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Orientation of polymers in die-drawing with superimposed transverse shear deformations

by

Shaun Mannell

A thesis submitted in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy of Loughborough University

September 1997

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ABSTRACT

For polymer materials to compete with metals in engineering applications, they must possess adequate mechanical properties. Some crystalline plastics are able to offer enhanced properties but these tend to be very expensive. Often a viable alternative is to modify commodity polymers through further processing techniques which introduce molecular orientation, thereby producing high modulus polymers.

Molecular orientation of polymers can be achieved by solid-state deformation through tensile drawing, extrusion and die-drawing. The present work is concerned with solid-state die-drawing. Whilst drawn polymers show clear improvements to the mechanical properties in the longitudinal direction, their transverse properties are very poor with compressive failure and fibrillation problems limiting the application of such products.

The work will show how hoopwise transverse orientation can be achieved by introducing a rotational shear to the conical flow deformation mechanism by using appropriately designed dies. It will demonstrate how this modification improves the drawn products and provides much evidence that even small amounts of transverse orientation superimposed upon the much larger longitudinal orientation will give substantial mechanical improvement to the transverse direction at little expense to the longitudinal direction. In particular, improvements in splitting resistance have been found. Further advantages in terms of process control are also shown, improvements in dimension stability and a reduction in the peak drawing force being key features.

Birefringence measurements on sections of drawn products show that orientation developed using rotational shearing dies lies at an angle to the die axis depending on the radial distance from the axis. The transverse orientation is zero at the axis and becomes a maximum at the largest radius.

Mechanical testing and thermal analysis further support the existence of transverse orientation in the drawn products.

Analysis of the deformation geometry will show how the distribution of deformation changes with the addition of rotational shear. A consideration of work done during the process accounts for the characteristics of the process.

Dimensional, optical and thermal properties of properties of material taken from the deformation region in the dies have been measured. They agree closely with those predicted from a knowledge of the deformation mechanism.
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Chapter 1 Introduction

The rapid development of the polymer industry is due mainly to the ease with which polymers can be processed, making them suitable for mass production. They are relatively inexpensive and offer a wide range of properties. Their volume usage worldwide now exceeds that of metals.

Compared with metals, the low stiffness and strength of polymers tends to limit their use for many engineering products. Some crystalline plastics, so called 'engineering thermoplastics', can offer much enhanced properties but these materials tend to be very expensive. A viable route is to enhance the properties of commodity thermoplastics through processing techniques which introduce orientation, thereby producing high modulus polymers.

1.1 POLYMER STRUCTURE

The properties of a polymer are dependent on the nature of the molecular chains, i.e. their structure and length, and their arrangement and interaction. There are two states within which a polymer chain can exist; (1) amorphous, where the chains are randomly coiled and entangled with no regular order, or (2) crystalline, where the molecular chains have a regular arrangement. The particular state in which a polymer chain exists under a given set of conditions depends principally on the molecular energy and the ability of the chains to pack closely together.

Many polymers do not exhibit any crystallinity at all. Where crystallisation occurs, the polymer will exist in a semicrystalline state in which both amorphous and crystalline regions coexist with the crystalline regions, known as crystallites, dispersed within an amorphous matrix. The process of crystallisation never reaches completion due to chain entanglements and so even highly crystalline polymers have some amorphous content. In highly crystalline polymers, molecules order themselves into lamellae which are thin...
plates of crystalline material with molecular alignment through their thickness. These lamellae collect and grow into spherulites. *Figure 1.1(a)* illustrates an amorphous structure and *Figure 1.1(b)* shows a folded chain model for polymer crystallinity. *Figure 1.1(c)* shows the lamellar structure for highly crystalline polymers.

Crystallinity content is dependent on the rate of cooling. Rapid quenching from the melt state produces a more amorphous polymer with substantially reduced mechanical strength and modulus but with enhanced toughness. The degree of crystallinity also depends on the molecular weight, higher molecular weight molecules have more entanglements which hinder the crystallisation process giving a higher amorphous content to the solidified polymer.

Polyethylene is a good example of a semicrystalline polymer, whereas polyethylene terephthalate can exist as either an essentially amorphous or crystalline polymer depending on the conditions under which it solidified. Rapid quenching from the melt does not allow sufficient time for rearrangement of the molecules and crystallisation to occur. This results in an amorphous product with very low crystallinity. Slow cooling on the other hand allows plenty of time for reordering to take place and a highly crystalline polymer to be formed.

### 1.2 POLYMER ORIENTATION

Orientation in the form of permanent molecular alignment is achieved by stretching the polymer in the rubbery or plastic state. It involves molecular arrangements in both crystalline and amorphous regions. The molecules align in the stretch direction and the higher the orientation, the more mutually parallel are the molecules, and the smaller is
the angle formed by them with the stretch axis. Since in theory a fully aligned long-chain polymer would exhibit mechanical properties higher than metals, the improvement in properties is significant even for moderate degrees of orientation. The Young's modulus of cold drawn high-density polyethylene for example can be increased by a factor of 10 or more above that of the bulk isotropic material, approaching a value expected for aluminium or glass fibres. They can exhibit an elastic modulus up to 30-50% of the axial modulus of the perfect crystal.

Monoaxial orientation in polymers is achieved by aligning the chains into one particular direction only. In fibre production, which is a monoaxial process, the alignment is achieved by cold drawing, orientation being in the machine direction. However the enhanced strength and stiffness in this direction is at the expense of the transverse properties which deteriorate rapidly with increasing deformation. Applied loads along the fibre are carried by the strong covalent bonds within the polymer chain, but transversely the loads have to be transmitted by van der Waals bonds which are substantially weaker.

This problem can alleviated by inducing biaxial orientation into the product, a principle which is used in the production of two dimensional products such as films and tapes. The material is stretched in two directions, either simultaneously or sequentially, and the molecules line up in a plane parallel to the stretch plane but within this plane they may occupy a preferential orientation. If the stretching is equi-biaxial then the orientation within this plane will not have a preferred direction and will be random. If the stretching is unbalanced then preferential orientation within the plane will be in the direction of greatest deformation.

As well as the much reported increases in mechanical properties, studies have shown that orientation can also produce a small increase in the melting point of the polymer and there is increasing recognition that it also enhances a number of other properties including, piezo and pyroelectricity, thermal conductivity, general fracture behaviour and resistance to solvents and permeation of gases and vapours.
Oriented polymer sections can be successfully produced by a variety of solid-state deformation techniques, principally of four types; ram extrusion, hydrostatic extrusion, tensile drawing and die-drawing. All the processes except for tensile drawing utilise a conical die to impart the deformation.

Cold drawing is the processes by which the polymer is stretched between two grips and, because of its simplicity, is one of the most well researched areas of solid-state deformation. The process is illustrated in Figure 1.2. The process can be either batch-wise, where the material is stretched between two grips, as in a tensile test, or a continuous process utilising two capstans rotating in the same sense but at different speeds. A good example of the latter is fibre production. A very high degree of orientation can be developed quickly and efficiently using this technique. However, the process does not allow a great deal of control over the final cross-sectional area or shape of the product. These are strongly affected by the material characteristics, processing conditions and initial size and shape of the undrawn material. This process can only be used where precise size and shape of the product are not critical.

The extrusion processes have the ability to produce much larger section products and the die gives greater control over the size and shape. The material contacts the die surface all the way through the die and so, allowing for elastic effects, a die exit-sized and shaped product is obtained. However, a consequence of the dependence of flow stress
with pressure means that these processes are extremely slow. Also, containment within the high pressure apparatus means that they have to be batch processes and for this reason extrusion has not achieved commercial significance. Extrusion is sometimes used for specialist materials or applications where specific orientation is required, which can only be achieved by this route.

It is die-drawing which is of primary interest in this project. Die drawing can offer a good compromise between the speed offered by the tensile drawing processes and the control of the deformation mechanism as in the conical-die processes. The commercial potential of the process has been recognised and as a result it has been extensively investigated over recent years. The process is illustrated schematically in Figure 1.4.

The technique involves pulling an isotropic polymer billet through a shaped conical die to produce the polymer section, reduced in size and containing substantial molecular orientation in the axial direction. In this process, because the working force is applied to the drawn product at the die exit, the billet is free to neck down within the die and will leave the die wall at some point in order to follow a preferred strain and strain-rate path. The final product cross-section will be smaller than that of the die exit and has been found to be highly influenced by the drawing speed. Thus some loss of control
over size and shape is experienced, but not to the degree as in cold drawing. The deformation mechanism is much more favourable than for extrusion and consequently the speed limitations are much reduced. Combining this benefit with continuous production, the commercial advantages of die drawing are obvious.

1.4 COMMERCIAL INTEREST

This project has been set up between the Institute of Polymer Technology and Materials Engineering and Bridon Ropes Limited with the aim of continuing an investigation into the potential of the die-drawing process for producing drawn polymer cores for use in the manufacture of wire rope. Bridon Ropes manufacture a wide range of wire rope utilising various core materials including synthetic or natural fibre and steel.

The construction of a wire rope involves the spinning of steel wires into strands which are then closed over a central core. The wires are drawn using high speed wire drawing machines which may have 10 or more dies, reducing the wire diameter in a series of steps up to draw ratios of 20. There are usually six strands to a rope which consist of several layers of wire spun around a central king wire. The number and size of the wires depends upon the intended use of the rope; large wires offer greater corrosion and abrasion resistance but are relatively inflexible, smaller wires being used where flexibility is important.

Generally steel wire ropes have a steel or fibre core and the main function of this core is to provide a stable support for the strands both during rope construction and under
working conditions. Fibre cores generally consist of man-made fibres of polypropylene although some may still utilise natural fibres. Steel cores can be either a single wire for small ropes or be of a rope construction for larger diameter ropes. They tend to provide better support than fibre cores and the stress distribution throughout the rope is more even.

Due to a demand for synthetic cores with improved performance, Bridon Ropes Limited have developed a method of manufacturing solid polymer cores with a fluted profile, produced using a two stage extrusion. The helical, fluted profile is extruded over a circular polymer core and is generated by rotating the extrusion die. The rate of rotation is determined by the lay of the rope.

Whilst it may be commercially viable to produce larger cores with this extrusion process, where smaller ropes are required the production process is much faster. Not only must the core be manufactured at a faster rate therefore but also it must be able to withstand the larger stresses imposed by these faster speeds without stretching significantly. The die drawing process has the potential to allow both these objectives to be realised.

To successfully manufacture polymer cores of acceptable quality by die drawing, a number of criteria must be satisfied. The main requirements are given below;

- **Size Control.** It must be possible to predict the draw ratio accurately to enable the core size to be controlled within fine limits and ensure uniformity. Previous feasibility studies at Leeds University have shown that shape and size uniformity of the product are difficult to control and vary considerably along the length. It has been suggested
as a target that the variation must be reduced to an acceptable tolerance of ±1% of the
root diameter.

- **Shape Control.** The shape of the core must be consistent.

- **Process Speed.** The speed of production must be maximised whilst maintaining
  product quality. Velocities up to 20 m/min have been shown to be feasible from work
carried out at Leeds University.

- **Tensile Strength.** The tensile strength must be sufficient to withstand the
  manufacturing process.

- **Stiffness.** Whilst it is important that the product is stiff enough to resist undue
  stretching during rope manufacture (which will cause a reduction in cross-section) it
  must not be too great since the rope requires a certain flexibility.

- **Compressive Properties.** The radial compressive properties must be sufficient to resist
  undue deformation. Also continuous bending and compression of the rope core will
  tend to cause fibrillation. This will result in a loss of shape and dimensional stability
  with support to the surrounding strands being much less effective. Splitting resistance
  must be enhanced to minimise this problem.

### 1.5 HYPOTHESIS

The limitations of conventional monoaxial die-drawing are well known. Ultra-high
modulus, high strength polymer materials obtained by die-drawing show many benefits in
terms of longitudinal mechanical properties, but their transverse properties are very poor
with compressive failure and fibrillation problems limiting the application of such
products. There is much evidence that even small amounts of transverse orientation
superimposed upon the much larger longitudinal orientation will substantially improve
the transverse properties of a product at little expense to the longitudinal mechanical
properties. Such improvements could result in much greater use in a wider range of
applications.

It is proposed that it is possible to introduce elements of biaxial orientation to die-
drawing processes which are normally carried out monoaxially. It has been shown by
other workers\textsuperscript{3-13} that shearing processes can affect the molecular orientation produced in
an otherwise extensional deformation and it is believed that this could be a route to
obtaining transverse orientation in die-drawing. This principle is illustrated schematically
in Figure 1.6.
Conical flow leading to monoaxial orientation

Conical flow with shear leading to biaxial orientation

Figure 1.6: (a) Conventional conical flow - straight flow paths. (b) Conical flow with superimposed rotational shear - helical flow paths.

Conventional die drawing uses a straight channel, conical die which causes the material to deform along straight flow paths as shown in (a), resulting in monoaxial orientation. If the die is such that material is forced to deform along a helical path as shown in (b), it should show both a component of orientation in the draw direction and a component of orientation in a hoopwise direction. It is proposed that the hoop orientation will increase from zero at the axis of deformation to a maximum on the surface of the product. The drawn products would show enhanced transverse mechanical properties which can be predicted with a knowledge of the deformation mechanism.

It is anticipated that by introducing shear deformation into the mechanism, the distribution of strain, and hence strain hardening, of the material as it passes through the die would be affected.

The experimental work is to demonstrate how transverse orientation is achieved using an appropriately designed die and the effects of shear components on the deformation mechanism are to be investigated, not only in terms of properties of the drawn products but also from a processing point of view, i.e. process stability and drawing forces. The magnitude and type of any orientation produced is also to be identified.

The investigation aims to explain the changes in the deformation mechanism through a numerical analysis by considering the distribution of forces and work done at points within the die.
1.6 OBJECTIVES

The main objectives of this project work can be summarised as follows:

1. Identify a means by which transverse, hoopwise orientation may be imposed to a polymer when die drawn longitudinally through a conical die. The best material strain and strain rate profile should be recognised in order to achieve optimum orientation in the drawn product.

2. Design and manufacture appropriate dies capable of applying the required deformation profile to the polymer during drawing. A minimum of three dies are required in order to impose varying degrees of rotational deformation (these include one conventional straight die with zero rotational deformation).

3. Conduct an experimental programme to produce die-drawn polymer products of polyethylene and polyethylene terephthalate using the above dies under different processing conditions. The main process variables for the experimental die drawing include polymer grade, nominal draw ratio, draw temperature and draw speed.

4. Identify the direction and magnitude of the orientation produced in the drawn products by means of birefringence.

5. Determine the likely mechanism by which the orientation pattern is developed from considerations of strain history and deformation rate. Confirm this by analysis of partially drawn polymer obtained from the die mid-process, i.e. polymer samples containing undrawn billet material, the neck region and the drawn product.

6. Determine the mechanical properties of the drawn products in both longitudinal and transverse directions. Mechanical tests will include both tensile and compression testing.

7. Measure thermal properties using differential scanning calorimetry techniques and shrinkage tests in order to quantify changes in the degree of crystallinity and melting point brought about through the orientation process. Identify any differences in the crystallinity produced by different dies.

8. Demonstrate the influence of the main variables of polymer grade, nominal draw ratio, draw temperature and draw speed on the process and drawn products. Determine any differences which can be attributed to the rotational deformation mechanism imposed by the dies.
Chapter 2 Literature Survey

2.1 INTRODUCTION TO ORIENTATION

There are a number of routes to produce high modulus polymer products. These methods can be divided into essentially two categories; (a) spinning high modulus fibres from a melt, solution or gel, which allows the chains to crystallise into a chain extended form, and (b) aligning the chains to a preferred direction through solid-state deformations. The former technique will not be discussed in detail because it is the solid state deformation processes which are of interest in this research work.

The orientation of polymeric materials may be discussed by considering their viscoelastic behaviour. When a polymer is stretched above its glass transition temperature, \( T_g \), a number of different forms of deformation can occur and will contribute to final morphology of the material according to the conditions of the process. Elastic deformation is an instantaneous, reversible form of deformation and as such does not play a role in the final degree of orientation. It occurs because of distortions in valence angles and bond stretching. Viscous flow, restrained by molecular entanglements, is irreversible since it results from the molecules moving passed each other under the applied stress. The uncoiling of molecular chains results in a more linear molecular arrangement and this may be retained if the polymer is cooled below \( T_g \) but is slowly recoverable above \( T_g \). Its contribution to the overall orientation will therefore vary according to the deformation conditions. Ideal orientation occurs when maximum chain alignment is maintained on releasing the stress with minimal viscous flow during stretching. Therefore it is obvious that the effectiveness of orientation is both rate and temperature dependent.
Orientation enables crystallites to form also from formerly amorphous regions by both orienting the molecules and by bringing them closer together. The crystallinity of polyethylene has in fact been observed to increase with drawing.\textsuperscript{18,19}

### 2.1.1 Amorphous orientation

Amorphous regions in semicrystalline polymers become partially oriented when the polymer is drawn, the extent of this orientation depends on the molecular weight, temperature, original morphology and material preparation and draw ratio. Post draw annealing will have a significant effect on the amorphous contribution to orientation. It is proposed that amorphous orientation exists in a similar manner to that of the crystal phase,\textsuperscript{20} but the problem becomes more complex above the $T_g$ because there will be some segmental motion which will tend to reduce the orientation of the amorphous phase.

Amorphous orientation has been found in drawn polyethylene by polarised infrared spectroscopy.\textsuperscript{21} Chappel\textsuperscript{22} found that orientation of crystalline regions exceeded that of the amorphous regions at all stages of drawing. Stein and Norris\textsuperscript{23} also found this with polyethylene and discovered that at high extension ratios, amorphous orientation reaches a limit. This however was not observed by Chappel for samples of Nylon 66.

### 2.2 STRUCTURAL MODELS

#### 2.2.1 The Peterlin model of deformation

The crystalline regions of a semicrystalline polymer are interlinked by amorphous chains of relative disorder. Peterlin,\textsuperscript{24,25} who worked mostly with polyethylene, has proposed that the strongest element of a drawn fibre is a microfibril, consisting of highly oriented folded chain crystals which are connected by means of many tie molecules within the amorphous layers separating the crystals. It is these extended-chain tie molecules that are primarily responsible for the increase in Young’s modulus associated with orientation. Peterlin\textsuperscript{24,25} and Becht \textit{et al.}\textsuperscript{26} found that the Young’s modulus of the oriented material is essentially determined by the proportion of tie molecules which produce links between the crystalline blocks in the fibre direction.

The starting isotropic material has stacked folded chain lamellae arranged in a spherulitic morphology, \textit{Figure 2.1(a)}. Through a complex deformation mechanism these lamellae are transformed into highly aligned microfibrils,\textsuperscript{25,27} \textit{Figure 2.1(b)}. The starting lamellae within the spherulites are about 20nm thick and typically 1000nm wide and the
Figure 2.1: (a) A stack of densely packed parallel lamellae of the microspherulitic structure in the starting material. (After Peterlin\textsuperscript{25}). (b) Necking of a parallel lamellae stack into a bundle of aligned microfibrils to form a fibril. (After Peterlin in Ciferri and Ward\textsuperscript{16}). (c) Tie-chains and crystalline regions in an oriented fibre. (After Becht et al\textsuperscript{25})

Microfibrils that result from the transformation are usually some μm in length and about 10nm in thickness.\textsuperscript{16}

Peterlin\textsuperscript{25} has identified three distinct stages to the deformation process; (1) the plastic deformation of the original spherulitic structure, (2) transformation of the lamellae in the spherulites into a fibre structure and (3) plastic deformation of the formed fibre structure. The first stage concerns deformation which occurs not only between the spherulites but also between lamellae within each spherulite. The distribution of the stress and strain field is non-uniform across the structure and the more compliant amorphous regions will deform to a greater extent than the lamellae. As a general guide, the modulus of the amorphous layers is about 10% of that of the perfect crystal. Distortion of the
spherulites during yielding results in a restructuring mechanism involving lamellae slipping past each other if they lie parallel to the applied stress or, if they are perpendicular to the stress they tend to separate, in both cases by overcoming the van der Waals forces between them. In the second case the spherulites may break up under the influence of lateral forces rather than involving slippage of lamellae.

The transformation of the lamellae into microfibrils results from partial unfolding and pulling off blocks of folded chains from the crystal and so each microfibril consist of amorphous, extended-chain, tie molecules between crystalline blocks. The microfibrils collect to form bundles - "fibrils", Figure 2.1(c). A detailed study of the work done per unit volume during this deformation has indicated that in polyethylene the transformation to microfibrils is complete at an extension ratio of 9.8. However tie molecule content has been found to increase up to a draw ratio of about 20 due to pulling out of molecules from the folded chain blocks.\(^{16}\) This also appeared to show up as changes in modulus and birefringence response with deformation ratio in hydrostatic extrusion reported by Gibson \textit{et al.}\(^{28}\)

For non-homogeneous drawing, the spherulitic structure is transformed into microfibrils by micronecks concentrated in the macroscopic neck, whereas in homogeneous deformation the micronecks are distributed throughout the deforming polymer.

The deformation of the fibril structure occurs through slipping of the microfibrils past each other axially and continues to the ultimate deformation of the polymer. An analysis on the fibrils has shown that axial displacement of the microfibrils is due to shear forces.

Peterlin\(^{29}\) proposes that some tie molecules run laterally between the microfibrils and are extended as the microfibrils slide past one another and so fibre strength is due to these interfibrillar tie molecules as well as from the intrafibrillar tie molecules.

X-ray diffraction of drawn polyethylene fibres show some periodicity and Peterlin accounts for this by the folded chains in the microfibrils,\(^{18}\) while the partially extended tie molecules provide the strength to the fibre.

Peterlin\(^{30}\) also suggests that the stresses acting on the tie molecules should vary throughout the sample because they are of different lengths. The most highly strained chains become taut and rupture, the fibre becomes gradually weaker until, finally, microcracks develop and lead to final fracture of the fibre. This microcrack phenomenon is observed in many polymers, which include polyethylene, when subjected to tensile stresses near their ultimate tensile strength.
2.2.1.1 Strain hardening

Peterlin\textsuperscript{31} has incorporated the effects of strain hardening into his model by considering point vacancy defects caused by the ends of microfibrils incorporated into the microfibrillar superlattice. The fracture of the polymer is assumed to originate from these defects and it is proposed that as the fibrils slide over one another the improved contact between them heals the point vacancy defect. As draw ratio increases, the van der Waals forces which act over the long molecular chain will increasingly resist the deformation resulting in strain hardening. For the same reason the drawn fibre will have increased resistance to elastic deformation and a higher tensile strength.

2.2.2 The aggregate model of anisotropy

The mechanical properties of an anisotropic polymer product will depend on the molecular arrangements, i.e. molecular orientation and crystalline morphology. Investigations undertaken by Pinnock and Ward\textsuperscript{32} on PET fibres at room temperature have shown that mechanical properties, in particular Young's modulus and torsion modulus are affected by molecular orientation to a much greater extent than by the crystallinity. From these findings, an aggregate model was proposed. This model consists of an aggregate of units, each of which has anisotropic mechanical properties, but with each unit oriented randomly resulting in an isotropic material on a macroscopic level. Orientation is produced in the polymer when these units rotate under stress to align with the direction of draw. The maximum orientation possible is achieved when all the units are aligned, giving a maximum contribution to the overall anisotropy of the drawn material.\textsuperscript{33}

To obtain elastic constants for the isotropic aggregate it is possible to use two approaches; one method assumes a uniform stress throughout the aggregate, \textit{Figure 2.2}: The aggregate model (a) for uniform stress and (b) for uniform strain (After Ward et al\textsuperscript{15})
2.2(a), the other assumes a uniform strain, Figure 2.2(b). In the former case, a series arrangement of units will have a total strain equal to the summation of the strains imposed on each unit. This implies a summation of their compliance constants and the average is known as the Reuss average. In the other, a parallel arrangement of units will share a total stress equal to the summation of the stress on each unit. This implies a summation of their stiffness constants and the average is known as the Voigt average.

Observations for low-density polyethylene (LDPE)\textsuperscript{34} and nylon 66\textsuperscript{35} show that as draw ratio increases the birefringence obtained increases, rapidly at first but approaching a maximum asymptote. On this basis, the proposed model was extended by Crawford and Kolsky\textsuperscript{34} by considering the material to consist of transversely isotropic, rod-like units. Assuming constant volume and that deformation occurs by rotation of the rods towards the line of the applied force with their axes rotating in the same way as a line drawn on the macroscopic material, the model becomes pseudo affine. However, this model does not account for a change in length, such as the length of the line drawn on the macroscopic material. On the other hand, an affine model also assumes changes in length within the model as the deformation is applied and can be used to describe the deformation of natural rubber for example.

This extension of the aggregate model also gives good approximations for the birefringence behaviour of polyethylene terephthalate,\textsuperscript{36} and polypropylene,\textsuperscript{37} and gives the basis for extending the original model still further to predict mechanical properties. More recently, Zhao and Mascia\textsuperscript{38} have used a similar model as a basis for evaluation of biaxially oriented extrudates from constant area (shear) convergent-divergent dies.

The success of the model in predicting mechanical anisotropy with different polymers is varied. The model only predicts that the mechanical properties will lie between the two theoretical bounds given by Reuss and Voigt. Ward \textit{et al.}\textsuperscript{39-41} compare the calculated values for five polymers with the actual values obtained. Low density polyethylene lies close to the properties predicted by the Reuss curve. This is further supported by work carried out by Odajima and Maeda\textsuperscript{42} in comparing the averages of single crystals with measured values, but there are some discrepancies. LDPE experiences a minimum in the transverse modulus curve, apparently attributable to mechanical twinning,\textsuperscript{43} and this does not show in the model. Also the development of mechanical anisotropy with draw ratio is much greater than predicted by the model. Kausch\textsuperscript{44} has suggested that this increase is due to additional orientations within each unit of the aggregate and for LDPE it has been concluded that this is in fact due to orientation of the crystalline regions. Experiments
using wide-angle X-ray diffraction and nuclear magnetic resonance\(^45\) have allowed corrections to the model to be made.

For PET the experimental elastic behaviour lies between the two bounds and in fact cold drawn fibres lie almost exactly on the median.\(^45\) There is much evidence to suggest that PET is in fact best represented by a network structure which will be described in detail in a later section. A network structure model has an advantage over the rod model in that it allows better representation of high strain properties.\(^46\) Nylon lies closer to the Voigt average.

This aggregate model has been shown to be reasonable for application to the mechanical anisotropy of many non-crystalline polymers whose deformation is of a \textit{pseudo affine} nature. However the aggregate model does not seem to be so applicable in the case of the semicrystalline polymers of high-density polyethylene and polypropylene, except at low draw ratios. With these polymers it seems likely that factors other than molecular orientation are also responsible for determining the mechanical properties of the polymer. An alternative two phase model, the Takayanagi model, described in the following section is more appropriate in these cases.

### 2.2.3 Takayanagi model for semicrystalline polymers

In oriented high-density polyethylene a lamellar structure and its orientation plays a vital role in the mechanical properties of the polymer in addition to the molecular orientation. The Takayanagi model for oriented crystalline polymer assumes the polymer to be

![Takayanagi model](image)

\[\text{Figure 2.3: The Takayanagi model and the dependence of parallel and perpendicular dynamic modulus on temperature.}\]
constructed from two phases, Figure 2.3, one of crystalline material and the other amorphous material. These two components lie in series in the drawn direction of the polymer and are parallel in the transverse direction. Once again the Reuss and Voigt averages can be used for a prediction of the mechanical properties. Since in the draw direction there is a 'series' arrangement, each component experiences the same state of stress so the compliances are added. In this direction therefore, the lower stiffness of the polymer at higher temperatures is a result of the highly compliant, amorphous phase. In a transverse direction however, the amorphous phases are 'in parallel' with the crystalline phases and experience the same strain. The Voigt average applies and since the stiffness constants are added, a comparatively high stiffness is obtained. The crystalline regions are able to support the applied stress at the higher temperatures. In this manner it is possible to see that there should be a cross-over point between the two curves for parallel and transverse moduli with temperature, Figure 2.3. However the model does fall short in that the amorphous region will always be constrained to a certain degree by the crystalline phase. The cross-over was observed by Takayanagi et al with their work on drawn and annealed sheets of high density polyethylene and polypropylene, and later by Gupta and Ward in drawn and annealed sheets of low-density polyethylene.

In more detailed studies conducted by Stachurski and Ward, low-density polyethylene sheets were prepared with well defined crystallographic and lamellar structures. This technique was first used by Hay and Keller. By using dynamic mechanical analysis they were able to establish that a major deformation process involves shear in the amorphous regions between the rigid lamellae and that this could account for the dynamic mechanical loss spectra observed.

### 2.2.4 Models for ultra-high modulus polyethylene

The Young's modulus of drawn polyethylene fibres as a function of draw ratio tends to depend only on the final draw ratio and is relatively independent of the initial morphology of the polymer. The models were subsequently adapted to depend on the structure produced during the deformation process rather than that of the starting material. Two models were proposed by different workers; the crystalline fibril model, and the crystalline bridge model, Figure 2.4.

The crystalline fibril model consists of discontinuous fibrils of high aspect ratio arranged in a compliant matrix, Figure 2.4(a). Post-neck drawing results in an increase in stiffness of the polymer and was assumed to be a consequence of an increase in aspect ratio of the fibrils which then become more effective for reinforcing the matrix. The
model was found to agree closely with observations made by Arridge et al.\textsuperscript{55} and Barham et al.\textsuperscript{66} as long as the polymer was assumed to draw homogeneously with an affine deformation of the fibrils. The model explained observations of self-hardening of linear polyethylene fibres by a stiffening of the matrix. These workers also found that highly drawn samples held at fixed length relax at elevated temperatures with a concomitant decrease in modulus. However when held for long times at room temperature the modulus (and density) increased substantially. During the heating process, stressed tie molecules detach from the fibrils and recrystallise in the usual chain folded manner. In this way the model explains the observed drop in modulus, the persistence of X-ray orientations, the increase in lamellar content, and the absence of large contractions in subsequent reheating of these aged fibres.

The Takayanagi model was extended by Gibson et al.\textsuperscript{68} to account for the discontinuous nature of the crystalline phase. This 'crystalline bridge' model assumes that the crystalline blocks are linked by crystalline bridges and these bridges form a continuous phase with the consequence of an increase in polymer stiffness, \textit{Figure 2.4(b)}. The equivalent Takayanagi model is then a continuous phase of crystalline bridges in parallel with a series arrangement of the remaining lamellar and amorphous material. The crystalline bridges are similar in concept to the amorphous tie molecules proposed by Peterlin as
described above and that the increase in mechanical properties with draw ratio results from an increase in the proportion of material existing in the crystalline bridges.

2.3 POLYETHYLENE

2.3.1 Introduction to polyethylene

Polyethylenes are a group of polymers which are produced from ethylene monomer as the main component and can be represented by the formula \((CH_2CH_2)_n\). The polymer chains tend to have methyl end groups (-CH3) or vinyl end groups (-CH=CH2).

