PLASTIC DEFORMATION OF ORIENTED POLYETHYLENE

A thesis submitted to the
Faculty of Mathematical and Physical Sciences
of the University of Surrey
for the degree of Doctor of Philosophy.

LESLIE AINSLEY SIMPSON

November 1972
ABSTRACT

Tensile test specimens were cut from high density polyethylene sheet that had been fully cold drawn. The angle ($\lambda_o$) between the tensile axis and the initial draw direction was varied from $0^\circ$ to $90^\circ$ and the specimens deformed between the temperatures of $-10^\circ$C and $120^\circ$C. With the aid of a dot printing technique, analysis of the macroscopic strains revealed an approximate simple shear process, for specimens with angles of less than $90^\circ$ and greater than $0^\circ$. Deviation from simple shear, which was accounted for in terms of a shear reorientation model, was found to be approximately independent of $\lambda_o$, although temperature sensitive. It is shown that the shear process beyond yield can be described in terms of a flow criterion, the parameters of which were dependent upon $\lambda_o$ and temperature.

The elastic and pre-yield deformation behaviour for specimens with angles between $70^\circ$ and $30^\circ$ was investigated at $22^\circ$C, and it appeared that the onset of the flow criterion occurred before the yield point (load maxima) at a critical shear strain. Specimen deformation was also analysed in terms of the relationship between resolved shear stress and shear strain, and this was found to be independent of $\lambda_o$.

Changes in the morphology during redrawing were revealed by using a combination of wide and low angle X-ray diffraction techniques together with macroscopic strain measurements. Assuming a principle of superposition of shear strains, two modes of slip parallel to the oriented chain axis, intracrystalline slip and fibrillar slip, were postulated in order to account for the observed macroscopic shear strain. It was found that both modes were temperature sensitive.
Dedicated to

My Parents
<table>
<thead>
<tr>
<th>CONTENTS</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>2</td>
</tr>
<tr>
<td>CHAPTER 1: General Introduction</td>
<td>8</td>
</tr>
<tr>
<td>1.1 Introductory Remarks</td>
<td>8</td>
</tr>
<tr>
<td>1.2 Flow Criterion</td>
<td>8</td>
</tr>
<tr>
<td>1.3 Geometry of Deformation</td>
<td>9</td>
</tr>
<tr>
<td>1.4 Yield Point and Pre-Yield Studies</td>
<td>10</td>
</tr>
<tr>
<td>1.5 Structural Studies</td>
<td>11</td>
</tr>
<tr>
<td>CHAPTER 2: Specimen Preparation and Experimental Techniques</td>
<td>13</td>
</tr>
<tr>
<td>2.1 Material Specification</td>
<td>13</td>
</tr>
<tr>
<td>2.2 Specimen Preparation</td>
<td>13</td>
</tr>
<tr>
<td>2.3 Density Measurements</td>
<td>15</td>
</tr>
<tr>
<td>2.4 Tensile Testing Machines and Heating Units</td>
<td>15</td>
</tr>
<tr>
<td>2.5 Photography and Microscopy</td>
<td>17</td>
</tr>
<tr>
<td>2.6 X-ray Diffraction</td>
<td>18</td>
</tr>
<tr>
<td>2.7 Irradiation</td>
<td>21</td>
</tr>
<tr>
<td>CHAPTER 3: Post-Yield Flow Behaviour of Oriented Polyethylene</td>
<td>27</td>
</tr>
<tr>
<td>3.1 Introduction to Yield Criteria</td>
<td>27</td>
</tr>
<tr>
<td>3.2 Application of Yield Criteria to Polymers</td>
<td>29</td>
</tr>
<tr>
<td>3.3 A Flow Criterion</td>
<td>32</td>
</tr>
<tr>
<td>3.3.1 Experimental Procedure</td>
<td>32</td>
</tr>
<tr>
<td>3.3.2 Measurements</td>
<td>33</td>
</tr>
</tbody>
</table>
CHAPTER 4: The Geometry of Deformation of Oriented Polyethylene

4.1 Introduction

4.2 Experimental

4.2.1 Procedure

4.2.2 Measurements

4.3 Geometry of Simple Shear

4.4 Results

4.4.1 Dependence on $\lambda_0$ at Room Temperature

4.4.2 Effects of Temperature on the Deformation Geometry

4.4.3 Annealed Specimens

4.5 Discussion

CHAPTER 5: Stress-Strain Phenomena during Pre-Yield and Post-Yield Deformation

5.1 Introduction

5.2 Experimental
5.3 Results
5.3.1 Maximum Load Point
5.3.2 Pre-Yield Stress-Strain Behaviour
5.3.3 Strain Rate Effects
5.3.4 Recovery Behaviour
5.3.5 Post-Transition Point Stress-Strain Behaviour

5.4 Discussion

CHAPTER 6: A Correlation Between the Macroscopic and Structural Changes that occur in Oriented Polyethylene during Deformation

6.1 Introduction
6.1.1 X-ray Diffraction
6.1.2 Structural Model
6.1.3 Shear Deformation Modes
6.1.4 Orientation
6.1.5 Irradiation

6.2 Experimental
6.2.1 Procedure
6.2.2 Measurements

6.3 Results
6.3.1 Check on Fibre Symmetry
6.3.2 Deformation
6.3.3 Orientation Changes
6.3.4 Changes in Void Size during Deformation
6.3.5 Deformation of Slightly Crosslinked Oriented Polyethylene

6.4 Discussion

CHAPTER 7: Summary and Suggestions for Further work

ACKNOWLEDGEMENTS

REFERENCES
CHAPTER 1

General Introduction

1.1 Introductory Remarks

When a solid polymer undergoes large plastic deformation, considerable changes occur in the morphology, with the result that the polymer chains and crystallites align in the direction of the applied stress, consequently there is a preferred orientation. The effects of orientation on the physical properties of the polymer are profound. Due to orientation, an anisotropy in the mechanical properties of the polymer is produced with the result that the polymer is much stronger in the direction of orientation than at right angles to it. Knowledge of this anisotropy is of importance especially as the use of oriented synthetic polymers in the form of films and fibres is increasing in society.

The aim behind this project was, therefore, to analyse the effect of this anisotropy upon the tensile deformation behaviour of oriented high density polyethylene (Rigidex type 2) at various temperatures. The rest of this chapter will be a brief survey of the project, with few references, as it is considered more applicable to leave them to the appropriate chapters.

1.2 Flow Criterion

Work carried out by Hinton and Rider (1968) on the tensile deformation of oriented polyethylene at room temperature, was the starting point for work in this project. They found that specimens
cut out at various angles to the draw direction, yielded in accordance with a stress criterion for yield, suggested by Coulomb (1773). In their work, the yield point was assumed to be the position of maximum load on the usual load-extension curve, referred to below as load maxima.

At this particular stage of the project, only deformation after load maxima was of interest and not the significance of yield point. It was found that the Coulomb criterion could satisfactorily explain the deformation after load maxima, and for this reason it seemed appropriate to use the concept of a flow criterion rather than a yield criterion. The application of this criterion was tested between the temperatures of 0°C and 120°C and it was found to be valid, although the parameters in the theory were temperature sensitive.

1.3 Geometry of Deformation

The term 'flow' is generally taken to mean irrecoverable shear, and although it is often associated with liquids, it is also evident in viscoelastic materials such as polymers. It was found that the mode of deformation of oriented polyethylene was to a good approximation simple shear parallel to the oriented polymer chain axis direction, referred to as the c direction. Therefore associated with a flow stress criterion there was also a corresponding simple shear mechanism. Extensive studies into the geometry of deformation carried out between the temperatures of 22°C and 120°C, revealed a gradual increase in deviation from simple shear with temperature rise. Specimens were also annealed at temperatures of
up to 120°C in air, and then tested at room temperature, in order to find out if there were any difference in deformation behaviour between annealed specimens and those deformed at the equivalent elevated temperatures.

1.4 Yield Point and Pre-Yield Studies

A yield criterion is a criterion for the onset of plastic deformation and is generally defined in terms of the applied stresses, although occasionally in terms of strain. Studies into the recovery or elastic behaviour of deformed specimens with various initial orientation angles (\(\lambda_0\)) were made at room temperature, and it was found that irrespective of \(\lambda_0\), the elastic region was of the order of 2% tensile strain, whereas the yield point which was taken to be load maxima, varied between 4% and 50%, depending upon \(\lambda_0\). When true stress rather than nominal stress was considered, it was found that only stress maxima occurred for those specimens that had \(\lambda_0\) values greater than 55°. Interpretation of load maxima as having any intrinsic meaning in terms of yield was therefore in doubt. After analysing the resolved shear stress and resolved shear strain data from specimens with \(\lambda_0 < 55°\), it was found that flow began much earlier on in the deformation process, rather than at load maxima, as previously assumed. It was in fact found that the onset of flow, in terms of the criterion used, began at a critical resolved shear strain.

