s} have some deficiencies. The instruments produce relatively poor results because of differences in operator interpretation. Also particle boundaries are often quite poorly defined and there is considerable operator subjectivity in deciding which ones to measure. Despite these deficiencies they have made very important contributions. However, many manufacturers are still unable to assess dispersion in their products very quickly without
having to invest in advanced image analysing equipment. An image analyser is however a versatile piece of equipment for work in a whole range of microstructural problem solving and therefore not economical for a manufacturer only interested in dispersion to invest in such a dispersion outfit because of the cost involved.

There is therefore a great need for a simpler and less costly approach to quantitative dispersion studies. It is essential to develop a simpler and therefore less costly quantitative dispersion equipment than image analysers such as the Quantimet. Such an equipment if developed will be within reach of small scale manufacturers. So the approach is basically towards cost cutting.

In this chapter, a simple procedure involving the use of a microscope photometer and transmitted dark field illumination is described. The procedure nevertheless does not give a single figure as an index of dispersion in plastics. It offers a contribution towards the improvement of quantitative dispersion methods through its ability to classify the dispersion of pigment particles in planar specimens as randomly distributed or aggregated. It also allows a description of the degree of aggregation quantitatively when they are found to be so.

The main feature of the procedure is the measuring of light intensities scattered by pigment particles within varying areas of the photometer aperture by scanning the surface of the specimen. (A given aperture of the photometer will be referred to as a "Quadrat" henceforth). The light intensities were then linearly related to the number of primary pigment particles (by assumption to be stated later) in the field of view. The procedure may have however suffered some theoretical inadequacies due to the simplification lent to it by the assumptions made. This became necessary because of the desire by the author to stimulate interest in quantitative dispersion procedures for practical applications. The other reason is that a fully consistent theoretical treatment of the theory involved may have proved too complex to be used.
5.3 THEORETICAL CONCEPTS

5.3.1 Notation

\( A_p \) = area of photometer aperture
\( P \) = photometer output reading
\( N \) = number of primary particles
\( K, K' \) = constants
\( N_A \) = number of particles per unit area
\( SD \) = standard deviation
\( \delta \) = diameter of primary particles

5.3.2 Assumptions

1. The photometer output \( (P) \) linearly relates to the number of primaries in the viewing area \( (A) \) so long as extreme aggregation does not occur in which case particles within the aggregate are prevented from scattering light by those on top of them.

2. The distribution of primary particle size is constant i.e. all primaries are the same size.

3. The sections studied are thought to be sufficiently thin so that problem is regarded as a two-dimensional one.

4. Depth of field of the objective is greater than the thickness of the section i.e. everything seen down the microscope is in focus. (Depth of field of a 20x objective is \( \sim 8 \, \mu m \) and since 5 \( \mu m \) thick sections are being dealt with, the assumption holds).

Similarly, the other assumption, the distribution of primary particle size is constant, is justified because some pigment particles such as titanium dioxide are known to have a very narrow particle size distribution. The small section thickness employed makes the first assumption reasonable.
5.3.3 Measurable Quantities

Pigment particles have an inherent ability to scatter light. The photometer responds to the scattered light intensity at various areas of the specimen by giving an intensity signal which can be amplified and recorded on a chart recorder. The photometer output relates to the number of pigment particles in the viewing area.

Considering an idealised array of pigment particles (Figure 5.1) as a symbolic representation of a plastic pigment system of area $A$, the number of primary particles per unit area can be derived as follows.

In dark field transmitted light microscopy (to be described later), scattered light from inclusions such as pigment particles come from the surface of the pigment particles. The photometer output therefore is proportional to the total perimeter of pigment particles within the aperture area ($A_p$) of the photometer i.e.

$$ P \propto \text{Total particles perimeter} $$

$$ P = K \cdot \text{Total perimeter} \quad (1) $$

Given that $N_A$ is the total number of primaries per unit area and that the photometer aperture area is $A_p$, then from (1):

$$ P = K \cdot N_A \cdot 2\pi \frac{\delta}{2} \cdot A_p $$

i.e.

$$ P = K \cdot N_A \cdot \delta \cdot A_p $$

$$ N_A = \frac{1}{N_A \delta} \cdot \left(\frac{P}{A_p}\right) $$

from where

$$ N_A = k' \cdot \frac{P}{A_p} $$
FIGURE 5.1: An Idealised Array of Particles Within the Field of View of Microscope
5.3.4 Number of Primaries per Unit Area for Varying Degrees of Dispersion

Consider once again an idealised representation of two systems with good particle dispersion (Figure 5.2a) and another of bad dispersion (Figure 5.2b) along with the ratio of the number of primaries to a given area over a number of area locations for each of the two systems determined respectively, their standard deviations (SD) would compare according to the level of dispersion in each case. In other words, for a perfect dispersion, a plot of the standard deviations of \( N_A \) against experimental areas would be a straight line parallel to the area axis so long as the areas employed are large compared with the primary particle dimension (i.e. \( A >> \delta^2 \)). This implies that in the event of departure from this ideal, the point of a departure from the expected would indicate the point at which agglomeration becomes significant.

5.4 MODEL EXPERIMENT

A model experiment to test the approach outlined above was carried out by a statistical analysis of a simulated particle distribution on a squared paper.

Four hundred circular slide tags were randomly placed on a 28 cm x 18 cm squared paper as shown in Plate 5.1. Three other simulations shown in Plates 5.2, 5.3 and 5.4 were prepared by agglomerating the same number of tags to varying degrees and patterns respectively on three other squared papers.

The number of primary tag particles per unit area were determined by counting for each of the four models. The standard deviation of the number of primary tag particles per unit area (\( N_A \)) in each of the area locations for each model using manual scanning procedure similar to that illustrated in Figure 5.8(b) was calculated and graphs of \( N_A \) plotted against area (Figure 5.3). The procedure was repeated for all
FIGURE 5.2: Two Systems with (a) Good Dispersion, and (b) Bad Dispersion
PLATE 5.1: RANDOMLY DISTRIBUTED SLIDE TAGS ON SQUARED PAPER

PLATE 5.2: SLIGHTLY AGGLOMERATED SLIDE TAGS ON SQUARED PAPER
PLATE 5.3: HIGHLY AGGLOMERATED SLIDE TAGS ON SQUARED PAPERS

PLATE 5.4: AGGLOMERATED AND ALIGNED TAGS ON A SQUARED PAPER
models for area locations in the form of a Raster i.e. scanning procedure similar to that schematically shown in Figure 5.8(a) (Figure 5.4).

A model experiment was considered useful because of the obvious advantage it has over a real system in terms of developing the necessary concepts and idealising the nature of the specimen.

5.5 EQUIPMENT AND HARDWARE

The instrumentation shown in Plate 5.5 is based on a PZO Biolar light microscope equipped with a transmitted light dark field condenser lens. This microscope is also fitted with a computer driven and specially designed stepping stage that moves in steps of 2.5 μm in two orthogonal directions in its own plane. The microscope is also equipped with a Leitz MPV compact microphotometer (Figure 5.5) that has been fitted with a rectangular diaphragm for precise specification of specimen areas for intensity measurements. The photometer output is connected to the computer for data acquisition. The Apple II microcomputer printer allows a print-out of results while a disc drive unit stores both the system program and input data from the photometer. An interesting feature of the microcomputer is an interface board which controls the pulsing of the stage stepping motors and synchronised data acquisition.

5.5.1 Software and Data Acquisition

An interactive menu driven software was employed. Test specimens are entered easily before a given run. Parameters to be entered at the start of every run include the reading interval, scan length, scan width and number of scans. These parameters specify the areas or quadrats to be analysed by the distance between measurements taken. The other parameters, reading interval, scan length and total number of scans altogether define the total number of readings finally obtained.
FIGURE 5.3  STANDARD DEVIATION OF NUMBER OF PARTICLES
PER UNIT AREA OF FOUR MODELS OF 'HAND
SIMULATED DOTS ON A (280 x 180) mm²
RULED PAPER
FIGURE 5.4  GRAPH OF STANDARD DEVIATION OF NO OF PARTICLES PER UNIT AREA (RASTER) TO AREAS IN MICRONS
FIGURE 5.5: A Leitz MPV Compact Microphotometer
The 'set up mode' allows the manipulation of the stage from the microcomputer keyboard. Figure 5.6 shows a flow chart for the mode of operation of the scan systems. The systems programme 116 is given in the Appendix.

5.6 EXPERIMENTAL

5.6.1 Sample Preparation

Specimens for scanning were prepared by thin sectioning pigmented extrudates of high density polyethylene and polypropylene using an MSE Base Sledge microtome. About 1 cm x 0.5 mm piece of the polyolefin under investigation is firmly held down on the microtome and using a sharp steel knife, 5 μm thick sections were sectioned and mounted in silicone oil between a glass slide and coverslip. It is most important that sections to be studied be flat and free of knife marks and strain free to ensure good dark field illumination.

The suitability of a section for subsequent microscopical examinations is not only judged on the basis of the above (i.e. quality) but also on thickness. The major difficulty encountered in the sample preparation during this work is that of coping with curling or buckling, particularly for the high MFI HDPE. This effect was reduced by cutting 5 μm thick sections as opposed to thicker sections which might otherwise have been more appropriate.

5.6.2 Dark Field Optics

The principle of dark field transmitted light microscopy is shown in Figure 5.7. In a dark field system, only light scattered from the object on the stage reaches the eye. Dark field systems can be achieved in several ways. Light can be controlled as closely as is done in bright field illumination. Once this is achieved, the object is usually evenly illuminated to give a clear image provided the optical arrangement is symmetrical.
FIGURE 5.6: Flow Chart for Mode of Operation of Scan System
In one form of transmitted dark field, a central stop in a ring diaphragm in the condenser aperture area produces a circular cone-shaped beam whose apex is the stage object. The cone formed on the far side is directed outside that accepted by the objective, so that it receives only light scattered by the object. This requires that the image of the filament formed in the condenser-aperture area must be as wide as the outer diameter of the ring diaphragm.