Polyethylenes are categorized by their densities and fall into four main categories; High density polyethylene (HDPE), Low density polyethylene (LDPE) and Linear-low density polyethylene (LLDPE).

2.3.1.1 High density polyethylene (HDPE)

With a density of 935-965 kg/m³, high density (linear) polyethylene has less than 10 short side chains per 1000 main chain atoms. It can be made by either of two processes, one based on Ziegler-type catalysts, the other on mixed oxide catalysts (e.g. the Phillips process). HDPE made by the latter of these processes tend to have the highest densities.

The chain linearity means a higher degree of crystallinity, typically 65 - 90%, which forms more rapidly from the melt than for LDPE and the crystalline melting point is 130-135°C. HDPE is much stronger and stiffer and the high molecular weight grades are tough even to low temperatures. Applications include dustbins, barrels, water butts, bottle crates, petrol tanks and other general purpose fluid containers. Extruded pipes of HDPE and a tougher medium density polyethylene (a lower density form of HDPE 930-940kg/m³) are used for natural gas distribution.

2.3.1.2 Low density polyethylene (LDPE)

LDPE has a density of 915-935kg/m³. It contains typically about 20 to 40 branches per 1000 main chain atoms. It is manufactured at high pressures (1500 - 3000bar) and high temperatures (150 - 250°C). Molecular weight and its distribution are controlled by modifiers, temperature and pressure, and by the type and concentration of the initiator. The side chain branches are unable to fit into the crystalline phase and therefore reduce the crystallinity significantly to a level typically 50 to 65%. This is dependent on the molecular weight with higher molecular weight grades having a lower degree of
crystallinity. Melting point is about 105 - 115°C and will vary with density. This polymer is both tough and flexible and finds major applications in the packaging industry for films.\(^6\)  

2.3.1.3 **Linear low density polyethylene (LLDPE)**

This polymer was first introduced by Union Carbide in 1977. It is manufactured by a low pressure process and has similar structure and properties to low density polyethylene except that it has short chain branches of typically 2 - 8 carbon atoms. Control of the cooling rate from the melt enables the molecules to link together, forming a stiffer polymer with a higher yield strength and greater ductility than LDPE. The strain behaviour is not limited by the long chain branching of LDPE or the large amounts of crystallinity of HDPE and as a result the draw ratio obtainable is much higher. LLDPE has taken over 30% of the traditional LDPE market.\(^6\)

Being a semicrystalline polymer in its isotropic state, polyethylene contains crystallites dispersed with random orientation in an amorphous matrix. The crystallites form when clusters of chains exhibit local alignment and pack closely to form a dense, highly ordered rigid state and because they are large enough to scatter light the polymers are usually translucent or opaque. Because of its regular structure, short chain repeat distance and high chain packing density, polyethylene crystallises rapidly compared to most other semicrystalline polymers. As polyethylene cools from the melt, the crystallinity begins with the formation of lamellae which are of a plate-like structure with the chains folded through the thickness. Chain folding results from the lowering of conformational energy by regular folding of long molecules so that van der Waals interactions come into play. The surfaces of the lamellae provide nucleation sites for further crystallisation of lamellae layers. The ribbon-like lamellae grow with a spherical front forming a so called 'spherulite' and this continues until it impinges on a neighbouring spherulite growing towards it. The lamellae only contain ordered chains, but these are surrounded by a remaining amorphous matrix within the spherulite. Lindenmeyer\(^6\) suggests that the composition of a polymer crystal will differ from that of the melt because short molecules increase the free energy of the crystal and longer molecules increase the free energy of the liquid. Therefore there is a tendency for both very short and very long molecules to diffuse away from the crystal and remain in disordered states within spherulites and at spherulite boundaries. The alternating dark rings observed in many spherulites are believed to be due to a twisting of radiating fibrils.\(^6,4\)
The degree of supercooling affects the growth of spherulites. At rapid cooling rates, the spherulites become more numerous and therefore grow to a smaller size as their boundaries impinge. If polyethylene crystallizes nearer the melting point, a consequence of slower cooling, fewer spherulites are nucleated, but these are able to grow larger and the result is a higher crystallinity than the rapidly cooled material. Note that spherulite size has also been found to be influenced by additives present, for example colourants in partially crystalline polymers tend to behave as nucleating agents. Spherulite size is a feature in determining the mechanical and physical properties of the polymer as explained below.

2.3.2 Deformation of polyethylene

Polymers that can be cold drawn have characteristic stress-strain curves that have three distinct regions. The stress rises rapidly at first in a typically linear manner as the sample is stretched. This deformation is elastic and is therefore reversible with the polymer returning to its original size and shape with the removal of the stress. The curve then reaches a maximum as a neck forms in the sample and then falls off to a point where it remains almost constant while the neck propagates as stretching is continued. This is plastic deformation and is non-reversible. At the point where all the sample is drawn there becomes an increase in stress with further strain because the molecules aligned on necking resist further elongation, i.e. there is a strain hardening process that comes about as a result of the orientation of the molecules.

The natural draw ratio is defined as the uniform draw ratio which can be given to a fibre or a film when it is oriented by cold drawing. This natural draw is affected by experimental conditions and polymer molecular weight for any given polymer. Amorphous polymers, such as amorphous PET are generally most easily cold drawn just below the glass transition temperature, but semicrystalline polymers, such as polyethylene, may be cold drawn from below $T_g$ up to near the melting point. If drawn at temperatures above or below the cold drawing range the deformation does not result in the same extent of molecular orientation as obtainable by cold drawing.

It has been suggested that cold drawing occurs because a non-uniformity develops in the specimen under tensile stress which may be due to a region of smaller cross sectional area or because of some stress concentrations. This local increase in stress causes an increase in strain, resulting in thinning at that point which leads to continued instability and neck formation. The edges of the neck deform rapidly, producing a local heating and temperature rise, allowing the neck to propagate without plastically deforming other
parts of the sample. It has been found that polyethylenes of a higher density exhibit a sharper neck and a larger natural draw ratio and also that the geometric profile of the neck is related to the strain rate and molecular weight of the material.\textsuperscript{67}

Deformation relating to spherulites has been investigated by Hay and Keller.\textsuperscript{68} They used high density polyethylene film as a starting material and employed polarised light microscopy, X-ray diffraction, and electron microscopy techniques to investigate the development of spherulite deformation in the material as it was stretched. They noted two types of spherulitic deformation during tensile drawing; homogeneous, where all parts of a given spherulite extend simultaneously and in proportion, and inhomogeneous, where the spherulites and/or regions between them, yield selectively with the rest of the microstructure remaining unaltered. They also observed that the deformation within a spherulite is often greater than that in the material between the spherulites, reflecting some sort of weakness within the spherulites themselves. The spherulite deformations are not \textit{affine}.

The deformation of polyethylene by cold drawing and the development of anisotropic mechanical properties has been given much attention and an account of the mechanical properties and the success of modelling these properties with various models is presented by Ward.\textsuperscript{69}

The deformation behaviour and deformed material properties seem to be dependent on three main factors including strain rate, molecular weight and temperature. Post deformation annealing also plays a significant part in the final product behaviour. Each of these parameters will be discussed individually below.

\subsection*{2.3.3 Molecular weight}

Capaccio and Ward\textsuperscript{70} have proposed that molecular weight and molecular weight dependent parameters such as the extent of crystal nucleation, crystal growth, and segregation of low molecular weight material influence the initial morphology and thus the subsequent drawing behaviour of polyethylene.

Andrews and Ward\textsuperscript{71} performed cold drawing experiments on high density polyethylene and reported the effects of molecular weight, strain rate and temperature. Whilst in this study they found that the yield and drawing stress of high density polyethylene to be independent of molecular weight, in a later study by Capaccio and Ward\textsuperscript{72} the yield stress increased with molecular weight at constant temperature. They concluded that the
longer molecules in the distribution can form a network superstructure due to physical cross-linking by molecular entanglements.

The draw ratio obtained, i.e. the natural draw ratio, has been found to decrease with increasing average molecular weight. Higher molecular weight material provides a greater number of tie molecules which hinder the orientation, causing a lower natural draw ratio. A greater concentration of interlamellar ties increases the rate of strain hardening.\textsuperscript{73} Vincent\textsuperscript{66} has shown that there is a lower limit of molecular weight for cold drawing, below which there is insufficient strain hardening to stabilise the neck. However Barham and Keller\textsuperscript{74,75} found that a component of low molecular weight was necessary to achieve high draw ratios.

In a study by Capaccio and Ward\textsuperscript{70} which concentrated on the initial morphology of polyethylene, they found that it was the highest molecular weight material within the molecular weight distribution that determined the highest tensile modulus attainable. This was supported in the later paper\textsuperscript{65} which concluded that variations in the high molecular weight tail in the molecular weight distribution was the likely dominant feature influencing drawing characteristics. Tensile strength, affected by molecular weight was investigated in another paper.\textsuperscript{76}

Capaccio and Ward\textsuperscript{72} found that the yield stress increases with the crystallinity of the original high density polyethylene for a given molecular weight. Slow crystallisation of the starting material to control the initial morphology has been seen as an important requirement for obtaining high draw ratios by Barham and Keller\textsuperscript{75} who investigated drawing of single crystal mats.

Barham and Keller\textsuperscript{74} also concluded that complete pulling out of chain folds during the drawing process could not be achieved because they always found a contraction on heating the drawn fibre close to the melting point. Hay and Keller\textsuperscript{68} found chain folding even in highly drawn structures.

Work conducted by Capaccio \textit{et al.}\textsuperscript{77,78} emphasised the notion that the drawing behaviour of polyethylene was best understood in terms of a molecular network by considering the drawability of different molecular weight grades of polyethylene. In this molecular network, both physical entanglements and crystalline regions can form network junction points. In low molecular weight materials, the crystalline regions form the majority of the network junction points, whereas in higher molecular weight grades, physical entanglements form play a more dominant role.
2.3.4 Strain rate

The effect of strain rate on the yield stress is similar to that reported earlier by Allison and Ward for polyethylene terephthalate.45 As the strain rate increases, the process appears to become more adiabatic resulting in a reduced drawing stress. At low strain rates, the heat generated by deformation is conducted away and as strain rate increases, the rate of heat generation increases more rapidly than the rate of dissipation. The result is an increase in the effective drawing temperature, hence the reduction of drawing stress. The natural draw ratio was found to be sensitive to strain rate in this study and there appears to be a particular strain rate at which there is a sudden increase in the natural draw ratio. It is suggested that this sudden increase is due to void formation. It happens at a lower strain rate than for PET and this has been attributed to the higher thermal conductivity of polyethylene, thus removing heat from the deformation zone much more efficiently.

Andrews and Ward71 later tested a number of processing parameters in drawing tests on a high density polyethylene and observed similar effects. They found that the yield stress appeared to be a linearly increasing function with the logarithm of strain rate. Drawing stress was also found to increase up to a point after which it diminished with increased strain rate. The natural draw ratio was found to be independent of strain rate up to about $5 \times 10^{-2} \text{sec}^{-1}$, above which it increased rapidly.

2.3.5 Temperature

The effect of temperature has been found to decrease both the yield and draw stress of the polymer. Successful drawing can be achieved at very high temperatures, close to the melting point, provided a sufficiently high molecular weight material is used.78

Andrews and Ward71 found the natural draw ratio to be affected by temperature, decreasing slightly up to $100^\circ\text{C}$, possibly due to annealing, then increasing as the drawing temperature was raised further.

Extrudates obtained by hydrostatic extrusion at higher processing temperatures have shown signs of an increase in melting temperature. This is a result of the crystals being larger and more perfect.79

2.3.6 Annealing behaviour

Isothermal annealing is usually an irreversible process. Sanchez80,81 suggests that the process is an irreversible thermodynamic process resulting in crystal thickening. This is
due to unequal free energies of the fold and lateral surfaces of the polymer crystal. However Pope and Keller\textsuperscript{82} found reversible changes of long spacing in oriented polyethylene with temperature and proposed that the increase in overall periodicity was a result of partial melting of small or imperfect lamellae.

Peterlin\textsuperscript{18} has identified post drawing annealing as a major influence on the final properties of a drawn fibre. On annealing cold-drawn polyethylene at or above $118{}^\circ$C, rapid relaxation occurs with an increase in the heat content of the amorphous component to the value of completely relaxed chains. The number of tie molecules is significantly reduced. However annealing of highly drawn crystalline polymers heals crystal defects and increases the long period of the crystal lamellae, with an associated increase in crystallinity and hence density.

Mead and Porter\textsuperscript{83} studied the effects of annealing on a highly oriented linear polyethylene morphology containing approximately 15% extended chains. They found that by annealing between $126{}^\circ$C and $132{}^\circ$C the melting endotherm of the material split into two peaks. It was suggested that the first corresponded to the melting point of the unoriented starting material and the latter the melting point of the unannealed fibre.

### 2.3.7 Creep and stress relaxation

An overview of the methods of enhancing the creep properties of polyethylene is given by Ward.\textsuperscript{84}

Whilst the effect of higher molecular weight, copolymerisation and lower crystallinity may reduce the obtainable draw ratio, studies by Wilding and Ward\textsuperscript{85-88} have indicated that these materials have the advantage of improved long-term creep behaviour. In these studies two components of viscoelastic behaviour were observed; (1) a linear recoverable component, and (2) a non-linear irrecoverable component which can be modelled as an activated creep process. The recoverable part was found to be not greatly affected by draw ratio or molecular weight, but the irrecoverable creep was affected substantially by these two factors.

The authors suggest a continuity between drawing and irrecoverable creep behaviour for polyethylene because both relate to permanent plastic deformation. They use this to explain the differences in creep behaviour between low and high molecular weight grades. Low molecular weight materials appear to reach a plateau of creep rate at high stresses. Higher molecular weight materials do not reach this plateau and experience a more pronounced strain hardening. The low molecular weight grade shows a reduction in irrecoverable creep with increasing draw ratio because a crystalline deformation
process such as the pulling out of chain folds by crystal slippage dominates in this case. In a high molecular weight material however it seems that the mechanism is quite different where it relates to a localised molecular process such as the breaking of an inter-crystalline tie molecule or pulling out of a chain entanglement. Deformation requires that physical entanglements be destroyed or that chain scission occurs. This explains why the higher molecular weight grades require a critical stress level for irrecoverable strain to occur.

From these results they propose that irrecoverable creep occurs through two distinct processes. The first appears to be primarily affected by draw ratio and is little affected by polymer molecular weight, copolymerisation or cross-linking. This process relates to the deformation of crystalline regions. The second process is not significantly affected by changes in structure or chemical composition but rather molecular weight, cross-linking and copolymerisation. It relates to deformation of the molecular network. A similar proposal for polypropylene is made by Duxbury et al.\textsuperscript{89}

The effect of irradiating isotropic low molecular weight polyethylene by $\gamma$-irradiation had the same effects as increasing the molecular weight on improving creep behaviour. This can be expected because the irradiation process should give rise to network junction points, chemical cross-links, with similar consequences to the increased molecular entanglements of the high molecular weight.\textsuperscript{90} The irradiation process is best carried out after orientation since the cross links will otherwise hinder the development of higher draw ratios.\textsuperscript{91}

These studies along with another by Hope et al.\textsuperscript{92} who investigated small diameter isothermal hydrostatic extrusion on different grades of polyethylene (in particular copolymers), had shown that copolymers gave enhanced creep resistance over similar molecular weight homopolymers. However, in another study by Hope and coworkers,\textsuperscript{93} who used an adiabatic thermal regime, it was found that creep behaviour was better for homopolymers. This contradiction was explained by the fact that the latter study was conducted with lower deformation ratios and lower stresses and thus the tests were performed in a region where the creep properties were dominated by the recoverable component of deformation. At higher stresses and deformations, the permanent flow process dominates and the copolymer performs better. For this reason it seems reasonable that for applications in which creep behaviour at a given strain is important, the copolymer is preferable, but for constant loading applications involving low stress levels, the homopolymers are superior by virtue of a higher initial moduli. A comparison
of tensile, compressive and torsional creep behaviour for both isotropic and oriented polyethylene is given by Philip et al.\textsuperscript{94}

### 2.4 POLYETHYLENE TEREPTHALATE

#### 2.4.1 Introduction to polyethylene terephthalate (PET)

Polyethylene terephthalate (PET) is a saturated polyester and was discovered in 1941 by J. R. Whinfield and J. T. Dickson. Polyesters are a group of polymers containing the ester group in their main chain and are produced from a di-carboxylic acid and a glycol. A whole range of different polyesters can be obtained by varying the diacid and glycol used in their manufacture. Aliphatic polyesters have a limited commercial use due to their thermal and hydrolytic instability. For this reason they are used mainly as modifiers. Aromatic polyesters have increased intermolecular forces and are more rigid due to the introduction of the aromatic ring. Only the ethylene (PET) and butylene (PBT) terephthalates have any commercial significance and PET is in fact a mixed aliphatic and aromatic polyester.\textsuperscript{94}

PET is produced by either direct esterification of ethylene glycol with terephthalic acid or by an ester exchange process between ethylene glycol and dimethyl terephthalate. The latter of these two reaction processes has been replaced by the former because the ester exchange process requires a first stage catalyst and the initial esterification product is a low molecular weight mixture of PET oligomers.

Polyethylene terephthalate has a relatively high melting point and glass transition temperature (255°C and 75° respectively). It is a crystallisable polymer and its morphology depends on the processing conditions. The amorphous form is obtained by rapidly quenching the melt below the glass transition temperature $T_g$. When heated above the $T_g$ the polymer crystallises, forming an opaque material exhibiting spherulitic morphology. Amorphous PET is of little commercial significance because it has low mechanical properties and low dimensional stability. These properties may vary depending on the molecular weight and can be significantly enhanced by orientation and heat treatment. PET has commercial uses which fall into four main categories including fibres, films, food and beverage containers, and precision mouldings.

PET fibres tend to be of low molecular weight grades and are used for fabrics, carpeting tyre cords etc. The polymer is first extruded and solidified into an amorphous form before being stretched above its $T_g$ to give high uniaxial orientation. The resulting fibres
have extremely high strength and modulus and resist chemical attack and can be heat treated to enhance their higher temperature properties.

Films are produced by biaxially stretching amorphous sheets of polymer produced by extrusion. The biaxial stretching produces orientation and crystallinity which enhances tear strength and hinders diffusion through the polymer, thus lower water absorption and gas permeability. By heat setting the film its dimensional stability and high temperature performance can be improved and coatings are often applied to optimise the film for a particular application. The films are suitable for photographic film, magnetic tape media, and food packaging.

PET bottles are now used extensively as containers for both alcoholic and non-alcoholic drinks, other foodstuffs, pharmaceutical products, toiletries and chemicals. They are produced by stretch blow moulding an amorphous preform produced by injection moulding. The blow moulding process produces significant orientation within the bottle walls which in turn improves its barrier properties.

Heat crystallisable grades are suitable for injection moulded products. The properties of moulded products are comparable with components made with polyamides but on short term exposure to moisture they are much better at retaining their mechanical properties and dimensional stability.95 Engineering products demand high levels of consistent crystallinity. Molecular weight has a significant effect on the crystallisation. Lower molecular weight molecules have a greater mobility and hence the crystallisation rate is faster. Crystalline products of higher molecular weight grades are only available at mould temperatures of 140°C because quenching occurs at lower temperatures before crystallisation commences. Higher molecular weight grades can be made to crystallise faster by introducing nucleating agents and thus cycle times and mould temperatures may be reduced with these grades. Also available are engineering grades with fibre-glass or mineral reinforcement. Filler levels of 30 to 45% are typical but levels up to 55% are possible.

2.4.2 Degradation considerations

PET is a hygroscopic polymer and will absorb moisture extremely rapidly. During processing at melt temperatures, thermohydrolytic degradation occurs which results in a reduction in molecular weight.96 Its melt stability is strongly affected by the amount of water absorbed prior to processing. Thermal degradation reactions result from chain scission of ester bonds to form carboxyl end groups and vinyl ester. Reactions of the vinyl ester end groups is accompanied by the formation of acetaldehyde and the re-
establishing of ester bonds, thus thermal degradation may not lead initially to a reduction in viscosity. If the acetaldehyde remains in the melt, as it would for enclosed processing conditions such as an extruder, it participates in secondary reactions to form water which causes further degradation. When this occurs the degradation by the combined effects of thermal and hydrolytic degradation is rapid. Zimmerman\(^{96}\) studied hydrolytic degradation in relationship to carboxylic end group concentration. His findings showed hydrolytic degradation to be autocatalytic and dependent on initial carboxylic content. A low carboxyl content is essential for thermal and processing stability.

The effects of hydrolysis are not only confined to the melt processing of PET. It is assumed that water diffusion proceeds initially in the amorphous regions of PET and so hydrolysis in the solid phase occurs primarily within this region. Solid state hydrolysis is also significant and exposure to water at 50°C has a detrimental effect on properties, most notably to the impact strength and toughness of the material.\(^{95,97}\) Where the polymer is not in direct contact with moisture it has been suggested that it does not suffer deterioration below temperatures of about 87°C.\(^{97}\)

Water sorption depends on a variety of parameters, most notably temperature, relative humidity, ratio of volume to surface area and microstructure and morphology of the polymer matrix. Another investigation on amorphous PET films\(^{98}\) concluded that PET absorbs moisture as a function of temperature, relative humidity and time. The equilibrium moisture content increases linearly with relative humidity. The amount of water absorbed is independent of molecular weight, but has pronounced effects on the glass transition temperature and crystallisation temperature, decreasing them both. For a given draw ratio, the molecular orientation, density and mechanical properties of PET are reduced as a result of increased moisture absorption prior to orientation and these effects are enhanced with increasing temperature.

The equilibrium water content of PET is about 0.3% at 25°C and 50% relative humidity. It has been suggested by Mills\(^{99}\) that high molecular weight grades need to be dried to a water content of 0.003% (30ppm) with this content causing a drop in the intrinsic viscosity from 0.73 to 0.71. Further examples of the effect of hydrolysis are given by ICI.\(^{100}\) They suggest that 16ppm moisture content results in a drop of 0.01 dl/g in the intrinsic viscosity corresponding to a drop in the molecular weight of about 500g/mol.

The need for controlled drying is clear. Hydrolytic degradation results in lower molecular weight and lower melt viscosity. This in turn makes processing, especially extrusion, more difficult. Most manufacturers suggest drying to at least a moisture content of less than 0.004% (40ppm) and for this a source of dry air is required, typically
0.001% (10ppm) moisture or less. The slowest step of the drying process is the diffusion of the water through the solid granules. The diffusion coefficient rises with temperature, but as the temperature rises, hydrolysis of the polymer begins to occur. A compromise is required and different methods have been used by various workers depending on the dehumidifying equipment available.\textsuperscript{9,99,101}

### 2.4.3 Orientation of PET

The drawing behaviour of PET has been studied for both cold drawing (i.e. drawing the material below $T_g$) and hot drawing (drawing above $T_g$). The formation of craze marks occurring in the undrawn region of amorphous PET during cold drawing has been observed.\textsuperscript{45} A number of workers\textsuperscript{45,102,103} have reported that there is a temperature rise occurring within the neck of the polymer. Utilising the steady-state drawing stress and the draw ratio, a modulus can be obtained and by comparing this modulus with Young's modulus and shear modulus-temperature data for small strains, the rise in temperature occurring within the neck during cold drawing can be predicted. It has been suggested that the temperature rises to approximately 80°C. When cold drawing PET at various strain rates it is noted that as strain rate rises, the stress also increases to a peak after which it decreases with further increases in strain rate. This has been attributed to the process becoming more adiabatic and the effective drawing temperature increasing accordingly - a decrease in stress. Hot drawing occurs above the $T_g$ at about 80°C and homogenous drawing is observed throughout the entire sample.

Following work done by Pinnock and Ward\textsuperscript{104}, investigations have attempted to verify the network structure model proposed. Cold drawing of PET fibres\textsuperscript{35,45,105,106} and hot drawing\textsuperscript{107} have shown the model to hold for a variety of deformation conditions. Evidence suggests that when deformations are small, there is no great change in the overall topology of the molecular chains. Rietsch et al\textsuperscript{108} have found that deformation above 80°C is consistent with the network theory, although above a draw ratio of about 1.7 the stress-optical properties diverge from this model. This discrepancy has been supported by the work of Engelaere et al\textsuperscript{109} and Bhatt et al\textsuperscript{110} who also found divergence at higher draw ratios.

Work by Ward and co-workers\textsuperscript{104,108,111,112} has suggested that the natural draw ratio depends on the pre-orientation of the material and the total natural draw ratio. That is, the sum of pre-orientation and drawing orientation has been found to be approximately constant at a value of about four. However, work done by Engelaere\textsuperscript{109,113} on two-stage drawing of PET, has disputed this and found that for a low molecular weight material the
total extension increases linearly with pre-orientation. Padibjo and Ward later explained this by assuming that the overall orientation produced reaches a limiting value when crystallisation occurs. In a two stage drawing operation the network’s extensibility is increased.

2.4.4 Strain induced crystallisation

In addition to thermal crystallisation, PET also undergoes strain-induced crystallisation during the orientation process which results in the crystallinity increasing with draw ratio. Bourvellec et al. have shown that for a given temperature, the kinetics of crystallisation during stretching are controlled by the evolution of amorphous orientation and so rate of crystallisation increases with strain rate. The rate of crystallisation induced during stretching is completely controlled by the strain rate, the beginning of crystallisation being delayed at higher temperatures because of a lower amorphous orientation in the material. At low temperatures and high extension rates, the stress-strain relationship demonstrates a finite strain with a increasing stress before the material fractures. This can be attributed to strain-induced crystallisation. At high temperatures and low strain rates, where there is a sufficiently long 'dwell time' at the drawing temperature there is also an upswing in the stress-strain curve and this is due to thermal crystallisation. Flow drawing as reported by Gupta et al. occurs when the drawing temperature is so high, typically 20 - 30°C above the T_g, that the relaxation of molecules is predominant and the molecular orientation is almost negligible. This illustrates an important point; it is the stress that is more important than the amount of strain. The stress causes the orientation making it possible for either the orientation to be frozen in by cooling the polymer below T_g or for the polymer to crystallise. Absence of the stress, regardless of strain, results in flow drawing. The yield behaviour of PET has been studied by Foot et al.

At temperatures below T_g the polymer shows a yield point and cold draws. As the temperature increases, above T_g yielding no longer occurs and homogeneous drawing takes place instead. As PET is stretched, the load increases to a plateau where the polymer experiences large deformation at essentially constant load, i.e. the so called "cold drawing condition". There is alignment of the molecules and this leads to strain-induced crystallisation. At this point the stress/strain curve shows an upswing and this effect is called strain hardening. DeVries studied both uniaxial and biaxial stretching to investigate the effect of molecular orientation between stress and recoverable strain.
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A number of studies have been conducted on PET to determine the development of orientation and its associated molecular structure. Also the crystallisation process which occurs during orientation in PET has been studied to determine the influence of draw ratio, temperature and strain rate.

Heffelfinger and Schmidt have studied the structural changes that occur within oriented PET films. They proposed that the resulting properties are dependent on three structural factors including (1) the kind of perfection of crystalline orientation, (ii) the amount and direction of the trans-gauche isomerisation in the amorphous regions and (iii) the amount of crystallinity. During drawing there is a change in the rotational isomerism of molecules in the PET. The existence of two possible rotational isomeric forms in PET is a result of differences in conformations of the ethylene glycol linkage. The gauche isomer only appears in amorphous material whereas the trans isomer occurs in both crystalline and amorphous regions. During stretching, gauche PET from the amorphous phase is changed to the trans conformation and when these isomers are brought into close contact by molecular alignment, the material crystallises. Some chain segments remain entangled in the amorphous regions but these are strained, lying between the crystallites and fibrillar structure. Since the trans isomer is the extended form, the more highly strained these amorphous regions, the greater the content of the trans isomer. In fact the analysis has shown that the amount of trans structure at a given level of crystallinity is a measure of the tautness of the amorphous regions and is directly related to modulus, strength, elongation etc. This was experienced in two-stage drawing conducted by Padibjo and Ward where these samples showed superior modulus values over single-stage drawing. This was found to be due to the increased orientation of trans isomer in the amorphous regions which was found irrespective of crystallinity.

The molecular morphology has been studied in the glassy state, the semicrystalline state and after cold drawing. Cold drawn samples of PET with a macroscopic draw ratio of 4.9 exhibit a molecular draw ratio of 2.8 thus deforming less than affinely at the macroscopic level.

Bonnebat et al have studied the effects of molecular weight on both uniaxial and biaxial stretching of PET. By stretching at temperatures near the glass-rubber transition, the material may not undergo a uniform deformation unless the draw ratio exceeds a "critical" value (the natural draw ratio). They also found that the extension ratio at the onset of strain-hardening depends upon the molecular weight, an increase in the molecular weight of the polymer decreases the draw ratio required for the onset of strain-hardening. This draw ratio is also strongly dependent upon the temperature where
a decrease in temperature decreases the required draw ratio. An increase in strain rate also reduces the required draw ratio although this effect is small.

Studies\textsuperscript{127} have also shown that when PET is stretched biaxially, oriented rod-like superstructures are formed, Chu and Smith\textsuperscript{135} found that the degree of crystallinity increased with increasing annealing temperature although the anisotropic shrinkage remained unchanged. By small angle light scattering techniques it was found that rod-like superstructures existed and tended to be oriented in the machine and transverse directions with biaxially oriented films, the number of these rods did not change on orientation but the order increased within the superstructure. Annealing increases the perfection within crystallites, owing to the partial release of frozen in strain.

Jabarin\textsuperscript{136} investigated the molecular orientation achieved in PET dependent upon four independent but interrelated variables; extension, extension rate, molecular weight and temperature. It was found that biaxially oriented PET film demonstrated strain induced crystallisation and the amount of crystalline material was dependent upon strain rate. The orientation increases with strain rate and this influence on orientation is extremely significant at higher temperatures. In addition, the mechanical properties for a given amount of molecular orientation, measured by birefringence, increase with molecular weight. Molecular orientation achieved and mechanical properties increase with draw ratio but decrease with increasing temperature, although this effect is reduced at high strain rates and when higher molecular weight materials are used.

Gumther and Zachmann\textsuperscript{137} have shown that an increase in molecular weight of PET leads to an increase in orientation for tensile drawing of PET films, probably due to the increase in viscosity and any viscous flow becoming less important.

In a recent series of papers by Chandran and Jabarin\textsuperscript{138-140} the orientation characteristics of PET with respect to stretching mode, strain rate, draw ratio and temperature have been investigated. They have proposed the use of a 'strain hardening parameter' which is a measure of the extension ratio at the onset of strain hardening. They have found that when PET is biaxially drawn the strain hardening parameter, SHP, decreases with increasing the strain rate, while it increases with temperature. Further they found that for specimens stretched in a uniaxially constrained manner, the upswing in the stress strain curve occurred at a point corresponding to the completion of strain-induced crystallisation. Thus the onset of strain hardening occurs upon completion of the strain induced crystallisation.
2.4.5 Thermal shrinkage

When an oriented amorphous polymer is heated above its glass transition, the oriented chains tend to regain their random orientation and this results in shrinkage of the oriented product. For crystalline polymers, on the other hand, the recoiling of oriented molecules is hindered by the crystalline material although this effect is reduced with increasing temperature. Most shrinkage of a crystalline polymer is observed fairly near the melting point, above which no orientation remains.