A region of deformation still however existed between the elastic limit and the onset of the flow criterion. This region was therefore investigated and a simple empirical expression developed in order to
predict the effect of $\lambda_o$ upon the observed relationship between the resolved shear and normal stresses acting on the slip plane.

1.5 Structural Studies

With this last section of work, it was hoped to find a correlation between the macroscopic and structural changes during the deformation of oriented polyethylene. Oriented polyethylene has a well defined fibre texture, thus morphological changes during redrawing were easily investigated using wide and low angle X-ray diffraction techniques.

The structural model adopted for oriented polyethylene is similar to that suggested by Peterlin (1971), in which the basic element is the microfibril that consists of alternate crystalline and amorphous layers stacked along the fibre or c direction. The microfibrils are connected to one another by tie molecules, and the space between the microfibrils is associated with microvoids in the material.

It was found that the macroscopic deformation, which was approximately simple shear, could be accounted for on a submicroscopic level in terms of slip within the crystalline regions, referred to as intracrystalline slip, and slip between microfibrils referred to as fibrillar slip. At room temperature the initial mechanism was intracrystalline slip, although later on in the deformation process a transition point was reached, after which fibrillar slip began. This transition from intracrystalline to fibrillar slip occurred at the same macroscopic shear strain, irrespective of $\lambda_o$. Studies
were also carried out at elevated temperatures, although mainly at 105°C, and it was found that the two modes of shear were temperature sensitive.

Orientation changes during deformation were investigated using birefringence and wide angle X-ray techniques, and a simple mathematical model suggested by Modlen (1969) was fitted to the (002) pole density distribution. The possibility of void closure due to shear strains was also considered, although no evidence was found in the specimens tested.

Finally, specimens were slightly crosslinked by irradiation in order to find out if either of the two postulated modes of shear could be inhibited in any way.
CHAPTER 2

Specimen Preparation and Experimental Techniques

2.1 Material Specification

Studies were carried out on a high density polyethylene, manufactured by B.P. Chemicals Ltd. (Rigidex). This was a homopolymer of melt index 0.2 (type 2) with a density of 0.96 g cm\(^{-3}\), and had a high crystallinity together with a high molecular weight (\(M_w = 115,000\)). The manufacture of Rigidex type 2 has now been discontinued.

2.2 Specimen Preparation

The polyethylene was initially received in pellet form. An isotropic sheet was produced when the pellets were compression moulded at 190°C, and quenched in water which was at a temperature of about 15°C. A photograph of the isotropic sheet, moulded in the form of a dumb-bell, is shown in Figure 2.1, together with the mould and pressing plates. In the moulding process, aluminium foil was placed between the polyethylene pellets and pressing plates, so as to prevent adhesion between specimen and plate surfaces. The resulting dumb-bell sheet was 17.5 cm long, 6 cm across the neck, and approximately 0.11 cm thick, with a density of 0.958 g cm\(^{-3}\), and negligible birefringence, confirming the isotropy of the sheet. Oriented polyethylene was then obtained by cold drawing the isotropic sheet at a crosshead speed of 10 mm min\(^{-1}\) using an E-type tensometer as shown in Figure 2.2. When high density polyethylene is cold drawn, it necks, stress whitens, and produces a natural draw ratio of about
8. Investigations into the effect of strain rate and temperature on the natural draw ratio were performed by Andrews and Ward (1970), who found that the draw ratio was almost independent of strain rate.

A grid system stamped onto the polyethylene prior to cold drawing enabled the draw ratios in the direction of draw ($R_y$), and perpendicular to the draw in the plane of the sheet ($R_x$), to be calculated. Specimen thickness ratio ($R_z$) was calculated from micrometre measurements. The results shown in Table 2.1 give values of $R_y$, $R_x$, and $R_z$ obtained from four different cold drawn specimens, where it appears that on average a natural draw ratio ($R_y$) of 8.5 was obtained, and that deformation occurred with approximately constant volume (i.e. $R_x R_y R_z = 1$). In fact, changes in density of polyethylene on drawing revealed a small increase in volume of about 4%.

Using a half tone printing plate, an orthogonal grid of ink dots 0.2 mm apart was then printed onto the drawn material, with one of the principal grid directions parallel to the oriented chain axis direction (c direction). The error in getting the grid and c directions parallel was found to be within 0.5°. This dot technique was adopted in order to measure specimen strains during the subsequent stage of the deformation process. Finally, dumb-bell shaped tensile test specimens with a 10 mm long parallel region and 2.4 mm wide, were cut out of the drawn sheets with the aid of a hand press and die, at various angles to the c direction. A photograph of the central region of such a dumb-bell shaped specimen is shown in Figure 2.3, where the principal grid direction (c direction) is denoted by g.d.
2.3 Density Measurements

A few density measurements were carried out on polyethylene using two density gradient columns, manufactured by Davenport. The two columns used consisted of a water and ethanol mixture that gave a density range from 0.91 g cm\(^{-3}\) to 0.98 g cm\(^{-3}\).

2.4 Tensile Testing Machines and Heating Units

Two tensile testing machines were used in the course of the work. The first was the E-type Tensometer as mentioned in section 2.2, which was used for cold drawing the isotropic sheet and redrawing the small dumb-bell shaped specimens. This machine was used if either a high load was required, or a load-extension curve needed. A 25 Kg load cell was used for most of the work which gave a range of sensitivities from 1 Kg to 25 Kg full scale deflection (F.S.D.) on the chart recorder. The 2.5 Kg F.S.D. was usually used for room temperature tests, but at higher temperatures the 1 Kg F.S.D. was required. A range of crosshead speeds were obtainable by changing a gear ratio, although the values of 10 mm min\(^{-1}\) and 0.67(\(\frac{2}{3}\)) mm min\(^{-1}\) were generally used. The chart speed was directly related to the crosshead speed, and various ratios were possible, however for most work carried out, only a chart to crosshead speed ratio of 20:1 was used. Checks on the recorded load and crosshead speed were found to be within 1%. Attached to the Tensometer was an environmental chamber manufactured by Sondes Place Research Laboratories, that enabled specimens to be tested between the temperatures of -70°C to +250°C, to an accuracy of 1°C.
The second tensile testing machine shown in Figure 2.4, was built so that a specimen could be deformed and viewed under a microscope at the same time. A mains operated synchronous motor manufactured by Smith's Clocks and Watches Ltd. was used for driving the crosshead, the speed of which was generally $0.67 \text{ mm min}^{-1}$. No load recording facilities were available. It was possible to hold the deformed specimen at constant length, after the motor had been removed, by clamping the drive screws, using clamp C shown in Figure 2.4. The purpose behind this particular facility is explained in the X-ray diffraction section.

To investigate the deformation of specimens at elevated temperatures under the microscope, a small heating chamber plus temperature controller was designed and built. The small tensile machine was housed in the chamber, and the specimen viewed through optical windows (see o.w. in Figure 2.5). As shown in Figure 2.5, the heating chamber consists of two units, the inner most unit made of aluminium was surrounded by two heating elements that consisted of nichrome tape ($0.15 \text{ cm} \times 0.015 \text{ cm}$) wound around strips of mica. The heating elements were then insulated from the aluminium body using more mica. Finally, the inner unit was enclosed by another chamber made from Sindanyo, a material that has very good thermal insulating properties.

The temperature controller circuit diagram is shown in Figure 2.6. This was based on the Wheatstone bridge principle, where a thermister which has a negative temperature coefficient of resistance was placed inside the heating chamber, and incorporated in one arm of the bridge. The other arm of the bridge consisted of a variable resistance which enabled a particular temperature to be
selected. The out of balance current from the bridge was amplified, and used to control the power to the heating elements in the chamber. Due to thermal lag of the system, a maximum time of about 2 hours was needed before a steady temperature of about 120°C was reached. Calibration of the temperature controller was performed by measuring independently the temperature of a specimen mounted in the grips, using a chromel-alumel thermocouple attached to the specimen surface, for various values of the variable resistance. The calibration chart is shown in Figure 2.7, and a check on the temperature stability of the specimen showed that at 120°C it was within 0.5°C.

2.5 Photography and Microscopy

When specimens were deformed in the E-type Tensometer, photographs were taken with a 35 mm camera (Exakta) fitted with an f2.8, 100 mm focal length lens (Trioplan), using Ilford Pan F film. An event marker on the chart recorder was used to indicate when each photograph was taken. To check the accuracy of the system, photographs were taken of a printed grid (Letratone by Letraset) of known spacing (0.298 mm), set up in the Tensometer. It was found that linear measurements taken from the prints had a maximum error of 0.6%, and angular measurements a maximum error of 0.5°. These errors include errors arising from lens distortion, film and print shrinkage, and print measurements, obtained by the use of a fine scale rule and protractor.