5.6.3 Sample Scanning

Sample scanning was done by the microscope stepping stage controlled by computer in such a way that it scanned specimens in either of two modes of movement orthogonally in its own plane, viz:

a) **Raster Movement:**

The stage was programmed to move linearly in specified steps (usually of 2.5 μm), scan length and width to describe a track in the form of a raster as shown in Figure 5.8(a).

b) **Drunkard's Walk:**

The other method of scanning the specimen allowed the stepping stage to describe a drunkard's walk on the surface of the specimen. A schematic representation of the stage motion on the specimen is shown in Figure 5.8(b).

The major problem which arose during scanning of samples is that sometimes either or both of the stepper motors traverse their entire possible length before the number of scans was completed. This situation usually occurred when the traverse did not start from the beginning i.e. the stage motors had perhaps traversed some distance after a previous run. The inconvenience caused by a problem like this was overcome by remembering to use the 'set-up-mode' to manipulate the motors back to their initial positions before any run.
FIGURE 5.7  PRINCIPLE OF DARK-FIELD TRANSMITTED LIGHT MICROSCOPY
a(i) Scan

Aggregate made up of primary particles

Primary Particles

b(ii) Drunkard's Walk

FIGURE 5.8 GENERAL SYSTEM OF SCANNING PROCEDURES
5.6.4 **Scan Area**

The area of a given sample being analysed is controlled by the microphotometer variable aperture. The actual aperture area (i.e. quadrat size) under investigation is measured by adjusting the aperture to form a square whose dimensions are measured using a microscope graticule. Areas of 100 \( \mu m^2 \), 400 \( \mu m^2 \), 900 \( \mu m^2 \), 1600 \( \mu m^2 \) and 3600 \( \mu m^2 \) have been used to scan the specimens.

In order to maintain a constant aperture area for all specimens, any given apertures are measured out and set, remain unaltered until all samples are scanned for that particular area. In this way error due to aperture area measurement is reduced and equally spread to all samples.

5.6.5 **Preliminary Runs**

Initially, sample scan intensities as measured by the photometer were recorded on a chart recorder. This enabled a visual assessment of microphotometer aperture and variation on pigment dispersion.

5.7 **RESULTS AND DISCUSSION**

5.7.1 **Model Experiment**

Figures 5.3 and 5.4 show the variation of the standard deviation of the number of tags per unit area with varying quadrat areas. As can be seen from these figures, significant changes in standard deviation appear at varying quadrat area levels for the four models. The areas at which the standard deviation change significantly increase from model 1 shown in Plate 5.1 through models 2, 3 and 4 (Plates 5.2, 5.3 and 5.4). The theory suggested in Section 5.3 therefore very well differentiates the degrees of dispersion of the tags in each of the four models.
5.7.2 **Intensity Patterns in Varying Photometer Aperture Areas**

Figure 5.9 shows the variation of light intensities as measured by the photomultiplier at two different photometer aperture areas, output on a chart recorder. It can be seen from this that the photometer response to the scattered light intensities differs appreciably for the two areas. The pattern for the smaller aperture area (Figure 5.9(a)) contains both high, intermediate and low peaks, while the intensity pattern for the higher photometer aperture area is tending towards peaks of the same height. Following the suggestions made by the model experiment and the analysis discussed in Section 5.3.3, a statistical treatment of the intensity variation which is a linear function (by assumption) of the number of primary particles in the viewing area could be a useful tool for determining the level of agglomeration of pigment particles.

1. **Variation of standard deviation with aperture areas:**

Figure 5.10 shows the variation of the standard deviation of the number of pigment particles per unit area for three samples of 6.0 MFI high density polyethylene extruded at low temperature/high shear rate, low temperature/low shear rate and high temperature/low shear rate. It can be seen from this figure that the point at which the standard deviation increases sharply varies for the three extrudates. The aperture area at which the standard deviation increased sharply is 1450 $\mu$m$^2$ for the high temperature/low shear rate extrudate, 1175 $\mu$m$^2$ for the low temperature/low shear rate extrudate and 850 $\mu$m$^2$ for the low temperature/high shear rate extrudate. These values are very interesting judging from the visual examination of the dark field photomicrographs of the three samples shown in Plate 5.6. Visually, it is difficult to distinguish these three samples.
FIGURE 5.9  INTENSITY PATTERNS OF VARYING APERTURE AREAS
FIGURE 5.10: Graph of Standard Deviation of NO of Particles per Unit Area Vs Aperture Area (nm²) in Three Samples of Dispersed 6.5 MEU UP.
PLATE 5.6: DARK-FIELD PHOTOMICROGRAPHS OF SECTIONS OF PIGMENTED 6.0 MFI HDPE
Figure 5.11 shows the variation of the standard deviation of the number of pigment particles per unit area with varying photometer aperture areas for extrudates of 0.2 MFI, 2.0 MFI and 6.0 MFI obtained under the same processing conditions of 170°C die temperature and 10 rpm screw speed. It can be seen from these curves that there is not a significant difference in the aperture areas at which the standard deviation rises sharply. This observation suggests that dispersion of pigment is not affected by the expected melt viscosity difference at the processing condition used.

Based on the curves shown in Figures 5.10 and 5.11, determination of the point at which the standard deviation of the number of pigment particles per unit area rises sharply is subjective. To overcome this difficulty, graphs of log, of standard deviation were plotted against area. These are shown in Figures 5.12 and 5.13.

2. **Effect of aperture size on detection of non-randomness:**

On theoretical grounds, it can be readily shown that in any agglomerated population, the use of Poisson Series (to be discussed shortly) and test of departures from it will show both random, agglomeration and regular distribution as the size of quadrat is steadily increased. This is illustrated in Figure 5.14.

The anomalous values of log standard deviation at very high aperture area (at > 3500 μm²) could have been due to the fact that we begin to pick up streaks such as exist on the photomicrographs shown on Plate 5.6. For example, if we consider the streak contained in Plate 5.6B with a width of about 32 μm, the aperture area at which these anomalous points occurred is far greater than the width of these streaks and are expected to pick them up in addition to the pigment particles.
FIGURE 5.11: Graph of Standard Deviation of Number of Particles per Unit Area vs Aperture Area ($\mu$m$^2$) in 0.2, 2.0 and 6.0 MFI HDPE Extruded Under the Same Processing Conditions
FIGURE 5.12: Graph of $\log_{10} 10^5$ Standard Deviation of Particles per Unit Area Against Aperture Area in Sections of 6.0 MFI HDPE
FIGURE 5.13: Graph of $\log_{10}$ Standard Deviation of Number of Particles Per Unit Area Against Photometer Aperture Area

- 0.2 MFI HDPE: Processed at a die temperature of 170°C and screw speed of 10 rpm
- 2.0 MFI HDPE: Processed at a die temperature of 170°C and screw speed of 10 rpm
FIGURE 5.14: Schematic Representation of the Relationship Between Quadrat Size and Standard Deviation
Sampling with a photometer aperture of area A, B and C would show agglomeration while D and E would appear to tend towards random/regular distribution, with each containing approximately the same number of particles. Thus the most marked demonstration of agglomeration would be with the quadrat having an area approximately equal to the area of the clump.

With this theoretical analysis in mind, it is reasonable to relate the area of the photometer aperture in Figures 5.10 and 5.11 at which the standard deviation rose steeply to be the region of significant agglomeration and therefore area of pigment clumps. The area (as obtained from Figures 5.12 and 5.13) and size of pigment clumps in the pigmented 6.0 MFI HDPE extruded at varying conditions is shown in Table 5.1 while the area and size of pigment clumps in varying grades of HDPE extruded at low temperature/low shear rate processing conditions is shown in Table 5.2. The sizes shown in Tables 5.1 and 5.2 have been calculated by assuming that the clumps are circular and of area \( \pi r^2 \) (\( r = \) radius of particle clump).

3. Test of Randomness

A number of approaches have been made to the determination of non-random distribution of individuals of the same species. The earliest accounts of non-random distribution studies are those of Gleason and Svedberg on the distribution of plants in a community. Svedberg's approach to the problem has since become one of the standard methods of detecting non-randomness in vegetation. His approach consists of the use of \( \chi^2 \) goodness of fit and variance:mean ratio. This botanical approach may be of use in the characterisation of pigment dispersion in plastics. This is because looking down the microscope and counting pigment aggregates is very similar to quadrat counting of plants in a vegetation.
TABLE 5.1: AREA AND SIZE OF PIGMENT AGGREGATES AT SIGNIFICANT AGGLOMERATION LEVELS FOR 6.0 MFI HDPE EXTRUDED AT VARYING CONDITIONS

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Clump Area $10^2 , \mu m^2$</th>
<th>Clump Diameter $\mu m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low temp/low shear extrudate</td>
<td>26.75</td>
<td>2.92</td>
</tr>
<tr>
<td>Low temp/high shear extrudate</td>
<td>22.75</td>
<td>2.66</td>
</tr>
<tr>
<td>High temp/low shear extrudate</td>
<td>29.25</td>
<td>3.05</td>
</tr>
</tbody>
</table>

TABLE 5.2: AREA AND SIZE OF PIGMENT PARTICLE AT SIGNIFICANT AGGLOMERATION LEVEL IN 0.2, 2.0 AND 6.0 MFI HIGH DENSITY POLYETHYLENES

<table>
<thead>
<tr>
<th>Sample ID-Melt Flow Index (g/10 min)</th>
<th>Extrusion Condition</th>
<th>Clump Area ($\mu m^2 \times 10^2$)</th>
<th>Clump Diameter ($\mu m$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Die Temp ($^oC$)</td>
<td>Screw Speed (rpm)</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>190</td>
<td>10</td>
<td>26.75</td>
</tr>
<tr>
<td>2.0</td>
<td>170</td>
<td>10</td>
<td>24.25</td>
</tr>
<tr>
<td>6.0</td>
<td>170</td>
<td>10</td>
<td>26.50</td>
</tr>
</tbody>
</table>
a) \( \chi^2 \) Goodness-of-fit

The \( \chi^2 \) goodness-of-fit approach has been employed to characterise the dispersion of pigment particles in two grades of high density polyethylene (6.0 MFI and 0.2 MFI) which have been pigmented by the use of green LDPE pigment masterbatch (VBM 301-22380). Tables 5.3 and 5.4 show the \( \chi^2 \) goodness-of-fit of pigment particles in varying photometer aperture areas. The procedure consists of relating the observed number of individuals per quadrat (a quadrat refers to a given aperture area) to the expected number derived from the Poisson Series \( e^{-m}, me^{-m}, \frac{m^2e^{-m}}{2!}, \frac{m^3e^{-m}}{3!}, \frac{m^4e^{-m}}{4!}, \ldots \)

where \( m \) is the mean density of individual pigment particles. Successive figures of the series give the probability of quadrats containing 0, 1, 2, 3, 4, ... pigment particles respectively and the expected number can be readily calculated. It can be seen from the tables referred to above that the difference between the observed and the expected numbers of occurrences of pigment particles for all quadrat areas studied is highly significant, the chances of this stated differences arising accidentally are very much less than 0.005 (i.e. the probability of a chance difference is much less than 200:1). The observed data shows a poor fit with the expected series and the population of pigment particles sampled was non-randomly distributed.