With PET the strain-induced crystallisation effects will affect thermal shrinkage and it is possible to reduce thermal shrinkage further by inducing thermal crystallisation on an oriented sample. This technique is known as heat setting. During heat setting, the polymer is heated (annealed) above the glass transition temperature but its physical dimensions are retained, preventing shrinkage. The temperature encourages thermal crystallisation and it is this that hinders the recoiling of any remaining amorphous regions of the polymer, even at temperatures higher than the $T_g$.

Shrinkage has also been found to be reduced by applying shear to the deformation process, thereby producing more strain induced crystallisation.

Statton et al have concluded using infra-red techniques that the shrinkage occurring in PET is the result of chain folding, with higher annealing temperatures resulting in more regular chain folding and this is particularly true for a sample that is free to contract. An external tension applied to a sample during an annealing treatment will determine the internal shrinkage tension caused by the molecules during subsequent reheating.

Other studies, most notably by Pinnock and Ward on spun fibres, have been conducted on the basis that the amorphous polymer behaves like an amorphous network formed during solidification and that the origin of anisotropy of PET during spinning is the deformation of this network, although they restricted their work to draw ratios below 2, i.e. before strain induced crystallisation becomes significant. An alternative view presented by Wilson suggests that PET behaves as a two phase system, the shrinkage observed is a result of disorientation of the amorphous regions. This was further supported by work by Bhatt and Bell. The applicability of the network theory to the amorphous phase however has been found to be limited to draw ratios of up to 3.5. In these studies crystallisation by chain folding as above was only found to be significant at higher temperatures.
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2.5 COMPARISON OF SOLID-STATE DEFORMATION PROCESSES

The work of Coates and Ward\textsuperscript{143} presents the idea of true stress-strain-strain rate surfaces for given polymers. In this study the polymers of interest were linear polyethylene (LPE) and polyoxymethylene (POM), under given conditions of temperature, pressure and initial material treatment. It is assumed that for a given temperature and strain rate, there is a unique relationship between true stress and strain; the strain imposed on the material at an instant determines the relationship between true stress and strain rate, \textit{Figure 2.5 (a) and (b)}. The fact that such a true stress-strain-strain rate surface exists implies that any deformation process at a given temperature may be described by taking an element of material along a specific path across this surface. Ward and Coates used samples of material with differing initial morphology in order to investigate the nature of deformation prior to and after necking and found that there was a close agreement of stress-strain-strain rate relationships.

The concept is further supported by Davis and Pampillo\textsuperscript{144} who investigated LPE using a single specimen exposed to a jump in strain rate during drawing. Also Wu and Turner\textsuperscript{145} performed strain rate jump experiments and discovered that when a change in strain rate is imposed, the flow stress shifted to a new value corresponding to the stress-strain curve at the new strain rate.

The flow stress-strain-strain rate surface may be used to explain why hydrostatic extrusion of polymers is unfavourable for large deformation ratios and why the material draws away from the die wall during die drawing, \textit{Figure 2.5 (c)}.

In a uniaxial tensile test the variation of stress-strain-strain rate in the neck region is complex. In the neck, the strain rate will rise sharply, where the draw ratio is small, to some maximum value. The neck stabilises and moves along the material and the strain rate decreases with the increasing draw ratio imposed. The true stress increases indicating strain hardening. Where there is homogeneous drawing of the material beyond the neck, the strain rate is inversely proportional to draw ratio.

In hydrostatic extrusion the material passes through a conical die and as such the strain rate field is determined by the geometry of the die. Coates, Gibson and Ward\textsuperscript{146} have investigated the hydrostatic extrusion process and have found the process flow path for extrusion is therefore quite different to tensile drawing, simply because a different strain rate path has been imposed. The strain rate is such that the highest levels of plastic deformation occur as the polymer nears the die exit. The work of Coates and Ward\textsuperscript{143}
has shown that the strain rate sensitivity of the flow stress increases rapidly with plastic strain and so at the die exit, where the deformation ratio reaches a maximum, there are very high stresses and detrimental die pressures. These high strain rate fields imposed by the process make it impossible to use fast production rates under isothermal conditions.\textsuperscript{147,148}

By contrast, in die-drawing the billet is free to neck down at any point within the die because the stress flow paths make it more favourable for it to do so. The strain rate field in the deforming polymer is imposed by the polymer itself and the drawing conditions. The profile that the material adopts on leaving the die wall reflects the optimal strain rate field for the polymer under these conditions. The strain rate field is
such that the highest strain rates are encountered at low levels of deformation. By
careful control of the strain rate field imposed on the material by the geometry of the die
it can be seen that it might be possible to control the position at which the material necks
away from the die wall. It is evident that for different strain rates, i.e. velocity, and
temperature the stress strain relationship will change and so it is quite certain that a
different optimum die geometry will exist for different drawing conditions.\textsuperscript{149}

A product smaller in cross section than the die exit may be obtained, in contrast to solid
state extrusion where the polymer remains in contact with the die so that a die-exit size
product is produced. Strain hardening behaviour allows the neck to stabilise in die
drawing and steady state deformation is obtained at a constant velocity. In comparison
to hydrostatic extrusion, the deformation ratio increases with draw speed. The limited
deformation ratios of the high molecular weight materials are not as pronounced in die
drawing.

The high hydrostatic pressures involved in extrusion also inhibit the process, in particular
for crystalline polymers. LPE, POM and PP\textsuperscript{147,148} are typical examples. The dependence
of flow stress of polymers on pressure has been well investigated.\textsuperscript{146} It is found that flow
stress of the material rises with increasing applied pressure, plastic strain and strain-rate,
thus limiting the extrusion velocity at the die exit for greater deformation ratios.

At higher deformation ratios, the tie molecules will play an important role in the
deformation since this occurs by slipping along the c-axes. Deformation could be
initiated locally by shear stresses acting where the tie molecules connect with the
crystalline zones (a localised Coulomb yield criterion). Therefore the influence of normal
stresses acting at these points will affect the process and this leads to the pressure
dependence.

With die-drawing on the other hand, the low hydrostatic stress component eliminates
much of this problem. The polymer in contact with the die wall in die drawing will
experience a pressure from the die wall but this only occurs at low deformation ratios
where the pressure effects are small.

In summary, the ultimate limitations of the hydrostatic extrusion process are associated
with output rates; it is essentially a batch process, requiring a discrete billet of material to
be loaded into a temperature controlled pressure vessel. The equipment used for
hydrostatic extrusion has a high capital cost compared to that used for die drawing. The
combined effects of high strain rates at high stress and the pressure dependence of the
flow stress taken together account for the limitation of hydrostatic extrusion speed.
These combined effects lead to high cycle times making it impossible as a means of producing large section high stiffness polymers at commercially acceptable production rates.

2.6 PROCESSES FOR CONICAL DIE DEFORMATION IN THE SOLID PHASE

Solid state deformation can be divided into two basic types involving orientation by means which is essentially an extensional deformation or orientation by means where a shear component is present. Elongation deformation is important for obtaining chain extension in an axial direction but in shear deformations, the velocity gradient normal to the flow direction induces a superposed motion of rotation and translation on each material element. Recently Mascia and Zhao have examined the principles of shear deformations on solid-state extrusion of ultra-high molecular weight polyethylene (UHMWPE) and polytetrafluoroethylene (PTFE) through convergent-divergent dies.2-6

Whilst this research work will deal with solid-state die-drawing, the similarities between this process and that of solid-state extrusion means that much of the research so far conducted on the latter becomes relevant. There are specific phenomena which are unique to the extrusion process, but nevertheless an understanding of these may help to explain other observations made in die-drawing. For this reason the literature review will consider the two solid-state extrusion processes, ram extrusion and hydrostatic extrusion, as well as die drawing. Schematic diagrams of these processes are shown in Figure 2.6.

2.6.1 Solid-state extrusion

In solid-state extrusion, a solid polymer billet is forced through a conical die under high pressure. There are two types of solid-state extrusion processes which differ principally in the way that the extrusion pressure is transmitted to the extruding polymer. In ram extrusion, otherwise termed cold extrusion, the polymer is pushed through the die with a ram and the polymer is in contact with the die, containing vessel and ram causing a lot of friction. These frictional losses are essentially eliminated by hydrostatic extrusion as the billet is surrounded by a pressurised lubricant which transmits the extrusion pressure. Because of the effect of the lubricant between the billet and the die, the extrusion pressures required are usually lower than required for ram extrusion under comparable conditions. The deformation approximates more closely to convergent flow and so the
amount of deformation attainable for hydrostatic methods should be greater than ram extrusion.

In extrusion processes, the deformation ratio is referred to as the extrusion ratio. As the polymer passes through the die, it deforms such that the molecules tend to align themselves along the extrusion direction with the result of enhanced mechanical properties of the extrudate in this direction.
2.6.1.1 Ram extrusion

Ram extrusion has been successfully applied to a range of polymers, including high density polyethylene\textsuperscript{150-157} low density polyethylene\textsuperscript{158,159} polypropylene\textsuperscript{157,160} nylon\textsuperscript{73,155} and polyvinylchloride and polyoxymethylene.\textsuperscript{157} The attainment of high extrusion ratios with the most efficient molecular orientation has been found to occur at an optimum temperature between the glass transition temperature and the crystalline melting point.\textsuperscript{161,162} It is more usual for this optimum temperature to be fairly close to the transition temperature, $T_g$, because as the melting point is approached, the deformation becomes ever more viscous with much reduced orientation efficiency. Nakamura \textit{et al}\textsuperscript{161} found the optimum extrusion temperature for polypropylene to be 110°C which is exactly the transition temperature.

Extrusion temperature appears to have a significance when considering post die annealing of the extrudates.\textsuperscript{163,164} It appears that where extrusion temperatures are lower, little annealing occurs downstream of the die during the process. For polyethylene extruded at 80°C for example,\textsuperscript{164} the extrudates showed elastic after effects such as shrinkage at higher temperatures. When extruded above 100°C, on the other hand, they remained dimensionally stable. This implies that either post die annealing occurs at these higher temperatures or that amorphous deformation only occurs at lower temperatures. There is a further suggestion by Maruyama \textit{et al} that extrusion temperature has an effect on the coefficient of friction between the material and die wall. An increase in temperature has been observed to lower the coefficient of friction for polyethylene by some workers.\textsuperscript{165}

Extruding the materials below $T_g$ makes it extremely difficult for the molecules to rearrange because of the mechanical cross-linking effects at these temperatures. The covalent bonds tend to rupture before the folded chain crystals can be pulled out into extended chains. If extrusion must be carried out below $T_g$ then extremely long extrusion times are necessary. The alternative of raising the extrusion pressure in an attempt to increase the process rate will most likely result in a fractured extrudate.

Fractured extrudates have also been observed as crazes and cracks at high extrusion ratios.\textsuperscript{155,161,166} The fractures occur at lower extrusion ratios as the extrusion temperature is reduced. The defects have been found to be small fractures oriented at different angles to the extrusion direction and these affect the tensile properties of the extrudate significantly.\textsuperscript{166}
In an attempt to understand extrusion phenomena, and in particular the observed fractures, reference has been made to melt extrusion through conical dies by a number of workers.\textsuperscript{167-169} It was concluded that fracture originates from points in the flow where essentially extensional deformation exists with less shear.

It is generally observed that lubricants allow attainment of higher draw ratios and reduce the extrusion pressure required for a given extrusion ratio. The effect of using lubricants on the conical interface has been investigated with respect to the balance between shear and extensional deformations. Shaw\textsuperscript{169} found that a lubricant eliminated shear stress almost completely with the balance moving in favour of extensional flow. This results in high tensile stresses which in turn are responsible for fracture. So, despite lower extrusion pressures, the fracture in the extrudate becomes worse. The flow is forced to follow the sharper convergence within the die rather than establishing a more gradual convergence, typically a wine glass-shaped flow pattern, as found in un-lubricated flow. Die design for minimum pressure drop is at odds with the production of sound extrudates.

Predecki and Statton\textsuperscript{175} found that whilst the lubrication reduced the extrusion pressures, the efficiency of molecular orientation was reduced. Zhao\textsuperscript{6} found that pigments in polyethylene produce a lubricating effect which reduces the effectiveness of the orientation. Porter and co-workers have found that lubricants tend to affect extrudate clarity because of ingress of the lubricant into the extrudate surface, but did not find this detrimental to the mechanical properties.\textsuperscript{20}

Die angle has an affect on the extrusion pressure as investigated by Imada, Takayanagi and co-workers.\textsuperscript{170} An increase in die angle increased the required pressure and this can be accounted for by considering slip-line theory and integrating the theoretically required force between the die wall and deforming material, thus following the ideas of Hill.\textsuperscript{171} Takayanagi\textsuperscript{170} attributes the pressure increase with die angle as a consequence of a change in stress and velocity distribution, in particular around the die entrance.

Molecular weight was found to have a limited effect on extrusion pressure by Nakamura \textit{et al}\textsuperscript{161} who worked with polypropylene. They proposed that molecular interaction was a more dominant feature in solid state extrusion. Later Zachariades and co-workers\textsuperscript{172} reported that molecular weight had significant effects on the extrusion speed with lower speeds for a higher molecular weight polymer extruding at the same pressure. They also found that molecular weight affected the modulus of the extrudates and there was a linear increase in tensile strength with molecular weight.
2.6.1.2 Hydrostatic extrusion

Products successfully produced by hydrostatic extrusion methods include sections in linear polyethylene, polypropylene, polyoxyethylene, polymethylmethacrylate and glass fibre reinforced polyoxyethylene. The rods produced range in diameters from 2mm to 25mm.

The mechanism of deformation is almost identical to that of ram extrusion but the lubrication provided by the pressurised fluid means that observed deformation pressures are lower. The lubrication is more efficient than a lubricated ram extrusion and so generally the lubrication effects noted for this process are more extreme for hydrostatic extrusion.

Nakayama and Kanetsuna have studied hydrostatic extrusion using high density polyethylene. Extrusion pressure, temperature and extrusion rate relationships were investigated and found to support observations made by other workers. The minimum pressure required for extrusion was found to decrease with increasing temperature. The temperature had a significant impact on the rate at a given pressure.

Die angle also has an effect on the extrusion pressure for hydrostatic extrusion and was reported in another paper by Nakayama and Kanetsuna. They used different die angles and extrusion temperatures and found that higher temperatures produced the best quality extrudates, with low temperatures, higher die angles and high extrusion ratios being less appropriate conditions. In this study and another they found an optimum die angle relating to a minimum pressure. This result is in conflict with observations made by some other workers, most notably Takayanagi and co-workers, but is supported by evidence for a similar effect found in the extrusion of metals.

Gibson et al studied the hydrostatic extrusion of high density polyethylene to an extrusion ratio of about 20. They found that modulus increased linearly with extrusion ratio for extrusion ratios up to about 10, at which point the modulus started to increase more rapidly with extrusion ratio. This coincides with the point at which the birefringence of the extrudates tends to level off at a constant value after initially rising rapidly with extrusion ratio, a point at which the deformation changes from an extension of chains to deformation of the formed structure by chain slippage.

Davis found that a coating of PTFE on the die surface improved the process by reducing the slip-stick effect encountered otherwise. Davis and co-workers recognised that hydrostatic extrusion was a possible means of dealing with materials which cannot be processed by traditional means. This was later realised by Porter et al who used the
technique to process aromatic polyamide polymers with extremely high melting points (>300°C).

2.6.2 Die-drawing

For convenience of comparison with other work in the field the notation adopted throughout this report and the project will follow that used by Ward and co-workers. The technique involves pulling a polymer billet through a shaped conical die. The billet may be isotropic or may contain some pre-orientation introduced by a previous deformation. The billet which has an initial cross-sectional area of $A_o$, is drawn through the die (which has an exit cross-sectional area of $A_e$) and eventually attains a cross-sectional area of $A_f$.

For a given die, with a constant cross-section at its exit the nominal draw ratio is determined by the cross-section of the billet. Obviously if the deformation is to follow the die controlled deformation, the cross-section of the billet cannot exceed that of the die entry. The nominal draw ratio is given by;

$$\lambda_n = \frac{A_o}{A_e}$$

However since the product cross-section is expected to be smaller than the die exit, due to deformation outside the die, assuming constant volume the actual draw ratio obtained will be;

$$\lambda_f = \frac{A_o}{A_f}$$

The major process variables are billet and die geometry, billet and die temperature, rate of drawing and tensile drawing. Because the drawing occurs in the presence of a neck, the stress will vary with location along the die. The maximum stress occurs outside the die where the maximum draw ratio exists. A stress calculated based on the initial cross section, that of the billet, is the minimum stress and corresponds to the initial yield of the material. It is important to remember that at low deformation ratios near the entrance of the die, the strain rate is much higher than at higher deformation ratios experienced outside the die.192,193

The work of Ward194 has identified three regions of deformation occurring as the polymer passes through the die, refer to Figure 2.6. These can be summarised as follows.
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1. Convergent flow under conditions approaching isothermal where the deformation is governed by the geometry of the die. Strain rates are relatively low.

2. Necking away from the die wall under isothermal conditions if strain rates are small.

3. Further necking down beyond the die under non-isothermal conditions. The material progressively cools through zone three and deformation ceases at some point beyond the die.

Even at low drawing speeds, the actual draw ratio has been observed to be smaller than the nominal draw ratio indicating that a significant amount of post-die deformation.\textsuperscript{195}

Under the chosen drawing conditions, a stable neck can only be reached if the polymer has a sufficiently high strain hardening behaviour.\textsuperscript{143} Another factor that aids the stability of the process is the temperature profile. The polymer in the die can be considered to be isothermal. As the polymer moves axially away from the die it will cool progressively and the non-isothermal behaviour of the post-die deformation means that the polymer will experience a complicated thermal and strain rate history. The cooling acts as a stabilising influence on the process since it will counteract the effects of deformational heating and also it is known that drawing at lower temperatures is more effective in producing a greater improvement in properties.

The drawing will effectively cease when the stress at the highest deformation ratio element becomes insufficient to deform the material at the prevailing temperature of that element. The length of the non-isothermal zone will depend on heat transfer, being influenced by velocity and scale of the process. It will be smaller for slower deformation rates. As the draw speed is increased it is possible that the temperature gradient along the product may be altered considerably. Deformation in the die region and post die zone may in fact tend towards an adiabatic state whereby the work done in deformation is not dissipated quickly to the surroundings. This effect might be more pronounced in a larger scale process where the ratio of volume to surface area is increased. The length of this zone has also been found to vary for different polymers and different molecular weights. This is a result of the influence molecular weight has on strain rate and temperature dependence of the polymer.

One problem associated with the die drawing method is that of starting the process. The original isotropic material of the polymer billet cannot withstand the drawing load for a deformation ratio greater than 2.72.\textsuperscript{196} The load time curve typically demonstrates a peak in the initial stage of drawing, followed by a steady load which remains throughout the drawing process. The peak often causes the material to break at the neck.
One method suggested by Ward and coworkers\textsuperscript{195,197} utilises a stepped billet having steps in diameter along its length increasing from the nose which is small enough to thread through the die up to the uniform diameter of the billet. The idea behind this method is that at low diameters, or cross sections, the draw ratio is small and the associated maximum drawing stress experienced by the undrawn, isotropic material outside the die will be small enough to prevent it from breaking. As the first stage of drawing at this diameter is completed, proceeding to a larger diameter the draw ratio increases and the stress rises correspondingly. The initial undrawn material may not be strong enough to support this load, but the oriented material resulting from the first drawing stage will be stronger and by re-gripping on this material the drawing can continue. The number of stages required depends upon the final value of nominal draw ratio. The maximum increase in diameter with each stage will depend on the draw stress and the strength of material obtained from drawing the previous stage.

An alternative method provides a continuous increase in the nominal draw ratio and involves machining a conical section on the end of the billet, having a conical semi-angle which is substantially less than the die angle. The nominal draw ratio increases smoothly with this method.

Another method of starting is to produce an oriented nose on the billet to the required draw ratio by hydrostatic extrusion, producing oriented material of sufficient strength to support the die drawing stress. A swaging method, as used in wire drawing, may also produce an oriented tag.

\textbf{2.6.2.1 Stability of the process}

The drawing load, or tension in the product, at a given temperature provides the work for deforming the material in the die. Considering the strain rate dependence of the yield stress in polymers one would expect the drawing load to increase as the velocity increases, corresponding to the increase in work done per unit volume in the deformation zone. However this effect is counteracted because an increase in strain rate also causes the material to leave the die wall at an earlier point and this reduces the work done. The length of Zone I, i.e. the length over which die contact is made, therefore acts as a control mechanism for stabilising the draw load. This phenomenon has been observed in practice when drawing polyethylene.\textsuperscript{198} It has been found that it is difficult to measure the actual point at which the material leaves the die wall because of the elastic recovery and thermal dimensional changes that occur when the billet is removed from the die.
The die angle affects the amount of work done on friction at the die-billet interface. The surface area decreases with increasing die angle and frictional work done decreases accordingly. The magnitude of the shear component of work done in deforming the polymer (redundant work) increases with increasing angle. A small angle, and with additional lubrication, is likely to shift the ratio of shear stress to tensile stress in the direction of a more tensile process and thus increased extensional flow. Suggested lubricants include PTFE spray. Predecki and Statton have proposed that the optimum die angle for extrusion of polyethylene is about 4°. An improvement of strand quality with a reduction of die angle has been observed by Capriati et al and this was attributed to the longer residence time in a die for a given draw ratio. With a slower draw rate there is a more gradual development of tensile stress.

### 2.6.2.2 Die-drawing process variables

Small scale die drawing, making use of an Instron machine has been performed on polypropylene, polypropylene copolymer, polyethylene, polyoxymethylene, polyvinylidene fluoride and Polyetheretherketone (PEEK). Larger scale die-drawing has been conducted on polyoxymethylene, polyethylene in square-section and sheet form, polyvinylidene fluoride, polyethylene terephthalate and polyvinyl chloride.

It is apparent that for a given billet size an increase in drawing temperature leads to a reduced response in draw ratio to strain rate. Also in order to maximise draw ratio, a high nominal draw ratio is appropriate and a lower drawing temperature. Maximum drawing stress responds to actual draw ratio and hence total strain. At each drawing temperature a unique and substantially linear relationship is apparent between actual draw ratio and maximum stress. The relationship between Young's modulus and actual draw ratio shows little dependence on temperature for the temperature range 90-110°C. However at 120°C the drawing is less effective in enhancing stiffness. By operating at 120°C, the lower relaxation times are sufficient to reduce the number of crystalline bridges between crystalline blocks during deformation.

Parsons and Ward have performed compression tests on LPE drawn with a draw ratio of 14 and modulus of 20GPa. An ultimate tensile strength of about 500MPa was observed whereas the ultimate compression strength was only 60MPa. They discovered that in compression, signs of shear failure were apparent with longitudinal splitting at high deformations. The oriented system is susceptible to buckling in compression axially.
Gibson and Ward\textsuperscript{198} have conducted die drawing experiments on glass reinforced polypropylene GFPP. This material was found to produce slightly different results from the unfilled polymer in that the draw ratio/velocity relationship is convex and the drawing load increased progressively as velocity increases rather than level off. In a fibre reinforced polymer, two mechanisms contribute to the mechanical properties as the polymer is stretched; the orientation of the fibres and the stiffening of the polymer matrix.

One application of die drawing which demonstrates commercial significance is the production of tubular products with enhanced properties.\textsuperscript{198,204-209} Tube drawing represents a biaxial drawing process with an initially isotropic, tubular billet being drawn over a mandrel causing an axial elongation and a hoop-wise expansion. It has been found that the same modulus/deformation ratio relationship exists for the tubular products as for rods produced by uniaxial deformation.

Multi-filament drawing has also been investigated\textsuperscript{194,198} where a bundle of fibres are drawn through a single die. Gibson\textsuperscript{198} discovered that LPE filaments can be drawn to a draw ratio of 20 with a Young's modulus of 44\text{GPa} by this method. The filaments tend to take a prismatic form due to their contact between the die and other fibres.

The following sections describe the process parameters of die-drawing in more detail;

\subsection*{2.6.2.2.1 Nominal draw ratio;}

The point at which the upturn in the draw ratio/draw speed curves occurs is dependent on nominal draw velocity and decreases with increasing nominal draw ratio. Since the material tends to leave the die wall, the value of nominal draw ratio does not have the same significance as it does with hydrostatic extrusion and its use with die drawing can be a little misleading. It is in fact the initial cross section of the material that has an influence. At lower velocities however, the polymer will tend to stay in contact with the die nearer the exit. The ratio of nominal draw ratio to actual draw ratio, i.e. diameter of die exit cross-section to product cross section, may be expected to have a greater influence in this case. The closeness of the die wall to the product during the transition from the isothermal to non-isothermal conditions may affect the heat transfer for example.

\subsection*{2.6.2.2.2 Drawing temperature;}

Increased drawing temperature reduces the dependence of draw ratio on the strain rate and also decrease the maximum attainable draw ratio. The maximum drawing speed
possible increases with temperature. The maximum draw stress is reduced by an increase in temperature and at a given temperature it is dependent on the draw ratio.

2.6.2.2.3 Molecular Weight;
The optimum temperature for large plastic deformations depends to some extent on molecular weight.

It has been observed that for a given nominal draw ratio, increasing the polymer weight average molecular weight reduces the slope of the draw ratio against haul-off velocity relationship. That is, increasing molecular weight reduces the influence of haul-off velocity on draw ratio. Gibson and Ward investigated small-scale die drawing of LPE homopolymers with various molecular weights at 100°C. They found that high molecular weight material reduced the maximum possible draw ratio to less than 12. An increase in molecular weight creates a more effective network during initial crystallisation and this hinders the subsequent drawing process. Lowering the molecular weight on the other hand reduces the maximum attainable haul-off velocity.

The higher molecular weight materials tend to yield a lower moduli for a given draw ratio. Higher molecular weight LPE tends to be easier to process into billets by extrusion, however. Higher temperatures are required to draw these materials to achieve their optimum properties, such as stiffness.

2.6.2.2.4 Crystallinity;
Molecular weight and copolymerisation affect the type of crystallinity for a given thermal history. The crystallinity of the polymer is usually affected by the preparation method employed on the polymer billet. When billets are prepared by rapid cooling from the melt, they are considered to contain a low crystallinity and lead to a greater proportion of molecules being incorporated into more than one lamella. This leads to a denser network structure and the increased number of entanglements affect the drawing behaviour by reducing the overall strain.

High crystallinity can be attained by careful control of the cooling process. A slow oven cooled technique can be utilised. Capaccio et al. have prepared high density polyethylene with a high crystallinity content by melt spinning at 200°C and crystallising in a glycerol bath at 118°C.

2.6.2.2.5 Copolymerisation;
Copolymerisation has a similar effect to that of using a high molecular weight. It decreases the maximum attainable draw ratio and modulus (although some investigations
have reported that copolymerisation has no effect on modulus\(^{219}\) and increases the maximum haul-off velocity that can be achieved for a given set of conditions. The draw ratio response to velocity is somewhat flatter. Gibson and Ward initially reported the opposite\(^{195}\) but this was due to an error in material identification.\(^{194}\)

Copolymerisation has shown benefits for production of polyethylene pipe.\(^{209}\) The copolymer grade could be processed at much faster rates compared with a homopolymer and, more importantly, the stress rupture of the copolymer pipe was substantially enhanced unlike the homopolymer where this property was unaffected by orientation. Under given conditions of temperature, the copolymer did not show significant post die deformation in contrast to a homopolymer.

2.6.2.2.6 Scale effects;
An increase in scale means that the billets surface area to volume ratio decreases and as a result it is feasible that the heat of deformation in the neck may be retained more effectively in a large scale process. As a result the actual drawing temperature in the deformation zone increases. This is consistent with the observations made for LPE and POM\(^{194}\) as an increase in scale has been observed to reduce the draw ratio obtained at a given strain rate and to decrease the maximum attainable draw ratio. Drawing stress was also found to change with scale according to the deformation ratio. For a given strain rate it follows from the stress-strain-strain rate surface that since the drawing stress is reduced, a lower strain will be imposed.

2.6.2.2.7 Haul off velocity;
Drawing of polypropylene copolymer\(^{197}\) shows that the drawing load increases slowly with an increase in haul off speed.

The main effect of increasing the draw velocity as observed in many studies by various workers is that the draw ratio increases. At higher draw speeds the relationship of draw ratio and speed steepens and a limiting value of draw speed is reached for a given temperature. The limiting value increases with molecular weight. Given the steepness of the curve of this relationship there is an obvious of the need for good stability of the draw velocity if a product of consistent profile is to be obtained.

Increasing the value of nominal draw ratio decreases the draw speed required to obtain a particular value of draw ratio, but does not affect the maximum attainable draw ratio.

An interesting effect was observed by Parsons et al.\(^{194}\) when drawing polyethylene sheets at various draw speeds and temperatures. It was found that above a certain temperature,
the speed versus draw ratio relationship shows a cusp such that above a certain strain rate, the draw ratio tends to decrease before increasing once again. This apparent shift towards higher velocities for a given draw ratio is consistent with a rise in drawing temperature. This may be attributed to a greater retained heats of deformation. The stress vs. velocity curve reflects this shift. Lazurkin\textsuperscript{211} has in fact suggested that in order to eliminate any retained heat of deformation draw speeds have to be minimised and a typical value given was that when drawing 2mm samples, a draw speed of less than 0.6mm/min must be employed.

\textbf{2.6.2.2.8 Draw ratio;}

Previous studies for tensile drawing and hydrostatic extrusion\textsuperscript{58} have shown that modulus values obtained could be considered to be approximately a unique function of draw ratio, holding for a range of polymer grades. These two processes are carried out under approximately isothermal conditions and it is possible that the differences experienced between grades for die drawing is a consequence of the non-isothermal nature of post-die zones.

\textbf{2.6.2.2.9 Draw load;}

The draw load is generally found to be independent of draw speed, although it has been observed to have lower values at low draw speeds.\textsuperscript{195,209} Also at the highest draw ratios where the sensitivity if draw ratio to speed is greatest, the draw load tends to decrease.

Hope \textit{et al}\textsuperscript{174} have investigated the hydrostatic extrusion of non circular sections. Their findings, although based on hydrostatic extrusion will be borne out for the die drawing process also. Higher strain rates for a given product will be experienced at various points within the die as the material takes on the new profile and an increased surface to volume ratio causes a significant increase in the frictional component of work done.
Chapter 3 Biaxial orientation in die-drawing

The purpose of this chapter is to present the idea that shear deformation, in particular rotational shear, superimposed on a conical flow deformation would provide a viable route to biaxial orientation in die-drawn products. A detailed review of recent developments in solid-state processing by Mascia and Zhao\textsuperscript{1-6} on which the current work builds is given. Analytical expressions for magnitude of rotational shear strain at different points through a special helically shaped die show that the orientation developed should depend on the rate at which twist is applied to the material when it passes through the die.