Specimens under test in the small tensile machine were examined using either a Zeiss photomicroscope or Wild stereomicroscope. In
both cases, polarized light was used to enable the c direction, as
determined by the extinction direction, to be obtained, and photomicrographs of specimens during deformation were also taken.
Birefringence measurements were made on the Zeiss microscope using
an Ehringhaus rotating calcite compensator. The maximum error in
angular measurements obtained from the rotating stage of the Zeiss
microscope was 0.2°, and the maximum birefringence error estimated
to be about 2.5%. The large error in birefringence arose mainly
from fluctuations in specimen thickness (4 μm) that could not be
accurately measured.

Thickness measurements were made by using a dial gauge, the
accuracy of which was within 0.5 μm.

Some fracture surfaces of specimens were observed through a
scanning electron microscope ('Stereoscan' mark IIA), and this could
give surface magnifications from 20X to 5000X with a possible
resolution of 2500 Å. A conducting layer of gold-palladium was
deposited onto the surfaces studied, using a vacuum coating unit.

2.6 X-ray Diffraction

Various X-ray cameras were used in the structural studies of
oriented polyethylene, one of which was a Unicam S-25, that was used
to obtain wide angle X-ray diffraction patterns on either flat or
cylindrical film. The camera employed a pin-hole collimator of
diameter 0.5 mm, and nickel-filtered Cu Kα radiation was always
used. Exposure times varied between 2 and 6 hours.

A flat film cassette was used to verify the fact that the
extinction direction obtained using the polarized microscope,
coincided with the [001] direction, as inferred from the wide angle diffraction pattern. For (002) reflection studies, the normal flat film cassette was inadequate in detecting this rather weak reflection, thus a technique was adopted involving the cylindrical film cassette. Procedures used for both flat and cylindrical film are discussed in detail in section 6.2.

Most of the structural studies involved the use of a Rigaku-Denki, pin-hole collimation goniometer. The advantage of this camera was that wide and low angle diffraction patterns were obtained simultaneously. The camera consisted of two collimators of diameters 0.5 mm and 0.3 mm, that were separated by a distance of 26 cm. This resulted in a beam diameter of about 0.4 cm at the specimen, which was positioned 4 cm away from the second collimator. Specimen to film distance was usually 3 cm for recording the wide angle diffraction pattern, and 33 cm for the low angle diffraction pattern. A system of pin holes along the edge of both film cassettes was used to produce a fiducial mark on each film, which enabled wide and low angle diffraction patterns to be aligned to an accuracy of 0.5°. Cold drawn polyethylene did not produce strong low angle reflections, unless it had been annealed, thus long exposure times of about 24 hours for unfiltered radiation were required, and even longer times for filtered radiation. High speed X-ray film was used (Kodak - Industrex D), and all measurements were taken directly from the film.

The specimen holder was designed and built so that X-ray patterns could be obtained whilst the specimen was in tension. After the specimen had been deformed using the small tensile machine, the specimen length was held constant as described in section 2.4, whilst
the electric motor and drive gears were removed for convenience from the tensile machine. The small tensile machine with specimen in position was then fixed into a jig (see Figure 2.8) to enable it to be attached to the X-ray camera. Two adjusting screws marked X and Y in Figure 2.8 enabled the specimen to be moved in the horizontal or vertical directions, thereby positioning the specimen in front of the X-ray beam. X-rays were also occasionally passed through the specimen edge, and this was possible by rotating the cylindrical grips through an angle of 90°.

The final piece of X-ray equipment used was a Schulz Texture Goniometer made by Philips, and the use of this instrument is well described by Cullity (1956). This machine was mainly used for checking fibre symmetry, although it was also used to verify the assumption that the (002) reflection maxima was at right angles to the two (110) reflection maxima. All reflections were detected using a counter, and the intensity of the reflections were plotted on a chart recorder, the speed of which was related to the rotation of the specimen. Nickel-filtered Cu Ka radiation was used at all times. Use of this apparatus is discussed further in section 6.2.

For some of the diffraction patterns obtained on wide and low angle X-ray films, intensity measurements were required. A Wooster microdensitometer was employed in order to measure the optical density of photographic emulsions. A light beam, 0.5 mm in diameter was passed through the film, and its intensity registered on a chart recorder. It was possible for the beam to oscillate over a distance of 2 mm in one direction (y), and the film to move at right angles to this direction (x). This technique was used when scanning low angle diffraction patterns in the x direction, and the distance
travelled by the film was directly related to the chart drive. The film carrier could move in both x and y directions, and also rotate about the beam direction. This facility was used when measuring the intensity distribution of the (110) reflection, by rotating the (110) arc about the centre of the diffraction pattern, and scanning the light beam across the reflection.

Intensity measurements were assumed to be accurate to 1% (manufacturers specifications), and the angular measurements obtained from the rotating carrier were accurate to 0.2°. Error in film distance obtained from the chart was of the order of ±0.05 mm.

2.7 Irradiation

To prevent oxidation of cold drawn specimens during irradiation, specimens were initially placed into glass tubes that were subsequently evacuated using a mercury diffusion pump with an oxygen trap attached. After a pressure of about $2 \times 10^{-5}$ torr had been reached, the tubes were sealed and irradiated for various times in a Cobalt 60, γ ray source ("Super Hotspot") at room temperature. The radioactive source produced γ rays at a dose rate of 0.125 Mega rads hr$^{-1}$ as measured by a Perspex (Red 400) dosimeter.

To check whether carbonyl and peroxide bonds had formed due to the possible presence of oxygen, infra-red spectra of specimens were obtained using a Unicam S.P. 200 infra-red spectrophotometer.
Figure 2.1: Moulding plates and resulting isotropic polyethylene sheet.

Figure 2.2: Cold drawing of polyethylene sheet using an E-type Tensometer.
Table 2.1: The three draw ratios $R_x$, $R_y$ and $R_z$ obtained from four cold drawn polyethylene specimens.

<table>
<thead>
<tr>
<th>$R_y$</th>
<th>$R_x$</th>
<th>$R_z$</th>
<th>$R_xR_yR_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.77</td>
<td>0.57</td>
<td>0.20</td>
<td>0.99</td>
</tr>
<tr>
<td>8.20</td>
<td>0.59</td>
<td>0.19</td>
<td>0.92</td>
</tr>
<tr>
<td>8.36</td>
<td>0.54</td>
<td>0.22</td>
<td>0.99</td>
</tr>
<tr>
<td>9.05</td>
<td>0.52</td>
<td>0.21</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Average Values

<table>
<thead>
<tr>
<th>Average</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.52</td>
<td>0.56</td>
</tr>
<tr>
<td></td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>0.98</td>
</tr>
</tbody>
</table>

Figure 2.3: A photomicrograph of the central region of a dumbbell shaped test specimen, which was cut out at an angle of 27° with respect to the draw direction (dot spacing = 0.2 mm).
Figure 2.4: Small tensile testing machine.

Figure 2.5: Temperature controller and heating chamber.
Figure 2.6: Circuit diagram of temperature controller.
Figure 2.7: Calibration chart for temperature controller.

Figure 2.8: Specimen holder for X-ray camera.
CHAPTER 3

Post-Yield Flow Behaviour of Oriented Polyethylene

3.1 Introduction to Yield Criteria

Most materials behave elastically at low stresses. However, when the stresses are increased, these materials either yield at some point, if they are ductile, or fracture if they are brittle. The term yield is used in reference to the onset of plastic deformation, and various criteria involving generally the principal stresses at yield have been formulated to explain this transition.

One such theory which is based on a maximum shear stress concept suggested by Tresca, is described by Jaeger (1969). If \( \sigma_1, \sigma_2, \) and \( \sigma_3 \) are the principal stresses at a point where \( \sigma_1 > \sigma_2 > \sigma_3 \), then it is shown that the maximum shear stress has a value of \( \frac{1}{2}(\sigma_1 - \sigma_3) \), and occurs in a plane whose normal bisects the angle between the greatest and least principal stresses. Tresca's yield criterion states mathematically that when:

\[
|\sigma_1 - \sigma_3| = \text{constant} \quad (3.1)
\]

yield occurs. This criterion satisfies the following three assumptions: (a) the material is isotropic, (b) there is an independence of the hydrostatic component of stress, and (c) the yield behaviour is the same in tension and compression.