Having reached the above conclusions, it should be pointed out, that the \( \chi^2 \) method of sampling is not particularly convenient for a population where the number of individuals in a given quadrat can be as high as 100 as is the case with population of pigment particles distributed in a plastic system. This might be overcome by grouping the data in such a way that intensity values of between 1 to 10 be regarded as one pigment particle, 11 to 20 as 2, and so on in which case it was possible to get the number of individuals per quadrat in the form of 0, 1, 2, 3, 4, ...
TABLE 5.3: DENSITY DATA OF NUMBER OF PIGMENT PARTICLES FROM PIGMENTED 6.0 MFI HDPE EXTRUDED AT A DIE TEMPERATURE OF 170°C AND SCREW SPEED OF 10 rpm SHOWING CHANGE OF AGGREGATION OF PIGMENT PARTICLES DETECTED WITH CHANGE OF SCANNING AREA

b) \( x^2 \) - goodness of fit

<table>
<thead>
<tr>
<th>Quadrat Size (( \mu m ))</th>
<th>Mean</th>
<th>( x^2 ) Observed</th>
<th>( x^2 ) (from Tables) Expected</th>
<th>Degrees of Freedom (n)</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>10.4</td>
<td>21.44</td>
<td>22.00</td>
<td>8</td>
<td>0.005</td>
</tr>
<tr>
<td>225</td>
<td>4.77</td>
<td>17.66</td>
<td>16.70</td>
<td>5</td>
<td>0.005</td>
</tr>
<tr>
<td>400</td>
<td>3.18</td>
<td>32.60</td>
<td>10.60</td>
<td>2</td>
<td>0.005</td>
</tr>
<tr>
<td>900</td>
<td>2.22</td>
<td>20.80</td>
<td>10.60</td>
<td>2</td>
<td>0.005</td>
</tr>
<tr>
<td>1600</td>
<td>1.27</td>
<td>40.65</td>
<td>10.60</td>
<td>2</td>
<td>0.005</td>
</tr>
</tbody>
</table>

TABLE 5.4: DENSITY DATA OF NUMBER OF PIGMENT PARTICLES OF PIGMENTED 0.2 MFI HDPE EXTRUDED AT A DIE TEMPERATURE OF 190°C AND SCREW SPEED OF 10 rpm SHOWING CHANGES OF AGGREGATION OF PIGMENT PARTICLES DETECTED WITH CHANGE OF SCANNING AREA

<table>
<thead>
<tr>
<th>Quadrat Size (( \mu m ))</th>
<th>Mean</th>
<th>( x^2 ) Observed</th>
<th>( x^2 ) (from Tables) Expected</th>
<th>Degrees of Freedom (n)</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>99.60</td>
<td>13.33</td>
<td>21.96</td>
<td>8</td>
<td>0.005</td>
</tr>
<tr>
<td>225</td>
<td>40.83</td>
<td>35.64</td>
<td>16.75</td>
<td>5</td>
<td>0.005</td>
</tr>
<tr>
<td>400</td>
<td>28.85</td>
<td>36.82</td>
<td>10.60</td>
<td>2</td>
<td>0.005</td>
</tr>
<tr>
<td>900</td>
<td>17.85</td>
<td>228.60</td>
<td>31.32</td>
<td>14</td>
<td>0.005</td>
</tr>
<tr>
<td>1600</td>
<td>10.91</td>
<td>619.26</td>
<td>21.96</td>
<td>8</td>
<td>0.005</td>
</tr>
</tbody>
</table>
b) Variance:Mean Ratio

Tables 5.5 and 5.6 show the variance:mean ratios of the sampled population in the specimens referred to in Section 3(a). The variance mean ratio shows that the population in the 6.0 MFI HDPE has apparently some degree of aggregation at a quadrat area of 100 μm². This difference tested from the expected ratio of 1 applying a t-test is significant because the probability of this difference arising by chance is very much less than 200:1. However, as the quadrat size used for sampling increased, the variance mean ratio approached the expected value of 1. This is not surprising because as mentioned earlier on in Section 5.7.2 (2) all quadrats tend to contain approximately the same number of individuals. Similar calculations for the 0.2 MFI high density polyethylene (Table 5.6) give variance mean ratios less than 1 and very different from values obtained for the high MFI polymer. This suggests different pattern of pigment distribution in the two polymers.

5.8 CONCLUSIONS

1. Model experiments employing microscope tags on squared papers show that it is possible to establish the point at which agglomeration of particles dispersed in a system becomes significant by comparing the standard deviation of the number of particles per unit area to the area of the system sampled. The area at which the standard deviation rises sharply is the area at which agglomeration becomes significant (see Figures 5.3 and 5.4).

2. Experiments based on the theory previously described (Section 5.3.3) and employing techniques similar to the model experiment lead to the conclusion that the degree of pigment dispersion of a polyolefin plastic can be quantitatively described by relating the variation of the standard deviation of particles per unit area to the aperture area of the microscope microphotometer as illustrated in Figures 5.10 and 5.11.
### TABLE 5.5: Variance: Mean Ratio of Particles Distribution in Varying Sample Areas of a Section of 6.0 MFI HDPE

<table>
<thead>
<tr>
<th>Quadrat Size (microns)</th>
<th>Variance: Mean Ratio</th>
<th>t</th>
<th>P</th>
<th>Degrees of Freedom</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>6.68</td>
<td>26.34</td>
<td>0.005</td>
<td>54</td>
</tr>
<tr>
<td>225</td>
<td>6.71</td>
<td>29.66</td>
<td>0.005</td>
<td>54</td>
</tr>
<tr>
<td>400</td>
<td>2.47</td>
<td>7.63</td>
<td>0.005</td>
<td>54</td>
</tr>
<tr>
<td>900</td>
<td>1.62</td>
<td>3.22</td>
<td>0.005</td>
<td>54</td>
</tr>
<tr>
<td>1600</td>
<td>1.13</td>
<td>0.69</td>
<td>0.005</td>
<td>54</td>
</tr>
</tbody>
</table>

### TABLE 5.6: Variance: Mean Ratio of Particles Distribution in Varying Sample Areas of a Section of 0.2 MFI HDPE

<table>
<thead>
<tr>
<th>Quadrat Size (microns)</th>
<th>Variance: Mean Ratio</th>
<th>t</th>
<th>P</th>
<th>Degrees of Freedom</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.63</td>
<td>1.47</td>
<td>0.005</td>
<td>54</td>
</tr>
<tr>
<td>225</td>
<td>0.31</td>
<td>4.62</td>
<td>0.005</td>
<td>54</td>
</tr>
<tr>
<td>400</td>
<td>0.25</td>
<td>3.90</td>
<td>0.005</td>
<td>54</td>
</tr>
<tr>
<td>900</td>
<td>0.21</td>
<td>2.75</td>
<td>0.005</td>
<td>54</td>
</tr>
<tr>
<td>1600</td>
<td>0.19</td>
<td>4.21</td>
<td>0.005</td>
<td>54</td>
</tr>
</tbody>
</table>
3. The procedure not only quantifies the degree of dispersion but also enables the effect of melt temperature and shear rate on the degree of dispersion. For example, the point at which the standard deviation of the number of particles per unit area increases sharply (i.e. onset of significant agglomeration) for the low temperature/low shear rate extrudate is 1175 μm², 850 μm² for the low temperature/high shear rate extrudate and 1450 μm² for the high temperature/low shear rate extrudate and therefore describes the effect of processing on degree of dispersion.

4. Melt flow index has no effect on degree of pigment dispersion of a given pigment masterbatch in varying grades of HDPE studied as shown in Figure 5.11 where there is no significant difference in the aperture areas at which the onset of agglomeration becomes important.

5. The Poisson series applied to data acquired by the microphotometer enables a characterisation of pigment dispersion similar to that used by botanists in the characterisation of plant distribution in a vegetation. This is because looking down the microscope and using a microphotometer to count particles in a pigment/plastic system is similar to quadrat counting of plants in a vegetation.

6. In addition to being able to use the described technique to quantitatively measure the point of onset of significant agglomeration the use of χ² goodness-of-fit and variance:mean ratio also enables the characterisation of dispersion as being random or aggregated.

These conclusions suggest that this technique can be applied on a routine basis for the characterisation of pigment dispersion in plastics.
6.1 INTRODUCTION

It is common today to employ polyolefin/polyolefin polyblends in the manufacture of coloured polyolefin products or elastomer/elastomer polyblends in the manufacture of automotive tyres and other products. This type of blending where one component of the polyblend is an additive masterbatch complicates the problem of dispersing pigments. Although a lot has been reported on the dispersion of carbon black masterbatch in rubbers, not much attention has been paid to pigment dispersion in polyolefin polyblends.