3.1 REVIEW OF RECENT WORK

Deformation occurs as a result of work done on a material. The total amount of work required and the distribution of work relative to the increasing deformation ratio will depend on the process used. A typical deformation will comprise both useful and redundant work. The amount of useful work is the minimum required to produce the net deformation under ideal conditions and is equivalent to the work done during a homogeneous deformation. Redundant work is the additional work that is spent as a result of employing a particular process. It can arise through friction losses or through shear mechanisms occurring wherever the direction of material flow changes. Both these redundant contributions occur in conical flow processes.

Solid-state conical flow differs from conventional melt-state flow in that the solid polymer billet deforms plastically and slides at the metal interface, establishing a plug flow pattern whereby cross-sections of material remain planar and perpendicular to the flow direction. A typical convergent die as used to produce monoaxially oriented extrudates is shown in Figure 3.1. Flow is directed towards the die apex.
Assuming plug flow, the deformation of a cubic element of material moving through the deformation region would be expected to be as shown in the figure. Consider now the same material being forced through another die, but this time the profile being such that no net reduction in cross-sectional area, and hence no increase in longitudinal dimension, occurs across the deformation region. The final extension ratio would assume a value of 1. This is shown in Figure 3.2. Although there may be no apparent elongation or change of cross-sectional area or shape, there will still be orientation developed because shear deformation has been experienced by the material. The geometry of the emerging element is shown in the figure.

Biaxial orientation has been successfully achieved by solid-state extrusion by Mascia and Zhao\textsuperscript{1-4} who used convergent-divergent (C-D) dies to produce large section polymeric extrudates. The extrudates demonstrated improved transverse mechanical properties. The convergent-divergent dies had cross-sectional profiles which caused the polymer to deform by shear rather than extensional plastic flow.

In their work, Mascia and Zhao investigated the development of orientation within these shearing dies and established a number of routes to obtaining different orientation patterns within products of similar cross-sections formed from similar billets. They considered four differently profiled C-D dies in their study, three of which are shown in Figures 3.3, 3.4 and 3.5.

It can be seen that for each die the entry and exit cross-sectional areas were identical implying no net acceleration of the material as it passed through the die. In fact not all these dies were strictly pure shear dies since the cross-section did not remain constant through the die except in the case of the constant cross-section fish-tail die. Therefore, at some points within the die, longitudinal deformation may occur. This will essentially
be elongational where the die cross-section is reducing and retractive where the cross-section is increasing. So even if the net deformation appears to be purely shear, it does not mean that no elongational deformation has occurred during the process. The importance of this deformation history when considering orientations will become apparent later.

A true pure shear die must maintain the cross-section along the die axis at a constant value. Even then, the deformation is only truly pure shear if the cross-section is filled
with material at every point along the die axis. This point was demonstrated by Mascia and Zhao who used a so called Dual-Taper Die which had a cross-section of 125mm$^2$ at entry, exit and the mid section, but increased by up to 16% at intermediate sections, (Figure 3.6). The expansion fish tail die demonstrated an even greater increase in cross-sectional area at its mid point, almost 80%. This is also shown in Figure 3.6.

The resistance of the polyethylene to longitudinal compression, and hence transverse expansion, to fill the cross-section at these intermediate points at lower processing temperatures, meant that it did not contact the die walls at these intermediate sections. This resulted in a twisting deformation within the die as illustrated in the Figure 3.7. This phenomenon could only be visually recognised by opening the die mid-process. This was because extrudates produced by the Dual Taper die had the same cross-sectional shape and more or less the same cross-sectional area by the time the material emerged from the die exit, the twist having been apparently 'ironed out' and lost. The phenomenon was noted to disappear at higher processing temperatures and this was attributed to the reduction in longitudinal yield stress. At these higher temperatures the die remained full at every cross-section, the deformation defined by the die profile. As such there must have been local, longitudinal compression followed by elongation both before and after the mid-section of the die.

Figure 3.6; Showing the variation in cross sectional area for each of the dies used by Mascia and Zhao.
Chapter 3 Biaxial orientation in die-drawing

Figure 3.7: Showing twist deformation resulting from incomplete filling of the die. The twist deformation results in an orientation at an angle to the transverse axis.

Figure 3.8: Showing the development of transverse draw ratio for each of the fish tail dies.

Inspection of the extrudates using birefringence techniques showed that whilst they all contained transverse orientation, which was fairly uniform across the section and much higher than in the longitudinal direction, the orientation of the ‘twisted’ samples was found to lie at an angle with the extrudate axis. This provides evidence that the twist induced some rotational shear deformation and that the orientation developed by this was retained even with further deformation and when, the net macroscopic deformation appears to be the same. Thus, the amount and type of orientation achieved is not only dependent on the amount of deformation imparted to a material. Whilst the net deformation may be identical under similar processing conditions, the different route by which this deformation was obtained has a significant effect on the magnitude and direction of the orientation.

The investigation using fish-tail dies provided more evidence that the orientation produced within a given net deformation depends upon the deformation history of the material as well as processing conditions. Two fish-tail dies were used, both deformed a
Chapter 3 Biaxial orientation in die-drawing

billet of material 10mm by 10mm to a flatter profile of 50mm by 2mm. One of the fish-tails had straight boundary surfaces resulting in an increase in cross section at the centre whilst the other die had curvilinear convergent boundary surfaces to keep the cross-sectional area constant along the entire length of the die. The dies were referred to as Expanding Cross-section Fish-Tail (EXFT) and Constant Cross-section Fish-Tail (CXFT) respectively. The angle of convergence was much smaller than the angle of divergence for both these dies.

It was found that compared to the longitudinal orientation, the transverse orientation was higher and was developed much more effectively when using the constant area fish-tail die rather than the expanding-area fish-tail die. In order to explain this result it is useful to consider the deformation ratio and hence deformation rate that occurs along the axis of each die, Figure 3.8. Assuming the longitudinal draw ratio to be unity throughout the deformation, the rate of deformation for the expanding-area fish-tail was lower than for the constant area fish-tail die near the entrance of the die. The material deformation rate in the expanding fishtail die increases through the die and becomes higher than that in the constant area die near the die exit. The development of orientation with deformation would therefore appear to be more effective at the lower deformation ratios and using higher strain rates at lower strains gives rise to a higher orientation.

Using these findings it is possible to see how the deformation within die drawing may be affected by utilising a die which not only imparts a convergent flow but also a rotational shear in an attempt to provide a small degree of hoop-wise orientation. The deformation profile and the relative magnitude of the rotational shear should be key factors that affect both the deformation mechanism and the biaxial orientation produced.

3.2 ROUTES TO MATERIAL DEFORMATION

In this section notation is used to indicate differences between linear and rotation directions. Subscripts $l$ and $\varphi$ denote linear and rotational directions respectively; hence $\gamma_l$ represents linear shear strain and $\gamma_\varphi$ represents rotational shear strain.

Consider the possible routes that may be followed to deform a length of material to a given deformation ratio. The main components of work involved in a deformation process can be identified as;

1. Work of deformation (homogeneous process)
2. Work of redundant deformations (shear processes)
3. Work done against friction

The magnitude of each of the first component will depend upon the magnitude of the deformation ratio. The second is determined by the any changes in flow that the material experiences during the process and the frictional component will depend on any contact between the material and tools that are used to deform it. Both the latter two components are redundant because they play no useful part in the deformation.

3.2.1 Homogeneous processes

Homogeneous tensile drawing represents the most ideal in terms of minimising the amount of work required. In an ideal case, the absence of a neck means that material flow is unidirectional, and can be illustrated schematically as in Figure 3.9. No frictional, or shear losses are present.

3.2.2 Linear shear

Wherever a neck forms there will be localised changes in the direction of flow for any elements of material which are at some distance from the axis of symmetry. This is similar to the situation that occurs in conical flow processes such as die-drawing or solid-state extrusion. Here, changes in the flow direction occur at both the die entrance and die exit.

The flow is parallel to the die axis on approaching the die. As the material flows into the die it deforms by shear so as to flow towards the die apex. Material emerging from the die experiences a reverse shear to return its motion along a path parallel to the die axis. The work involved in these shearing processes does not contribute to the net deformation and is therefore redundant. Since the angle through which the flow changes...
is the same at a die entrance and exit, the linear shear strain applied to an element of material entering the die, $\gamma_o$, is the same amount applied at the die exit, $\gamma_f$.

Linear shear strain at the die entrance, $\gamma_o = \tan \delta_o$

Linear shear strain at the die exit, $\gamma_f = \tan \delta_f$

Where $\delta$ is the angle through which the flow direction changes for an element of material passing from parallel flow to conical flow at the die entrance and back to parallel flow at the die exit.

Since $\delta_f = \delta_o$,

$\gamma_f = \gamma_o$

It is clear that the component of work associated with linear shearing at the die entrance and exit depends upon the die angle.

### 3.2.3 Rotational Shear

Rotational shear can be imposed by causing relative rotations of adjacent cross-sections of material. The principle is shown in Figure 3.10. It is obvious that in order to realise a twisting deformation to a piece of material, it is necessary to have some sort of mechanical key to grip the material allowing opposing rotational forces to be applied to different cross-sections. For this reason round cross-sections are inappropriate and so square sections have been used throughout the analyses and in practical work.
The figure shows a square-section, undeformed, billet moving through a deformation region where it experiences an instantaneous rotational shear at point $A$. Each cross-section is rotationally displaced relative to the adjacent section coming through behind it and, assuming the deformation to be plastic, the result is a product of a helical shape. If transverse planes remain planar, it would be expected that the resulting product would have a square cross-section with the same cross-sectional area, but that some hoop-wise orientation would exist within each section. The rotational shear is applied about the axis of the billet and so the orientation should lie along tangents and depend on the radial distance from the axis. There should be a gradient of orientation from zero at the axis to a maximum at the largest radius.

For any element of material passing through plane $A$ the magnitude of the rotational shear strain, $\gamma_\phi$, will depend on the angle of twist, $\theta$, over length $l$, and on the radial distance, $r$, of the element from the axis of rotation.

\[ \gamma_\phi = \frac{r\theta}{l} \]

### 3.2.4 Rotational shear and extensional deformation

If a linear extensional deformation is imposed after a rotational shear, its effect will tend to reduce the contribution of rotational shear strain component to the total deformation of a particular element. This can be illustrated by considering the effect of tensile drawing the helical shaped product obtained above, as shown in Figure 3.11. Each element of material increases in length according to the draw ratio. The relative rotational displacement of the ends of the element remain the same but the ends become further apart. The magnitude of the rotational shear strain, after drawing, $\gamma_{\phi'}$ is the same
Chapter 3 Biaxial orientation in die-drawing

as that required to straighten the product. Since it is shear strain recovered, it has a negative value. Figure 3.12 shows rotational shear strain of an element on the surface of a cylinder in the helical product before and after tensile drawing, \( \gamma_{oo} \), and \( \gamma_{of} \) respectively.

From the figure it is clear that:

\[
\gamma_{oo} = \frac{r_o \theta}{l_o} \quad \text{and} \quad \gamma_{of} = -\frac{r_f \theta}{l_f}
\]

The initial and final lengths of the element \( l \), and the radial distances that it lies from the material axis before and after drawing, \( r \), can be related with reference to the draw ratio, \( \lambda \).

\[
l_f = \lambda l_o \quad \text{and} \quad r_f = \frac{r_o}{\sqrt{\lambda}}
\]

Therefore for tensile drawing the amount of rotational shear strain of an element after experiencing an extensional draw ratio of \( \lambda \) can be related to its initial rotational shear by the following expression:

\[
\gamma_{of} = -\gamma_{oo} (\lambda)^{-3}
\]

The difference between \( \gamma_{oo} \) and \( \gamma_{of} \) is equal to the shear strain removed by the extension, \( \gamma_{tensile} \)

\[
\gamma_{tensile} = -\gamma_{oo} \left(1 - \frac{1}{(\lambda)^{3/2}}\right)
\]

3.2.5 Rotational conical flow

Suppose now that a square section conical die is such that its cross-sections rotate at a constant rate along the die axis, i.e. constant pitch. This is shown in Figure 3.13. Assuming material is deformed plastically through this die it will emerge with a helical shape having a pitch equal to that of the die.

The constant rate of twist along the die axis can be expressed by \( \omega \), where \( \omega = \frac{\theta}{l} \). The rotational shear strain of an element at any point within the die at a distance \( r \) from the die axis is given by
Figure 3.12: The concept of rotation shear strain reduction resulting from axial extension.
Figure 3.13: Deformation constrained by the die geometry. The pitch is constant along its length.

\[ \gamma_\varphi = \frac{r\dot{\theta}}{l} = r\omega \]

At the die entrance an sudden rotational shear occurs, the magnitude of the rotational shear strain is;

\[ \gamma_{\text{entry}} = r_{\text{entry}} \omega \]

and at the die exit, the rotational shear strain of an element will be;

\[ \gamma_{\text{exit}} = -r_{\text{exit}} \omega \]

As before, this can be thought of as the amount of rotational shear required to straighten the element. Combining the above equations then gives a relationship for the rotational shear strain removed at the die exit in terms of that applied at the die entrance;

\[ \gamma_{\text{exit}} = -\gamma_{\text{entry}} (\lambda)^{-1/2} \]

The amount of reverse shear strain that must applied to a product in order to straighten it will therefore depend on the nature of the extension. Less reverse shear strain is required for a tensile drawn product helical product than for one drawn through a die with a constant pitch. This provides evidence of a third rotational shear component arising from deformation through the die. Although in both processes the shear strain of an element is reduced by extensional deformation, the amount is less when using a die. In
effect the die must provide some additional shearing as the material passes through it which compensates for that lost from the extension. The magnitude of this progressive shear strain applied by the die can be found from the difference between the reverse shears applied to the die drawn and tensile drawn products, where the initial shear strains are equal;

\[ \gamma_{\text{die}} = \gamma_{\text{entry}} \left( \frac{1}{\lambda} \right)^{-\frac{1}{2}} - \gamma_{\text{entry}} \left( \frac{1}{\lambda} \right)^{-\frac{3}{2}} \]

\[ \gamma_{\text{qdie}} = \frac{\gamma_{\text{entry}}}{\sqrt{\lambda}} \left( 1 - \frac{1}{\lambda} \right) \]

In summary, the three components of rotational shear strain experienced by an element of material passing through a conical die have a constant cross-section rate of rotation along its axis are;

- Sudden rotational shear strain at the die entry \( \gamma_{\text{entry}} = r_{\text{entry}} \)
- Through the die;

  Rotational shear strain due to linear extension \( \gamma_{\text{qentry}} = -\gamma_{\text{entry}} \left( 1 - \frac{1}{(\lambda)^{\frac{1}{2}}} \right) \)

  Progressive rotational shear strain through the die \( \gamma_{\text{qdie}} = \frac{\gamma_{\text{entry}}}{\sqrt{\lambda}} \left( 1 - \frac{1}{\lambda} \right) \)

- Recovered rotational shear strain at the die exit; \( \gamma_{\text{qexit}} = -\gamma_{\text{entry}} \left( \frac{1}{\lambda} \right)^{-\frac{1}{2}} \)

As expected, the sum of these components for a complete deformation resulting in a straight product is zero.

Figure 3.14 shows how the rotational shear strain components are developed for an element of material passing through a die which has a nominal draw ratio of 9. The curves are normalised with respect to the initial radial distance from the die axis and with respect to the rate of twist for the die. The three dotted curves represent the magnitude of each shear component and the solid line represents the total rotational shear of an element at that particular draw ratio. The reverse rotational shear at the die exit removes rotational shear from the drawn product.
Figure 3.14; Rotational shear strain through a helically profiled die.

It is clear from this graph that the highest rotational shear strains are present at low draw ratios which should, as discussed above, provide the optimum conditions for producing hoop-wise orientation.
Chapter 4 Die design and manufacture

This chapter describes the design and manufacture of the helical profile dies. The qualitative requirement for dies capable of imparting rotational conical flow has been described in Chapter 3. The die had to have a square cross-section with a constant die semi-angle (i.e. the angle between its axis and its boundary surface). The cross-sections rotate at a uniform rate along the die axis providing a rotational shear to the material cross-section at die entry, through the die, and at the die exit if a reverse shear is applied to straighten the product.

A straight channel die would be used as a control for all experimental work. It was reasoned that at least two dies with a helical profile would be required in order to establish firstly if rotational shear has an effect on the die drawing process and the products produced, and secondly, to what extent the magnitude of the rotational shear component affects the properties induced by such a deformation. All three dies would have the same length and nominal entrance and exit cross-section dimensions, giving the same convergence angle and nominal draw ratio.

4.1 SELECTION OF MANUFACTURING METHOD

With the geometry of the dies qualitatively defined it was then possible to consider means of manufacture. There were essentially two alternatives available; casting or machining from solid material. The main advantage with casting is that a one piece construction could be produced. This would prevent leakage of material through poorly mating surfaces which was a potential problem should multi-piece dies be used. However casting has a number of disadvantages with particular implications if used to manufacture these dies. There was no guarantee of eliminating distortions or accurately predicting the shrinkage and so good dimensional tolerances would be difficult to achieve. The surface finish of a cast component is also generally poor which would give
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an unpredictable variation in the coefficient of friction at the polymer/die interface. Polishing the internal surfaces would be difficult, particularly near the corners. The casting operation would require a core which itself would have to accurately reflect the shape and dimensions of the die profile. This could only be practically achieved if it were machined. By machining the die directly, the number of operations were reduced which minimised the sources of error that could be introduced during manufacture by casting.

4.2 DESIGN FOR MANUFACTURE

4.2.1 Die design

To machine the die from solid material, access to all internal die surfaces was required which necessitates splitting the die into a number of pieces. It was clear that the helical profile would not allow internal corners to be machined. It was logical to split the die into four similar ‘quadrants’ with each quadrant containing one face of the die profile. The mating surfaces at the profile corners would also form a helical shape, rotating around the die axis at the same rate as the profile. The quadrants are illustrated in Figure 4.1 in which (a) is a quadrant for Helical Die A and (b) is a quadrant of Helical Die B. The cross-section of a quadrant at any position along the die axis would contain two mating surfaces at right angles and the die profile surface at 45° to these mating surfaces as shown in the figure. It is clear that easy access for the cutting tool to all machined surfaces could be gained.

The die would be assembled by ‘screwing’ each of the quadrants in along the die axis from one end of the die. Plate 4.1 shows the finished die quadrants to illustrate the concept of how they are assembled to produce the die profile. In order to achieve a die cavity of accurate shape and dimensions, it would be necessary to provide some form of location for each of quadrants when assembled. This could be achieved by making the assembled die in the form of a cuboid and clamping this cuboid in a box as shown in Figure 4.2 and Plate 4.2. Relative movement between the quadrants could only occur by unscrewing about the die axis and this would be prevented by the clamping box.

The machining of the straight die did not require any special computerised techniques and was completed in the Departmental workshops. The completed die is shown in Plate 4.3. However the helical geometry of the surfaces on the helical dies combined with the three-dimensional cutting envelope of the tool prevented the use of manual machining methods. The manufacture of the helical dies required computational...
techniques for both die design and manufacture. These facilities were accessed through the Department of Manufacturing at Loughborough University.

(a)
(b)

Figure 4.1: The die quadrants for (a) Helical die A and (b) Helical die B

Plate 4.1: The machined die quadrants for Helical die A partially assembled.
Figure 4.2: A schematic of the die box assembly, used to clamp the die quadrants together.

Plate 4.2: The completed die box partially assembly.
Computer surface modelling can be used as a means of generating complex tool path data which allows machining by a one-dimensional (point contact) cutter. The computer calculates the tool path taken by the end of the cutter and the orientation of the cutter so that its axis is in a plane normal to the machined surface at the point of contact. A 12mm ball nosed cutter was used throughout. Machining the components in this manner required full 4-axis machining with all four axes moving simultaneously. The four axes involved included three linear motions along x, y and z and rotational motion about the y axis.

4.2.2 Die dimensions

All three dies were designed to have the same nominal draw ratio of 9, reducing isotropic billets from an initial cross-section 6mm by 6mm to 2mm by 2mm; it was considered that 6mm section was the practical limit for amorphous PET. The die length and rate of rotation were decided from a consideration of the machining operation. Vibration and deflection of the part was to be avoided which required a degree of part stiffness. As a result, the rate of rotation was limited to about 6°/mm. The two helical dies were made with rotations of 3°/mm and 6°/mm, referred to hereafter as Helical die A and Helical die B respectively. All dies were 60mm in length giving a total rotation of 180° for Helical die A and 360° for Helical die B.

4.2.3 Surface model of the dies

In order to generate tool paths, a virtual model of the part which defined the surfaces to be machined was produced. This model was constructed using a software package called DUCT, marketed by Delcam International, Birmingham UK. The model consisted of defined surfaces which represented the helical surfaces of the quadrant shape. The computer aided manufacture process provides a means of translating these defined surfaces into machine tool code which allows the surfaces, and hence the part, to be cut from a solid block of material. The following section describes how the helical profile surface was defined mathematically using a vector analysis and how the parametric equations generated from this analysis were used to construct a mesh-type representation of the surface in the computer. The computer then used this virtual surface to compute the machine tool paths.
4.2.3.1 Boundary surfaces

The geometry of the die can be defined more fully with a knowledge of the required draw ratio, die-semi-angle, entry and exit cross-section dimensions and the rate of cross-section rotation (die pitch). It is possible to obtain mathematical expressions to describe the boundary surfaces and the curves of the intersection of these surfaces.

Consider Figure 4.3. This shows a representation of the die channel lying in a Cartesian co-ordinate system such that the die axis of symmetry is coincident with the $x$ axis. The apex of the die lies at the Origin, $O$. It is assumed that at $x = 0$, the orientation of the cross-section is such that the angle it makes with the $y$ axis about the die axis, $\theta$, is zero. At any position along $x$, the section orientation will be given by:

$$\theta = \omega x$$

where $\omega$ is the rate of rotation of the cross-section with $x$. The die semi-angle, $\alpha$, is assumed to be measured in planes coincident with the $x$ axis (die axis) and passing through the mid-point of the line forming the side of the square cross-section, $M$. Any point on the boundary side can be specified by summing the two vectors $OM$ and $MP$.

Any point on surface $a$ with a known $x$ co-ordinate will lie at some displacement, $d$, from the mid-point, $M$, as shown.

The position vector of a point on the surface will be given by:

$$\mathbf{r}_a = x_a \mathbf{i} + y_a \mathbf{j} + z_a \mathbf{k}$$

where $x_a = x$

$$y_a = x \tan \alpha \cos \theta - d \sin \theta$$

$$z_a = x \tan \alpha \sin \theta + d \cos \theta$$

substituting $\theta = \omega x$ gives a position vector for any point on the surface defined in terms of $x$ and $d$.

$$\mathbf{r}_a = xi + (x \tan \alpha \cos \omega x - d \sin \omega x)j + (x \tan \alpha \sin \omega x + d \cos \omega x)k$$

similarly the other three boundary surfaces, $b$, $c$, and $d$, can be defined in terms of position vectors $\mathbf{r}_b$, $\mathbf{r}_c$ and $\mathbf{r}_d$ respectively.
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\[ \mathbf{r}_b = \mathbf{x}_i - (x \tan \alpha \sin \omega \mathbf{x} + d \cos \omega \mathbf{x}) \mathbf{j} + (x \tan \alpha \cos \omega \mathbf{x} - d \sin \omega \mathbf{x}) \mathbf{k} \]

\[ \mathbf{r}_c = \mathbf{x}_i - (x \tan \alpha \cos \omega \mathbf{x} - d \sin \omega \mathbf{x}) \mathbf{j} - (x \tan \alpha \sin \omega \mathbf{x} + d \cos \omega \mathbf{x}) \mathbf{k} \]

\[ \mathbf{r}_d = \mathbf{x}_i + (x \tan \alpha \sin \omega \mathbf{x} + d \cos \omega \mathbf{x}) \mathbf{j} - (x \tan \alpha \cos \omega \mathbf{x} - d \sin \omega \mathbf{x}) \mathbf{k} \]

The curves defined by the intersection of adjacent boundary surfaces form the corners of the die profile. The position vector of any point on the curve where boundary surface \( a \) meets surface \( b \) is given by position vector \( \mathbf{r}_{ab} \) such that:

\[ \mathbf{r}_{ab} = x_{ab} \mathbf{i} + y_{ab} \mathbf{j} + z_{ab} \mathbf{k} \]

Since the die profile section is square, the vector \( \mathbf{r}_{ab} \) can be found most easily by constraining the value of \( d \) such that it equals the distance of \( M \) from the die axis, i.e.;

\[ d = x \tan \alpha \]

This gives

\[ \mathbf{r}_{ab} = \mathbf{x}_i + (x \tan \alpha \cos \omega \mathbf{x} - x \tan \alpha \sin \omega \mathbf{x}) \mathbf{j} + (x \tan \alpha \sin \omega \mathbf{x} + x \tan \alpha \cos \omega \mathbf{x}) \mathbf{k} \]

\[ \mathbf{r}_{ab} = \mathbf{x}_i + x \tan \alpha (\cos \omega \mathbf{x} - \sin \omega \mathbf{x}) \mathbf{j} + x \tan \alpha (\sin \omega \mathbf{x} + \cos \omega \mathbf{x}) \mathbf{k} \]

Figure 4.3: Definition of boundary surfaces.
Similarly the other profile corners can be described using position vectors as below;

\[ r_{bc} = x_i - x \tan \alpha (\cos \omega x + \sin \omega x) j + x \tan \alpha (\sin \omega x + \cos \omega x) k \]

\[ r_{cd} = x_i + x \tan \alpha (\cos \omega x - \sin \omega x) j + x \tan \alpha (\sin \omega x + \cos \omega x) k \]

\[ r_{da} = x_i + x \tan \alpha (\cos \omega x - \sin \omega x) j + x \tan \alpha (\sin \omega x + \cos \omega x) k \]

### 4.2.3.2 Wire frame model

In order to produce an accurate surface model of the die it is necessary to first produce a ‘wire frame’ model which describes the part in terms of a network of laterals and longitudinals. The longitudinals pass along the surface of the die in a direction from the entry end of the die to the exit end. The laterals pass across the die surface. Typical longitudinals and laterals are shown on the die surfaces in Figures 4.1(a) and 4.1(b).

The surface shape at each node is defined by the direction cosines of the lateral and longitudinal passing through it. It can be seen that each quadrant will have four longitudinals which form the four corners of the die shape passing from the entry end to the exit end. The direction cosines of the two corner longitudinals forming the corner of the die cavity at any given value of \( x \) can be found by finding the tangent function to the curve defining the path of the longitudinal, i.e. the curve defined by position vector \( r_{ab} \) for example.

The position vector \( r_{ab} \) can be written in terms of a single parameter, \( t \), by putting \( x = t \). This gives \( r_{ab}(t) \).

\[ r_{ab}(t) = t i + t \tan \alpha (\cos \omega t - \sin \omega t) j + t \tan \alpha (\sin \omega t + \cos \omega t) k \]

The tangent function of the curve is found by differentiating with respect to \( t \) to give \( r_{ab}'(t) \).

To differentiate the vector with respect to \( t \), each term is differentiated separately;

\[ r_{ab}'(t) = x'_{ab}(t)i + y'_{ab}(t)j + z'_{ab}(t)k \]

\[ \frac{d}{dt} (t \sin \omega t) = \omega t \cos \omega t + \sin \omega t \]

\[ \frac{d}{dt} (t \cos \omega t) = -\omega t \sin \omega t + \cos \omega t \]

Therefore;
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\[ r'_{ab}(t) = i + \left[ \tan \alpha (-\omega t \sin \omega t + \cos \omega t + \omega t \cos \omega t + \sin \omega t) \right] j + \left[ \tan \alpha (\omega t \sin - \cos \omega t + \omega t \cos \omega t + \sin \omega t) \right] k \]

\[ r'_{ab}(t) = i + \left[ \tan \alpha ((1 - \omega t) \sin \omega t + (1 + \omega t) \cos \omega t) \right] j + \left[ \tan \alpha ((1 + \omega t) \sin \omega t - (1 - \omega t) \cos \omega t) \right] k \]

This tangent vector describes the direction of the curve for a given value of \( t \).

Its magnitude \(|M|\) is given by

\[ |M| = \sqrt{\left(x'_{ab}\right)^2 + \left(y'_{ab}\right)^2 + \left(z'_{ab}\right)^2} \]

\[ \left(x'_{ab}\right)^2 = 1 \]

\[ \left(y'_{ab}\right)^2 = \left(1 - 2\omega t + (\omega t)^2\right) \sin^2 \omega t + \left(1 + 2\omega t + (\omega t)^2\right) \cos^2 \omega t + 2\left(1 - (\omega t)^2\right) \sin \omega t \cos \omega t \]

\[ \left(z'_{ab}\right)^2 = \left(1 + 2\omega t + (\omega t)^2\right) \sin^2 \omega t + \left(1 - 2\omega t + (\omega t)^2\right) \cos^2 \omega t - 2\left(1 - (\omega t)^2\right) \sin \omega t \cos \omega t \]

Substituting these three equations to find \(|M|\)

\[ |M| = \sqrt{1 + 2(1 + (\omega t)^2) \sin^2 \omega t + 2\left(1 + (\omega t)^2\right) \cos^2 \omega t} \]

\[ |M| = \sqrt{1 + 2\left(1 + (\omega t)^2\right)} \]

The direction cosines are found by dividing each component by its magnitude; i.e.

\[ \cos \alpha = \frac{x'_{ab}}{|M|} \quad \cos \beta = \frac{y'_{ab}}{|M|} \quad \cos \gamma = \frac{z'_{ab}}{|M|} \]
Plate 4.3: The straight die

Plate 4.4: Helical Die A assembled
4.3 MACHINING

With the surface model complete, it was then possible to generate the tool paths which would be used by the CNC machine. The complexity of the network of tool paths depended upon the tolerances specified for the finished part. Two tolerance values relating to the part tolerance and cusp tolerance were used. Surface tolerance relates to the deviation that the tool tip may take from the specified geometry and the cusp tolerance relates to the amount of material that may be left between adjacent cuts. Close dimensional tolerances could be produced but these would lead to substantially increased machine cycles because the number of tool passes would increase accordingly. A good compromise was found to be a surface tolerance of ±0.01mm and a cusp tolerance of +0.05mm. A protruding ridge was relatively easy to remove in a manual finishing operation performed after machining.

The tool path geometry was converted into machine tool code and processed using another virtual software program called VERICUT. By specifying the material to be machined it was possible to verify that the machining operation was acceptable in terms of machining practice, specifically checking feed rates, depth of cut. The working envelope was also calculated at this stage which was used to check for cutter/tool collisions.