Mohr (see Jaeger (1969)) proposed a theory for failure in a plane whose normal and shear stresses were \( \sigma_n \) and \( \sigma_s \) respectively. Failure occurred when the stresses were related by some function:
\[ \sigma_s = f(\sigma_n) \]  

This relationship plotted on a \((\sigma_n, \sigma_s)\) plane is known as the Mohr circle diagram, and is a very useful way of representing data for two stresses on any one plane. It can be seen from equation (3.2) that if \(f(\sigma_n)\) is a constant, then this expression is the Tresca yield criterion, where \(\sigma_s\) is the maximum shear stress.

In 1773 Coulomb put forward a theory to explain the yielding of soils. This yield criterion states that for yielding to occur in any plane, the critical stress required, increases with the pressure applied normal to this plane. Thus:

\[ \sigma_s = \sigma_c \pm k \sigma_n \]  

(3.3)

where \(\sigma_c\) is the critical stress (a stress constant) and \(k\) a constant, frequently called the coefficient of internal friction. The \((\pm)\) sign is used depending upon whether the medium is tested in tension (\((-)\)) or compression \((+)\). An advantage of this simple criterion is that it not only gives the stress conditions for yielding, but also the direction in which the material will yield, which is not \(45^\circ\), as in the case of Tresca's criterion.

Other criteria have also been suggested in order to explain yielding, one of which is the von Mises criterion (see Cottrell (1964)). Although the theory was initially derived mathematically (see Ward (1971)) it has been interpreted physically in terms of (a) a critical elastic strain energy theory, and (b) a critical stress occurring in an octahedral plane (see Nadai (1950)). Modifications to the von Mises criterion have been successfully made when applying such a criterion to the yielding of polymers (see section 3.2).
3.2 Application of Yield Criteria to Polymers

Evidence has shown that the hydrostatic component of stress affects the yield behaviour of polymers. Thus, certain yield criteria have to be modified in order to describe the observed pressure dependence, and one, the von Mises criterion, is expressed by the simple equation:

\[ \sigma_{oct} = \sigma_k - k' \sigma_m \]  

(3.4)

where \( \sigma_{oct} = \frac{1}{3} [(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2]^{\frac{1}{2}} \), is the octahedral shear stress, and \( \sigma_m = \frac{1}{3} (\sigma_1 + \sigma_2 + \sigma_3) \) the mean normal stress; \( \sigma_k \) and \( k' \) are material parameters. This criterion has had wide application to the yielding of isotropic polymers, and further details are described in a review by Ward (1971).

The Coulomb criterion mentioned in section 3.1 already takes into account the effect of a normal stress on the slip plane by use of the term \( k \sigma_n \) in equation (3.3). This criterion has been satisfactorily applied to the yield behaviour of isotropic polymers such as polymethyl methacrylate (PMMA), by Bowden and Jukes (1968). They subjected PMMA to orthogonal compressive and tensile stresses simultaneously, and found that a value of \( k \) of 0.158 was obtained, in order to agree with the effect of the observed pressure upon a shear plane, which was at an angle of about 53° with respect to the plane of the sheet.

The testing of polymers has only been considered to take place under a standard loading path and a standard rate of loading, and the above-mentioned criteria have been successful under these con-
ditions. However, the mechanical properties of polymers are very sensitive to the variables of time and temperature. Work has been done on the viscoelastic nature of yield, and the starting point for much of this work has been the Eyring viscosity equation, which is:

\[ \dot{e} = A \exp \left( -\frac{\Delta U - \sigma y}{kT} \right) \]  

(3.5)

where \( \dot{e} \) is the strain rate, \( \sigma \) the applied stress, \( y \) the activation volume, \( T \) the absolute temperature, \( A \) a constant and \( \Delta U \) the activation energy for the flow process. This molecular theory for yield incorporates the variables of time and temperature, and has been applied to isotropic polymers such as polycarbonate and polyethylene terephthalate. Further details are in a review on the yield behaviour of polymers by Ward (1971).

In order to explain the yield behaviour of oriented polymers further modifications have to be made to the yield criteria, since oriented polymers are highly anisotropic, and the Bauschinger effect, in which tensile and compressive yield stresses are not equivalent, is evident. Also, when an oriented polymer is deformed in tension at an angle (\( \lambda_0 \)) with respect to the initial draw direction, under certain conditions yield is accompanied by the formation of a narrow deformation band. The angle the deformation band makes with respect to the specimen edge is dependent upon \( \lambda_0 \). Work carried out on the yielding of oriented polyvinyl chloride by Rider and Hargreaves (1969) showed that by using the von Mises criterion, extended by Hill (1950) for anisotropy, the band angle could be predicted, and good agreement with experimental data was obtained, after a Bauschinger term had been included.
Keller and Rider (1966) made detailed studies of band formation during the tensile deformation of oriented high density polyethylene, and found that the deformation bands formed, depended upon pre-treatment (annealing and rolling) of the drawn polymer. For cold drawn polyethylene specimens that were redrawn at room temperature it was, however, found that no deformation bands formed. The Coulomb criterion was successfully fitted to the upper yield points of specimens that had various pretreatments. The Coulomb criterion has, however, been modified by various people in order to explain band formation (see Hargreaves (1970)).

As a consequence of the work of Keller and Rider (1966), studies were carried out by Hinton and Rider (1968) on the tensile deformation of oriented polyethylene specimens that did not form deformation bands. As well as investigating the use of a Coulomb criterion, a detailed strain analysis was also made. Further details of the strain analysis will be mentioned in Chapter 4. However, it is sufficient to say that the deformation to a first order was simple shear parallel to the c direction. The Coulomb criterion was again fitted to the yield points of specimens with different initial orientation angles \(\lambda_0\), and the parameters \(\sigma_c\) and \(k\) obtained were subsequently used to predict satisfactorily the post yield deformation.

The simplest yield criterion for anisotropic materials is the critical resolved shear stress law, suggested by Schmid (see Schmid and Boas (1950)). This law states that when a resolved shear stress in a particular plane reaches a critical value, yield will occur. The criterion which is very similar to the Coulomb criterion, except
there is no normal stress term, has been applied successfully to explain the yielding of drawn and annealed high density polyethylene in compression, by Bowden and Young (1971).

3.3 A Flow Criterion

It appears from the findings of Hinton and Rider (1968) that the Coulomb criterion was not only adequate in satisfying the yield conditions, but also in describing the uniform deformation beyond yield, up to large plastic strains. It is therefore appropriate to refer to the Coulomb criterion as a flow criterion.

The rest of this chapter describes in detail an investigation into the validity of the flow criterion over a range of experimental conditions far wider than reported by Hinton and Rider (1968).

3.3.1 Experimental Procedure

Dumb-bell shaped tensile specimens, described in section 2.2, were cut out of the cold drawn polyethylene sheet at various angles ($\lambda_o$) to the c direction. These angles varied from $30^\circ$ to $80^\circ$. In order to minimize scatter in the results, most specimens were cut from the same sheet of material because the variation in results between nominally identical specimens was found to be less for specimens taken from the same sheet of material than for specimens taken from different sheets, even though care was taken to ensure that moulding conditions were the same for all sheets, and that the polyethylene pellets were from the same manufacturers batch. A few tests were therefore carried out on specimens from different sheets in order to determine the magnitude of sheet variation.
Test specimens were deformed in tension at a crosshead speed of 0.67 mm min\(^{-1}\) in the E-type Tensometer, at temperatures from 0°C to 120°C, and specimen deformation beyond yield recorded photographically (see section 2.5).

### 3.3.2 Measurements

Measurements were initially taken from the photographic negatives, although it was later found that the error in taking measurements from the negatives in preference to the prints was negligible. The two measurements taken (\(\lambda\) and \(\ell\)) are shown schematically in Figure 3.1. The grid direction was used to indicate the c direction during specimen deformation, although after tensile strains of about 300\%, the c direction and grid direction differed by about 3°. The initial values of \(\lambda\) and \(\ell\), \(\lambda_0\) and \(\ell_0\) respectively, were also measured.

When each photograph of the specimen was taken, an event mark was made on the load-extension curve. This enabled the nominal and true tensile stresses to be calculated at that point of deformation. Nominal tensile stress (\(\sigma\)), and true tensile stress (\(\sigma_T\)) are defined as follows:

\[
\sigma = \frac{\text{load}}{\text{initial cross-sectional area}}
\]

and

\[
\sigma_T = \frac{\text{load}}{\text{cross-sectional area}} = \sigma \frac{\ell}{\ell_0}
\]

where the initial cross-sectional area of the specimen was calculated from measurements obtained by using a travelling microscope and dial...
gauge. The true tensile stress was calculated from equation (3.7) assuming a constant volume deformation.