Polyolefin blends, in terms of the relationship between compatibility and additive distribution between the separate polymer zones, has received very little attention in plastics manufacture. There are suggestions from the work described in Chapter 3 of the present study, that the compatibility/dispersion relationship is an important aspect of degree of additive dispersion studies and additive incorporation by masterbatching. In that chapter, the distribution of Cyasorb 531 ultraviolet absorber in two different grades of high density polyethylene and polypropylene which were compression moulded into 200 μm thick films after extrusion was described. In particular, it was observed that whereas the degree of dispersion of ultraviolet absorber masterbatch in a 6.0 MFI high density polyethylene improved from bad to good dispersion with increased shear rates, the degree of dispersion of the same low density polyethylene ultraviolet masterbatch remained poor at equivalent processing conditions and indeed all the processing conditions studied for the 0.2 MFI HDPE sample. In this chapter, these observations are being examined and discussed along with the microstructure of these materials;
the idea being to try and find out how the microstructure of the polyolefin/polyolefin polyblends relate to the quality of additive dispersion.

Large scale production of polyolefin blends is carried out in two stages:

a) Dispersive Mixing: dispersive mixing typically involves melting and kneading of the components. The spatial distribution and the initial component grain size depend on the dispersive mixing efficiency.

b) Laminar Mixing: laminar mixing is typically carried out in extruders or intensive mixers. Better laminar mixing is realised if the viscosities of the components are 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 of the imparted strain. However a more viscous component will swim in a fluid sea of the major component without being dispersed. When additives are involved, this problem in relation to quality of dispersion can be compounded indeed. It will be interesting to see how the more fluid masterbatch base affects the quality of dispersion. In order to get this information one is interested in the compatibility of the LDPE masterbatch base and the base polymer.

Polymers are ordinarily blended to yield composites in which the individual components function in symbiotic relationship that ultimately results in improved use properties. Although these properties are not of interest here, the fact that we have had to disperse additives into a given polymer using polymer as a base for the additive makes it imperative that we examine the properties and morphology of such blends in relation to the quality of dispersion since morphology
in particular can influence the degree of additive dispersion. Since the utility of polymer blends obviously does not require miscibility as most of the multicomponent polymer systems used commercially are two phase blends, it is important to understand the effect of two phase systems on the degree of additive dispersion. This is important because in two phase systems containing additives, a gain in use property brought about by blending can quickly be eroded by poor additive dispersion brought about by the immiscibility of its components. Even when we have a one-phase system on mixing two components, it is still important to ascertain the degree of additive dispersion since miscibility does not suggest ideal molecular mixing in blends. All that miscibility suggests is that the level of molecular mixing is adequate to yield macroscopic properties expected of a single phase material. So in a miscible polyolefin blend defined as a stable homogeneous mixture which exhibits macroscopic properties expected of a single phase material, it remains to be seen if a single phase material comprising of a base polymer and another which constitutes the additive base, is a guarantee to good dispersion everything else being equal.

Polymer blends may be expected to exhibit incompatibility. Mechanical properties can also show a minimum when plotted against composition. Situations like these arise from a poor degree of interfacial adhesion between components which provide a multiplicity of defects for early failure. This is a dilemma that prohibits a more general use of blending two components. This situation can be further compounded when additives such as poorly dispersed pigments are involved because an agglomerate coming between the interface of incompatible components will obviously hasten failure. For a two phase system, the interfacial adhesion between the respective phases together with the degree of additive dispersion with particular reference to agglomerates positioned at interfacial regions may well govern the ultimate mechanical properties of such a blend. Even for polymers with a high affinity of each other, an additive agglomerate within phase interface is bound to represent a flaw which can possibly give rise to properties lower than that expected if the agglomerate was not there.
Several approaches have been utilised to study blends in relation to additive/filler dispersion. Phase contrast optical microscopy was advantageously employed by Walters et al. and Hess et al. as well as by Marsh and co-workers. Phase contrast procedure was successful in heterogeneous material blends system but less applicable to systems with poor interzone contrast such as in BR and SBR. Other useful methods which have been reported include hysteresis loss as a function of temperature, dielectric loss and dynamic modulus, modulus-temperature transitions and electron microscopy as well as DTA data.

The objectives of this chapter therefore are to investigate the effect of compatibility of polyolefin blends on the degree of dispersion using phase contrast microscopy, polarised light microscopy and DTA. Secondly, to investigate what happens to the particles of the minor component of the blend (in the event of immiscibility) as well as pigment agglomerates using scanning electron microscopy and isothermal crystallisation techniques.

6.2 EXPERIMENTAL

Blends of two different grades of HOPE and polypropylene with an LDPE based pigment masterbatch (VBM 301-22380 or drab green) were obtained employing exactly the same equipment and similar processing conditions used in the case of the UV masterbatch mentioned above (see Section 3.4.2). The only difference was that the extrudate obtained at a screw speed of 40 rpm and die temperature of 180°C for the 6.0 MFI HDPE/UV masterbatch blend (i.e. high temperature/high screw speed) is in this case (HDPE/pigment masterbatch blend) obtained at a screw speed of 10 rpm and die temperature of 180°C (i.e. investigating only the effect of increased temperature at low screw speed). Table 6.1 shows the screw speeds and die temperatures of the extrudates studied. Blends of HDPE or polypropylene with the UV masterbatch studied here were obtained as previously described (Section 3.4.2).
TABLE 6.1: SCREW SPEED AND DIE TEMPERATURE AT WHICH HDPE/PP AND PIGMENT MASTERBATCH WERE OBTAINED

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Screw Speed rpm</th>
<th>Die Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.0 MFI HDPE</td>
<td>10</td>
<td>170</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>170</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>180</td>
</tr>
<tr>
<td>0.2 MFI HDPE</td>
<td>10</td>
<td>190</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>190</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>200</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>10</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>210</td>
</tr>
</tbody>
</table>

6.2.1 Microtomy and Sample Preparation

All the polyblends were prepared for microscopical examination by means of frozen sectioning in the case of specimens for phase contrast, room temperature sectioning for other microscopical examinations and melt pressing for isothermal crystallisation experiments. The frozen sectioning operation was carried out on a Leitz Sledge type microtome using liquid carbon dioxide as the cooling agent. Sections were cut to a thickness in the range of 2 μm to 5 μm, using freshly made glass knives, for analysis under a phase contrast optical microscope. Sections studied were obtained in duplicate to enable comparison of results from the phase illumination to that obtained in the ultraviolet microscope. Sections for polarised light and bright field analysis were obtained using an LKB microtome using a sharp steel knife.
Slides were prepared from the cut sections using glycerol for specimens to be observed in ultraviolet light and Canada balsam for samples to be analysed in phase contrast, polarised light and bright field illumination.

6.2.2 Melt Pressing

The melt pressing method of sample preparation was used for specimens which were first isothermally crystallised before microscopical examination. This was done by melt pressing very small amounts of the extrudate to be studied between glass slide and coverlip on a hot plate at a temperature at which the material flows easily (160°C for polyethylene and 200°C for polypropylene) to give a thin film. The glass slide is rapidly transferred from the hot plate to the hot-stage fitted with a polarizing microscope and isothermally crystallised at 100°C for HDPE and 140°C for polypropylene for 3 hours respectively and slides prepared as mentioned in Section 6.2.1.

6.2.3 Microscopy

The microscopical examination of specimens obtained as previously described in Sections 3.4.2 and 6.2 were performed employing the following techniques:

a) Phase contrast microscopy

Phase microscopy was carried out with a Reichart Zetopan phase microscope equipped with a 40x phase objective. Sections were mounted in a liquid of refractive index close enough to the components of the blend. Canada balsam was selected for this purpose.

For optimum contrast, the thickness of the section to be studied needs to be of the order of 5 μm and free from cutting artefacts. Contrast is developed as a consequence of refractive index fluctuations in the specimen. Phase contrast microscopy is therefore employed to differentiate
the components in the blend (in case of immiscibility) and visually assess the frequency of occurrence of pigment particles in relation to the blend components (i.e. for polymer pigment masterbatch blend). Comparison of photomicrographs of specimens observed in phase contrast microscopy with equivalent specimens examined by ultraviolet microscopy was carried out in the case of polyolefin/UV masterbatch blend for the same reason as above for the polymer/pigment masterbatch blend.

The main problem encountered in phase contrast microscopy is the existence of haloes brought about by the nature of the system. This leads to confusion in the image seen and poses problems in the interpretation of results particularly where there is an overlap of blend components.

b) **Hot-stage microscopy**

A micro hot-stage fitted to a polarizing microscope was used to study the crystallisation behaviour of the polyolefin blends. Of particular interest is what happens to the masterbatch base particles as well as the additive particles under crystallisation conditions. The hot-stage microscope was employed because such information (i.e. dispersion and distribution of the masterbatch under crystallisation condition) can be of immense importance to manufacturers.

The experiment is an isothermal one in which a melt-pressed specimen is rapidly transferred from a hotplate, set at a temperature well above the melting point of the polymer being studied, into the hot-stage set at a chosen crystallisation temperature below the melting point.

This procedure is particularly relevant to the present problem because detection of phases may be aided by heating the material in the hot stage. For example, in a two-phase system a temperature can be chosen when one phase is melted and the other still crystalline and birefringent. At such a point, the phase separation becomes very much more evident and easier to observe.
6.2.4 Scanning Electron Microscopy

Specimens to be analysed were prepared by dropping extrudates into liquid nitrogen and leaving them for sufficient time of about 10-30 minutes and fracturing the cooled samples.

The fractured surfaces were next differentially etched in boiling xylene for a range of times of 5 seconds to 1 hour.

6.2.5 Differential Thermal Analysis

The melting points of the components of the blends were determined using a Du Pont 990 thermal analyser equipped with a 990 mechanical cooling accessory. A diagram of the calorimetric cell is shown in Figure 6.1. A sample pan and a reference pan were positioned on the two raised platforms of the constantan disc as shown. The cell operates at a constant heating rate using a single heating block as the heat supply for both sample and reference pans.

The temperature axis of the instrument was first calibrated using pure samples of indium and tin metals with melting points of 156.6°C and 231.9°C respectively.

About 10 mg of blends were scanned from room temperature to 200°C at a heating rate of 10°C/min and a sensitivity of 10 mV/cm.