Plate 4.5; Machining of the die quadrants.
The program was then proved by cutting a resin material using the actual fixtures and tools to be used when cutting the metal. The resin could be machined much faster than metal allowing a low cost, rapid assessment of the finished part. It also identified any errors in the program before metal was cut.

Finally the four quadrants for each die were cut from solid blocks of mild steel, Plate 4.4. The machined surfaces were finished manually, removing tool marks with a fine file before polishing with emery paper. The surfaces were polished using a metal paste.

### 4.4 DIE EVALUATION

The manufacture of the helical dies using these CNC manufacturing facilities was found to be successful. The die quadrants were found to mate closely together to form the square cross-section die without large joints along the mating surfaces. Initial drawing trials proved that provided the die is kept tightly clamped, no flash would formed.

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*Plate 4.6: Helical Die A assembled and showing the die profile.*
Chapter 5 Experimental Procedure

5.1 MATERIAL PREPARATION

Two polymers were used throughout the course of this work; polyethylene (PE) and polyethylene terephthalate (PET). Polyethylene was selected to represent polyolefins which have been identified as being the most likely die drawn polymers to find commercial applications. A number of workers have found that the polyolefin polymers polyethylene and polypropylene show similar behaviour when they are die-drawn. On this basis the qualitative results obtained in this work for polyethylene are likely to apply equally to polypropylene.

Polyethylene terephthalate was used to demonstrate the differences expected in the deformation mechanism between the dies. When PET is drawn from an initially amorphous state, it is susceptible to strain induced crystallisation. The rotational dies imposed additional shear to the material and it was reasoned that PET would illustrate this in the form of higher levels of crystallisation induced during drawing.

5.1.1 Polyethylene

5.1.1.1 Selection of polyethylene grades

Three grades of polyethylene were used in this work, differing in molecular weight. The higher molecular weight grades of polyethylene offer a number of improved properties including notched impact strength, wear resistance, heat distortion resistance, ultimate tensile strength at high temperatures and stress cracking resistance. However, as molecular weight increases the melt viscosity also increases making processing more difficult, and in particular screw extrusion. The three grades of polyethylene selected were manufactured by Hoechst. These grades represented high density polyethylene,
high-molecular weight polyethylene and Ultrahigh molecular weight polyethylene respectively.

The two lower molecular weight grades can be processed by screw extrusion, the high molecular weight material representing the limit of this capability. These grades were not expected to exhibit the level of properties possible with the ultra-high molecular weight grade but were representative of commercially viable materials used for continuous die-drawing that would necessarily be screw extruded.

5.1.1.2 Preparation of polyethylene billets

5.1.1.2.1 Machining polyethylene feedstock

The polyethylenes were obtained as semi-finished product in the form of sheet, 6mm in thickness and supplied by Poly Hi Solidur Limited, Lancashire, UK. The selected grades, HDPE, HMWPE and UHMWPE, were available under the names of Solidur 300, 500 and 1000 respectively. The 300 and 500 sheets were manufactured by extrusion and the 1000 by compression moulding.

The sheets were cut longitudinally into square section rods. Thus the 300 and 500 rods had the same axial properties that might be expected from extruded rod. The rods were finished to size by milling. The machined surfaces were refined with a 1200 grit wet and dry paper. Small scale billets were cut to 200 mm in length, large-scale billets left uncut at 1.5m.

5.1.1.2.2 Polyethylene tag formation

To begin the drawing process, the billet end has to be threaded through the die to allow it to be gripped. This was achieved by forming a tag on the billet which was both small enough to thread through the die exit and strong enough to withstand the drawing stress applied in the initial stages of drawing. There are a number of routes that could have been used to produce an oriented tag which are described in Chapter 2. For the polyethylene billets it was found that the most effective method was to draw a portion of material near the end of each billet to its natural draw ratio on a tensometer.

The billet was gripped using hand closed grips, initially separated by 40mm. The lower grip was attached to the end 20mm of material, the other attached so as to allow the billet to pass through the grip without excessive bending. Sand paper was also applied between this grip and the billet to minimise damage to material that would subsequently be die drawn. The tags were drawn using a cross-head speed of 40mm/min to a length in excess of 200mm. Control of this operation was improved by using a hair dryer to
selectively heat (or cool) areas along the length being drawn. Any notch damage present after tag formation was removed with a sharp knife.

5.1.2 Polyethylene Terephthalate

5.1.2.1 Selection of polyethylene terephthalate grade

The polyethylene terephthalate (PET) selected was a high molecular weight grade supplied in granular form from Eastman Kodak Company.\textsuperscript{213} The grade used was EBM PET Copolyester 13339 (Clear) and this particular grade had a very high intrinsic viscosity (IV) of 1.05. The high molecular weight allowed the polymer to be extruded more easily since a stiff, viscous melt was obtained which supported its own weight, retained the extruded profile in the molten state and was strong enough to withstand the haul off tension which had to be applied to obtain a straight product.

5.1.2.2 Preparation of polyethylene terephthalate billets

PET finds limited application in its amorphous state and as such it was not possible to obtain it as a semi-finished product from an external source. Therefore the amorphous PET billets of the required dimension had to be obtained by extrusion of the selected grade.

5.1.2.2.1 Extrusion of PET Feed Stock.

Extensive melt extrusion trials were conducted in an attempt to produce rods of PET which would make suitable billets for the die drawing experiments. The extrusion equipment consisted of a standard arrangement of extruder, water bath and caterpillar haul-off but also had a dehumidifying hopper which was used to dry the PET granules.

An extrusion die was manufactured with a concave square section profile, as shown in Figure 5.1. The concave nature of the orifice allowed for die swell so that a 'near square' section profile was obtained in the relaxed extrudate.

A calibration die attached to the water bath was used to refine the final dimensions of the extrudate and stabilise the shape to the required cross section. The rapid heat transfer from the extrudate, necessary to promote an amorphous structure, was facilitated by the calibrator which was manufactured with channels in each half through which chilled water was pumped. The size of the calibrator was 10% smaller than that of the extruder die to allow for draw down.
Figure 5.1: The extrusion die manufactured for melt extrusion of 6mm billets of PET.
Drying polymer granules prior to extrusion was most conveniently achieved using a
dehumidifying hopper on the extruder. Recommended drying times and temperatures
differ significantly between manufacturers and other workers with experience of PET
extrusion. Mills\textsuperscript{99} suggests drying for four hours at a temperature of 170°C while Birley
Haworth and Batchelor\textsuperscript{1} suggest that drying may be extended to up to 8 hours at a
temperature between 170 and 180°C. ICI recommend their Melinar grades to be dried at
150°C for 10 hours and 5 hours at 190°C\textsuperscript{100}. Fekkai\textsuperscript{9} on the other hand successfully
dried PET granules for 8 hours at a temperature of only 120°C.

The PET granules were taken from a new batch contained in a sealed polyethylene bag
and as such the initial moisture content was expected to be minimal. For convenience
the drying conditions were selected to be five hours at 170°C. The temperature was
reduced to 100°C at which the polymer was held prior to processing. The granules were
poured into the dehumidifier with the shutter at the throat of the hopper closed. The
shutter was only opened when drying was complete. The lid of the dehumidifier was
then sealed to prevent moist air from being drawn into the chamber as the material
passed down into the extruder.

The necessity to cool the extrudate rapidly to the amorphous form favoured a low
material output rate. In practice it was found that if the extruder screw speed was
increased beyond 10 rpm the extrudate began to become increasingly opaque from the
core outwards indicating the onset of crystallisation due to insufficient cooling at the
calibrator. However, at these lower screw speeds, surging began to cause significant
variation in the extrudate size. The calibrator could only operate effectively when it was
completely full of material. Under ideal conditions, the extruder output and haul-off
velocity could have been varied so that the calibrator was just full under steady state
conditions. However the surging caused periodic 'overfilling' of the calibrator, causing a
frozen plug to form as a result, leading to the eventual break down of the system.

Surging is a flow instability caused when the solid bed in the transition zone of the
extruder breaks up and causes pressure and temperature fluctuations. These fluctuations
can be eliminated by increasing the effective length of the metering zone to allow them
to dampen out before reaching the die. This was achieved in practice by lowering the die
temperature, thus increasing the head pressure and reducing the transport rate. The
temperature was lowered to a minimum, below which there was a tendency for the melt
to show non-homogeneous properties i.e. the onset of solidification before leaving the
die.
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The rods produced using this method proved to be satisfactory in terms of amorphous/crystalline content as measured using differential scanning calorimetry. On the other hand the surface finish and uniformity of cross section were found to be inadequate. Thermal shrinkage of PET during solidification caused one of two effects. Firstly it allowed the product to shrink radially inwards causing a concave surface shape. Alternatively material tended to shrink outwards towards the solidified skin, resulting in piping and void formation. This pipe formation was found to predominate at very low haul off rates. Since the former was more desirable, haul off speed was increased to 1.2 m/min at which the extrusion was completed.

It became evident during these trials that producing a consistent, good quality, amorphous PET product of large cross-section required a considerable amount of expertise and specialised, dedicated equipment. In particular greater control over the cooling and sizing arrangement was required.

The extrusion conditions used are as follows

- Screw diameter = 50 mm
- Temperature profile from feed = 265 / 285 / 285 / 275 / 275 / 280 °C
- Screw speed = 20 rpm
- Haul off speed = 0.8 m/min

5.1.2.2.2 Machining PET feedstock

The inconsistent size and shape of the extruded PET billets obtained from the extrusion process described above was improved by machining the billets using a milling operation. A long wooden clamp was made to hold individual billets to allow an initial face to be machined. This face was then used as the datum to machine the three remaining sides, forming a square section profile.

5.1.2.2.3 PET tag formation

It was found that the oriented tag could not be produced on the PET billets by tensile drawing as used for polyethylene. PET offered resistance to a draw ratio of greater than 4 using this method which was insufficient to allow it to thread through the die exit. The obtained draw ratio could increased to five by utilising a two stage drawing technique where the end of the billet was initially drawn to four at 80°C (just above its glass transition temperature) followed by further drawing at low speed (~5 mm/min) at room temperature. However this was still insufficient to allow it to thread through the die.

An alternative method was devised where the end of each billet was heated rapidly for 30 seconds between two hot plates at 200°C. The heated end was then gripped with a
pair of pliers and stretched quickly. The obtained tag cross-section was just smaller than the die exit and its strength was sufficiently high to support drawing loads.

5.1.3 Billet measurements

5.1.3.1 Dimension measurement

Difficulties in machining arose from the flexibility of the rods and inevitably the dimensions of all billets were found to vary along the length. This lead to variations in nominal draw. Although this would be unacceptable for commercial practice, variation in nominal draw ratio allowed its effects to be assessed over a limited range by using a single billet. From a knowledge of the dimensional profile of each billet before drawing and of the dimensional profile of the drawn product, it was possible to determine the effect of nominal draw ratio on the actual draw ratio obtained.

The billet dimensions were measured along its length at 20mm intervals. Dimensions were taken to the nearest 0.01mm using a micrometer screw gauge. At this stage each billet was given a reference number and labelled.

5.1.3.2 Thermal analysis

Differential scanning calorimetry (DSC) was conducted on the feedstock materials. Melting point and crystalline content were assessed for each material. The average initial crystallinities of the materials based on 10 DSC experiments are 58% for the high-molecular weight polyethylene and 4% for the PET. Example DSC traces are presented in Figure 5.2
Figure 5.2(a); A DSC Thermogram of High Molecular Weight Polyethylene (HMWPE). Undrawn material.

Figure 5.2 (b); A DSC Thermogram of Polyethylene Terephthalate (PET). Undrawn material as extruded.
5.2 DIE-DRAWING EXPERIMENTS

Small scale die drawing experiments were conducted using a standard tensometer. This was a means of drawing at predetermined drawing speeds up to 500mm/min which offered a convenient way of measuring drawing force. Most of the experimental work was completed using this technique. Its main advantage was the ability to maintain close control of the drawing process. The tensometer cross-head movement could be programmed to apply different speed profiles, eliminating many of the start-up problems that are usually encountered with other methods.

Die drawing of polymers on a large scale with the potential for a continuous process could not be achieved using the tensometer. The limited travel of the cross head only allowed short lengths of drawn material to be produced. At higher drawing speeds, there was insufficient time to be certain that the system had reached a steady state before the cross head ran out of travel. Also the cross head speed was limited to 500mm/min which is much lower than would be required for an industrial process.

A continuous draw bench was designed and manufactured which allowed long billets of material to be heated and drawn using a continuous caterpillar haul-off. The design was a development based on the equipment used by other workers investigating die-drawing, most notably Ward and co-workers at Leeds University.

5.2.1 Small-Scale Drawing

5.2.1.1 Equipment

The small-scale drawing experiments were carried out on a standard tensometer equipped with an environmental cabinet which served as a heating chamber for both the billet and the die block assembly. The tensometer was a Hounsfield 10KN machine and was fitted with either a 1kN or 10kN load cell according to the expected drawing load. A hand closed grip attached to the cross-head was used to pull the material from the die.

An airline was used as a means of cooling the area around the die exit. The air flow rate was monitored periodically using a standard flow meter.

The arrangement for drawing is shown in Figures 5.3 and 5.4. The die block was assembled prior to heating as shown in the Figure and this was supported within the chamber using extension tubes as shown.
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Figure 5.3; The Hounsfield tensometer showing general arrangement of small-scale die drawing equipment
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Figure 5.4: A detailed view of the equipment within the environmental chamber

- **Hand-Tightening Jaws.**
- **Air Flow.**
- **Rubber Hose.** Supplies cooling air to the drawn material as it exits the die in order to provide stability.
- **Die Box Assembly.** The die set and spacer are contained in the die box which serves to clamp the components together.
- **Die Set.**
- **Spacer Block.**
- **Adaptor.** This allows the die box to be fitted to the tensile test machines.
- **Extension Tubes.** Tubes of differing length allow polymer billets of varying length to be used.
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Draw speed was programmed using a computer. The computer was used to record drawing load and cross-head displacement. A printout of this information was obtained for each experiment.

5.2.1.1.1 Calibration of the environmental cabinet.
The environmental chamber was used as a recirculating air oven with temperature control obtained via a thermocouple positioned within the chamber. The manufacturer states that the temperature in the chamber remains within ±1°C of that set. In order to verify this, and to ensure a uniform temperature distribution a second thermocouple, connected to an independent electronic thermometer, was used to measure the actual temperature at different locations in the chamber. Readings were taken at each node of an imaginary three dimensional grid of spacing 5cm. The thermocouple was mounted on a thermally insulating wooden dowel and this was held in a retort stand positioned so as to minimise its effect on the air flow around the thermocouple. The chamber was allowed to reach steady state conditions before a temperature reading was taken. It was found that the temperature variation was ±1°C at the top of the chamber and ±3°C at the bottom. Since the die was positioned near the top of the chamber, the fluctuation was considered to be within acceptable limits.

5.2.1.1.2 Control of the temperature profile
The stability of the drawing process depends significantly on the temperature of the drawn material immediately leaving the die. By using differing lengths of extension tube it was possible to position the die to give different heating profiles downstream of the die exit. A shorter extension tube meant the drawn product emerged from the die into the chamber and thus remained at isothermal drawing temperature conditions for longer than if the die exit were near the top of the chamber. The longest extension tube positioned the die so that its exit was exposed to ambient conditions through the hole in the top of the chamber. The temperature immediately downstream of the die exit was then somewhere between that of the chamber and ambient and diminished with increasing distance from the die exit. By using a controlled supply of compressed air to forcibly cool this region, uniform isothermal conditions at any desired temperature between that of the chamber and ambient were obtained along a length of about 60mm. For each set of conditions, the temperature profile moving away from the die exit was measured using a thermocouple.

The temperature profile of the drawn product, i.e. its cooling rate, relative to that of its surroundings depended on both the surrounding temperature and the drawing speed.
5.2.1.2 Experimental procedure

5.2.1.2.1 Heating of the billet materials

For each run of drawing experiments at any given drawing temperature the die block and auxiliary components were loaded into the chamber and allowed to heat up prior to loading a polymer billet. Using a thermocouple embedded in the block it was found that 1½ hours were required to allow the block to heat through and attain steady state conditions.

Polyethylene is a thermally inert polymer and can be held at the drawing temperatures indefinitely without significant morphological change. Polyethylene terephthalate on the other hand will crystallise when heated above its $T_g$, the rate of crystallisation depending on just how far above $T_g$ the polymer is heated. In order to minimise the dwell time and hence the amount of thermal crystallisation occurring, drawing should begin at the instant the polymer reaches drawing temperature. At temperatures between $T_g$ and about 100°C the crystallisation process is sufficiently slow to allow a short billet of PET to be drawn without thermal crystallisation having a significant effect. At temperatures above 100°C however, thermal crystallisation becomes extremely rapid and this means that as drawing proceeds the billet morphology changes and the drawing characteristics may be completely different at the end of a drawing run than they were at the beginning. This may also be apparent at the lower temperatures where a longer billet is used since the dwell time for the end part of the billet will become excessive.

It was not possible to have access to monitor each billet temperature during drawing and so an indirect method was required to ensure that each billet was at the correct temperature before drawing but also was not held at that temperature for too long. The time for billet heating is mainly affected by the specific heat capacity of the polymer, the billet dimensions and the temperature required. For each material and billet size, a billet was prepared in the usual manner but in addition, a small 0.5mm diameter hole was drilled along its axis. A thermocouple wire, connected to an electronic thermometer, was then fed into the billet to allow measurement of its core temperature. The depth of the hole in the billet and position of the thermocouple was such that the temperature was being measured at approximately the mid point of the die block. Particular care was taken when drilling the hole to ensure that it remained concentric to the billet. This was best achieved using a clamping jig which always presented the billet parallel to the drill.
Chapter 5 Experimental procedure.

Each billet was loaded into the die block in the usual manner and placed in the chamber. The core temperature was measured from the instant the billet was loaded into the die and readings were taken at appropriate time intervals as heating commenced. The heating profiles are shown in Figure 5.5. It can be seen that there is a well defined point in time where the temperature stabilises and this time interval was used consistently for heating all billets of the same material type and dimensions.

5.2.1.2.2 Billet Loading

The end of the billet tag was cut off to allow it to be threaded through the die. As a cross-section of material passes through the die it will rotate according to the die profile. The tag drawn on the end of each billet has a sharp neck and initially the billet will only contact the die at the shoulders of the neck. As the billet begins to draw it will progressively fill the die cavity and the tag end of the billet will try and rotate to orientate itself with the cross section of the die at the point of contact. When the die is completely full the tag should have rotated by the same amount as the die profile over the deformation zone of the die. If however the tag is not free to rotate in the exit of the die, which occurs if the tag cross-section is sufficiently large, then a counter shear occurs near the end of the die. In order to avoid this problem the billet tag is twisted to match the die profile prior to loading so that the orientation of the tag passing through
the die exit is as if it had followed the die profile. A mark is made along one side of the billet and tag which assists in orienting the billet in the die.

The billet is loaded into the chamber and the required heating time allowed. The grips were attached to the tag and a small tension of about 15 to 20 N was applied during heating to prevent any shrinkage in the drawn tag. After the allotted heating time drawing commences. The drawing load is recorded versus displacement of the cross-head.

Drawing experiments were conducted for different billet sizes and material grades to investigate the effects of both drawing speed and drawing temperature. Drawing speeds up to 500 mm/min at intervals of 100 mm/min were used. The range of drawing temperature was determined by the material. Tables 5.1 to 5.5 show the experimental conditions used for each of the dies with the materials indicated. The notation indicates whether a particular experimental condition was used and whether drawn product was successfully produced. The symbol '✓' indicates a successful experiment with drawn product produced. The results of these experiments can be found in the Appendix. The symbol 'B' indicates that that particular sample broke during drawing due to some instability and so no drawn product could be obtained. A '✗' indicates that these experiments were not attempted.

5.2.2 Large Scale Drawing

5.2.2.1 Equipment

The continuous drawing apparatus comprised of main process areas which the material passes through in sequence; heating, drawing, cooling and haul off, Figure 5.6 and Plate 5.1. The design requirement and how these were realised will be discussed in the following section.

5.2.2.1.1 Heating

Consistent, uniform heating of the polymer billet is essential since the draw characteristics are strongly influenced by this parameter. This became more difficult to achieve over long billet lengths. The billet lengths were 1.5-2m and so the heating solution had to be able to maintain a steady state temperature over this length.
### Table 5.1: Experimental conditions for UHMWPE - nominal draw ratio of 7.1

<table>
<thead>
<tr>
<th>Draw Speed (mm/min)</th>
<th>100</th>
<th>200</th>
<th>300</th>
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<tr>
<td>Temperature (°C)</td>
<td>ST</td>
<td>HA</td>
<td>HB</td>
</tr>
<tr>
<td>90</td>
<td>B</td>
<td>x</td>
<td>x</td>
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<tr>
<td>100</td>
<td>✓</td>
<td>✓</td>
<td>B</td>
</tr>
<tr>
<td>110</td>
<td>✓</td>
<td>✓</td>
<td>B</td>
</tr>
<tr>
<td>120</td>
<td>B</td>
<td>x</td>
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### Table 5.2: Experimental conditions for UHMWPE - nominal draw ratio of 4.5

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<thead>
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<td>HB</td>
<td>ST</td>
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<td>B</td>
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<tr>
<td>120</td>
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### Table 5.3: Experimental conditions for HDPE - nominal draw ratio of 4.5

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<td>B</td>
<td>B</td>
</tr>
<tr>
<td>100</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>110</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>120</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>
Chapter 5 Experimental procedure

<table>
<thead>
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<th>Draw Speed (mm/min)</th>
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<td>115</td>
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Table 5.4: Experimental conditions for HPMWPE - nominal draw ratio of 7.1

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</tr>
<tr>
<td>115</td>
<td>✓</td>
</tr>
<tr>
<td>120</td>
<td>✓</td>
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Table 5.5: Experimental conditions for PET - nominal draw ratio of 4.5

A number of heating options were considered but a recirculating air chamber similar to that used on the small-scale apparatus was chosen. The advantage of heating with air as opposed to water or glycerol for example was that it did not contaminate the surface of the billet before this was drawn through the die. Baffles placed around the chamber ensured that the flow was broken to avoid hot spots and dead zones. A 25mm diameter copper pipe was used to house the billet in the chamber whilst it was being heated. This kept the billet straight and prevented it from sagging or touching the chamber walls where it was more likely to encounter uneven heating. The recirculating heating chamber allowed operating temperatures of up to 150°C.
Figure 5.6(a) A schematic of the large-scale drawing equipment.

DRAW DIRECTION

HEATING CHAMBER

LOAD CELL

DIE BLOCK

WATER BATH

HAUL OFF

AIR PIPE
Figure 5.60: Large-scale drawing equipment - detailed view of the die housing.

SECTION A-A

<table>
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<th>PART NO.</th>
<th>DESCRIPTION</th>
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<td>12</td>
<td>GROUND SHANKS</td>
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<td>SHAFT ENDS</td>
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<td>SHAFT SUPPORTS A</td>
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<td>SHAFT SUPPORTS B</td>
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<td>BASE PLATE</td>
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<td>16 (A)</td>
<td>DIE BLOCK LOAD CELL BRACKET L/H</td>
</tr>
<tr>
<td>16 (B)</td>
<td>DIE BLOCK LOAD CELL BRACKET R/M</td>
</tr>
<tr>
<td>17 (A)</td>
<td>FRAME LOAD CELL BRACKET L/H</td>
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<td>17 (B)</td>
<td>FRAME LOAD CELL BRACKET R/M</td>
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<td>CARTRIDGE HEATERS</td>
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<td>21</td>
<td>LINEAR BEARINGS</td>
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<tr>
<td>28</td>
<td>CAP SCREWS - M6x15mm</td>
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</tbody>
</table>
5.2.2.1.2 Calibration of the heating chamber.
The temperature distribution within the chamber was measured using a thermocouple in a similar way to that used for the small scale work. The temperature profile was found to vary by less than ±1°C

5.2.2.2 Die heating
The die was held within the same die block assembly as used with the small scale apparatus as shown in the diagram. This was housed in a large steel block complete with six cartridge heaters positioned symmetrically around the die axis to provide an even heat distribution to the whole assembly. The block was split in half and the top half could be removed to allow easy access to the die. The large mass provided sufficient thermal inertia to eliminate any temperature fluctuation at the die axis due to the heating cycle or chilling effects of draughts etc. The stability of the temperature in the die block was checked using a thermocouple and was found to vary by less than ½°C.

5.2.2.3 Load measurement
The drawing load was transferred from the haul-off to the die block through tension in the drawn product. In theory it was feasible to measure the drawing load at any point
between the haul off and the die block fixing. In practice however, downstream force effects, may have been present which would be included in a force reading taken at the haul off. This was avoided by measuring drawing force at the die. The die block was supported by linear bearings running on ground shafts, providing a 'frictionless' running of the die block along the drawing axis. The die block was held in position by a pair of cantilever load cells positioned symmetrically on either side, each capable of supporting a measured load of up to 1000N. The drawing load was then measured by summing the loads supported by the two load cells. The load cells were thermally insulated from the die block to prevent damage to the circuitry and to avoid divergence from the linear calibration. Force measurement was measured to the nearest Newton (N).

5.2.2.4 Cooling

Cooling of the drawn product emerging from the die was provided by two sequential processes. Firstly chilled, compressed air was used to provide immediate quenching at the die exit, and secondly a water bath provided additional cooling downstream. The need for rapid quenching became apparent after initial trials were conducted with polyethylene. Using the water bath by itself did not quench the product sufficiently near the die exit to give it stability and prevent breakage at relatively low drawing loads.

The chilled air was blown through a tee piece as shown in the diagram, Figure 5.6(b). A further advantage was offered by this technique. The pressure created in the tee prevented water from leaking from the tank through the diaphragm.

The water bath was positioned as close to the die as possible. Water was circulated by a pump to ensure a uniform temperature distribution. A chiller was used in series with the pump to allow sub ambient cooling temperatures to be achieved. This also gave greater stability to the water temperature.

5.2.2.5 Haul off

Haul off was provided by a caterpillar fitted with rubber belts providing a steady, continuous haul off. The unit was driven by a dc shunt wound motor which has the advantage of providing a near constant speed for any load in its operating range. Speed control was provided by a control rheostat and an approximate speed measurement was provided by monitoring field current of the motor. The electronic motor speed controller provided a ramped start up allowing the operating speed to be reached without shock loading. Haul off speed was continuously variable between 0.5m/min and 20m/min.
5.2.2.6 Experimental procedure

Billets were prepared in the same way as for the small scale work, the only difference being their length, now 1.5m to 2.0m. Billet dimensions were measured at intervals of 50mm. The billets were loaded in to the die and given a pre-twist according to the die profile as described. The drawn tag was threaded through the diaphragm and a loop was tied on the end to allow attachment to a hook on the end of a braided rope. This rope was used during start up to draw the end of the tag to the caterpillar. A braided rope was used to illuminate twisting under tension.

After drawing sufficient material to allow the caterpillar to grip the drawn product, the process was stopped, the rope removed and the belt pressure increased to improve the grip on the rubber belt surfaces. Excess water was removed from the surface of the drawn product using an absorbent wipe before it was pulled into the haul-off. Failure to dry the surface properly reduced friction resulting in slippage, particularly at high drawing loads.

Drawing load was monitored throughout the duration of the experiment and recorded every 10 seconds. Although haul-off speed could be read from the tachometer on the haul off unit, in practice a better method was to measure the time taken to draw a known length of product. This was because there was no guarantee of zero slippage between the belt and product, particularly at the higher draw speeds and drawing loads.

The drawn sample was coiled and labelled.

The experimental conditions used for the large scale drawing are given in Table 5.6.

<table>
<thead>
<tr>
<th>Draw Temperature (°C)</th>
<th>Die</th>
<th>Draw Speed (mm/min)</th>
</tr>
</thead>
<tbody>
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<td>80</td>
<td>ST</td>
<td>429 814 843 B</td>
</tr>
<tr>
<td></td>
<td>HA</td>
<td>488 683 918 B</td>
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<td>HB</td>
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<td>ST</td>
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<td></td>
<td>HA</td>
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<tr>
<td></td>
<td>HA</td>
<td>434 581 737 996 1141 1950 3228 B</td>
</tr>
<tr>
<td></td>
<td>HB</td>
<td>416 709 1076 1463 2463 B</td>
</tr>
</tbody>
</table>

Table 5.6: Experimental conditions for HMWPE drawn on the large scale drawing equipment - nominal draw ratio of 4.5
5.2.3 Neck profile investigation

The geometry and morphology of material in the neck region developed during drawing is dependent upon the optimum stress-strain-strain rate characteristic of the polymer under the given drawing conditions. An investigation of the effects of the rotational shear in terms of both the mechanics of the drawing process and the development of the modified structure was achieved by partially drawing billets under various conditions, halting the process and removing the material from the die.

Billets were prepared in the usual manner but in this case a grid was marked onto the four surfaces allowing differing macroscopic deformations of different elements of material to be identified. Billets were first given a surface treatment using plasma which improved the durability of the grid markings. These grid markings, spaced by 2mm were applied using a fine tipped waterproof marker.

Billets were heated and drawn in the normal way except that once steady state conditions were reached, the process was suddenly halted and the drawing force immediately removed. The drawing was halted with the cross-head at a known position which allowed the elastic recovery of the material to be accounted for in the geometric analysis. Also, before the billet was removed from the die, the point of die entry and die exit were marked onto its surface. To remove the billet, the die was first extracted with care from the die block and immersed in chilled water to cool the assembly. This was done to avoid any distortion of the partially drawn billet which would inevitably occur if it were removed hot. The partially drawn billet was labelled for later reference.
5.3 PRODUCT CHARACTERISATION

5.3.1 Dimension Measurements

5.3.1.1 Drawn product dimensions

The dimensions of the billet and drawn product were used to establish the actual draw ratio obtained for a given set of conditions. For the small scale work, the drawn product was obtained in a number of shorter lengths (~150mm). Each length was numbered according to the order in which they were produced. The total length of drawn product from each billet was obtained by reconstructing the lengths in the order and direction they were produced. The dimensions were then taken at intervals of 50mm at three points, avoiding measurement at the damaged portion where the grips were located. For the large scale work, the entire drawn length was obtained in one piece. Dimensions were measured at 150mm intervals.

In order to obtain exact values of draw ratio at specific points in the drawn product, it is necessary to identify the same points in the billet. This is complicated where the billet dimensions are not uniform along its length because this will affect the draw ratio along the product. This implies that it is not possible to identify the equivalent points on the product simply by length measurements. If the density is assumed to be unaffected by drawing then the equivalent points can be found by equating the cumulative volume of material from the beginning of the billet and product. Where the entire billet is drawn, it is possible to check the accuracy of the method because the total volume of drawn product should equal that of the original billet. Elements of material at the beginning and end of the billet are the same elements at the beginning and end of the drawn product respectively.