The expression for the Coulomb criterion when applied to a specimen in tension is:

\[ \sigma_s = \sigma_c - k\sigma_n \]  

(3.8)

The values of \( \sigma_s \) and \( \sigma_n \) were obtained by resolving the true tensile stress into a shear stress and a normal stress, thus:

\[ \sigma_s = \sigma_T \cos\lambda \sin\lambda \]  

(3.9)

and

\[ \sigma_n = \sigma_T \sin^2\lambda \]  

(3.10)

3.4 Results

When the resolved normal and shear stresses were plotted in a way similar to that of the Mohr circle diagram, a linear relationship between \( \sigma_s \) and \( \sigma_n \) was obtained for each test temperature. The results are shown in Figure 3.2 for specimens with the same \( \lambda_o \), tested over the temperature range of 22°C to 119°C. It can be seen from the data that the relationship between \( \sigma_s \) and \( \sigma_n \) is of the form expressed in equation (3.8), and that the two parameters, \( \sigma_c \) (the intercept) and \( k \) (the slope) are temperature dependent.

For a given test temperature it was found that \( \sigma_c \) was approximately independent of \( \lambda_o \), while \( k \) was dependent upon \( \lambda_o \). The data for specimens tested at 70°C is shown in Figure 3.3, and the values of \( \sigma_c \) and \( k \) obtained, are shown in Table 3.1.
It was first thought that there was a range of values of $\lambda_o$ between approximately $70^\circ$ and $45^\circ$, forming a central region, in which there was little variation in $\sigma_c$ and $k$ (see Simpson and Hinton (1971)). In this work a master curve of tensile stress ($\sigma_T$) against orientation angle ($\lambda$) was used to superimpose the data from specimens within this region. The master curve used was obtained from equations (3.8), (3.9) and (3.10) and was of the form:

$$\sigma_T = \frac{\sigma_c}{(\cos \lambda \sin \lambda + k \sin^2 \lambda)}$$  \hspace{1cm} (3.11)

The data from the three specimens (see data marked * in Table 3.1) within the central region in Figure 3.3 was plotted in Figure 3.4, and a master curve drawn through the data, by a least squares fitting method. Similarly, data from specimens within the central region at temperatures of $22^\circ$C and $105^\circ$C was also plotted, and this is shown together with the $70^\circ$C data in Figure 3.5. The parameters $\sigma_c$ and $k$ required for the fitting of the three master curves are shown in Table 3.2.

Upon inspection of further data, it was found that rather than there being a plateau in the $k$ values within the central region, there was in fact an approximately linear relationship between $k$ and $\lambda_o$ of the form:

$$k = m(90^\circ - \lambda_o)$$  \hspace{1cm} (3.12)

where $m$ is temperature dependent. The variation of $k$ with $\lambda_o$ for a series of tests carried out at temperatures of $22^\circ$C, $50^\circ$C and $90^\circ$C are illustrated in Figure 3.6.
The effect of temperature on $\sigma_c$ and $k$ has already been illustrated in Figures 3.2 and 3.6. However, it is shown in detail in Figure 3.7 where specimens with the same $\lambda_o$ are compared. An increase in temperature therefore results in an increase in $k$, but a decrease in $\sigma_c$.

All results shown, apart from those in Figure 3.6, are of specimens obtained from the same cold drawn polyethylene sheet (ref CD.144). The results of tests performed on specimens from a further two cold drawn sheets (ref CD.141 and CD.148) are presented in Table 3.3. The values of $\sigma_c$ and $k$ are from specimens with approximately the same value of $\lambda_o$, and the various test temperatures are listed. It appears that $\sigma_c$ is less sensitive than $k$ to sheet variation.

Plastic deformation after yield has been analysed above in terms of the relationship between the resolved shear stress and normal stress components, and it appears that $\sigma_n$ plays an important part in influencing the flow stress behaviour. If, however, post yield deformation is considered in terms of resolved shear stress and shear strain (see Chapters 4 and 5) behaviour, there is little evidence to indicate that $\sigma_n$ has any affect upon the flow stress for different specimens ($65^\circ > \lambda > 30^\circ$). In Figure 3.8, a plot of $\sigma_s$ against $\gamma$ (shear strain) for two specimens deformed at $22^\circ$C with $k$ values of 0.22 ($\lambda_o = 62^\circ$) and 0.55 ($\lambda_o = 42.5^\circ$) shows little difference in deformation behaviour. Data presented in the two forms is therefore paradoxical, and in section 5.3.5 analysis of the situation is discussed further.
3.5 Discussion

3.5.1 Application of the Flow Criterion

For all specimens tested between 0°C and 120°C with different values of $\lambda_0$, the flow stress criterion is well obeyed. However, when considering the exactness of fit of equation (3.9) to the data, and also comparing the values of the parameters $\sigma_c$ and $k$ with those reported in other work, both the effect of shear strain rate ($\dot{\gamma}$) upon the flow stress, and the use of true stress rather than nominal stress, have to be taken into account. In earlier work on yielding, nominal stress was generally used, and in the studies of yielding of PMMA by Bowden and Jukes (1968), nominal stress was described as having a real interpretation, since it was proportional to the 'stress per molecule'. The value for $k$ when true stress was considered was 0.158, whereas it was 0.256 for nominal stress, although there was little change in the value of $\sigma_c$. It was also later indicated by Bowden and Jukes (1970), for polymers such as high density polyethylene (unoriented), that the use of nominal stress compared with true stress increased the value of $k$. Since the series of tests described in this chapter involved large plastic strains with considerable changes in the cross-sectional area of specimens, true stress values were used.

Another aspect to be considered when comparing absolute values of $\sigma_c$ and $k$ with those obtained by other workers, is that $k$ is not only sensitive to changes in the types of high density polyethylene used, but also to changes between one sheet of material and another. Values of $\sigma_c$ and $k$ parameters obtained from three cold drawn sheets showing such variation are listed in Table 3.3. In some cases
k has differed by a factor of 2, although there has been little change in $\sigma_c$. This fluctuation in $k$ does not mean that the trend expressed by equation (3.12) for the variation of $k$ with temperature is incorrect, but that $m$ does not have a unique value for a given temperature.

The presentation of data in the form of a master curve is very convenient, particularly as the data is that which is directly measured and not processed in any way. Thus, any deviation between experimental data points and the master curve can be seen in relationship to the experimental error. However, this method of handling the data is not very sensitive to small changes in the parameters $\sigma_c$ and $k$. Consequently, a variation in $k$ of 1.63 to 1.30 which was obtained for a variation in $\lambda_0$ of 46° to 71° (see Table 3.1), did not make a significant difference to the master curve.

It is, however, interesting to compare the value of $k$ obtained by other workers with the range of values obtained in this project, in which a value of $k = 0.3$ was obtained as a mean value at room temperature. Keller and Rider (1966) fitted the room temperature upper yield points of specimens with various $\lambda_0$ values to the Coulomb theory and found that $k = 0.45$. The polyethylene used was Marlex 50, the crosshead speed was 1.6 cm min$^{-1}$, and only nominal stress was considered. In the work by Hinton and Rider (1968), on Rigidex type 2, at a lower crosshead speed of 0.5 mm min$^{-1}$, a value of $k = 0.2$ was obtained when fitting nominal tensile yield stress data to the Coulomb criterion. The value of the parameter $k$ in Hinton and Rider's (1968) yield analysis was, in fact, adequate in describing the flow stress behaviour after yield for a specimen with a $\lambda_0$ value of 66°. It is, however, shown in section 5.3.1 that
there is a difference in $k$ values when the criterion is fitted to
(a) the yield points, and (b) the post yield stress data, contrary
to that found by Hinton and Rider (1968). The two types of $k$
values are therefore not strictly comparable.

The variation of $k$ with $\lambda_o$ is clearly illustrated in
Figure 3.6, where at $22^\circ$C, $k$ varies between 0.2 ($\lambda_o = 80^\circ$) and
1.0 ($\lambda_o = 30^\circ$). In considering the variation of the parameters
$\sigma_c$ and $k$ it is important to note that $\sigma_s$ and $\sigma_n$ are not
independent (see equations (3.9) and (3.10)). Thus, the relative
magnitudes of $\sigma_s$ and $\sigma_n$ cannot be independently controlled.
The ratio of the stresses is given by:

$$\frac{\sigma_n}{\sigma_s} = \tan \lambda_o$$  (3.13)

The fact that this ratio is a rapidly changing function, particularly
at high angles ($\lambda_o > 80^\circ$) may account for the fact that experimentally
$k$ approaches zero for $\lambda_o = 90^\circ$, for all temperatures. Another
possible reason for this dependence upon $\lambda_o$ is that deformation
prior to yield is dependent upon $\lambda_o$, and the pre-yield deformation
may influence the parameters in the flow criterion. Detailed studies
into the pre-yield deformation of specimens are described in section
5.3.2, where it certainly appears that $\lambda_o$ eventually dictates the
parameters $\sigma_c$ and $k$.