6.3 RESULTS AND DISCUSSION

6.3.1 Phase Contrast Microscopy and Ultraviolet Microscopy

a) 6.0 MFI HDPE

Plates 6.1 and 6.2 show photomicrographs of melt pressed samples of polypropylene and low density polyethylene ultraviolet masterbatch blend viewed in phase contrast and ultraviolet microscope respectively. Plate 6.1A reveals various sized globules of the minor LDPE phase very
FIGURE 6.1: Calorimetry Cell of Du Pont 990 Thermal Analyser
PLATE 6.1: PHASE CONTRAST AND UV MICROGRAPHS OF MELT PRESSED POLYPROPYLENE/MASTERBATCH BLEND
A = PHASE CONTRAST; B = UV
PLATE 6.2: PHASE CONTRAST AND UV MICROGRAPHS OF MELT-PRESSED HDPE/UV MASTERBATCH BLEND
A = PHASE CONTRAST; B = UV
clearly. Although the ultraviolet photomicrograph of an equivalent specimen reveals non-uniform absorber distribution as shown in Plate 6.1B, it unfortunately does not say much regarding the position of the UV absorber with respect to the separate phases observed in Plate 6.1A. The melt pressed sections give too much detail in regions of high UV absorption perhaps because of high thickness of pressed melt sections or because there might be UV absorbing species in the polypropylene base material that makes the blend give rise to intense UV absorption. However, regions of higher ultraviolet absorption are differentiable from among the UV absorbing regions themselves, these regions could be LDPE rich regions. Similarly Plate 6.2A reveals the LDPE as light regions which show high absorption in the UV photomicrograph as revealed in Plate 6.2B.

In order to clarify this, 2 μm thick microtomed sections of the same blend were observed similarly in phase illumination and ultraviolet microscope. Although phase microscopy shows two-phase system (Plate 6.3) consistent with the result shown in Plate 6.1 for a thick melt pressed section, the ultraviolet microscopy of an equivalent thin section does not give enough contrast to resolve the all important question regarding the position of UV additive in relation to low density polyethylene. Based on what is previously known on the distribution of stabilising additives in crystalline polymers (they are rejected within the crystalline regions by the spherulite), it is expected that the UV absorber will be located more in polypropylene which is about 50% crystalline compared to 70% in polyethylene so that if this expectation is attained, the ultraviolet absorber should associate more with polypropylene. On the other hand there are two possible reasons why the absorber could have remained largely in the low density polyethylene rather than polypropylene. Polypropylene crystallises earlier than the masterbatch base so that before ever the LDPE starts to crystallise, polypropylene had already pushed off some of the absorber within the polypropylene phase thus creating a differential distribution. The other possible explanation against absorber preference for polypropylene is that when the two polymers are inadequately mixed, it could not
PLATE 6.3: PHASE CONTRAST MICROGRAPH OF A SECTION OF POLYPROPYLENE/UV MASTERBATCH BLEND
be surprising to have high absorbing regions within the LDPE phase as it originally has 1.3% ultraviolet absorber concentration.

b) **0.2 MFI HDPE/UV Masterbatch Blend**

Plate 6.4 shows low temperature microtomed sections of 0.2 MFI HDPE extruded at low temperature/low shear and respectively examined in phase contrast illumination and ultraviolet microscopy. The light rod like structure in Plate 6.4A is the low density polyethylene while the matrix is the HDPE. Compared to Plate 6.4B, which is a section of the same blend seen in ultraviolet light, it can be seen that high ultraviolet absorbing regions correspond to the low density polyethylene phase. So phase microscopy shows that the masterbatch base and the low MFI HDPE are not miscible while the ultraviolet microscopy shows that the UV absorber prefers to be associated with the LDPE.

c) **6.0 MFI HDPE/Pigment Masterbatch Blend**

Plate 6.5 shows a phase contrast photomicrograph of 6.0 MFI HDPE/LDPE pigment masterbatch blend. The light areas represent the low density polyethylene phase. Although it is difficult to reach an absolute conclusion on dispersion of pigment particles with the polyblend in relation to their position within the separate phases, it can apparently be seen that the pigment particles have no special preference for either the small particles of the LDPE masterbatch base or the big particles of the base polymer. Strictly speaking, the LDPE phase appears to have been stripped bare of pigment particles.

6.3.2 **Isothermal Crystallisation**

One of the principal aims of this work as stated earlier has been to find out what happens to particles of the low molecular weight additive base and pigment particles under crystallisation conditions. Plate 6.6 shows a polarised light photomicrograph of masterbatch pigmented polypropylene which has been isothermally crystallised for 3 hours at 140°C.
PLATE 6.4: PHASE CONTRAST AND UV MICROGRAPHS OF SECTIONS OF HDPE/UV MASTERBATCH BLEND
(A = PHASE CONTRAST; B = UV)
PLATE 6.5: PHASE CONTRAST PHOTOMICROGRAPH OF MELT PRESSED SAMPLE OF POLYPROPYLENE/PIGMENT MASTERBATCH
PLATE 6.6: POLARISED LIGHT PHOTOMICROGRAPH OF ISOTHERMALLY CRYSTALLISED POLYPROPYLENE/UV MASTERBATCH BLEND
It can be seen from this photomicrograph that particles of the order of 2-5 μm in size are seen aligned at spherulite boundaries and also distributed within the spherulite. Larger particles of the type referred to above of the order of 10 μm are observable within some of the spherulite structures.

It is tempting to interpret these particles at the spherulite boundaries and within as particles of the masterbatch base which have been squeezed out to spherulite boundaries during crystallisation and those which escaped the effect of the force imposed on the particles during growth. This temptation is reinforced by the thermogram of the polypropylene copolymer shown in Figure 6.2(a) which does not show any polyethylene peak. The melting point of the copolymer from the thermogram ~163°C indicates that the ethylene must have been in very small proportions not to have influenced the melting point of polypropylene. It may well be therefore that what we are seeing in Plate 6.6 is the LDPE masterbatch base.

On the other hand, because the sample is a copolymer, it is also quite possible that what is being seen is the ethylene rich phase of the copolymer. This is because the ethylene in a polypropylene copolymer is known to occur as droplets when a sample of the copolymer is slow cooled.

Plate 6.7A is a polarised light photomicrograph of polypropylene and UV masterbatch isothermally crystallised under the same conditions as the sample shown in Plate 6.6. Identical results (i.e. particles at spherulite boundaries and within the spherulites) as was obtained for polypropylene/pigment masterbatch blend are observed. Similar experiments were designed and performed for high density polyethylene/UV masterbatch blend. As can be seen in Plate 6.7B, the small and numerous spherulites do not offer a chance of relating what is seen here to what was observed in the case of polypropylene blends.
PLATE 6.7: POLARISED LIGHT PHOTOMICROGRAPHS OF ISOETHERMALLY CRYSTALLISED POLYPROPYLENE/UV MASTERBATCH BLENDS (A = POLYPROPYLENE, B = POLYETHYLENE)
If these particles in the case of polypropylene blends are LDPE from the masterbatch, then the result is very significant because it can influence the mechanical properties of the blend. The particles at the boundaries of spherulites and within the spherulites can serve as stress concentrators and failure can very easily start off and propagate from such points.

6.3.3 Bright Field Optical Microscopy for Qualitative Assessment of Pigment Dispersion in Polypropylene and Varying Grades of High Density Polyethylene

A bright field microscopic examination of pigmented polypropylene and three other grades of high density polyethylene extruded at varying processing conditions was undertaken. The idea was to find out the effect of expected varying degrees of miscibility between the masterbatch base and different melt flow index HDPE on pigment dispersion. Also sought is the effect of processing on the degree of dispersion in the blends.

Plates 6.8, 6.9 and 6.10 show comparisons of photomicrographs of each of 6.0 MFI, 0.2 MFI high density polyethylenes and polypropylene respectively extruded at low temperature/low shear, low temperature/high shear, and high temperature/high shear conditions. It can be seen from these that increased shear improves the blending operation for all blends but apparently without a significant effect on dispersion (i.e. the particle size distribution). A cross comparison of the three different polyolefins shown in Plates 6.8, 6.9 and 6.10 reveal that at low temperature/low shear rate and low temperature/high shear rate respectively, pigment blending is distinctly poorer for the 0.2 MFI HDPE and polypropylene compared to the 6.0 MFI HDPE. Indeed, dispersion of pigment masterbatch in polypropylene is atrociously bad. The progressively poorer dispersion in the high MFI, low MFI HDPE and polypropylene correlates with the expected greater difficulty in the mixing of the low molecular weight pigment-base with base polymers of high melt viscosities.
Low temp/low shear rate 100 µm

High temp/high shear rate 100 µm

Low temp/high shear rate 100 µm
PLATE 6.9: TRANSMITTED BRIGHT-FIELD MICROGRAPHS OF MASTERBATCH PIGMENTED 6.0 MFI HDPE EXTRUDED AT VARYING CONDITIONS
PLATE 6.10: TRANSMITTED BRIGHT-FIELD MICROGRAPHS OF MASTERBATCH PIGMENTED POLYPROPYLENE EXTRUDED AT VARYING CONDITIONS
6.3.4 Differential Thermal Analysis (DTA)

The use of DTA in the study of polymeric blends has been extensively described in the literature. More recently, several authors \(97,136\) have applied DTA to polyolefin blends and have suggested that detection of crystalline melting point appears to be the most unambiguous criteria for miscibility determination and that comparison of obtained values with individual component crystalline melting points gives some idea of the degree of miscibility. They also suggested that for heterogeneous blends, DTA curves show an unchanged summation of the individual responses of the blend constituents. Homogeneous or miscible blends may give either a single crystalline melting point at one of the blend components depending on the blend proportions or a single crystalline melting point at some intermediate level. In other words, 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.

As fusion in semi-crystalline high polymers invariably takes place over a range of temperatures, the total disappearance of crystallinity at a sharply defined temperature is usually taken as the "melting point". The melting point may be read from the position of the peak in the thermogram. The crystalline melting points as obtained from the position of the peak in the thermogram are shown in Table 6.2.