Therefore for any element of material in the undrawn billet it is possible to identify its location in the product and calculate the draw ratio for that element according its cross-sectional area. The nominal and actual draw ratio can be plotted for each billet and this will give an indication of the process sensitivity to nominal draw ratio under those drawing conditions. This procedure also allows the results to be normalised with respect to nominal draw ratio.

Dimensions were measured to the nearest 0.01mm using a micrometer screw gauge. For each billet a graph was constructed of cross-sectional area against distance from the front of the billet. A similar graph was constructed for the drawn product. Further
graphs were constructed of draw ratio versus accumulated volume (area under above graph). Suitable points were then selected to establish the relationship between nominal draw ratio and actual draw ratio. In practice, these points were selected to account for the range of nominal draw ratio for the given billet. The corresponding locations on the drawn product were identified and its draw ratio at these points interpolated from the graph.

5.3.1.2 Neck profile dimensional measurements

The partially drawn billets were measured to establish the geometry of the neck formed under steady state drawing conditions. Since a significant amount of post die axial drawing was expected under any drawing conditions, it was necessary to take measurements from the un-deformed billet through to some distance beyond die exit where uniform dimensions were measured. For the small scale work, this was generally found to be almost to the grips. The profiled sample was marked using a waterproof pen at 2mm intervals along its length, starting from 10mm behind the mark denoting the die entry. Measurements were taken to the nearest 0.01mm using a micrometer fitted with point contacts. These contacts improve the accuracy with which the micrometer can be positioned over non-parallel surfaces, as with the neck region. The cross-sectional area and cumulative volume of material up to the measured point were calculated.

5.3.2 Tensile Testing

Tensile tests were carried out on short lengths (~150mm) of drawn product in order to establish Young’s modulus values. Other workers, most notably Ward and co-workers, have used a bend test method to establish the modulus of drawn products. The advantages of this method are claimed to be that it produces a more accurate result because it is not affected by the end effects associated with the gripped ends of material in the standard tensile test. However, one of the assumptions made when calculating the result for the bend test is that the material concerned is isotropic which is clearly not the case with a drawn polymer. Also the necessarily short lengths of drawn polymer available here (150mm) made this method unfeasible and so the tensile test method was used.

5.3.2.1 Equipment

The tensometer used was a J. J. Lloyd machine fitted with a 50kN load cell and a laser extensometer. The machine was controlled by computer using Dapmat software (version 4.2). Load measurement was achieved using a load cell fixed to the cross-head.
Chapter 5 Experimental Procedure

The Lloyd machine offered three alternative means of extension and hence strain measurement. The first was simply recording the cross-head displacement. This assumes that the end of the gauge length of the sample moves by the same amount as the cross-head and that the other end remains stationary. This is a fairly crude method because it is difficult to determine the actual gauge length over which deformation is measured and invariably some deformation will occur in the grip region. In this case, it was not even possible to machine the sample to form a dumbbell shape which would confine most of the deformation to a known waist length. This method was therefore considered to be unsatisfactory.

The second method utilises a clip-on extensometer which attaches to two specific points on the sample, the material between the two points of contact forming the gauge length. The contacts were knife edges, sharp enough to avoid slippage of the contact but not sharp enough to produce notch effects. This is an accurate means of extension measurement because deformation of material outside the gauge length has no effect. However the small cross-section of drawn material (≈ 2 × 2mm) makes attachment of the device impossible. The clips required the contact surface to be at least 5mm in width. Also there was a risk of damaging the sample when attaching the device over such a short contact length.

The alternative method available, using a laser extensometer, eliminates the need for physical contact between the strain transducer and the sample. The laser extensometer (Laserscan 100) works by scanning a narrow parallel laser beam along the central vertical axis of the sample. A sample is first prepared by attaching two very small reflective markers separated by a standard gauge length. The reflective markers are strips of tape which are coated with a special optical material containing retro-reflectors which returns most of the incident light back along the same path. The extensometer measures the relative change in distance between the two reflective marks. Sample end effects are eliminated. This method was selected. The key to the laser’s accuracy was in its calibration and considerable attention was given to this procedure.

5.3.2.2 Calibration of the extensometer

The sensitive nature of the laser extensometer means that in order to obtain consistent, accurate data using this technique, it is vital that the calibration procedure is strictly adhered to and that it is repeated both before and during experimental runs. Calibration was achieved by using a reference gauge of the required working length, 150mm. Reflective tapes were positioned at the 25% and 75% points along the gauge. The
distance between the markers was then 75mm, 50% of the working length. This gauge was used consistently to calibrate the Laserscan. The reference gauge was placed in the tensometer and the laser aligned along the axis with the gauge positioned so that approximately equal lengths of scan line were above and below the marks. The working length that corresponds to the reference mark separation was entered into the computer and the calibration was then completed by adjusting a potentiometer on the laser unit until an LED panel indicated that the laser read the separation as 75mm. Re-calibration was conducted before each run of experiments and after every 25 measurements.

**5.3.2.3 Experimental procedure**

All tensile specimens were taken from length no. 3 from each drawing experiment to ensure consistency of sample history. The gauge length of approximately 75mm was marked on the mid-section of the sample and reflective markers attached. The extensometer recognises the lower edge of a reflective mark and as such its accuracy did not depend on the width of each marker. Strips of reflective tape 1mm in width were cut using a sharp knife and stuck horizontally across the sample. Accurate positioning of the markers was not essential since the laser measured their separation accurately before the test commenced.

The sample dimensions were measured to 0.01mm at three positions along the gauge length using a micrometer screw gauge. The average cross-sectional area was calculated. The cross-head of the tensometer was positioned so that the grips were approximately 110mm apart, giving about 20mm of gripping length at either end of the sample. The laser only reads the first two reflected pulses and so false reflections were eliminated by positioning the grips so that the beginning of the laser scan started immediately below the first reflective marker on the sample. Further precautions against false reflections were taken by to covering the grips with a matt tape. The grips were also rotated so that the surface of a sample would be at a slight angle to the incident laser beam.

The grips were tightened by hand and load measurement was zeroed before each test was started. The test was conducted at a cross-head speed of 10mm/min, equivalent to a strain rate of 9%/min = 0.0015 s⁻¹. The load applied and the extension of the gauge length were recorded by the computer at a rate of 10 readings/second. A load-extension and hence stress-strain curve could be derived. The expected accuracy limits are ± 0.5% between 10% and 90% of the working length, ±1.0 % outside these limits, and the linearity between these limits is 0.03 %/deg.
Chapter 5 Experimental Procedure

5.3.2.4 Method of analysis

The load-extension curves were taken with the initial cross-sectional area of the sample and the recorded gauge length to produce nominal stress-strain curves. The initial Young’s modulus was calculated from the slope of the curve at very low strain.

5.3.3 Compression Testing

Compression tests can offer benefits over the tensile test in that the strain measurement is much easier to make. Gripping problems are eliminated and thus strain can be related to the movement of the cross-head. However there are strong objections to compression tests. The most frequent of these arise from the presence of friction between the sample and the die applying the compressive force. Friction effects are difficult to determine and eliminate. It tends to inhibit the lateral deformation of the material between the die surfaces leading to barrel distortion. Where the material is able expand over the die surfaces the surface area of contact will increase as the test progresses leading complexities in stress measurement. Also greater attention has to be given to the test piece geometry, ensuring parallelism of the surfaces in contact with the die.

Drawn polymer samples tend to have extremely low transverse mechanical strength and compression offers a means by which this can be quantified. Two compression tests were used in this work. The first, plane strain compression, measures compressive stress-strain properties assuming that the area under load remains constant. This eliminates many complexities concerned with the calculation of stress and has been successfully used with polymers by Williams and Ford.\textsuperscript{14}. The second method, transverse compression, was used to assess the effectiveness of any biaxial orientation in preventing splitting along the direction of draw.

5.3.3.1 Plane Strain Compression

The plane strain compression test can be used to obtain a quantitative assessment of the compressive properties of polymer materials\textsuperscript{214}. Two highly polished flat dies are forced into a sample from either side as shown in Figure 5.7. There is no constraint to elongation in the direction normal to the dies and as the dies are pushed into the specimen, material is extruded in each direction along this path. When testing a plate type specimen, the deformed material under the tool is restrained by the undeformed material on each side of the dies and so essentially no deformation occurs along this axis. Thus the area under the tools remains constant during the test. This condition can similarly exist with a drawn sample. There tends to be a limited amount of material on
either side of the dies but since in this case the polymer is already highly drawn, it is unlikely to deform significantly in this direction before yielding occurs in the transverse direction.

If $h_0$ is defined as the initial sample thickness and $h$ is the sample thickness at any point after deformation begins then the deformation strain will be:

$$\varepsilon = \frac{h}{h_0}$$

The work of Williams and Ford\textsuperscript{214} demonstrated that the effects of friction can be minimised and essentially eliminated when working with polymers if a suitable lubricant is used between the die surfaces and the polymer. They investigated a number of lubricants and found graphite grease to offer the best performance. Vaseline offered acceptable lubrication for polyethylene, stress measured being typically 4% higher than the value obtained from using graphite grease.

Green\textsuperscript{215} has suggested that the accuracy in comparison of material properties is dependent on the relative dimensions of the sample under test, most notably the ratio of width to thickness, since this changes throughout the course of the experiment. Where absolute values for mechanical properties are sought, the width/thickness ratio should lie
within certain limits according to the geometry of the dies. In this work, the samples are necessarily square, the width/thickness nominally being 1.0. The theoretical solution proposed by Green for this value suggests that the measured stress value is independent of die geometry where this condition exists. In any case the aim is to provide comparative data rather than absolute mechanical property data.

5.3.3.2 Experimental procedure

Samples were taken from the front end of the drawn product in order to minimise variations in sample thermal history. The gauge length is the thickness of the sample and was measured to the nearest 0.01 mm using a micrometer screw gauge.

The die surfaces were prepared before each experimental run by polishing them on a flat surface using a metal polish. Care was taken to remove all traces of the polish before using the dies. Before each test Vaseline was applied to the sample and both die surfaces using a small paintbrush.

Strain measurement was inferred from the cross-head displacement measured using the computer. To prevent over loading the load cell, movement of the cross-head was restricted to limit the die separation to 0.5 mm. Load was measured using a load cell attached to the cross-head. Load was zeroed before inserting the sample in each test.

Ideally, the test should begin with the upper die surface just contacting the surface of the sample, load being applied immediately as the cross-head begins to move. Practically it is not possible to position the cross-head with such precision. The test was therefore started with the die some distance above the sample. Also the means by which the plane-strain compression jig was attached to the tensometer allowed a certain amount of free movement of the upper die along the loading direction before loading could take place. The displacement recorded by the computer was corrected to account for both these effects.

The cross head speed was 1 mm/min, relating to a nominal strain rate of 0.0083 s⁻¹.

5.3.3.3 Method of analysis

The compressive modulus was calculated as the gradient of the stress strain curve from the test. This gradient was calculated as a secant modulus between load limits of 10 and 50N.
5.3.3.4 Transverse compression

In these experiments, a compression test was conducted with the die axis perpendicular to the length of the sample so as to squash a specific length, in this case 4mm. Lateral expansion of material between the die surfaces caused the uncompressed material on either side of the dies to split along the direction of draw, Figure 5.8. The amount of splitting, assessed by measuring the split length, is an indication of the ability of the material to resist splitting due to compression under point contact.

The experimental procedure was identical to that used for plane strain compression except for the orientation of the sample. Cross-head displacement was stopped when the compressive strain reached 50% for each sample. The split length was measured using vernier callipers.

5.3.4 Birefringence

5.3.4.1 Introduction to birefringence

The refractive index ($n$) of a material is defined as the ratio of the velocity of light in vacuum to that in the material for a specific wavelength of light. For an isotropic
material, there exists only one refractive index which remains the same for any direction of observation. Doubly refracting, or birefringent, materials show different refractive indices in different directions. The optical anisotropy of a material can be defined in terms of three mutually perpendicular refractive indices, \( \alpha \), \( \beta \) and \( \gamma \). The chemical structure of a polymer chain causes a difference between the refractive index along the polymer chain axis and that across the chain axis. In this sense the polymer molecule is birefringent. If there is a truly random arrangement of molecules within a bulk sample of material then the birefringence observed for the bulk will be zero, the material having the same refractive index in all directions. A material having its molecules aligned in some preferred direction however will show anisotropic refractive optical properties as well as mechanical anisotropy, the magnitude of the birefringence will depend on the degree of molecular orientation.

The correlation between orientation and birefringence is a straightforward one for amorphous polymers, but when the polymer is semicrystalline the crystalline regions and amorphous regions have to be considered separately if accurate interpretations are required. In practice it is generally possible to assume that the orientations are similar and obtain an 'average' value of birefringence. Separation can be achieved by X-ray diffraction, for example, which will measure the crystalline orientation which can then be 'subtracted' from the birefringence reading to give the orientation of the amorphous regions.

Birefringence which is defined as the maximum algebraic difference between refractive indices measured along two orthogonal directions becomes a convenient measure of the orientation of the molecules.

\[
\Delta n_{xy} = n_x - n_y
\]

Polarised light incident on an anisotropic material splits into two light components which vibrate in mutually perpendicular planes. The velocity of each component through the material will be different depending on the refractive indices in these directions. When the two light components emerge from the material they will be out of phase and this can be measured as an optical path difference, OPD. The OPD will depend on the thickness, \( t \), of material for the given observation direction. The birefringence can then be calculated from the further definition as follows;

\[
\Delta n = \frac{OPD}{t}
\]
Uniaxially drawn materials have two principal refractive indices and an optic axis along which polarised light may travel without being modified. Where a material is biaxially oriented, there will be three principal refractive indices and two optic axes will exist. If the direction of observation is directly down the optic axis, the birefringence measured will be zero and the sample will be dark even when it is rotated between the polaroids. If however the direction of observation is coincident with the principal axes the birefringence measured will be a principle measurement.

5.3.4.2 Birefringence Measurement

Birefringence can be measured by either using a Michel-Levy colour chart or by using a compensator. The Michel-Levy chart method allows an OPD value to be obtained by comparing the colours observed through the microscope with those printed on the Michel-Levy chart. This method is fairly subjective and therefore not the most reliable. The compensator method was therefore selected following the guidelines set out by Hemsley.

The method of optical path difference measurement is a standard technique and the method was used throughout this work. It is described as follows.
A mounted oriented sample is placed between crossed polars on the microscope stage. When the stage is rotated it is found that the specimen will go dark, or extinguish every 90° of rotation. When this occurs the principle axes of the sample coincide with the vibration directions of the light waves from the polariser. At positions midway between the extinction points, i.e. at 45°, the sample is observed to be at maximum brightness. The sample has to be rotated to a position of maximum brightness in order to measure birefringence. Practically, it was found that this was best achieved by first finding an extinction point, which the eye can detect much more easily, and then rotating the stage through 45°.

A beam of monochromatic light passes through the polariser so that it is constrained to vibrate in one plane only. The beam enters the sample and splits into two with planes of polarisation mutually perpendicular and each lying at 45° to the original direction of polarisation. The beams pass through the sample at different speeds according to the refractive indices such that they emerge out of phase. The beams are orthogonal and so do not interfere. They pass into the compensator. A compensator is a doubly refracting device which can produce variable optical path differences. The compensator is adjusted to give an OPD equal in magnitude but opposite in sign to that of the sample. The resulting OPD of the light waves emerging from the compensator will then be zero. The two light waves then pass into the analyser where the beams are again split into two, being absorbed by the analyser in one direction but being transmitted in the other. The transmitted waves are now in the same plane and can interfere with each other. The compensated part of the image will usually appear black and is referred to as the zero order fringe. On either side of this fringe lies a sequence of coloured fringes ascending in order. The rotation of the compensator in degrees is converted into OPD values from the manufacturer calibration equation. This conversion was carried out using a spreadsheet.

Note that throughout this work optical dispersion effects have been neglected but would become significant where the sample thickness and hence the measured optical path difference becomes large. The type of compensator used throughout was an Ehringhaus compensator of Quartz or Calcite depending on the material and sample thickness.

Practically, the optical path difference is measured for different section thickness because the strains induced at the surface of a section during microtoming can affect the accuracy of the measurement. If the cutting strain is constant and independent of section thickness then birefringence can be calculated from the gradient of a graph of OPD.
versus section thickness. The intercept of this line is the OPD resulting from the cutting strain.

5.3.4.3 **Sample preparation**

5.3.4.3.1 **Microtoming**

Microtoming produces sections of material between 1 and 40 microns thick which are suitable for transmitted light microscopy. The method of preparation is as described by Hemsley\(^{193}\). The sections were cut using a standard base sledge microtome which provided the rigidity which was essential for good quality sections. Before each cutting operation the base was oiled well to give free running and the required section thickness was set on the microtome. Glass knives were found to be the most satisfactory for sectioning giving strain free sections with minimal marks from blade imperfections or judder. The knives were made with a blade angle of 40°. Knives were only used on the day they were made because it was found that the sharpness would deteriorate significantly overnight. The knives were clamped on to the microtome and their angle relative to the plane of cutting was set to the optimum. This was found by trial and error to be between 18° and 22°. The knife edge was perpendicular to the direction of sledge movement. It was found impossible to produce strain free sections at room temperature and also the more highly oriented samples seemed to show some relaxation when being section at this temperature. To overcome these problems a freezing stage was used. The sample was placed on a drop of water on the stage and CO\(_2\) gas allowed to expand through the base of the stage, causing the water to freeze. More water was added so as to completely embed the specimen in ice. The CO\(_2\) was used in bursts of about 10 to 20 seconds to maintain a sufficiently low temperature and prevent the ice from melting during sectioning. It was necessary to allow the sample to dry before mounting it on the microscope slide.

Mounting the section on a microscope slide was done using Canada Balsam to give a permanent mount. Each slide was labelled and stored in a slide box before examination under the microscope.

5.3.4.3.2 **Sectioning direction**

To obtain a complete picture of the three dimensional structure it is necessary to section the material in more than one plane. For biaxially oriented polymer materials, two birefringences, measured from two orthogonal planes are required to describe the orientation. By knowing the expected structure, the orientation of the planes of section can be decided upon.
In the drawn samples to be investigated in this work, the primary orientation direction was expected to lie along the direction of draw. In the straight die drawn samples, no transverse orientation was expected to be present. In the helically drawn samples however, rotational transverse orientation was expected. The best way to observe this would have been to take sections across the drawn material. However cutting such sections was impossible due to the extremely high orientation, even when using the cryo-techniques described above. On the other hand, it was very easy to cut sections along the draw direction. By cutting two orthogonal sections as shown in Figure 5.8 it was possible to measure the birefringence at points A, B and C.

Four sections of thickness 5, 10, 15 and 20 µm thickness were cut from the surface and mid-section of each sample. The optical path difference was measured at the centre and outside edge of each section. The OPD measurements were plotted against section thickness for each position and the birefringence calculated from the gradient of the line.

5.3.4.4 Orientation direction measurement

For the helically drawn samples it was noted that the direction of the principal axis tended to lie at some small angle to the draw direction and hence the axis of the sample. This angle was found to depend on the position from which the section was cut from the sample. Four adjacent sections of thickness 5, 10, 15 and 20 µm were cut at intervals of 0.25 mm through the thickness of samples produced under identical conditions from each of the three dies. The birefringence at each point of interest was measured and the angle made by the principle axis with the edge of the section was measured with the aid of the rotating microscope stage. Readings were taken to the nearest 0.1 degree.

5.3.5 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is a technique for recording the energy flow necessary to establish and maintain a zero temperature difference between a sample and a thermally inert reference, whilst they are subjected to a controlled temperature programme of heating or cooling. This allows physical and chemical changes that are accompanied by a thermal effect to be measured as a function of temperature. Any thermal change in the sample is measured against the heat-stable reference material and a plot of energy flow versus temperature results in a thermogram.

DSC differs from Differential Thermal Analysis (DTA) in that the latter technique measures the temperature difference between a sample and a thermally inert reference sample where both sample and reference are subjected to the same heating programme.
The DTA apparatus uses a single heating source to heat both the sample and reference and so any chemical or physical changes that occur to the sample that involve heat transfer results in a temperature differential between the sample and the reference. DSC uses separate heating elements and temperature sensing devices for the sample and reference and these are both maintained at an identical temperature by electronically controlling the rate at which heat is individually supplied to the test and reference samples. It is generally accepted that the two techniques offer equally good analytical capabilities although differential thermal analysers are capable of wider temperature ranges and differential scanning calorimeters give better results at very low heating rates. The temperature ranges required for analysis of the polymers in this work are relatively small (20 - 200°C for HMWPE and 20 - 300°C for PET) and so for this reason and convenience of equipment availability, the DSC technique was selected.

The DSC apparatus used was a Du Pont Instruments 910 Differential Thermal Analyser and is illustrated in Figure 5.9. It consists of a sample holder which accommodates both the sample and reference containers. In this case the containers are pressed aluminium pans with lids about 6mm in diameter. The heating source to each pan is controlled by a computer which supplies energy so that a linear rate of temperature change is maintained. The temperature of the sample and reference are measured with differential thermocouples which are in intimate contact with the pans. The heat flow to and from the sample relative to the reference is recorded by the computer and produces a DSC trace.
Chapter 5 Experimental Procedure

A typical DSC curve will consist of one or more exothermic (upswing) and/or endothermic (downswing) peaks along with changes in the height of the trace above the abscissa between transitions of the sample.

As the temperature increases at a linear rate, a small but steady difference in heat flow will be present between the test sample and reference. (represented on the trace by an offset in the baseline from its zero position). This is because the specific heat capacities of the sample and reference will differ and so one will require more heat in order to maintain the linear temperature increase. Any further changes in the height of a trace above the abscissa along the trace reflects a change in the specific heat capacity of the sample resulting from a chemical or physical transition.

At a point the curve may begin to deviate from the base line due to an exothermic or endothermic process. The onset temperature is defined as the temperature at which this process first becomes detectable by DSC. The exothermic peak corresponds to the maximum rate of heat evolution and the endothermic peak corresponds to the maximum rate of heat absorption. A peak does not necessarily correspond to the end of the process. A peak yields the transition temperature, and the area under any given peak with reference to an interpolated baseline is a quantitative measure of the total amount of heat flow to or from the sample during the change. The enthalpy change is not affected by the heat capacity of the sample.

5.3.5.1 Experimental Procedure

The main experimental parameters considered included type of atmosphere, heating rate and sample size. Because changes resulting only from a phase transition were of interest, rather than those resulting from a chemical reaction (for example a decomposition), the importance of these parameters might reasonably be expected to be very small. However because the differences in melting point and crystallinity between analysed samples were expected to be small, it was considered that every effort should be made to improve consistency and hence enhance the detection of such differences.

5.3.5.1.1 Atmosphere

Atmosphere has very little effect on any phase transition. Nevertheless all DSC experiments were carried out under a dry nitrogen blanket.

5.3.5.1.2 Sample Size

The main effect of sample size is to change the peak height. Large samples lead to higher heat changes and therefore give an increase in sensitivity. However a large
sample is also likely to develop a larger temperature gradient between its centre and the pan and leads to an increase in thermal lag, particularly at high heating rates. Large samples also decrease the obtainable resolution. The advantages offered by small samples include sharper peaks and a reduction in baseline drift as the properties of the sample approach that of the reference.

5.3.5.1.3 Heating rate

Heating rate was selected by considering three factors; thermal lag, resolution required and time restraints. Although the temperatures measured at the pans will be the same, the temperatures at the centres of the sample and reference will lag behind that of the furnace, the magnitude of the lag depends primarily on the thermal conductivity and heat capacity. Thus transition temperatures deduced from peaks on the DSC trace may be higher than their true value if the heating rate is sufficiently high. For the highest accuracy a heating rate of 2°C has been recommended. On resolution, the effect of a low heating rate is similar to that obtained by having a small sample; sharper peaks and a high resolution. For most applications a heating rate of about 10°C to 20°C per min is recommended since this seems to offer a compromise between quality of resolution and time taken per experiment. HMWPE samples were heated at 10°C per minute to 200°C making each run about 18 minutes long. PET was heated to 300°C at 20°C per minute giving run times of about 15 minutes.

5.3.5.2 Sample preparation

It was recognised that the thermal history of a sample analysed by thermal techniques could have significant effects on the measured properties. In order to minimise thermal history effects and therefore allow any effects of the drawing conditions to be clearly seen, samples were taken from the same point along the drawn products. This was the front end of length no 3 in each case.

The crystallinity of the drawn samples tends to depend on the strain experienced during drawing. Therefore imparting further strain on the DSC sample when trimming it from the material bulk should be avoided. For this reason a two stage technique was used. A small piece of material was cut away from the bulk of the drawn sample. Deformation imposed during this cut was found to be confined to about 1mm from the cut. This deformed portion of material was then removed by slicing thin layers from the cut end. In this manner further deformation is confined to the slice rather than the bulk of the sample. The remaining material then only contains deformation, and hence crystallinity,
imposed from the drawing operation. Samples taken from the drawn material taken from the full cross-sectional area.

Reduction in thermal contact between the sample and its container may result in poor transmission of any thermal changes in the sample to the detecting thermocouple and also poor heat transfer from the heater to the sample. Where oriented polymeric samples are heated, the container must be able to resist relaxation of the sample and ensure that contact between the sample and pan is maintained as this relaxation occurs. Accurate positioning of the sample containers over the thermocouples and heaters is also vital. Unless a similar thermal contact is made for each run, serious base-line drift can be expected.

The contact area between the sample and the pan was found to vary significantly because of the relaxation process experienced by the sample during heating. In some cases relaxation was so great that the sample tended to throw the lid off the pan base. To avoid this, each sample pan was crimped around its top edge to lock the top and bottom halves of the container together. The pan was then squashed around the sample inside to prevent the sample from moving. This was done on a flat surface to ensure that the base of the pan remained flat to provide good contact with the DSC cell. Inspection of the samples and pans after testing confirmed that this technique prevented the polymer samples from losing contact with the pan base.

The differences between samples was recognised as being small from an early stage. In order to reduce scatter and allow identification of trends and small differences between samples it was necessary to repeat experiments a number of times. For most samples, five DSC runs were completed, the results taken as an average of these runs. However where scatter was still judged to be significant for a few samples, the number of DSC runs was increased accordingly.

5.3.5.3 Method of Analysis

A DSC trace allows measurement of heat capacity, crystallisation enthalpy, melt enthalpy and transition temperatures such as the glass transition temperature $T_g$, crystallisation temperature $T_c$ and melting temperature $T_m$. From these measurements, other information such as percentage crystallisation can be calculated.

5.3.5.3.1 Glass transition temperature ($T_g$)

The glass transition temperature involves changes in specific heat, thermal expansion coefficient and free volume and is shown by change in baseline on the DSC trace. The
transition temperature is not always well defined and varies with the heating or cooling rate due to a time dependence of the relaxation of long chain molecules. A high heating rate results in an overestimate for $T_g$ whereas low heating rates not allow the $T_g$ to be detectable to DSC, the change in specific heat occurring over a long period of time.

5.3.5.3.2 Thermal crystallisation
Thermal crystallisation is an exothermic process and is represented as a sharp exotherm before the melting of the sample, as in PET. This is heating rate dependent and may be eliminated if the heating rate is too high, the molecules having less time to reorder themselves before melting occurs. If heating is carried out sufficiently slowly to allow complete crystallisation then the enthalpy change during this process is a measure of how much thermal crystallisation has occurs to complete the crystallisation of the sample. The amount of amorphous material present in the sample before thermal crystallisation can then be calculated.

5.3.5.3.3 Melting point
Melting or fusion is represented as a sharp endotherm. Fusion of the polymers involves transitions in the ordered crystalline regions or crystallites and the heat of fusion is the amount of energy needed to overcome the intermolecular forces in transforming a polymer from the crystalline or partially crystalline state to the completely disordered amorphous state. The entropy of fusion is a measure of the increase in degree of disorder. Entropy of fusion of the various polyethylenes varies directly with their crystallinity as would be expected since the fusion process involves a transition from different degrees of order to complete randomness.

An endothermic fusion peak is the point at which the heat effects are balanced and most closely approximates to the temperature at which all crystallinity is lost. Fusion in semicrystalline polymers takes place over a range of temperatures, and so the total disappearance of crystallinity at a sharply defined temperature is taken as the melting point. A low initial melting temperature and a broad melting range are indications of a wide distribution in crystallite size, smaller crystallites melting at a lower temperature than the larger ones.

Crystalline polymers exhibit a sharply defined melting point, whereas amorphous materials show a more gradual softening over a temperature range. The crystallinity in polymers requires a substantial amount of latent heat in order for the polymer to melt. With higher degrees of deformation, the melting point and heat of fusion rises.
5.3.5.3.4 Degree of crystallisation

The heat of fusion represents the enthalpy difference between crystalline regions and amorphous regions of the whole sample, and so it can be used as a measure of the degree of crystallinity in the sample immediately before melting.

If the heat of fusion of a perfectly crystalline polyethylene $\Delta H_{fo}$ is known, then the percentage crystallinity $x$ may be derived from the equation:

$$x = \left[ \frac{(\Delta H_f - \Delta H_c)}{\Delta H_{fo}} \right] \times 100$$

where $\Delta H_f$ and $\Delta H_c$ are the enthalpies of fusion and crystallisation respectively. Note that no crystallisation enthalpy was observed for the polyethylene samples and so only $\Delta H_f$ was measured. These values were calculated from the DSC trace by the computer which constructs a baseline across the peak in order to calculate the peak area. This baseline construction is the most arbitrary part of a calculation based on peak area. The baseline should reflect the progressive change of the sample properties. In all work carried out on the polyethylene and PET, the interpolated baseline has been a straight line between two specified temperatures.

For $\Delta H_{fo}$ of the hypothetically perfect crystalline polyethylene, the heat of fusion of crystalline, straight chain paraffin hydrocarbon, dotriacontane has been used by several workers. Bacon\textsuperscript{218} reports a value of 64.6 cal/g and Parks and Rowe\textsuperscript{219} report a value of 61.6 cal/g. Dole\textsuperscript{220} reports 66.3 cal/g, Billmeyer\textsuperscript{21} 65.9 cal/g. The heat of fusion for a perfect PET crystal has been taken to be 32.5 cal/g\textsuperscript{222,223}

5.3.5.4 Through-Die DSC

DSC was conducted on both HMWPE and PET neck samples as produced from partially drawn billets. The DSC samples were taken from positions along the axis of the billet from die entry through to 3cm beyond the die exit, at intervals of 0.5cm.

5.3.6 Shrinkage Measurement

5.3.6.1 Experimental procedure

Shrinkage measurements were conducted on drawn PET samples by immersing them in a constant temperature bath. Three samples 40mm in length were cut from length no 2 for each of the drawing conditions. The initial length of each was measured using vernier callipers.
Chapter 5 Experimental Procedure

The three samples were immersed for two minutes in the constant temperature bath at 85°C, 100°C and 120°C respectively. The bath contained water for both 85°C and 100°C experiments and oil for 120°C.