The critical stress constant $\sigma_c$ (equation (3.8)), is equal to
the shear stress $\sigma_s$, in the c direction, when the normal stress
compontent $\sigma_n$ is zero ($\lambda = 0^\circ$). This means that irrespective of
$\lambda_o$, $\sigma_c$ would be expected to be constant, since $\sigma_c$ is the limiting
resolved shear stress for all specimens after complete rotation of the
c axis \((\lambda = 0^\circ)\). Experimentally, the value of \(\sigma_c\) was found to be approximately independent of \(\lambda_o\) for a given temperature, as shown in Figure 3.3, which would indicate that \(\sigma_c\) is an intrinsic parameter of the material as suggested above. The room temperature results show that \(\sigma_c\) has a value of about 8 N mm\(^{-2}\), which is close to that of 8.7 N mm\(^{-2}\) obtained by Keller and Rider (1966).

Finally, it is important to point out two factors that were not considered when fitting data to the flow criterion. First, during the deformation of a specimen, there is a gradual deviation between the c direction and the grid direction, such that \(\lambda > \lambda_c\) (c direction). After tensile strains of about 300%, the difference between the grid direction and c direction \((\lambda - \lambda_c)\), is about 3\(^\circ\). Thus, the resolved normal and shear stresses to the c direction would be slightly less than those recorded. Secondly, the total strain of a specimen consists of plastic and elastic strain, and since only plastic strain is applicable to a flow criterion, the elastic strain should be removed. This would result in an increase in \(\lambda_c\) by about 1 or 2\(^\circ\) (see section 5.3.4), hence tending to cancel out the effect mentioned above. It was, in fact, found that after considering both effects for the last experimental point of deformation shown in Figure 3.2 for the 22\(^\circ\)C data, the normal and shear stresses were decreased by about 13\% and 7\% respectively (see data point marked + 0). Therefore, a small curvature to the data on a \((\sigma_n, \sigma_s)\) plot would be expected, when considering resolved stresses perpendicular and parallel to the c direction.
3.5.2 Temperature Dependence

When considering the effects of temperature upon the flow stress parameters, there are two types of resistance to motion that should not be confused. One is a viscous resistance to flow and the other, the already familiar Coulomb friction (see Alfrey (1965)). The two effects differ in that (a) the viscous resistance is rate dependent whilst the frictional resistance is not, and (b) the viscous resistance which is based upon molecular motion, is extremely temperature dependent, whereas the Coulomb friction being ideally a purely mechanical effect is practically independent of temperature. The effect of temperature upon the parameters $\sigma_c$ and $k$ is therefore of particular interest.

The parameter $\sigma_c$ decreases with temperature as illustrated in Figure 3.7 in such a way as to suggest that the stress constant is of a viscous nature. Work was done by Simpson and Hinton (1971) on the temperature dependence of the stress constant, where an activated energy process for molecular motion was considered. The attempt however was over-simplified since strain rate was not accounted for. The difficulty in dealing with a parameter such as $\sigma_c$ is that it is rather an indirect quantity, in so far as $\sigma_c$ is not actually measured, but only a consequence of the theory. If $\sigma_c$ is to be investigated in any detail, then simple shear experiments of the form performed by Robertson and Joynson (1968) would have to be adopted.

It can be seen from Figure 3.7 that $k$ is also temperature dependent. The concept of temperature affecting $k$ is contrary to the above-mentioned ideas on classical Coulomb friction, in which in the case of a polycrystalline fibrous material (see Chapter 6) such
as oriented polyethylene, the frictional force might be envisaged to arise from slip between adjacent crystallites. The simple assumption made is that there is no other interaction between such slip planes (crystallites). However, it is shown in Chapter 6 that temperature sensitive constraints exist between the slip planes. Consequently, this effect is reflected in the variation of $k$ with temperature.

Results show that as the test temperature approaches the melting point of polyethylene, $k$ increases, indicating that normal stress is becoming the predominant stress. However, in Chapter 4, the geometry of deformation of specimens tested at 120°C can still be described in terms of an approximate simple shear mode parallel to the $c$ direction, which confirms that shear stress is still the dominating factor. Also, a value of $k > 1$ is difficult to appreciate in terms of the criterion used, since only the complete resolved normal stress ($k = 1$) can be exerted on the slip plane. Thus, at elevated temperatures, the criterion may not be appropriate. One point of interest is that below 22°C there is little variation in $k$, this phenomenon also being observed by Keller and Rider (1966) when they deformed specimens at 22°C and 4°C.

3.5.3 Strain Hardening

When analysing an increase in the resolved shear stress during plastic deformation, difficulty arises in differentiating between a decrease in $\sigma_n$, strain hardening, and an increase in shear strain rate (see section 3.5.4). Results shown in Figure 3.8 clearly illustrate the possibility of strain hardening, and an independence of $\sigma_n$ during deformation at 22°C. If there were no strain hardening, all specimens would flow after yield under the same constant
shear stress $\sigma_c$, independent of $\lambda_0$ (assuming $\sigma_n$ has no effect), which is not the case. Strain hardening in a material is related to its crystalline texture, and in Chapter 6 a structural model for oriented polyethylene is discussed, in which tie molecules between crystalline regions, influence the deformation properties of the polymer. It is therefore possible that strain hardening could be attributed to a gradual increase in the constraints on such tie molecules.

It is well known that certain single crystals yield according to a critical shear stress law ($k = 0$), and during subsequent deformation there is little strain hardening. Consequently, a successful attempt was made by Bowden and Young (1971) to produce a highly crystalline bulk specimen that reflected the flow properties of a single crystal. In their work, samples of oriented high density polyethylene (RigideX 9) were annealed at 200°C under a hydrostatic pressure. The samples were then deformed in compression at room temperature, and a value of 15 N mm$^{-2}$ was obtained for the flow stress constant ($\sigma_c$).

3.5.4 Strain Rate

When data was considered in terms of the flow criterion, it was implicitly assumed that an increase in the resolved shear stress ($\sigma_s$) was solely due to a decrease in the normal stress ($\sigma_n$) exerted on the slip plane. It is known that for many viscoelastic materials such as polymers, strain rate has an effect on the applied stress (see Kumar (1969)), and the expression suggested by Eyring (see equation (3.5)) indicates that an increase in strain rate results in an increase in stress.
When dumb-bell shaped tensile test specimens deform in simple shear parallel to the c direction, the constraints of the grips cause the c direction to rotate towards the tensile axis. Since shear strain rate \( \dot{\gamma} \) is a function of the angle \( \lambda \), \( \dot{\gamma} \) is not constant during deformation. The relationship between \( \dot{\gamma} \) and \( \lambda \) is derived in section 5.3.3, equation (5.5), and it is shown that for the deformation of a specimen with \( \lambda_0 = 60^\circ \), \( \dot{\gamma} \) increases by a factor of about 2 when \( \lambda \) decreases from \( 60^\circ \) to approximately \( 20^\circ \). A plot of resolved shear stress against shear strain rate illustrates this effect in Figure 3.9, for a specimen \( (\lambda_0 = 62^\circ) \) deformed at \( 22^\circ \text{C} \). It is interesting to note the similarity between the curve in Figure 3.9 and that obtained from a non-Newtonian body, when subjected to an increase in shear rate (see Billmeyer (1962)). If oriented polyethylene behaves viscoelastically, then from data obtained by Hinton (1972), an increase in the shear strain rate by 2 is expected to produce an increase in the resolved shear stress of about 7%, which is relatively small compared with the measured increase value of \( \sigma_s \) (\( \approx 50\%) \).

It is, however, appreciated that strain rate affects the resolved stresses, and subsequently the parameters, \( k \) and \( \sigma_c \). Unfortunately, there was insufficient time to carry out a series of tests whereby the crosshead speed was varied so as to find out how \( \sigma_c \) and \( k \) changed with shear strain rate.
Figure 3.1: Diagram to illustrate the angle and length measured throughout the experiment.

Figure 3.2: Variation of shear stress with normal stress for various test temperatures, which are indicated in degrees centigrade. The value of $\lambda_0$ was approximately 78° for all specimens.
Figure 3.3: Variation of shear stress with normal stress for specimens of different initial orientation measured at 70°C. The values of $\lambda_0$ are indicated.

Table 3.1: Experimental values of $\sigma_c$ and $k$ obtained from various specimens at 70°C.

<table>
<thead>
<tr>
<th>$\lambda_0$ Degrees</th>
<th>$\sigma_c$ Nmm$^2$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>52</td>
<td>0.76</td>
</tr>
<tr>
<td>71</td>
<td>58</td>
<td>1.30*</td>
</tr>
<tr>
<td>60</td>
<td>5.4</td>
<td>1.44*</td>
</tr>
<tr>
<td>45</td>
<td>5.5</td>
<td>1.63*</td>
</tr>
<tr>
<td>29</td>
<td>5.7</td>
<td>232</td>
</tr>
</tbody>
</table>
Figure 3.4: Variation of tensile stress with orientation angle at 70°C. The data points are from three specimens within the central region, to which the master curve is fitted.