Thermograms of the two polyethylenes, polypropylene and masterbatch used are shown in Figure 6.2. It is interesting to note that although the polypropylene used is a copolymer, the thermogram shown in Figure 6.2 does not show the ethylene copolymer which means that it must have been in a very small amount. The LDPE peaks picked up in Figures 6.3 to 6.5 must be the masterbatch base. The thermograms obtained for the 6.0 MFI HDPE and UV absorber loaded LDPE blend which have been extruded at low temperature/low shear rate and low temperature/high
## Table 6.2: Crystalline Melting Points of Polyolefin Blends

<table>
<thead>
<tr>
<th>HDPE-1 MFI = 6.0</th>
<th>HDPE-2 MFI = 0.2</th>
<th>PP</th>
<th>LDPE</th>
<th>BLEND 1</th>
<th>BLEND 2</th>
<th>BLEND 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Base Polymer</td>
<td>MB Base</td>
<td>Base Polymer</td>
</tr>
<tr>
<td>135</td>
<td>135</td>
<td>164</td>
<td>111</td>
<td>(a) 130</td>
<td>114</td>
<td>135</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(b) 130</td>
<td>105</td>
<td>132.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(c) 135</td>
<td>107</td>
<td>135</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(d) 132</td>
<td>116</td>
<td>134</td>
</tr>
</tbody>
</table>

**Blend 1:**

a) HDPE, 6.0 MFI/LDPE MB extruded @ low temp/low shear rate  
b) HDPE, 6.0 MFI/LDPE MB extruded @ low temp/high shear rate  
c) HDPE, 6.0 MFI/LDPE MB extruded @ low temp/low shear and quenched at 4°C  
d) HDPE, 6.0 MFI/LDPE MB extruded @ low temp/high shear and quenched at 4°C

**Blend 2:**

a) HDPE, 0.2 MFI/LDPE MB extruded @ low temp/low shear rate  
b) HDPE, 0.2 MFI/LDPE MB extruded @ low temp/high shear rate  
c) HDPE, 0.2 MFI/LDPE MB extruded @ low temp/low shear rate and quenched  
d) HDPE, 0.2 MFI/LDPE MB extruded @ low temp/high shear rate and quenched

**Blend 3:**

a) PP/LDPE MB extruded @ low temp/low shear rate  
b) PP/LDPE MB extruded @ low temp/high shear rate  
c) PP/LDPE MB extruded @ low temp/low shear rate and quenched  
d) PP/LDPE MB extruded @ low temp/high shear rate and quenched
FIGURE 6.2: Melting Point of Base Polymers and Masterbatch (°C)
shear rate are shown in Figure 6.3. There are clearly double and depressed crystalline melting points for each of the blends. The low temperature/high shear rate extrudate however gives a broad crystalline melting point peak for the LDPE component compared to the sharp peak obtained for the same component in the case of the low temperature/low shear rate extrudate blend. This suggests that there is a higher level of molecular mixing in the former which prevents separate component crystallisation. This observation correlates well with the results and interpretation of the ultraviolet microscopy work described earlier on in Chapter 3 (Section 3.4.1 and Plate 3.4). The programme cooling curve for the same blend also shown in Figure 6.3 shows that the low temperature/high shear rate extrudate blend supercools at a temperature of 107°C about 2°C lower than the low temperature/low shear rate blend thus suggesting the nucleation of one of the blend components by the other.

The thermograms in Figures 6.4 and 6.5 are those of 33.3% by weight of UV masterbatch to 66.7% 0.2 MFI HDPE and same weight ratios of UV masterbatch and polypropylene respectively extruded at low temperature/low shear rate and low temperature/high shear rate. The melting peaks of the masterbatch in the two blends of 0.2 MFI HDPE retain similar shapes and area with characteristics that are quite different from the peaks obtained in the case of 6.0 MFI HDPE blend. This suggests that the LDPE and HDPE DTA curves for 0.2 MFI/masterbatch blend show an unchanged summation of the individual responses of the blend constituents and are therefore heterogeneous even at the higher shear rate. This again correlates well with the UV microscopy results shown in Plates 3.5 and 3.6. Similarly, the thermogram of polypropylene and masterbatch blend (Figure 6.5) show an unchanged summation of the individual responses of the blend components.

Quench extrudates of the specimens discussed above show similar trends with the base polymer in the high MFI HDPE blend showing a slightly more depressed melting peak at higher shear rate.
FIGURE 6.3: (a) Low Temperature/Low Shear Rate 6.0 MFI HDPE
(b) Low Temperature/High Shear Rate 6.0 MFI HDPE
Thermograms of Extrudates of 0.2 MFI HDPE.

FIGURE 5.4: (a) Low Temperature/Low Shear Rate 0.2 MFI HDPE

(b) Low Temperature/High Shear Rate-0.2 MFI HDPE
FIGURE 6.5: Thermograms of Extrudates of Polypropylene Masterbatch Blend

(a) Low temperature/low shear rate (PP)
(b) Low temperature/high shear rate
(c) High temperature/high shear rate
PLATE 6.11: SCANNING ELECTRON MICROGRAPHS OF PIGMENTED POLYPROPYLENE ETCHED AT VARIOUS TIMES IN BOILING XYLENE:

A = etched 30 seconds; B = etched 30 minutes, and C = etched 1 hour
6.3.5 Scanning Electron Microscopy

Scanning electron microscopy of etched samples prepared as previously described did not give any significant contribution to the solution of the problem, particularly for the HDPE/pigment masterbatch blend.

Scanning electron photomicrographs of etched polypropylene/pigment masterbatch blends are shown in Plate 6.11. It is easily seen that the specimens etched for 10 seconds, 30 minutes and 1 hour respectively contain a lot of voids. It is possible that these voids are due to the holes left by either a differential attack on the LDPE masterbatch base or pigment additive by the solvent used to etch the blend. However, the latter is less likely because the masterbatch contained mostly inorganic additives (see Table 2.1 for components of drab green masterbatch). The only non-inorganic being α-copper phthalocyanine which is an organometallic and consists of only 1.645% of the pigment components in the masterbatch.

If these holes are due to differential attack of solvent on the LDPE, the result correlates with microscopic and DTA analysis results that the masterbatch base is not compatible with the base polymer and should be used as additive base with great care.

6.4 CONCLUSIONS

1. Phase contrast microscopy coupled with ultraviolet microscopy leads to the conclusion that the UV absorber incorporated into polyolefins by the use of an LDPE masterbatch remains largely with the LDPE phase. This is illustrated by Plates 6.1, 6.2 and 6.4.

2. Pigment particles on the other hand do not have a special preference for the LDPE masterbatch base as is the case for UV absorber. This is illustrated by Plate 6.5 where the pigment particles are randomly distributed regardless of phase.
3. Isothermal crystallisation of polypropylene and masterbatch blend at 140°C supported by thermal analysis results of the base polymer (i.e. polypropylene copolymer) suggest that the LDPE is squeezed out to the spherulite boundary during crystallisation. See Plates 6.6 and 6.7A. However, this conclusion is tentative because the ethylene copolymer contained in the polypropylene is known to crystallise as droplets in a situation like this and the particles at the boundary could have been the ethylene copolymer.

4. The use of LDPE as a base for pigment masterbatch for purposes of colouring polypropylene is inadequate as demonstrated by the very poor pigment distribution at all the processing conditions studied and shown in Plate 6.10.

5. Differential thermal analysis shows that the LDPE masterbatch base and the base polymer exist as separate phases in the blend. This is illustrated by Figure 6.4.
CHAPTER 7
GENERAL REVIEW, CONCLUSIONS AND RECOMMENDATIONS

7.1 GENERAL REVIEW

The field of additive dispersion in polyolefins was chosen for further research because of the present need for greater understanding of the relationship between degree of additive dispersion and miscibility of natural polymers and the low molecular weight masterbatch base. Secondly, the current procedures for the determination of degree of additive dispersion are either qualitative, tedious or based on a high cost image analysing equipment such as the Quantimet. The Quantimet is a versatile piece of equipment for work in a whole range of microstructural problem solving and therefore not economical for small scale manufacturers. This makes it necessary that a low cost and fairly fast procedure for assessing additive dispersion quantitatively be developed. Additionally, a review of the literature has revealed that most of the quantitative dispersion models proposed have been based on the dispersion of carbon blacks in rubbers. Although it can be argued that these methods can be applied to additives in plastics, the methods are not always applicable because of the difference in sample preparation methods between rubbers and plastics. A lot more is known regarding the dispersion of blacks in rubbers than is of additives in plastics. More importantly, investigation of the degree of additive dispersion in masterbatches is largely unattempted.

Additive dispersion in eight different pigment masterbatches and one UV absorber masterbatch have been investigated. Also investigated is the degree of dispersion of one of the pigment masterbatches in two grades of high density polyethylene and polypropylene and also the dispersion of UV masterbatch in the same set of polymers. Blends of the polymers and the masterbatch were manufactured by melt mixing in an extruder under varying processing conditions viz low temperature/low shear rate, low temperature/high shear rate and high
temperature/high shear rate.

The resultant degree of dispersion within the blends has been investigated by four major techniques - X-ray microradiography, optical microscopy, ultraviolet microscopy (in the case of UV absorber) and photometer method. Some of these techniques yielded quantitative results in addition to qualitative assessment results. The ultraviolet additive dispersion studies were purely qualitative. From the results obtained, it has been possible to make recommendations on the use of masterbatches with polymers of varying molecular weights and also propose a model for a quantitative measurement of pigment dispersion in polyolefins.

Finally, the significance of conclusions drawn from UV photomicrographs of sections of the polyolefins was investigated by a simulated sunlight exposure measurement using compression moulded films.

The relationship between dispersion and microstructure of the blends was also investigated by various techniques viz transmitted light and phase contrast microscopy, isothermal crystallisation, differential thermal analysis and scanning electron microscopy.

7.2 GENERAL CONCLUSIONS

The main conclusions of the findings can be summarised as follows:

1. Pigment dispersion in low density polyethylene based pigment masterbatches is invariably bad. Significant results from the masterbatch studies are that:
   a) agglomerate sizes of up to 300 μm (maximum diameter) are present in some masterbatches;
   b) ferric oxide, barium sulphate, zinc sulphide, cadmium sulphide and β-copper phthalocyanines are poorly dispersed in an LDPE masterbatch base.
c) ferric oxide has the poorest dispersibility of all the heavy metal pigment components;

d) organometallic pigments even as small proportions of the pigment component show significant agglomeration in LDPE based masterbatches and therefore can be said to have a lower dispersibility than inorganics;

e) benzidine yellow (an all organic pigment) dispersed atrociously in LDPE base.