The samples were removed from the bath and immediately immersed in water at ambient temperature to eliminate residual shrinkage that might occur due to relaxation during slow cooling.

The final sample lengths were measured and recorded.

5.3.6.2 Method of analysis

The percentage shrinkage was calculated from the following equation:

\[ \% \text{ shrinkage} = \frac{L_o - L_f}{L_o} \times 100 \]

where \( L_o \) is the initial sample length and \( L_f \) is the final sample length.
**Chapter 6 Results**

During the course of this work considerable differences between polyethylene and polyethylene terephthalate, have been observed. These materials exhibit different features with respect to the die-drawing process as well as different characteristics of the drawn products. For this reason it is convenient to present the results separately for each material.

### 6.1 POLYETHYLENE

#### 6.1.1 Polymer grade

The experimental work has been conducted on three different grades of polyethylene; ultra-high molecular weight polyethylene, high molecular weight polyethylene and high density polyethylene. It was found that the grade of material (i.e. its molecular weight) had a significant influence on how easily the material was die-drawn.

##### 6.1.1.1 Ultra-high molecular weight polyethylene

In general, the ultra-high molecular weight material was found to have unstable die-drawing characteristics. At a nominal draw ratio of 7.5 (i.e. 6mm billets), it was only possible to draw at temperatures between 100°C and 110°C. At high temperatures, stability relies on rapid quenching as the drawn product emerges from the die exit. Whilst stability was improved by chilling the cooling air applied at the die exit, this was insufficient to allow speeds over 200mm/min to be attained.

The actual draw ratios obtained for the seven successful runs, drawing ultra-high molecular weight polyethylene to a nominal draw ratio of 7.5 are presented in *Table 6.1*. It was not possible to establish stability using helical die A at 200 mm/min and no products could be drawn using helical die B.
At lower nominal draw ratios of around 4.5, it was possible to draw through all dies but only in the restricted temperature range between 100°C and 120°C. The upper speed limit was 300mm/min achieved using the straight die and Helical die A. Helical die B demonstrated a lower speed limit of between 100 and 150mm/min. The results are shown in Table 6.2. The results show that at low draw speeds, 100 - 200mm/min, there is a reduction in the draw ratio when using Helical die A. Helical die B gives a much higher draw ratio. At the higher drawing speeds, no product could be produced from Helical die B and Helical die A produced a higher draw ratio than the straight die.

**6.1.1.2 High density polyethylene**

With respect to die-drawing the high density polyethylene proved to be the least successful. It could be drawn only at low nominal draw ratios (4.5) at speeds up to 100mm/min and at a temperature of 100°C. The actual draw ratio obtained under these conditions was high ~7.4. This value was approximately constant for all the dies. At high draw temperatures the product was found to become unstable, exhibiting periodic necking at the die exit. At low draw temperatures, the draw stresses were high and fluctuations in drawing load were observed. The combined effects prevented production of a suitable length of drawn product for further analysis.
6.1.1.3 High molecular weight polyethylene

High molecular weight polyethylene has been successfully die drawn at different drawing temperatures and speeds. Nominal draw ratios of 7.1 show the clearest distinction between the dies and these experiments were conducted on the small scale apparatus up to a draw speed of 500 mm/min. Large scale die drawing was also conducted on this material but was limited to lower nominal draw ratios. Drawing speeds of up to 3.5 m/min have been attained with this material. The results for this grade are presented in detail below.

6.1.2 Deformation zone geometry

In order to investigate the development of the deformation passing from the die entrance to the die exit, the geometry of the deformation zone was measured. Plate 6.1 shows the profiles obtained from partially drawn billets at temperatures of 80°C and 120°C. The grid pattern which was intended to illustrate the flow pattern of the surface material indicates that die controlled deformation of this material dominates near the die entrance.

The development of product draw ratio with that imposed by the die is shown in Figures 6.1 to 6.3. These graphs show a thick dotted line which represents the die profile. Hence below this line, the material has a lower deformation ratio than the die indicating that its cross-section is in fact larger than the die at this point. This occurs as a result of an elastic recovery of the material. Above the dotted line, material cross-sectional area is less than the die and results from the billet drawing away from the die wall through tensile drawing.

The elastic nature of the polymer means that it is likely that under the tensile drawing load, it actually leaves the die wall at some point nearer the die entrance than that indicated by the graph. This is because the graph is constructed from the dimensional measurements taken from the billets after they had been removed from the die and so it includes the recovered elastic component.

Figure 6.1 shows the graph for the straight die. The graph illustrating the material profile through drawing with the straight die shows the material to enter the die and deform elastically up to some point towards the die exit where there is an upswing of the graph. This upswing indicates the onset of plastic deformation where the polymer yields.
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Partially drawn billet profiles of HMWPE. Drawn at 80°C

Partially drawn billet profiles of HMWPE. Drawn at 120°C

Plate 6.1 Die geometry profiles for HMWPE billets
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Figure 6.1: Development of deformation ratio for a partially drawn billet of HMWPE using the straight die.

Figure 6.2: Development of deformation ratio for a partially drawn billet of HMWPE using Helical die A.
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At some further point along the die, the graph crosses the die line which is caused by the formation of a neck. The material leaves the die wall to follow a more favourable stress-strain-strain rate path.

For a higher drawing temperature the point at which the material leaves the die wall is nearer the die exit. The final draw ratio obtained is shown to depend on drawing temperature and draw speed.

The profile for Helical die A is shown in Figure 6.2 which demonstrates some subtle changes in the geometry of the deformation zone. The billet initially deforms elastically before yielding and eventually forming a neck. However the point at which the curve shows the material leaving the die wall (i.e. crossing where it crosses the die line) is much further along the die than for the straight die. This occurs at all drawing temperatures. The final draw ratios obtained tend to be lower than those for the straight die. Also the steady state draw ratio is reached nearer the die exit than for the straight die.

The geometry of Helical die B is represented by Figure 6.3. The observations made here are an extension to those made for Helical die A. The final draw ratio is the lower of all the dies. The material does not leave the die wall until almost at the die exit and so the
length of the tensile drawing zone is minimal. The steady state draw ratio is obtained much nearer the die exit than for the other dies.

6.1.3 Nominal draw ratio

Initial drawing trials indicated that nominal draw ratio had a significant influence on the actual draw ratios obtained. Figures 6.4 shows the variation of actual draw ratio with the nominal draw ratio for a given billet drawn at the temperatures indicated. The drawn product was obtained under steady state conditions of draw speed at 500mm/min. Each of the points represents a different point along the length of the billet. It is clear the there is a good correlation between the actual and nominal draw ratio. The curves indicate the relationship to be linear, but they do not extrapolate to zero which might imply that whilst the relation may appear to be linear over the small range of draw ratios being considered, the broader relation is more complex and almost certainly non linear.

It has been found that most drawing characteristics are sensitive to nominal draw ratio. By using curves generated from the length of each billet (i.e. over a range of nominal draw ratios) it has been possible to normalise the results with respect to nominal draw ratio. For the actual draw ratio curves, for example, it is possible to interpolate a value for the actual draw ratio at a given nominal draw ratio. For the range of billet dimensions in this work, it was possible to obtain a normalised values at nominal draw ratio of 7.1. The following results are presented and discussed with respect to the normalised values and so are no longer influenced by the nominal draw ratio.

6.1.4 Draw temperature

Draw ratio was found to decrease with increasing draw temperature. The relationship for billets drawn through the three dies is shown in Figure 6.5.

It is shown in these curves that for a given set of drawing conditions, the draw ratio obtained for the helical dies is always lower than for the straight dies, the lowest obtained using Helical die B. This was supported by the die profile measurements shown in Figures 6.1 to 6.3.

6.1.5 Draw speed

The effect of draw speed is illustrated in Figures 6.6 and 6.7. The results of the small scale experiments is shown in Figure 6.6 while the results from the large scale die-drawing conducted on at lower nominal draw ratios is shown in Figure 6.7.
Figure 6.4: Actual draw ratio vs Nominal draw ratio for die-drawn HDPE. Drawn at 50mm/min.
Figure 6.5: Actual draw ratio vs. Draw temperature for die-drawn HDPE
Figure 6.1: Actual draw ratio vs Draw speed for die-drawn HMPPE (Nominal draw ratio = 7.1)
Figure 6.7: Actual draw ratio vs. draw speed for the draw HMPE (Nominal draw ratio = 4.5)
These curves show clear trends towards actual draw ratios with higher draw speeds. Also apparent is that the effect of draw temperature is much less dominant in the helical dies, particularly Helical die B.

6.1.6 Drawing force and stress

6.1.6.1 Axial drawing force

Drawing force measured during the experiments are shown in Figure 6.8. The curves show that for a given draw temperature drawing force increases with actual draw ratio but under a given set of conditions, drawing force is consistently lower for the helical dies. Drawing force decreases with draw temperature which is attributable to the decreasing yield stress of the material.

6.1.6.2 Axial drawing stress

The graphs of figure 6.9 show the nominal axial draw stress (based on no-load cross-section) required to produce a given draw ratio at a given temperature. In effect these are draw speed curves plotted on an ‘actual draw ratio’ axis. The relationship is approximately linear for all temperatures. The curves generated by the helical dies are also shown.

By comparison of these curves, it is possible to see that the same relationship between draw stress and draw ratio exists for all dies.

6.1.6.3 Peak drawing forces

The drawing forces were recorded as a function of axial displacement of the drawn product and this is shown in Figure 6.10. The first stage of the die drawing operation involved drawing material through the die entrance to fill the die cavity. This was observed to be accompanied by a steady increase in drawing force, to a peak force when the die was completely full. The process then quickly established the slightly lower steady state drawing force.

Figure 6.11 illustrates the peak drawing force experienced when starting the process or whenever the drawing process was stopped and restarted during a drawing operation. The force displacement curves show that the helical dies considerably reduce the peak force generated at start up.
Figure 6.8: Axial drawing force vs drawing speed for die-drawn HMFPE (Nominal draw ratio: 7:1)
Figure 6.9: Axial draw stress vs. axial draw ratio for die-drawn HMFPE (Nominal draw ratio = 2).
Figure 6.10: Peak drawing force vs. draw temperature for die-drawn HNDFE.
6.1.7 Elastic recovery

The axial elastic recovery of the drawn samples was found to be appreciable after 48 hours. The values were calculated based on an initial drawn length of 100mm which after 48 hours was re-measured. The graphs of Figure 6.12 indicate that the greatest elastic recovery was obtained for product produced using the helical dies. All curves show a general trend of a lower elastic recovery for higher actual draw ratios. Elastic recovery is observed to be highest with lower drawing temperatures.

6.1.8 Orientation measurements

6.1.8.1 Initial surface measurement

The orientation in the drawn polyethylene products was measured using a polarising microscope. Initial birefringence measurements taken from sections near the surface of the drawn products demonstrated that the maximum birefringence value occurred for samples drawn at a draw temperature of between 100 and 105°C.
Figure 6.2: Axial elastic recovery vs actual draw ratio for die-drawn HPPE.
This was found for all dies. However no consistent correlation was observed with respect to the type of die used. It was expected that the helical dies would demonstrate a lower level of birefringence because they had been drawn to a lower draw ratio. From these results it was clear that under some circumstances the helical dies actually produced a higher birefringence.

6.1.8.2 Through-section orientation

These initial measurements were taken near the surface of the drawn product. It was observed that where the samples originated from the helical dies, the extinction points occurred with the section lying at an angle to the microscope stage. This implied that the principal orientation direction did not lie along the axis of the drawn sample. Since the section originated from near the surface of the drawn product, the observation would be consistent with the presence of some hoop-wise orientation superimposed onto a much larger axial orientation.

Figure 6.13 shows the results of a subsequent investigation to determine the relationship between the angle along which the maximum orientation was observed and the radial distance from the product axis. It shows that at the product core the principle orientation
lies along the product axis and no change in angle is observed until about 0.75mm from the surface of the product. The curve also shows the angle that would exist if the material deformed in an ideal manner according to the die geometry. It has been calculated from the helix angle at the radial distance concerned. The existence of a difference between the ideal principle angle and the measured angle can be attributed to the elastic properties of the material.

*Figure 6.14* shows birefringence measurement as a function of radial distance from the drawn product axis. Five measurements were taken from the axis to the surface. This shows that the birefringence for the straight die samples is approximately constant across the cross-section. the slight increase at the surface could be attributed to frictional effects at the die-material interface. Helical die A shows a similar birefringence magnitude at the die axis but increases towards the surface. On the other hand, Helical die B has a much lower birefringence along the axis rising to a higher value at the surface.
6.1.8.3 Product core measurements

The birefringence measurements at the core of the drawn product are shown in Figure 6.15 and Figure 6.16. They represent samples drawn at 500mm/min. Once again the maximum birefringence values are obtained at the draw temperatures of 105°C, Figure 6.15.

6.1.9 Thermal properties of drawn products

The results of the DSC analysis of drawn polyethylene have shown that the crystalline melting point is unaffected by the drawing conditions or by the type of die used and no correlation was observed, Figure 6.17. However, the melt enthalpy tends to increase with draw temperature, showing a maximum at the highest draw temperature of 120°C. This influence seems to be stronger for the helical dies, Figure 6.18.
Figure 6.16: Product core birefringence vs. Drawing temperature for die-drawn PE

- **Straight Die**
  - Drawn at 80°C
  - Drawn at 90°C
  - Drawn at 100°C
  - Drawn at 110°C
  - Drawn at 120°C

- **Helical Die A**
  - Drawn at 80°C
  - Drawn at 90°C
  - Drawn at 100°C
  - Drawn at 110°C
  - Drawn at 120°C

- **Helical Die B**
  - Drawn at 80°C
  - Drawn at 90°C
  - Drawn at 100°C
  - Drawn at 110°C
  - Drawn at 120°C

Actual draw ratio ($\lambda_d$) vs. Birefringence ($\Delta n^2$)
Figure 6.17: Crystalline melting point vs. Drawing temperature for die-drawn HDPE
Figure 6.8: Degree of crystallinity vs actual draw ratio for the drawn HMPP.

**Straight Die**

- 500 mm/min
- 400 mm/min
- 300 mm/min
- 200 mm/min
- 100 mm/min

**Helical Die B**

- 500 mm/min
- 400 mm/min
- 300 mm/min
- 200 mm/min
- 100 mm/min
6.1.10 Mechanical properties of drawn products

6.1.10.1 Tensile modulus

The tensile tests conducted on the drawn products have enabled the tensile Young's modulus to be calculated. The results are shown in Figure 6.19.

This clearly shows that the relationship between modulus and draw ratio is linear. The graphs show curves for products drawn at different temperatures and it appears that for a given draw ratio with a given die, the modulus is relatively unaffected by drawing temperature except where drawing occurs at 100°C, which produces the highest modulus.

For a given draw ratio the modulus decreases from products drawn through a straight die to those from the helical die B. However the gradient of the modulus-draw ratio relationship is the same for all three dies.

6.1.10.2 Compression test

The plane strain compression tests have not shown any correlation of compressive yield with draw ratio for any of the dies. There is no distinction between the dies. Compressive modulus on the other hand seems to depend on the type of die, Figure 6.20. Higher modulii tend to be obtained at higher draw temperatures, although at lower temperatures, there is no obvious correlation.

During the transverse compression tests all samples were subjected to the same level of compressive strain, applied so as to cause the material to deform in a transverse manner, promoting longitudinal splitting. The results have shown that the longitudinal splitting resistance of the products can be substantially improved by the drawing through the helical dies, Figure 6.21.

Figure 6.21: Degree axial splitting for HMWPE. (Left to right; Straight, Helical die A, Helical die B)
Figure 6.10: Actual Young’s modulus vs actual draw ratio for die-drawn HMWPE.
Figure 6.20: Compressive modulus vs actual draw ratio for die-drawn HiWPE.

### Straight Die

- Drawn at 80°C
- Drawn at 90°C
- Drawn at 100°C
- Drawn at 110°C
- Drawn at 120°C

### Helical Die B

- Drawn at 80°C
- Drawn at 100°C
- Drawn at 120°C

**Compressive modulus (GPa)**

**Actual draw ratio (R)**
6.2 POLYETHYLENE TEREPTHALATE

The die drawing experiments conducted in this work have shown that it is possible to successfully die draw PET to a draw ratio of up to 5:1 in order to produce an oriented, uniform, transparent product using both straight and helically profiled conical dies. The photographs of Plate 6.2 show samples of partially drawn PET billets which represent the profile of the deformation zone for the process conditions used.

6.2.1 Deformation zone geometry.

The graphs of 6.21 to 6.22 show the development of the deformation ratio of PET billets passing through the dies. The die profile is indicated by the thick dotted line. As with polyethylene, all profiles show that at some points, the material cross-section is bigger than that of the die due to the elasticity of the material which is recovered when the billet is removed from the die.

The point at which the material leaves the die wall appears to be less dependent on the process conditions for PET than for polyethylene.

For the straight die there is little deviation of the material from the die wall, regardless of processing conditions. The deformation is gradual from the die entrance to the exit. The neck is formed at a nominal draw ratio of about 2.5

The curves indicate that final draw ratio is independent of both drawing temperature, final actual draw ratio is the same for all temperatures. The material response to a higher drawing temperature is similar to that of polyethylene in that it necks away from the die wall at a point further along the die.

For helical die A the profiles show significant differences. Again there is a region ‘below’ the die line where the material cross-section is larger than that of the die and the deviation for each curve is much higher than for the straight die. It is also clear that in the region of deformation up to a die draw ratio of about 2.3, the actual deformation of the material is minimal. Both these features would indicate a higher level of elastic recovery for material in this area. The upswing in the curves occurs at a slightly lower nominal die draw ratio than for the straight dies and is much steeper. This would indicate the formation of a sharp neck which is also observed from the photographs.
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Partially drawn billet profiles of PET. Drawn at 80°C

Partially drawn billet profiles of PET. Drawn at 120°C

Plate 6.2 Die geometry profiles for PET billets
Figure 6.21; Development of deformation ratio for a partially drawn billet of PET using the straight die.

Figure 6.22; Development of deformation ratio for a partially drawn billet of PET using Helical die A.
The material stabilises away from the die wall and for all of the samples the final draw ratio is reached before the material emerges from the die. The range of total draw ratios is higher for this die. Helical die B demonstrates a more extreme profile than Helical Die A. This die differs significantly from the other die profiles in that near the entrance to the deformation zone, almost as soon as the material contacts the die, the billet profiles are measured as having a smaller cross section than the die. This region is essentially a neck where the material leaves the die wall and undergoes tensile drawing. Further along the die, the profile meets the die wall again and adopts the deformation imparted from the die profile, up to a die draw ratio of about 2.0. From this point the sample adopts a very sharp neck and does not contact the die wall again. The neck profile is most steep for samples drawn at 80°C and 120°C.

From the photographs it is apparent that the profile does not adopt the true shape of the die. At the point of the first neck, the material departs a sufficient distance from the die wall to allow it to rotate relative to the die cross-section. This in turn allows the billet surfaces to skip over the twist in the die to relocate on the die one quarter of a turn behind. This means that the overall twist imparted to the material is one quarter of a turn less than that of the die.
Figure 6.24: Actual draw ratio vs nominal draw ratio at different draw temperatures for PET billets.

The sample drawn at 100°C follows the die profile much more closely and adopts a lower final draw ratio than the samples drawn at 80°C and 120°. The order of final draw ratio with respect to draw temperature was also experienced with Helical die A.
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6.2.2 Final draw ratio

The draw ratio attained when die-drawing PET can be influenced by a number of factors. The main factors include draw temperature, draw speed and the development of crystallinity and orientation.

6.2.2.1 Nominal draw ratio

Unlike polyethylene, the actual draw ratio obtained when drawing polyethylene terephthalate does not seem to necessarily depend on the nominal draw ratio. This dependency appears to be related to the draw temperature and there is a definite temperature band only in which nominal draw ratio has an influence. The graphs of Figure 6.24 show how nominal and actual draw ratio are related for different draw temperatures. The figure shows the results for the straight die only, but the same effect has been observed for both the other dies.

At the lowest draw temperature of 80°C, there is almost no correlation between actual and nominal draw ratio. However, moving to a temperature of 90°C produces a much stronger correlation. Through 100°C the correlation is similar with a similar gradient implying that whilst draw temperature determines the existence of a relationship, it does not influence its nature. Moving up to 110°C and 120°C produces a more dispersed series of points and again there is no obvious existence of a relationship between nominal and actual draw ratio.

6.2.2.2 Draw temperature

PET also differs from polyethylene with its response to draw temperature. It is draw temperature which seems to play by far the most important role in determining the die drawing characteristics of PET. Figure 6.25 shows the actual draw ratios obtained for different drawing temperatures.

The straight die shows a clear trend with processing temperature. As drawing temperature is increased the draw ratio of the product decreases. The relationship is not completely linear and at the temperatures of 110 and 120°C, draw ratio is almost independent of draw temperature. Increasing the draw speed increases the draw ratio, an effect which is more noticeable at lower temperatures. However draw speed does not have the same effect on PET as it would for polyethylene when being drawn through a straight die. The increase in draw speed from 100 to 500mm/min only yields a 10% increase in draw ratio indicating that the process is relatively insensitive to the major die drawing influences.
Figure 6.25 Actual Draw Ratio vs Temperature for PET.
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The curves for the helical dies show a minimum draw ratio obtained at a draw temperature of about 100°C. For helical die A, the spread of draw ratio values for a given draw temperature is of a similar magnitude as for the straight dies. The regression curves for drawing speeds of 100 and 200 mm/min cross because at high temperatures the actual draw ratio is higher for a draw speed of 100 mm/min.

The existence of the minimum is more extreme for Helical Die B. It is clear with this die that all curves cross in the region where draw temperature is between 100 and 115°C. At temperatures below the cross over points, draw ratios higher where the draw speed is higher. At draw temperatures above the cross-over points, the draw ratio is higher for samples drawn at a lower speed.

6.2.3 Drawing force and stress

The observed drawing forces was found to be essentially a steady state load. This was rapidly achieved at start up. This is the case for all the dies.

At lower temperatures, however, the drawing force was found to fluctuate in a periodic manner. The frequency of this peak was about every 100 mm displacement for Helical die A and every 60 mm displacement for Helical die B. Examination of the drawn product found that these peak forces corresponded to a recovered twist in the drawn product. Unless a recovered rotational shear strain is applied to the material at the die exit, the material emerges from the die with a twisted profile matching that of the die. In the case of PET, the torsional stiffness of the drawn product is significant which prevents completion of the recovered shear process at the die exit. As a result the torsion in the product, applied between the die exit and the clamp on the cross head, accumulates until the torsional yield point of the product emerging from the die is reached. At this point the material yields producing a reverse twist in the product. Essentially, instead of recovering the rotational shear progressively as the drawing proceeds, as happens with polyethylene, the shear is recovered as discrete amounts of deformation. The increased frequency for Helical die B is a direct result of its rate of twist.

6.2.4 Crystallinity

The DSC results in Figure 6.26 show a distinct trend to a higher crystallinity with draw temperature which is undoubtedly due to the enhanced rate of thermal crystallisation at these higher drawing temperatures. This is evident even though the samples used for all the DSC measurements were taken from the front end of each drawn sample in order to
minimise the dwell time at the drawing temperature before drawing. This implies that the thermal crystallisation phenomenon is extremely rapid and has a significant role in the die drawing of PET.

The through neck DSC investigation did not show any trends. The development of crystallinity was extremely rapid from the die entrance, corresponding to the formation of the neck.

6.2.5 Shrinkage

Shrinkage was found to exhibit a maximum value in samples drawn at 100°C. This is much more evident in the straight die than the helical dies. As the rate of twist of the dies increases moving from straight to maximum rotational shear, the shrinkage reduces and becomes much less sensitive to draw temperature.
Figure 6.26 Degree of crystallinity vs drawing temperature for PET.
Figure 6.27 Axial shrinkage vs. drawing temperature for PET.
Chapter 7 Discussion

7.1 POLYETHYLENE

The experimental work has shown that particular grades of polyethylene have good die-drawing properties and all products have good integrity, uniformity and surface finish. Draw ratios of up to 9.0 have been achieved using high-molecular weight polyethylene. The drawn material appears white when drawn at low temperatures, becoming more transparent as the draw temperature increases.

The experimental work conducted on the three grades of polyethylene are shown in Chapter 6. Observations made from the successful die drawing experiments indicate that the same qualitative trends apply to each grade of material. A reasonable volume of results has been obtained for the high-molecular weight grade and so the results are discussed with reference to this grade. Similar observations would probably be made for each grade given optimum processing conditions such as temperature profile, die design and process scale.

It was found that the drawing characteristic of polyethylene was very sensitive to the temperature profile of the deformation zone, particularly at the die exit and the region immediately downstream of the die exit. This is because a substantial amount of post die axial deformation occurs for polyethylene and in order to achieve process stability, the deformation must be frozen at an optimum draw ratio for a given set of conditions. This can only be achieved if the post-die temperatures are sufficiently low to raise the yield stress of the drawn polymer to prevent further deformation. It is likely that this post-die temperature profile has a much larger influence on drawing behaviour than initially anticipated. The ambient post-die temperature must be carefully controlled and an optimum profile will exist for a given polymer grade, drawing temperature and draw...
speed. It is believed that this is the main cause of the problems experienced with the ultra-high molecular weight and high density polyethylenes.

The high molecular weight grade of polyethylene could be drawn most easily between 100° and 110°C. At the low temperatures, the yield stress of the polymer would be very high, requiring a high axial draw stress. It is likely that the required drawing stress would easily exceed the breaking strength of the product emerging from the die. The drawing is also hindered by the low die angles used in these experiments. A low die angle necessarily imposes a greater area of contact with the material and the larger frictional forces generated apply considerable additional load to the drawn product. At the higher temperatures, >110°C, the product stability is reduced because of insufficient quenching at the die exit. Because molecular relaxation becomes more significant at higher temperatures, the development of orientation is less efficient, despite the higher draw ratio.

At high nominal draw ratios, the draw ratio was consistently found to be highest for the straight dies, as shown in Figure 6.4, which meant that under a given set of processing conditions, producing axial orientation would be more effective using this die. This was also found to be true at most drawing speeds as in Figure 6.6. The idea that the straight die is more effective at orienting the polymer in the longitudinal direction is further supported by the fact that the drawing speed limit is lower for the helically drawn product.

As the drawing speed increases, it has been observed, in most cases, that the axial draw ratio of the helical dies reaches some point at which further increases in speed produce a sudden increase in draw ratio. This represents the drawability limit for the material at these conditions and it fractures with further increases in strain rate. This is clearly seen from the data in Tables 6.1 and 6.2.

The photographs in Plate 6.1 show partially drawn high molecular weight polyethylene billets. These profiles, produced at different draw temperatures and draw speeds, clearly show that material passing through the dies deforms according to the geometry of the die profile. The grid patterns show the distortions of the surface material to be consistent with die controlled deformations in which cross-sections of material remain planar as they move through the die. The photographs show no obvious visual indications that the draw conditions of temperature and speed have a significant effect on the deformation profile of polyethylene. However the investigation into the geometric profile of the partially drawn billets has revealed distinct differences between the dies.
As shown from this study, the helically die-drawn products tend to show a greater elasticity near the die entrance with the onset of plastic deformation occurring nearer the die exit. For the helical dies, most of the plastic deformation occurs near the die exit, refer to Figure 6.1 to 6.3.

The higher proportion of plastic deformation near the die exit implies that for a given draw speed, there must be a higher strain rate near the exit in these dies. A higher strain-rate would tend to make the mechanical response of the material more brittle and as such more sensitive to fluctuations in drawing conditions. This could also be a contributive factor in causing the helically drawn products to fail before attaining the higher draw ratios possible with the straight die.

It may also be interpreted that the effective yield point, with respect to location in the die, occurs nearer the die exit for a helical die. This in turn means that the effective nominal draw ratio (i.e. determined from the die geometry of the die at the location of this effective yield point) is lower for the helical dies. This phenomenon, which is enhanced with increasing the rate of twist is the same as would be experienced by processing the polymer at a higher temperature. This would suggest that phenomena with the helical dies might be connected to the material yield stress.

The state of stress of an element of material within the die will involve a distribution of normal and shear stresses. Yielding will occur where the state of stress satisfies yield criteria for the material. The rotational shear produced by the helical dies at the die entrance would produce additional shear stress to elements of material in the die thus changing the balance of stresses required to achieve the yield conditions. As the shear stress components increase, the magnitude of the normal stresses required to cause yielding will decrease. The change in stress distribution would be associated with a change in strain distribution resulting in different geometric profile.

As the strain rate increases with draw speed the stress-strain-strain rate field becomes less favourable for die drawing and more favourable for tensile drawing. This has been supported by the results of many other workers\textsuperscript{143} who have investigated die-drawing of polyethylene. This means that the material will leave the die wall nearer the die entrance. The location of the point of yielding will move towards the die entrance. Since this move towards the die entrance has been observed to occur for each die at higher drawing speeds, the location of the point of yielding for all dies will tend to become closer together. A proportionally higher degree of tensile drawing will occur in helical dies as the strain rate increases. The differences in deformation geometry between the dies at higher speeds is therefore reduced.
The observed lower peak loads, as shown in Figures 6.10 and 6.11, together with the lower steady state forces, Figure 6.8 implies that the material yields under a much reduced axial stress component which would further support the notion that the helical dies operate by changing the state of stress of elements of material in the die. This has potential benefits where the product is susceptible to breaking during the start-up procedure.

It is proposed that the two different rotational shear processes of the sudden shear at the die entrance and the progressive shear along the die are primarily responsible for the changes in drawing behaviour experienced when using helical dies to die draw polyethylene. The importance of these two mechanisms will vary according to the process conditions, the most influential of these being draw temperature and strain rate.

The sudden rotational shear at the entrance is experienced under all drawing conditions and the magnitude of this component remains essentially unchanged for all processes, if elastic deformations are ignored. However the progressive shear component will only be imparted to the material whilst it is in contact with the die wall. If contact is lost due to necking in order to follow a more favourable deformation route, there is no means of constraining the deformation to the helical profile of the die. The balance of these two rotational shear components will change with draw speed and it is reasonable to propose that it is the relative contributions made by each of these components that is most important for the observed changes in drawn product characteristics.

It is apparent that a unique relationship between axial draw stress and axial draw ratio exists. The regression lines drawn on each chart in Figure 6.9 are the same at any given draw temperature. Therefore, the relationship would seem to hold regardless of the type of die used. Furthermore, the gradients of the regression lines are similar regardless of draw temperature, at least over the draw ratios considered here. The existence of such a relation for straight channel dies has been supported by other workers\textsuperscript{194} but the results of this work suggest that it may be extended to include dies with rotational shear deformation components.

This observation can be used to formulate an empirical model relating axial draw stress to actual draw ratio. In this manner the required stress that must be carried by the drawn product in order to achieve a given draw ratio can be calculated regardless of the type of die to be used in the deformation.