Figure 3.5: Three master curves from three specimens, for each of three temperatures, which are indicated in degrees centigrade.
Table 3.2: The values of $c_\theta$ and $k$ obtained from the three master curve fittings.

<table>
<thead>
<tr>
<th>Temperature $^\circ$C</th>
<th>$c_\theta$ Nmm$^{-2}$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>8.0</td>
<td>0.30</td>
</tr>
<tr>
<td>70</td>
<td>4.9</td>
<td>1.05</td>
</tr>
<tr>
<td>105</td>
<td>3.8</td>
<td>1.74</td>
</tr>
</tbody>
</table>

Figure 3.6: Variation of $k$ with initial orientation angle at three temperatures, each temperature being indicated in degrees centigrade. The numbers in parenthesis refer to the particular cold drawn sheet used.
Figure 3.7: The effect of temperature upon the parameters $\sigma_c$ and $k$, for specimens with the same $\lambda_0$ value of 78$^\circ$.

<table>
<thead>
<tr>
<th>CD 144</th>
<th>Temp, °C</th>
<th>$\lambda_0$ degrees</th>
<th>$\sigma_c$, Nm^{-2}</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>22</td>
<td>59</td>
<td>7.6</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>77</td>
<td>6.0</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>75</td>
<td>47</td>
<td>0.99</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CD.141 and CD.148 (marked *)</th>
<th>Temp, °C</th>
<th>$\lambda_0$ degrees</th>
<th>$\sigma_c$, Nm^{-2}</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>22</td>
<td>60</td>
<td>8.1</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>50*</td>
<td>78</td>
<td>6.6</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>72</td>
<td>5.5</td>
<td>1.78</td>
</tr>
</tbody>
</table>

Table 3.3: Fluctuations in $\sigma_c$ and $k$, when specimens are obtained from three different cold drawn sheets.
Figure 3.8: Variation of shear stress with shear strain after yield for two specimens at 22°C.

Figure 3.9: The relationship between shear stress and shear strain rate, during the plastic deformation of a specimen ($\lambda_0 = 62^\circ$) at 22°C.
CHAPTER 4

The Geometry of Deformation of Oriented Polyethylene

4.1 Introduction

It was mentioned in the previous chapter that for oriented polymers, yield is often accompanied by the formation of a narrow zone, inside which the material is highly deformed. The circumstances under which these bands form in high density oriented polyethylene have been investigated in detail by Kurokawa and Ban (1964), Seto and Tajima (1966), and Keller and Rider (1966). In all cases the oriented polyethylene had to be annealed before well defined bands formed, although Keller and Rider (1966) found that deformation bands formed when unannealed oriented polyethylene was tested at a very high strain rate. Tests carried out at 4°C also showed band formation. It was, however, found by Keller and Rider (1966), that it was not only pretreatment to the oriented polyethylene that affected band formation, but also the value of the initial orientation angle ($\lambda_0$) of the specimen. Depending upon the value of $\lambda_0$ it was found that it was possible to produce two types of deformation band, referred to as type 1 and type 2 by Hargreaves (1970). Differences between the two types are discussed in section 4.4.1. Results published by Keller and Rider (1966) showed that for annealed polyethylene specimens with $\lambda_0$ values of up to 70°, deformation bands formed within 10° of the c direction, such that the angle between the band and tensile directions was always less than the angle between the c and tensile directions. On subsequent deformation considerable amounts of shear occurred in the band until there was a slip-off process. These results indicated that the plastic
deformation that had occurred in oriented polyethylene, approximated to slip in the c direction. Various other workers (see Darlington and Saunders (1970) and Young et al. (1972)) have also reported that the deformation mechanism of oriented polyethylene at room temperature can be described as simple shear in the c direction.

A detailed strain analysis in deformation bands would prove difficult because of the large shear strains involved, thus a strain analysis on specimens that did not form bands but underwent uniform deformation was performed by Hinton and Rider (1968). Their findings were that associated with a simple shear process there was a reorientation of material. Deviation from simple shear was assumed to be the consequence of a distribution of oriented chains about the draw direction. Referring to the mean direction of all the chain axes as the c direction, the model suggested by Hinton and Rider (1968) was as follows: (a) the first increment of deformation was simple shear in the c direction, (b) this shear process produced a new distribution of chains, with the c direction no longer parallel to the initial shear direction, and (c) the next increment of shear then occurred in the new c direction. This shear reorientation process was then continued and the resultant macroscopic strain in a tensile specimen calculated. Hinton and Rider (1968) found that if it was assumed that a shear increment of 1% produced a reorientation of 0.02° (θ) in the c direction, there was good agreement with experimental data. From the model, a deviation between the grid direction and c direction was therefore satisfactorily accounted for.

In Chapter 3 the flow criterion used also implies that there is an associated shear process in the c direction. It is therefore intended to extend the studies performed by Hinton and Rider (1968),
in order to describe the deformation behaviour of oriented poly-
ethylene at elevated temperatures.

4.2 Experimental

4.2.1 Procedure

Most specimens were deformed in the small tensile testing
machine, between temperatures of 22°C and 120°C. As in the previous
chapter, \( \lambda_o \) varied between 30° and 80°. In addition, a few tests
were carried out at temperatures of 0°C and -10°C, using the E-type
Tensometer and environmental chamber. The deformation of a few
specimens whose initial orientation angles were 0° and 90° were also
studied at room temperature, again using the E-type Tensometer.
Finally, some specimens were annealed without any constraints in air
for half-an-hour at temperatures between 50°C and 120°C. The cooling
rate was about 90°C hr^-1. Annealed specimens were then tested at room
temperature using the small tensile testing machine. In all cases
the crosshead speed was 0.67 mm min^-1.

4.2.2 Measurements

A few of the important measurements taken during the course of
studies in this chapter are illustrated in Figure 4.1, where there are
two micrographs of a typical specimen before and after deformation.
The various angles measured from the prints were; \( \omega \), the angle of
shear, and \( \lambda \). The angle the \( c \) direction made with respect to the
specimen edge (\( \lambda_c \)) was obtained from the calibrated rotating stage
of the microscope. In most cases, after specimen deformation,
\( \lambda > \lambda_c \) and this is shown in Figure 4.1, although not to scale.
Linear measurements taken from the prints were \( l \) (see Chapter 3), \( a \) - the distance between consecutive dots in the grid direction, and \( h \) - the perpendicular spacing between two rows of dots in the grid direction. The initial values of \( l \), \( a \), and \( h \) were \( l_0 \), \( a_0 \), and \( h_0 \) respectively. All measurements were made in the region where uniform deformation occurred, and the distances \( l \), \( a \), and \( h \) were averaged over five dot spacings. Specimen deformation continued until it was impossible to resolve adjacent dots for shear angle measurements.

Thickness measurements were taken of the specimen before and after deformation, and also birefringence values during the deformation process. It is, however, considered appropriate to discuss most of the birefringence results in Chapter 6 where orientation effects are considered.

4.3 Geometry of Simple Shear

Simple shear is illustrated in Figure 4.2 where a square of side \( a_0 \) (\( h_0 = a_0 \)) is sheared in the \( X \) direction (shear direction). Points \( p(x,y) \) on the unstrained square and \( p'(x',y') \) on the strained square are related by the two equations:

\[
x' = x + \gamma y
\]

and

\[
y' = y
\]

where \( \gamma = \tan \omega \), is the unit of simple shear strain. It can be seen from the figure that the perpendicular spacing \( (h_o) \) between
the two lines drawn parallel to the shear direction is constant, and the length of any line \( (a_o) \) in the shear direction remains unchanged. Thus, if simple shear occurs in one plane then the deformation is plane strain at constant volume.

When a specimen is deformed in tension, and simple shear occurs in the c direction, which is at an angle to the tensile axis, then due to the constraints of the grips on the specimen, the c direction will rotate towards the tensile axis. The geometry for this deformation is illustrated in Figure 4.3, where the two parallel lines drawn, each represent a row of dots in the c direction that are separated by a perpendicular spacing of \( h_o \). A simple shear of \( \gamma \) in the c direction would result in point A on the specimen edge moving to B, where AOB is the shear angle \( \omega \). However, since the specimen edge must be maintained in the tensile direction, B has to rotate by a value of \( \psi \) to A, or conversely B stays at A whilst the c direction rotates through the angle \( \psi \).