2. The above conclusions lead to a significant conclusion regarding the method employed in the manufacture of masterbatches viz: enough shear forces are not generated by the heavy duty internal mixers used in their manufacture, since very large agglomerates were observed in all the masterbatches.

3. In contrast to poor pigment dispersion in LDPE masterbatches, ultraviolet absorber distribution in the same type of carrier is uniformly distributed. I say distributed because the question of their dispersion has not been covered. Suggestions to this effect are discussed under recommendations.

4. The general belief in the plastic manufacturing industry that once a masterbatch is used to incorporate an additive is not true. This work has shown that at least with LDPE carriers, the manufacturer would have to work hard to obtain a good dispersion in the product.

5. High density polyethylene and polypropylene generally show very poor UV absorber distribution with LDPE UV masterbatches with all of them showing streaks or bands of undistributed additive. Other conclusions regarding UV absorber distribution in polyolefins are:
i) that the degree of distribution is dependent on the MFI of HDPE and therefore on polymer molecular weight distribution being poorer in the low MFI HDPE;

ii) increased molecular mixing (as was observed in the case of the masterbatch and 6.0 MFI HDPE at increased shear rate) improves distribution and therefore photostability.

6. Phase contrast microscopy shows that the streaks or bands of highly absorbing areas in the polyolefin extrudates are LDPE rich regions leading to the conclusion that the UV absorbers prefer to be associated with the masterbatch.

7. Increased UV absorber distribution increases the photostability of HDPE extrudates by as much as two times.

8. Isothermal crystallisation of polypropylene squeezes low molecular weight particles (which could be the ethylene copolymer of the polypropylene or LDPE carrier) to spherulite boundaries. For reasons stated in the text, we are tempted to think that these particles are LDPE masterbatch carriers.

9. The degree of dispersion of pigment masterbatches is not significantly affected by variation in the melt flow indices of HDPE, while in polypropylene, the masterbatch forms pigment streaks separated by regions not containing any pigment.

10. A semi-automatic procedure for the assessment of the degree of pigment dispersion in polyolefins has been developed. The setup is low cost and can be used by small scale manufacturers on a routine basis.
7.3 **RECOMMENDATIONS**

The study of the dispersion of pigment in low density polyethylene based masterbatches covered in Chapter 2 of the present work calls for a reassessment of masterbatch production processes. It is known that masterbatches are manufactured by dispersing high loadings of additives in a carrier using heavy duty internal mixers which are designed to generate enough dispersive forces to disperse additive agglomerates. Results given in Chapter 2 show conclusively that large agglomerates remain undispersed implying that either the dispersive force anticipated from the internal mixer is not attained, or that there are other factors to be considered in the dispersion of pigments in LDPE carriers using an internal mixer. It is therefore recommended that dispersion processes in the production of LDPE masterbatch be examined in more detail.

Sufficient solubility of functional additives in the polymer matrix is a necessary condition for their efficiency in polymer products. For ultraviolet absorbers, this has to be at ambient temperature. Overall there is scattered information regarding the solubility of UV absorbing and other stabilising additives in crystalline polyolefins. The solubility of UV absorbers in polyolefins need therefore to be investigated as a first step to understanding how actually the additives operate and transfer from the masterbatch to the polymer matrix.

The present work reached a number of conclusions that need further investigation. For example, it was concluded that LDPE masterbatch gives poor UV absorber distribution in low MFI (0.2 in this case). HDPE. In view of the fact that products examined by a variety of microscopical techniques were obtained by melt mixing in a single screw extruder, it will be interesting to investigate how the degree of dispersion obtained where a twin screw extruder or a single screw extruder coupled with mixing accessories compares with the result stated here.
The pigment masterbatches studied here are low load (only 3% pigment in LDPE). As stated dispersion in this concentration is indeed poor. The effect of additive load (i.e. additive concentration) on quality of dispersion in the masterbatch could be interesting. For example, increased pigment loading can increase generated shear rate and consequently the degree of dispersion. However, rheological factors are paramount in determining the concentration of additive loading in the carrier, the limiting factor being the viscosity of the mixture. Both cases need to be investigated and possibly correlated. This information can be of great importance to both the product and masterbatch manufacturers.

One very important aspect of masterbatch dispersion studies in products which were originally intended but eventually not covered because of the multiplicity of objectives, is the determination of the extent to which a given masterbatch carrier can be used in a polymer with a whole range of melt flow indices. The practice at the moment is to use a given carrier with a given polymer regardless of difference in melt flow index. A possible route to getting an answer to this is for instance finding out the effect of comparative flow properties of masterbatch and natural polymer on the degree of dispersion, since it can provide the answer to such questions as - which carrier in which polymer and therefore a streamlining of use of masterbatch and polymer.

A quantitative approach to the examination of UV absorber dispersion and distribution in polyolefin will be a good idea as this will remove the inevitable subjectivity in results obtained from qualitative studies. A procedure along lines employed by Scott et al. on the distribution of lignin in wood can clarify some of the points raised in the present study.

The determination of the point of significant agglomeration in a pigmented polyolefin product in the present work was carried out using 5 μm thick sections. It will be interesting to find out how variations in section thicknesses in a given product affect the point at which agglomeration becomes significant.
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APPENDIX

1. DESIGN OF DIE EMPLOYED IN THE EXTRUSION OF POLYOLEFINS
3. (a) Photometric Programming System for Semi-Automatic Pigment Dispersion Measurement