The model can be expressed in the form;

\[ \sigma_{\text{axial}} = \alpha \lambda_f + \beta + \left( \gamma / T \right) \]
where \( \alpha, \beta, \) and \( \gamma \) are constants. \( \alpha \) can be easily obtained by averaging the gradients of the lines of best fit through the data shown in Figure 6.9. These are calculated by the least squares method and the average gradient is then 20.6 MPa. This value can be substituted into equation 6.1 to give;

\[
\sigma_{axial} = 20.6 \lambda_f + \beta + \left( \frac{\gamma}{T} \right) 
\]

The term \( \beta + \left( \frac{\gamma}{T} \right) \) is the intercept of each line with the \( y \) axis, which can be calculated as an average of the three dies for each temperature. The following table gives the intercept values;

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( \beta + \left( \frac{\gamma}{T} \right) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>-54.2</td>
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<tr>
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</tr>
<tr>
<td>120</td>
<td>-99.5</td>
</tr>
</tbody>
</table>

These values can then be plotted against \( 1/T \) in order to find the constants \( \beta \) and \( \gamma \). The chart is shown in Figure 7.1.

![Figure 7.1](image.png)

*Figure 7.1; To calculate constants \( \beta \) and \( \gamma \).*

The constants are found to be \( \beta = -185 \) MPa and \( \gamma = 10400 \) MPa°C.

The model then becomes;

\[
\sigma_{axial} = 20.6 \lambda_f + \left( \frac{10400}{T} \right) - 185
\]
where draw temperature $T$ is expressed as °C and $\sigma$ is given in MPa. It is this relation that provides continuity between the different dies. It implies that draw stress and hence power requirement is determined only by actual draw ratio. (for a given set of drawing conditions). In producing a particular deformation ratio, the specific work per unit volume will be the same.

The lower drawing stress levels experienced with the helical dies is a direct consequence of the existence of a lower draw ratio. This in turn implies that some additional influence is responsible for preventing the higher draw ratios occurring in the helical dies. The investigation into the development of orientation has found that for a given set of drawing conditions, the maximum birefringence occurs on sections taken from near the product surface. (i.e. the product deformed at the furthest point from the die axis). Furthermore the maximum level of birefringence measured from the samples is similar regardless of the type of die used. This would suggest that near the surface, molecular orientation is reaching a similar magnitude. The rotational shear causes a much higher degree of deformation near the surface of the helically drawn products simply because the surface is furthest from the axis of rotation. The sudden rotational shear component experienced at the die entrance is likely to apply a significant amount of deformation before the material actually enters the conical deformation zone. The pre-orientation of this material will be higher. As axial deformation proceeds, the level of orientation will increase until it nears its limit for the processing conditions used. The high level of initial orientation for the helical dies means that this limit is reached at a lower axial draw ratio than would be obtained for a straight die. Relatively the straight die will show higher draw ratios.

The correlation observed between nominal draw ratio and actual draw ratio, *Figure 6.4* indicates that die-drawing processes are particularly sensitive to nominal draw ratio. The gradients of the curves on the actual draw ratio-nominal draw ratio graphs can be used to produce a draw ratio sensitivity index to relate the increase in actual draw ratio expected with an increase of billet dimension. This sensitivity index is plotted against temperature in *Figure 7.2*, and shows significant differences between the dies.

The most obvious trend is that the sensitivity tends to decrease with increasing drawing temperature. This can be attributed to the lower yield stress of the material at higher temperatures leading to lower drawing forces and decreased force fluctuation. Also at higher temperatures, the material tends to deform according to the geometry of the die, without necking.
The helical dies reduce this sensitivity still further, particularly at lower draw temperatures. This again is a trend normally associated with lower yield stresses and so provides more evidence that it is the stress distribution within the material that is responsible for the change in drawing characteristics.

This represents a significant improvement in process stability through two routes. Firstly the dependence of actual draw ratio with nominal draw ratio is reduced which means a consistently uniform product can be produced even when the dimensions of the billet vary significantly. Secondly the sensitivity is less dependent upon temperature. This provides a means of more accurately predicting the actual draw ratio for a given set of conditions without considering the effect of temperature fluctuations.

The lower draw ratios obtained for the helical dies is reflected in a lower draw stress under the same drawing conditions. The unique relationship between draw stress and axial draw ratio, also supported by other workers, is not confined to straight conical dies. The same relationship appears to apply for any die having rotational deformation components. It is the draw stress that provides continuity between the different dies. It implies that draw stress and hence the power requirement, for a given draw ratio is independent of the deformation mechanism.

The DSC results found that the melting point is unaffected by the drawing conditions or by the type of die used, Figure 6.17. This disagrees with observations made by some other workers who have found melting point to increase with increasing draw ratio. The differences here probably arise from the fact that the samples used for the DSC analysis taken from different drawing conditions do not have exactly the same nominal draw ratio. This has been shown to have a significant effect and so the small changes in melting point would not be detected.

The melt enthalpy tends to increase with draw temperature, showing a maximum at the highest draw temperature of 120°C, Figure 6.18. This peak occurs at a somewhat higher temperature than the peak birefringence which would indicate that it is not necessarily orientation related. It is likely that the high processing temperatures improve the crystalline structure of the material. This may also occur where the molecular relaxations during the DSC measurement provide a means of increased chain folding within the crystalline phase.
Figure 7.2: Draw ratio sensitivity index vs. draw temperature

**Straight Die**

![Graph of actual draw ratio vs. nominal draw ratio (β/β₀) for straight die](image1)

**Helical Die B**

![Graph of actual draw ratio vs. nominal draw ratio (β/β₀) for helical die B](image2)

**Drawing Temperature (°C)**

- 75
- 80
- 85
- 90
- 95
- 100
- 105
- 110
- 115
- 120
- 125

**Actual draw ratio / Nominal Draw Ratio (β/β₀)**

- 0.0
- 1.0
- 2.0
- 3.0
- 4.0
- 5.0
- 6.0
- 7.0
- 8.0
- 9.0
- 10.0
- 11.0
- 12.0

**Drawing Temperature (°C)**

- 0.0
- 1.0
- 2.0
- 3.0
- 4.0
- 5.0
- 6.0
- 7.0
- 8.0
- 9.0
- 10.0
- 11.0

**Straight Die**

- 500 mm/min
- 750 mm/min
- 1000 mm/min

**Helical Die B**

- 500 mm/min
- 750 mm/min
- 1000 mm/min
The tensile modulus clearly shows that the relationship between modulus and draw ratio is linear, Figure 6.19. The graphs show curves for products drawn at different temperatures and it appears that for a given draw ratio, the highest modulus values occur for products drawn at 105°C. This coincides with the temperature where maximum birefringence occurs.

The birefringence measurements have found the direction of orientation to lie at an angle with the product axis away from the core, Figure 6.13. The orientation is in effect along a helical path around the product axis. Although the pitch of this helical path is large, significant reduction in the load carrying capacity of these molecules in the axial direction will result. Furthermore, the birefringence measured at the core of the products was found to be much lower than helically drawn products, Figure 6.14. This indicates lower orientation and would give the material a lower axial modulus.

The plane strain compression tests have not shown any correlation of compressive yield with draw ratio for any of the dies. There is no distinction between the dies. Compressive modulus on the other hand seems to depend on the type of die as shown in Figure 6.20. For a given draw ratio, the yield stress is lower for samples produced from the helical dies. It might be expected that the hoop-wise orientation in these products would enhance the compressive properties to a greater extent. However the failure mode of these samples was found to be a shear along planes at 45° to the product surfaces, and passing through product axis. These shear planes are at 90° to any hoop-wise orientation and so the enhancement of transverse properties would not be observed. No correlation was observed between compressive yield, draw ratio of draw temperature.

The transverse compression tests were successful in causing failure in a transverse manner, promoting longitudinal splitting. The results have shown that the longitudinal splitting resistance of the products can be substantially improved by the introduction of the rotational shear mechanism. This provides additional qualitative evidence that hoop-wise orientation exists.

7.2 POLYETHYLENE TEREPTHALATE

The die drawing experiments conducted in this work have shown that it is possible to successfully die draw PET to a draw ratio of up to 5:1 in order to produce an oriented, uniform, transparent product using both straight and helically profiled conical dies. The photographs of Plate 6.2 show samples of partially drawn PET billets which represent the profile of the deformation zone for the process conditions used.
Chapter 7 Discussion

It is proposed that the differences in the geometric deformation profile and axial draw ratio exhibited by billets of PET drawn using the three different dies is primarily a result of the degree of crystallinity attained by the material as it passes through the deformation zone. A knowledge of the DSC data, Figure 6.26, shrinkage results, Figure 6.27 and from consideration of die geometry, it is possible to deduce the development of the crystallinity in drawn samples and how it affects the deformation.

Two mechanisms are responsible for the development of crystallisation in PET; stress-induced crystallisation and thermal crystallisation. At temperatures below about 100°C, it is known that thermal crystallisation does not occur and so crystallinity development in this temperature region arises from stress induced crystallisation alone.

Shrinkage of the drawn samples is shown to decrease with increasing draw ratio as in Figure 6.27. This is a result of the development of a crystalline phase within the material. The crystalline regions retard the recovery of the surrounding amorphous phase and so give the drawn products enhanced dimensional stability. The crystallites act as cross-links to restrict molecular relaxation.

Shrinkage shows a low value at the lowest drawing temperature for all samples and is the least for the helical die samples. The low degree of shrinkage at these temperatures can only be attributed to stress-induced crystallisation. Much lower shrinkage is observed for samples stretched under combined biaxial drawing with rotational shear deformation.

The rotational shear component at the die entrance and the rotational shear occurring within the die whilst the material is in contact with the die wall (hence deforming according to the die regime) must provide a means of introducing more stress induced crystallisation.

The maximum shrinkage values found at 100°C correspond to the lowest draw ratios obtained during the drawing process. At this temperature the rate of thermal crystallisation, if any is very small. The chain mobility at 100°C is such that the level of orientation and subsequent crystallinity are reduced. Combined, these effects explain the maximum shrinkage occurring at 100°C. For the helical dies however, the sudden rotational shear deformation at the die entrance will produce large strains which promote high levels of strain induced crystallisation, even at 100°C. This would account for the observed reduction in shrinkage.

The level of shrinkage is dependent also on the speed of drawing. At 100°C and 110°C in particular, the shrinkage decreases with increasing speed, much more so than for low
temperature drawing. It appears that at these temperatures, the chain mobility is such that the speed of the relaxation of the molecular chains is of the order of the speed of alignment due to the drawing. At low drawing speeds, the chains tend to lose their orientation and do not crystallise which would subsequently reduce shrinkage. As drawing speed increases, the stress induced crystallisation begins to take effect, reducing the subsequent shrinkage. The different dies show differing properties here. The decrease of shrinkage occurs at a lower drawing speed indicating that even at low drawing speeds and higher temperatures, the stress induced crystallisation resulting from the rotational shear is significant. Lowering the strain rate has a similar effect to increasing the draw temperature because the disorientation of the polymer chains has greater time to occur.

The shrinkage curves show that for draw temperatures below 100°C, increasing the draw speed tends to move the minimum shrinkage to a higher temperature. This might be caused by one of two effects. The most likely of these is that at a higher draw speed the strain rates are higher and the elastic property of the polymer responds to the applied strain faster that the viscous flow. The resulting higher stress levels accompanied by the reduction in the time available for the chains to relax give rise to higher orientation and crystallisation.

It may also be explained by considering local temperature effects in the deformation region. At 80°C the high draw ratio is primarily responsible for the low shrinkage. Moving to 90°C reduces the obtained draw ratio and so shrinkage tends to be higher. At the high draw speeds of 500mm/min, it is conceivable that significant localised heating in the die will occur. If the heat dissipation is low, the local heating effect adds to the ambient drawing temperature and it may be responsible for raising the local temperature to above that required for the thermal crystallisation. The additional crystallisation would tend to reduce the shrinkage.

At higher drawing temperatures, the percentage shrinkage is almost independent of draw speed indicating that thermal crystallisation proceeds so fast that it becomes by far the dominant crystallisation mechanism. This is further supported by the fact that there is little distinction between the dies at these temperatures, the proportion of crystallisation from the rotational shear at these temperatures is minimal.

Crystallinity development at high temperatures may also be aided by two other factors. The drawing stress at these temperatures is very low and so the efficiency of the chain orientation will be minimal which is enhanced from the high rate of relaxation at these temperatures. The orientation of the amorphous phase will therefore be minimal.
When annealed under constrained length, the shrinkage may be reduced significantly. At low drawing speeds and high draw temperatures, the dwell time in the region of the die exit zone is longer. The material emerging from the die is subjected to the drawing load and as such may undergo some annealing at this point. It is possible that even though the thermal crystallisation process dominates at these high drawing temperatures, that there is still some scope for removing internal stresses from the remaining amorphous regions. This may be the reason for the lower shrinkage measurements for the slower speeds at 120°C.
Chapter 8 Conclusions

The study of solid-state die-drawing of polymers through dies with superimposed shear deformations has been completed with the following conclusions

1. An innovative method has been devised of introducing rotational shear deformations into die-drawing processes which until now have been considered to be essentially extensional deformation processes.

2. Dies of a helical profile have been designed and manufactured using the latest computer aided manufacturing techniques. These techniques have proven to be extremely versatile and offer considerable flexibility and benefits over more traditional techniques in the design and manufacture of complex die profiles.

3. Die drawn polymers of polyethylene and polyethylene terephthalate can be successfully produced using both straight and helical conical dies which are designed to introduce rotational shear deformations as well as an axial draw.

4. The deformations occur such that increasing the amount of rotational shear delays the onset of permanent plastic deformation until much higher nominal draw ratios (imposed by the die geometry) are reached. It is believed that this is a direct consequence of a change in the state of stress distribution within the material.

5. Where rotational shear is present in the deformation, the balance of stresses is such that the drawing load is reduced. This is accompanied by a corresponding reduction in actual draw ratio. This will have implications as to the nominal draw ratio selected to produce the required actual draw ratio and will depend on the rate of twist.

6. For given processing conditions, a unique relationship between draw stress and actual draw ratio exists. The same relationship applies equally to processes involving a component of shear deformation. The relation can be represented by
an empirical model such that the drawing stress is given in terms of the actual draw ratio and draw temperature.

\[ \sigma_{\text{axial}} = 20.6\lambda_f + (10400 / T) - 185 \]

7. Rotational shear deformation components reduce the sensitivity of the drawing process to nominal draw ratio. This is a result of the greater degree of die controlled deformation. i.e. where material does not neck away from the die wall. This has particular implications for the rope making industry where control of the core root diameter size is critical.

8. The maximum level of molecular orientation developed in the product is constant under a given set of conditions. The distribution of orientation is such that the principal orientation direction lies along a helical path about the product axis. The magnitude of orientation is a maximum at the product surface and decreases towards the product core.

9. The transverse mechanical properties of the products drawn with rotational shear are much improved, most notably with respect to the axial splitting resistance.

10. The level of shrinkage of die-drawn PET when subsequently exposed to high temperatures can be reduced at all drawing temperatures by imposing a rotational shear component. The rotational shear increases the level of crystallinity in the product through strain-induced crystallisation. The degree of crystallisation depends on the amount of rotational shear.

11. Rotational shear applied to the process of rope core manufacture will significantly improve the products split resistance, particularly when the oriented polymer is subjected to high compressive loads or fatigue bending. Whilst the axial modulus will be reduced by the transverse orientation component, the benefits for applications where product integrity are of prime importance will allow these products to find many applications.

**Further work**

The limit of rotational shear that may be applied to a material is unknown. In order to investigate higher levels of rotational shear, dies with a greater degree of twist are necessary. These experiments have revealed that the die entry shear is by far the most dominant component and it is expected that this will be the root cause to limiting rotational shear. It may be possible to manufacture dies which have a gradient of twist along the axis with the die entry shear removed completely with progressive shear being
applied at an increasing rate along the die. Such dies should allow the deformation mechanism to be understood more easily.

The application of these processes to circular products is of commercial importance. In order to provide a mechanical means of applying the rotational shear to a circular billet, it may be possible to conduct the die-drawing process over a number of stages involving a number of deformations. The process may involve, for example, deforming an initially circular billet to an oval shape, followed by applying rotational deformation and finally returning the product to a circular profile.

Alternatively, it may be sufficient to rely on the friction between a conical die interface and a die-drawing polymer to provide the driving force to introduce a shear component to the deformation mechanism. A rotating conical die used to draw a billet that is held stationary would tend to shear the billet at the die entrance. Care would be required to control the frictional heating in this case which could have significant annealing effects on the drawn material. However the simplicity of such a process would be attractive both in terms of capital cost and process control.
References


References


References


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References


References


References


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Appendix

TABLE OF RESULTS
### Drawing of HMWPE - Actual draw ratio vs Draw temperature

**Description:** Nominal billet dimension 6.0 x 6.0mm  
Nominal draw ratio = 7.1  
All actual draw ratio values are normalised to a nominal draw ratio of 7.1

<table>
<thead>
<tr>
<th>Straight Die</th>
<th>Helical Die A</th>
<th>Helical Die B</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Draw speed</strong></td>
<td><strong>Drawing Temperature (oC)</strong></td>
<td><strong>Actual Draw Ratio</strong></td>
</tr>
<tr>
<td>100 mm/min.</td>
<td>Draw speed</td>
<td>Actual Draw Ratio</td>
</tr>
<tr>
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<td>80</td>
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</tr>
<tr>
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<td>80</td>
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</tr>
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**Drawing of HMWPE - Actual draw ratio vs Draw speed**

Description: Nominal billet dimension 6.0 x 6.0mm  
Nominal draw ratio = 7.1  
All actual draw ratio values are normalised to a nominal draw ratio of 7.1

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**Drawing of HMWPE - Actual draw ratio vs Draw speed**

**Description:** Nominal billet dimension 4.5 x 4.5mm
- Nominal draw ratio = 4.5
- All actual draw ratio values are normalised to a nominal draw ratio of 4.5

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<td>Actual Draw Ratio</td>
<td>Draw speed (mm/min)</td>
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| 1000°C      |              |               |               |
| Draw speed (mm/min) | Actual Draw Ratio | Draw speed (mm/min) | Actual Draw Ratio | Draw speed (mm/min) | Actual Draw Ratio |
| 450         | 7.00         | 450           | 6.32          | 509           | 6.32          |
| 693         | 6.23         | 620           | 6.68          | 905           | 6.88          |
| 760         | 7.00         | 703           | 7.00          |               |               |
| 955         | 6.68         | 1009          | 7.38          |               |               |

| 1250°C      |              |               |               |
| Draw speed (mm/min) | Actual Draw Ratio | Draw speed (mm/min) | Actual Draw Ratio | Draw speed (mm/min) | Actual Draw Ratio |
| 450         | 7.00         | 454           | 7.00          | 415           | 5.48          |
| 538         | 7.33         | 581           | 7.53          | 709           | 7.79          |
| 1162        | 7.73         | 707           | 7.73          | 1076          | 6.95          |
| 1754        | 7.97         | 596           | 7.87          | 1463          | 7.01          |
| 2135        | 8.06         | 1141          | 8.06          | 2463          | 7.06          |
| 3160        | 7.73         | 1950          | 7.73          |               |               |
| 3228        | 7.87         |               |               |               |               |
Description: Nominal billet dimension 6.0 x 6.0mm
Nominal draw ratio = 7.1
All actual draw ratio values are normalised to a nominal draw ratio of 7.1

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<th>Axial drawing force (N)</th>
<th>Drawing Temperature</th>
<th>Draw speed (mm/min)</th>
<th>Axial drawing force (N)</th>
<th>Drawing Temperature</th>
<th>Draw speed (mm/min)</th>
<th>Axial drawing force (N)</th>
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### Drawing of HMWPE - Nominal draw stress vs Actual draw ratio

**Description:**
- Nominal billet dimension 6.0 x 6.0 mm
- Nominal draw ratio = 7.1
- All stress values are calculated with respect to no-load cross-section

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<td><strong>Nominal draw stress (MPa)</strong></td>
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Drawing of HMWPE - Peak axial drawing force vs Draw speed

Description: Nominal billet dimension 6.0 x 6.0mm
Nominal draw ratio = 7.1
All actual draw ratio values are normalised to a nominal draw ratio of 7.1
Peak loads occurring at start-up

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<td><strong>drawing force</strong></td>
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<td><strong>(mm/min)</strong></td>
<td><strong>(mm/min)</strong></td>
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### Drawing of HMWPE - Elastic recovery vs Actual draw ratio

**Description:** Nominal billet dimension 6.0 x 6.0mm
Nominal draw ratio = 7.1
All actual draw ratio values are normalised to a nominal draw ratio of 7.1
% Elastic recovery calculated based on axial measurements of the drawn product whilst under draw load and 48 hours after the removal of the drawing load.

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<td><strong>% Elastic recovery</strong></td>
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Birefringence of HMWPE - Birefringence of drawn product core vs Actual draw ratio

**Description:** Nominal billet dimension 6.0 x 6.0mm
Draw ratio values are taken from the point where the birefringence sample was sectioned

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### DSC of HMWPE - Crystalline melting point vs Draw temperature

**Description:** Crystalline melting point calculated from peak of DSC trace

<table>
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<tr>
<th>Draw speed (mm/min.)</th>
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<th>Helical Die B</th>
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<td>Draw speed (mm/min.)</td>
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</tr>
<tr>
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<td>120</td>
<td>143.92</td>
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<tr>
<td>200</td>
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<td>60</td>
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<td>100</td>
<td>143.72</td>
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<td>300</td>
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DSC of HMWPE - Degree of crystallinity vs Draw temperature

Description: Crystallinity calculated from melt enthalpy of DSC trace
Based on the enthalpy change of a perfect crystal of 64.8 cal/g = 316.5 J/g

<table>
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<tr>
<th>Draw speed</th>
<th>Draw temperature (°C)</th>
<th>Degree of crystallinity (%)</th>
<th>Draw speed</th>
<th>Draw temperature (°C)</th>
<th>Degree of crystallinity (%)</th>
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<tr>
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<tr>
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<tr>
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<td>59.40</td>
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### Tensile tests on HMWPE - Axial modulus vs Actual draw ratio

**Description:**
Nominal billet dimension 6.0 x 6.0mm  
Nominal draw ratio = 7.1  
All modulus values calculated as a secant modulus at 0.5% strain

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Straight Die</th>
<th>Helical Die B</th>
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<td>Axial modulus (GPa)</td>
<td>Actual Draw Ratio</td>
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<tr>
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<tr>
<td>1100°C</td>
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<td>1200°C</td>
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Compression of HMWPE - Compressive modulus vs Draw ratio

Description: Axial draw ratios measured from the samples tested

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<td>Actual Draw</td>
<td>Compressive</td>
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<td>modulus (GPa)</td>
<td>Ratio</td>
<td>modulus (GPa)</td>
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<td>7.28 1.214</td>
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<td>7.47 1.328</td>
<td>8.28 1.237</td>
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<td>8.09 1.305</td>
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</table>
### Drawing of PET - Actual draw ratio vs Draw temperature

**Description:** Nominal draw ratio between 3.5 and 4.5.

*Note:* Draw ratios are not normalised because nominal draw ratio has little effect for this material.

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<th>Straight Die</th>
<th>Helical Die A</th>
<th>Helical Die B</th>
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<td><strong>Draw speed</strong></td>
<td><strong>Actual Draw Ratio</strong></td>
<td><strong>Actual Draw Ratio</strong></td>
</tr>
<tr>
<td>Draw speed</td>
<td><strong>Drawing Temperature (°C)</strong></td>
<td>100 mm/min.</td>
</tr>
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<td>4.25</td>
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<tr>
<td>90</td>
<td>3.93</td>
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</tr>
<tr>
<td>100</td>
<td>3.65</td>
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</tr>
<tr>
<td>110</td>
<td>4.08</td>
<td>100</td>
</tr>
<tr>
<td>120</td>
<td>3.92</td>
<td>120</td>
</tr>
</tbody>
</table>

| **Draw speed** | **Actual Draw Ratio** | **Actual Draw Ratio** | **Actual Draw Ratio** |
| Draw speed | **Drawing Temperature (°C)** | 200 mm/min. | 300 mm/min. | **Actual Draw Ratio** |
| 80 | 4.27 | 80 | 3.64 | 80 | 4.69 |
| 90 | 3.96 | 90 | 3.66 | 90 | 4.18 |
| 100 | 3.68 | 100 | 3.60 | 100 | 3.60 |
| 110 | 3.85 | 110 | 3.64 | 110 | 4.38 |
| 120 | 3.86 | 120 | 4.40 | 120 | 4.75 |

| **Draw speed** | **Actual Draw Ratio** | **Actual Draw Ratio** | **Actual Draw Ratio** |
| Draw speed | **Drawing Temperature (°C)** | 300 mm/min. | **Actual Draw Ratio** |
| 80 | 4.37 | 80 | 4.68 | 80 | 4.91 |
| 90 | 4.03 | 90 | 3.73 | 90 | 4.18 |
| 100 | 4.06 | 100 | 3.70 | 100 | 4.18 |
| 110 | 4.23 | 110 | 3.66 | 110 | 4.16 |
| 120 | 3.99 | 120 | 4.29 | 120 | 4.60 |

| **Draw speed** | **Actual Draw Ratio** | **Actual Draw Ratio** | **Actual Draw Ratio** |
| Draw speed | **Drawing Temperature (°C)** | 400 mm/min. | **Actual Draw Ratio** |
| 80 | 4.33 | 80 | 4.57 | 80 | 4.91 |
| 90 | 4.05 | 90 | 3.77 | 90 | 4.55 |
| 100 | 4.15 | 100 | 3.66 | 100 | 4.19 |
| 110 | 4.24 | 110 | 3.53 | 110 | 4.67 |
| 120 | 4.07 | 120 | 4.01 | 120 | 4.67 |

| **Draw speed** | **Actual Draw Ratio** | **Actual Draw Ratio** | **Actual Draw Ratio** |
| Draw speed | **Drawing Temperature (°C)** | 500 mm/min. | **Actual Draw Ratio** |
| 80 | 4.41 | 80 | 4.41 | 80 | 4.91 |
| 90 | 4.07 | 90 | 3.95 | 90 | 4.18 |
| 100 | 4.09 | 100 | 3.96 | 100 | 4.18 |
| 110 | 4.14 | 110 | 3.94 | 110 | 4.23 |
| 120 | 4.12 | 120 | 4.11 | 120 | 4.54 |
DSC of PET - Degree of crystallinity vs Draw temperature

Description: Crystallinity calculated from crystalline and melt enthalpies of DSC trace. Based on the enthalpy change of a perfect crystal of 32.5 cal/g = 159.3 J/g.

<table>
<thead>
<tr>
<th>Draw speed (mm/min)</th>
<th>Straight Die</th>
<th>Helical Die B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Draw temperature (°C)</td>
<td>Degree of crystallinity (%)</td>
<td>Draw temperature (°C)</td>
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<td>18.45</td>
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Drawing of PET - Axial shrinkage vs Draw temperature

Description: Axial shrinkage resulting from immersion in water at 100°C for 2 minutes.

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<th>Axial shrinkage (%)</th>
<th>Drawing Temperature (°C)</th>
<th>Axial shrinkage (%)</th>
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Description: Sensitivity index calculated as the gradient of the actual draw ratio vs nominal draw ratio curve

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How to use this guide

Welcome to the Pilkington Library. This guide has been designed to help you find your way around the library and its resources.

Within the building, a simple route is marked with consecutively numbered signs suspended from the ceiling. These are also marked on the maps inside this guide. Please follow the numbered signs from 1 to 25, pausing to read the information provided.

Detailed information is provided on posters and in leaflets situated at various points on the tour. If you have difficulty or(907,843),(999,995)Further details about Library Services(26,547),(371,798) are available from the Library Uncovered Leaflet.

Opening Hours

In Term
Monday-Friday 9.00am - 10.00pm
Saturday 9.00am - 5.30pm
Sunday 10.00am - 9.00pm

In Vacation
Monday-Friday 9.00am - 5.30pm

Loan periods
Undergraduates 10 items for 4 weeks
Course Postgraduates 15 items for 4 weeks
Research postgraduates and University staff 25 items for 12 weeks

Telephone Numbers
Information and enquiries (01509) (22)2360
Issue desk (01509) (22)2361

ULISEES
http://www.lboro.ac.uk/library/ulisees.html

July 2002
18 Ahead of you is the Information Desk. To your left the main book sequence starts at class number 500. First row of shelving contains oversize and pamphlets.

19 Note that the book sequence which ends here on the left continues across the aisle to your left.

20 As on Level 2 above, most of the study places are located around the edge of the building.

21 The main book sequence on this level restarts here.

22 To your left are more photocopiers, the University Archives and Group Study Room 1A.

23 Back copies of Serials from classmark 500 start here.

To the left are more Workstations and Individual Study Carrels.

24 Turn to your right and walk back towards the stairs. On your left is the final part of the Serials sequence on this level. Now return to Level 3 by staircase A where the tour ends at 25.

25 Ahead of you is the way out through a Security Barrier.

Remember to have your library books stamped at the Issue Desk before you leave.

As you leave the Library there is a Café on the left and a Shop on the right.
11 Ahead of you is the Information Desk.

The book sequence starts to your left. The first row is where books are kept until they are reshelved.

The following rows on your left are the Oversize Books, Pamphlets and Loughborough University Theses.

12 Here you will see that many of the study desks are located around the edge of the building. Turn right.

13 The book sequence continues here. Look for the class numbers which are shown on the ends of the shelves.

14 Across to your left is the first part of the Serials sequence. Back copies of Serials are shelved here.

In front of you are more photocopiers.

15 To your left are more PCs for viewing the Library Catalogue (OPAC). In front of you are more Workstations.

16 To your left and right are the final parts of the Serials sequence on this level.

Now do a 'U' turn to go to 17.

17 Return to Staircase A. Toilets + study carrels are located either side of staircase A. The tour continues at 18 downstairs on Level 1.
1. The tour begins to your left at Information and Enquiries. Ask here for help in using the Library.

   Ahead of you is the Issue Desk, where you may borrow and return books.

2. The turnstile in front of you leads to the Short Loan Collection.

   Turn to your left to see the New Books Display.

3. Current Serials are shelved here. Self-service Photocopiers and copy card dispensers are located in this area. Now walk across to 4 keeping the Issue Desk to your left.

4. The PCs in front of you are for viewing the Library Catalogue (OPAC).

5. The Workstations in this area allow you to access the University networked services including Electronic Databases and CD-ROMs.

6. The shelves to your right contain Reference Books. The Information Workroom is located behind this section.

7. Inter-Library Loans is to your left. There are more Workstations in front of you.

   Next to Inter-Library Loans is Group Study Room 3A.

   Now walk through the Abstracts section to B.

8. The Enquiry Desk for serials and new books is to your left through the Audio Visual Area.

9. Here is the Library Newspaper Area. To your left is Group Study Room 3B.

   Retrace your steps past Inter-library Loans to 10.

10. Ahead of you is staircase A, the main stairs. Your tour resumes at 11 on the floor below (Level 2).

Open out the leaflet to continue