10 DIM A(10), B(10), M1(10), M0(10), M2(10), M(10)
12 DIM X(10)
15 CC = 4933: PC = 49330: PB = 49329: PA = 49328
20 KY = -16384: KS = -16388: R1 = 0: R2 = 0
22 S = 0: OS = CHR$(4)
25 TEXT: HOME
30 UTAB(1): HTAB(8): PRINT "DISPERSION ANALYSIS PROGRAM"
35 UTAB(2): HTAB(8): PRINT "PHOTOGRAPHY-MODEL COMPUTER STAGE"
40 UTAB(3): HTAB(12): PRINT "CONTROL VERSION"
45 UTAB(4): HTAB(12): PRINT ".............."
90 UTAB(20): PRINT "PRESS ANY KEY TO CONTINUE": GET AS
100 GOTO 100
110 HOME: REM AUTO RUN
112 R1 = 0: R2 = 0
115 FOR W = 1 TO 10
120 Z1 = INT (4 + RND (1) + 1)
130 Z2 = INT (2 + RND (1) + 1)
140 Z3 = INT (2 + RND (1) + 1)
150 Z4 = INT (2 + RND (1) + 1)
220 IF Z4 = 1 THEN 250
230 A(W) = Z1: B(W) = 1
240 GOTO 260
250 B(W) = Z1: A(W) = 1
260 IF Z2 = 1 THEN M1(W) = 66: M0(W) = 32
270 IF Z2 = 2 THEN M1(W) = 114: M0(W) = 40
280 IF Z3 = 1 THEN M2(W) = 66: M0(W) = 2
290 IF Z3 = 2 THEN M2(W) = 87: M0(W) = 3
310 PRINT Z1, Z2, Z3, Z4
340 PRINT
350 PRINT A(W) ;":(W)
360 PRINT
350 PRINT M1(W), M0(W), M2(W), M0(W)
360 PRINT: NEXT
400 INPUT "ENTER SPEED CODE (1...260)"; S
465 HOME
410 REM 3.T.MOTOR DRIVER
415 POKE CC,148: POKE PC,255
420 FOR W = 1 TO 10
480 FOR T = 1 TO 50
580 REM DATA LOG
580 FOR N = 1 TO A(W)
590 POKE PC, M1(W)
600 FOR T = 0 TO S: NEXT
10 POKE PC, M0(W)
710 IF M0(W) = 32 THEN R1 = R1 + 1
710 IF M0(W) = 40 THEN R1 = R1 - 1
716 UTAB(16): HTAB(12): PRINT "
717 UTAB(16): HTAB(12): PRINT R1
720 NEXT
730 FOR N = 1 TO B(W)
740 POKE PC, M2(W)
750 FOR T = 0 TO S: NEXT
760 POKE PC, M0(W)
762 IF M0(W) = 2 THEN R2 = R2 + 1
764 IF M0(W) = 3 THEN R2 = R2 - 1
765 UTAB(16): HTAB(12): PRINT "
REM UTAB (18): HTAB (12): PRINT A$.
770 NEXT
780 NEXT
785 PRINT "": REM F**,I.
800 NEXT
805 PRINT "": PRINT "".
810 UTAB (10): PRINT "TEN SCANS DONE"
815 UTAB (22): PRINT "PRESS ANY KEY": SET A$.
820 GOTO 1000
1000 HOME : REM MENU
1010 UTAB (1): HTAB (8): PRINT "DISPERSION ANALYSIS PROGRAM"
1020 UTAB (2): HTAB (8): PRINT "PHOTOHETER-COMPUTER STAGE"
1030 UTAB (3): HTAB (12): PRINT "CONTROL VERSION"
1040 UTAB (4): HTAB (12): PRINT "……………".
1050 UTAB (4): UTAB (8): PRINT "SELECT MODE"
1060 HTAB (7): UTAB (10): PRINT "(1) SET UP"
1070 HTAB (7): UTAB (12): PRINT "(2) AUTO RUN"
1080 HTAB (7): UTAB (14): PRINT "(3) RF RUN"
1090 HTAB (7): UTAB (16): PRINT "(4) PRINT RESULTS"
1100 HTAB (7): UTAB (18): PRINT "(5) SAMPLE SCAN"
1110 HTAB (7): UTAB (20): PRINT "(6) TO STOP"
1120 PRINT : PRINT
1130 INPUT " MODE NO. ": F
1140 IF F = 1 THEN 1500
1150 IF F = 2 THEN 110
1160 IF F = 3 THEN 2000
1170 IF F = 4 THEN 2500
1180 IF F = 5 THEN 3000
1190 IF F = 6 THEN 3500
1200 GOTO 1010
1210 REM SET UP
1220 POKE CC,148: POKE PC,255
1230 HOME
1240 R1 = 0: R2 = 0
1250 HTAB (14): UTAB (1): PRINT "STAGE SET UP"
1260 HTAB (14): UTAB (2): PRINT "……………"
1270 HTAB (18): UTAB (4): PRINT "Y X"
1280 FOR I = 1 TO 9
1290 HTAB (20): UTAB (4 + I): PRINT "!
1300 NEXT
1310 HTAB (12): UTAB (8): PRINT "K _____________________________x"
1320 HTAB (18): UTAB (12): PRINT "R Y"
1330 PRINT : PRINT : PRINT
1340 PRINT "PRESS LETTER TO MOVE"
1350 PRINT
1360 PRINT "PRESS C TO CONTINUE"
1370 GOSUB 4210: REM KEY BOARD
1370 POKE KS,0
1380 IF KB = 195 THEN 1900
1390 IF KB = 193 THEN 1810
1400 IF KB = 194 THEN 1830
1410 IF KB = 216 THEN 1850
1420 IF KB = 217 THEN 1870
1430 GOTO 1510
1440 K2 = 200: GOSUB 4010
1450 GOTO 1510
1830 K1 = 200; GOSUB 4050
1840 GOTO 1510
1850 K2 = 200; GOSUB 4110
1860 GOTO 1510
1870 K1 = 200; GOSUB 4170
1880 GOTO 1510
2000 HOME: FLASH
2010 HTAB (15); VTAB (4); PRINT "RE-TRACING"
2020 Normal
2030 PRINT: PRINT
2110 IF R1 < 0 THEN 2210
2120 :IF R1 > 0 THEN 2260
2130 IF R2 < 0 THEN 2310
2140 :IF R2 > 0 THEN 2360
2150 GOTO 420
2160 K1 = ABS (R1)
2220 GOSUB 4170
2225 R1 = 0
2230 GOTO 2130
2260 K1 = R1
2270 GOSUB 4050
2275 R1 = 0
2280 GOTO 2130
2310 K2 = ABS (R2)
2320 GOSUB 4110
2325 R2 = 0
2330 GOTO 420
2350 K2 = R2
2370 GOSUB 4010
2375 R2 = 0
2380 GOTO 420_...
2500 REM DATA PROCESSING
2505 HOME
2510 UTAB (8); PRINT ".";
2515 INPUT "INSERT DATA DISC ** ENTER FILE NAME "; FS
2520 PRINT D$; "OPEN"; FS
2530 PRINT D$; "READ"; FS
2540 INPUT NR
2545 SZ = 0
2550 FOR I = 1 TO NR
2552 INPUT Z(I)
2554 SZ = SZ + Z(I)
2560 NEXT
2570 PRINT D$; "CLOSE"; FS
2580 PR = SZ / NR
2600 FOR I = 1 TO NR STEP 5
2610 PRINT Z(I); Z(I + 1); Z(I + 2); Z(I + 3); Z(I + 4)
2620 NEXT
2630 PRINT: PRINT "MEAN PR= "; PR
2645 PRINT: PRINT: PRINT "PRESS ANY KEY"
2646 GET A2$
2647 HOME
2650 GOTO 1010
3000 REM: SAMPLE SCAN MODE
3005 HOME: R1 = 0: R2 = 0: N = 0
3010 HTAB (14): UTAB (1): PRINT "SAMPLE SCAN"
3020 HTAB (14): UTAB (2): PRINT "............."
3030 HTAB (8): UTAB (6): PRINT "........................"
3040 FOR I = 1 TO 4
3050 HTAB (32): UTAB (1 + B): PRINT "."
3060 NEXT
3070 HTAB (8): UTAB (10): PRINT "........................"
3075 UTAB (12): PRINT "."
3080 INPUT "SCAN LENGTH "; SL
3085 PRINT
3090 INPUT "READING INTERVAL "; RI
3095 PRINT
3100 INPUT "SCAN WIDTH "; SW
3105 PRINT
3110 INPUT "NUMBER OF SCANS "; NS
3115 PRINT
3120 INPUT "EDIT(Y/N)... "; E$
3130 IF E$ = "Y" THEN 3005
3140 SL = SL + 2.5: RI = RI + 2.5: SW = SW + 2.5: TR = SL / RI
3150 POKE CC, 144: POKE PC, 247
3155 REM ********************
3160 INPUT "DATA FILE NAME "; F$
3170 HOME: NR = 0: UTAB (8): PRINT "FOCUS H/SCOPE"
3175 PRINT "SWITCH ON & SET CONTROL PANEL": PRINT : PRINT : PRINT "PRESS ANY KEY WHEN READY": GET A$
3180 MH = 114: ML = 40
3190 GOSUB 3220
3200 IF N = NS THEN 3400
3210 MH = 67: ML = 3
3220 GOSUB 3280
3230 MH = 36: ML = 32
3240 GOSUB 3320
3250 IF N = NS THEN 3400
3260 MH = 67: ML = 3
3270 GOSUB 3280
3280 GOTO 3220
3290 REM ********************
3300 FOR G = 1 TO SW
3310 POKE PC, MH
3320 POKE PC, ML
3330 R2 = R2 - 1
3340 NEXT
3350 RETURN
3360 N = N + 1
3370 REM PRINT 
3380 REM READ DATA
3390 GOSUB 4500
3400 FOR I = 1 TO TR
3410 FOR G = 1 TO RI
3420 POKE PC, MH
3430 POKE PC, ML
3440 IF ML = 40 THEN R1 = R1 - 1
3450 IF ML = 32 THEN R1 = R1 + 1
3460 NEXT
3470 REM PRINT 
3480 REM READ DATA
3375 GOSUB 4500
3380 NEXT
3385 RETURN
3400 GOSUB 4700
3405 K2 = ABS (R2)
3410 GOSUB 4110
3415 IF R1 = 0 THEN 3430
3420 K1 = ABS (R1)
3425 GOSUB 4170
3430 PRINT
3432 PR# 1
3434 PRINT "PRINT : PRINT : PRINT FS"
3436 PRINT SL * 2.5, R1 * 2.5, SW * 2.5, NS
3438 PRM 0
3440 INPUT " RE-SCAN (Y/N) " ; E$
3450 IF E$ = "Y" THEN N = 0: GOTO 3216
3460 GOTO 1000
3470 HOME:
3480 HTAB (18); UTAB (10); PRINT "*END*"
3500 END
3510 PRINT "H2 ..................CHS"
3515 FOR I = 1 TO K2
3520 POKE PC.67
3525 POKE PC.3
3530 NEXT
3535 RETURN
3540 PRINT "H1 ..................CHS"
3545 FOR I = 1 TO K1
3550 POKE PC.114
3555 POKE PC.40
3560 NEXT
3565 PRINT "H2 ..................CHS"
3570 FOR I = 1 TO K2
3575 FOR I = 1 TO K1
3580 POKE PC.96
3585 POKE PC.32
3590 NEXT
3595 RETURN
3600 PRINT "H1 ..................CHS"
3610 FOR I = 1 TO K1
3615 FOR I = 1 TO K2
3620 POKE PC.86
3625 POKE PC.2
3630 NEXT
3635 RETURN
3640 PRINT "H1 ..................CHS"
3645 FOR I = 1 TO K1
3650 POKE PC.96
3655 POKE PC.32
3660 NEXT
3665 RETURN
3670 REM KEY BOARD
3680 KB = PEEK (KY)
3690 IF KB > 192 THEN RETURN
3700 GOTO 4220
3710 REM DATA ACQUISITION
3720 NR = NR + 1
3730 X = PEEK (PA); U = PEEK (PB); Y = INT (X / 16); L = (10 + Y + (X / 16) - Y) * 16 + 10
3750 V1 = INT (U / 64)
3760 IF V1 = 1 THEN K = K + 1: U = U + 64
3770 IF U1 = 0 THEN K = 1
4550 U2 = INT (U / 32)
4560 IF U2 = 1 THEN U = U - 32
4570 E = INT (U / 16): W = 10 * E + (U / 16 - E) + 16
4580 G1 = K * (10 * W + L); Z(NR) = G1
4590 RETURN
4600 REM OPEN DATA FILE
4710 PRINT D$, "OPEN"; F$
4720 PRINT D$, "WRITE"; F$
4725 PRINT NR
4730 FOR I = 1 TO NR
4740 PRINT Z(I); NEXT
4750 PRINT D$, "CLOSE"; F$
4760 RETURN
3. (b) Program for Calculating Standard Deviation from Photometer Readings

5 DIM A(8)
10 D$ = CHR$(4)
30 HOME
35 DIM NK(400), MEAN(10), STD(10)
36 DIM P(490)
37 FOR X = 1 TO
38 READ AK(X)
40 UTAB (8); PRINT
50 INPUT "INSERT DATA DISC ** ENTER FILE NAME"; F$
50 PRINT D$; "OPEN"; F$
70 PRINT D$; "READ"; F$
80 INPUT NR
90 FOR I = 1 TO NR
100 INPUT NK(I)
110 NEXT
120 PRINT D$; "CLOSE"; F$
130 REM NUMBER OF PARTICLES PER UNIT AREA PROGRAM
180 REM INITIALIZE QUANTITIES
190 SUM1 = 0
200 SUM2 = 0
210 REM SET UP LOOP TO VALUES
220 REM AND CALCULATE SPECIFIED QUANTITIES
230 FOR I = 1 TO NR
240 P(I) = NK(I) / A(X)
250 SUM1 = SUM1 + P(I)
260 SUM2 = SUM2 + P(I) * 2
270 NEXT
280 REM CALCULATE MEAN AND STD
290 MEAN(X) = SUM1 / NR
300 STD(X) = (SUM2 * 2 - (SUM1 / NR) * 2) / (NR - 1)
305 HOME
310 NEXT X
320 REM PRINT RESULTS
330 HTAB 4; HTAB 8; PRINT "A MEAN STD"
340 FOR I = 1 TO
350 PRINT ; HTAB 8; PRINT I; TAB(1); MEAN(I); TAB(25); STD(I)
360 NEXT I
370 REM AREA DATA IN MICRONS
380 DATA 144.0, 256.0, 400.0, 1444.0, 1600.0, 3600.0