As \( h_o \) is constant for simple shear, it follows from the diagram that:

\[
\frac{h}{h_o} = \frac{x_o \sin \lambda_o}{z \sin \lambda} \quad (4.3)
\]

and

\[
h_o = k \sin \lambda \quad (4.4)
\]

From equations (4.3) and (4.4) the familiar Schmid and Boas (1950) relationship derived for slip in metal single crystals is obtained, which is:

\[
\frac{\frac{z}{x_o}}{\frac{z}{h_o}} = \frac{\sin \lambda}{\sin \lambda_o} \quad (4.5)
\]
where $\frac{\lambda}{\lambda_o}$ is the extension ratio. Now:

$$\text{A.B.} = h_o \tan \omega = h_o \gamma \quad (4.6)$$

and

$$\frac{AB}{\sin \psi} = \frac{\lambda_o}{\sin \lambda} \quad (4.7)$$

Thus, combining equations (4.3), (4.6), and (4.7), it can be shown that:

$$\gamma = \frac{\sin \psi}{\sin \lambda_o \sin \lambda} \quad (4.8)$$

and since

$$\sin \psi = \sin(\lambda_o - \lambda) \quad (4.9)$$

the shear strain is:

$$\gamma = \cot \lambda - \cot \lambda_o \quad (4.10)$$

By combining equations (4.5) and (4.10), it can also be shown that:

$$\gamma = \left(\frac{\lambda^2}{\lambda_o^2 \sin^2 \lambda_o} - 1\right)^{\frac{1}{2}} - \cot \lambda_o \quad (4.11)$$

Equations (4.10) and (4.11) therefore express the amount of simple shear strain in terms of either $\lambda$ and $\lambda_o$, or $\lambda_o$ and the extension ratio of the specimen.
4.4 Results

4.4.1 Dependence on $\lambda_o$ at Room Temperature

It was found then when specimens with $\lambda_o$ values of $90^\circ$ were tested in tension, brittle fracture always propagated parallel to the $c$ direction. A typical specimen after fracture is shown in Figure 4.4, and a point of interest is the fibrous texture along the fracture surface. Associated with this fracture was a tensile strain of about 6% at right angles to the $c$ direction, with no resulting shear strain. Thus $\frac{l}{k_o}$ was equal to $\frac{h}{h_c}$. In order to describe the fracture mechanism, a morphological model for oriented polyethylene is required, and this is discussed in Chapter 6.

When $\lambda_o$ was reduced from $90^\circ$ to $80^\circ$, specimen deformation was no longer fracture, but was by the formation of a deformation band that extended across the specimen. The micrograph in Figure 4.5 shows the formation of such a band after a specimen ($\lambda_o = 81^\circ$) had undergone a tensile strain of about 10%. Polarised light was used to show up the orientation change across the band. An important feature of the band is that the $c$ direction and band boundary are inclined to each other at a large angle (approximately $80^\circ$). This kind of band was referred to as type 2 by Hargreaves (1970), in contrast to the type 1 band in which the band boundary and $c$ direction were within about $10^\circ$ of each other. Various other workers (see Seto and Tajima (1966) and Keller and Rider (1966)) have also reported such bands, referred to as kink bands, in oriented polyethylene tensile test specimens with large $\lambda_o$ values. A study into kink band formation was not intended but only an investigation into the deformation behaviour within the band. The onset of a kink band
such as that shown in Figure 4.5 was difficult to assess especially as the kink boundaries were not well defined, but as the tensile test continued, the band expanded as the two kink boundaries moved apart. A kink band during its later stages of development is shown in Figure 4.6, where it can be seen that the material outside the band is relatively undeformed compared with the shear that has taken place within the band. For specimens with $\lambda_o$ values of about $80^\circ$, deformation within the band was uniform until $\lambda$ was approximately $57^\circ$, thereafter deformation within the band ceased to be uniform, resulting in curved grid lines, thus making shear strain measurements difficult. The limiting angular condition for kink band formation was found in specimens with $\lambda_o$ values of about $70^\circ$. However, unlike the $80^\circ$ ($\lambda_o$) specimens, deformation within the band was uniform for large strains, and characteristic of specimens with $\lambda_o$ values equal to that value of $\lambda$ within the band, as shown below.

Specimens with $\lambda_o$ values between $70^\circ$ and $30^\circ$ deformed uniformly in a simple shear mode approximately parallel to the grid direction. In Figure 4.7 data is shown for a specimen with a $\lambda_o$ of $61^\circ$, that has been deformed until a shear strain of about 2.4 was attained. The straight line in Figure 4.7 is obtained from equation (4.10) for simple shear, whilst the dotted line is a mean path through the experimental points. Deviation from simple shear appears to occur after a shear strain of about 0.8, and this trend was also evident in other specimens with different values of $\lambda_o$, except for $\lambda_o$ of about $30^\circ$ where there was no measurable deviation. It should, however, be noted that $\gamma$ is measured with respect to the grid direction and not the c direction, which deviates away from the grid direction by a maximum of about $3^\circ$ after a shear strain of about 2,
as a result of reorientation. The angle of deviation, \( \delta \), is given by:

\[
\delta = \lambda - \lambda_c
\]  

and in Figure 4.8 there is typical variation of \( \delta \) with extension ratio for a specimen that has a \( \lambda_o \) value of 59°. The deviation between simple shear and experimental results as shown in Figure 4.7 can, however, be considered in terms of changes in the parameters \( \frac{h}{h_o} \) and \( \frac{a}{a_o} \) which are very sensitive to changes in the direction of shear (\( \lambda_c \)). Thus, if no reorientation took place during simple shear, \( \delta \) would remain zero, and the parameters \( h \) and \( a \) would remain constant. However, this is not the case (see Figure 4.8), therefore changes in \( h \) and \( a \) indicate the effect of the reorientation process, as shown in Figure 4.9, where \( \frac{h}{h_o} \) and \( \frac{a}{a_o} \) are plotted against shear strain. It can be seen from Figure 4.9 that for specimens tested with \( \lambda_o \) values between 73° and 41.5°, deviation from simple shear is independent of \( \lambda_o \), whereas for the specimen with a \( \lambda_o \) of 30° there is good agreement with simple shear (as mentioned above) since \( \frac{h}{h_o} = \frac{a}{a_o} = 1 \). The shear reorientation model suggested by Hinton and Rider (1968) is fitted to the data in Figure 4.9, and the continuous curves are the predicted changes in \( \frac{h}{h_o} \) and \( \frac{a}{a_o} \) with \( \gamma \), when \( \theta = 0.01^\circ \) (reorientation angle) for 1% shear. The estimated experimental error of data is indicated by the error bar, and arises in some measure due to the fact that initially the grid and c directions are not always exactly parallel (maximum error of 1°), consequently a small scatter in data between specimens of different values of \( \lambda_o \) is expected.

Thickness measurements taken of specimens before and after deformation showed no change (within experimental error of 2%), indi-
cating plane strain deformation. Values of the product 
\( \frac{a - \lambda}{a_o} \times \frac{h}{h_o} \) calculated from measurements shown in Figure 4.9 for a
typical specimen (\( \lambda_o = 61^\circ \)) during deformation are listed in
Table 4.1, and since the product is unity, within an estimated
experimental error of 2%, deformation is assumed to be at constant
volume.

Specimens with \( \lambda_o \) values of 0\(^\circ\) extended uniformly in the
c direction up to strains of about 12\% (\( \frac{a - \lambda}{a_o} = 1.12 \)), thereafter the
defformation was non-uniform until fracture occurred at strains of
about 30\%. The resulting unclean fracture edge is shown in Figure
4.10, and the ink dots on the specimen surface portray the rather
irregular deformation that has taken place. Careful examination
indicated that the deformation was approximately non-uniform simple
shear in the tensile direction.

4.4.2 Effects of Temperature on the Deformation Geometry

As at room temperature, kink bands formed when specimens with
\( \lambda_o \) values greater than 70\(^\circ\) were tested at temperatures between -10\(^\circ\)C
and 120\(^\circ\)C. Detailed deformation studies were therefore confined to
specimens that deformed uniformly (70\(^\circ\) > \( \lambda_o > 30\(^\circ\) \)) at the temper­
atures of 50\(^\circ\)C, 70\(^\circ\)C, 90\(^\circ\)C, 105\(^\circ\)C, and 120\(^\circ\)C.

It was found that as the test temperature increased, there was
further deviation from simple shear. In Figures 4.11 and 4.12, \( \frac{h}{h_o} \)
is plotted against \( \gamma \) for specimens tested at 50\(^\circ\)C and 90\(^\circ\)C
respectively. It can be seen from the data that deviation from
simple shear for specimens tested at 50\(^\circ\)C is not significantly greater
than room temperature tests, although at 90\(^\circ\)C there is considerable
increased deviation. A fit to the 90°C data was made using the shear reorientation model (continuous curve) with $\theta = 0.03^\circ$. As at room temperature, low angle specimens ($\lambda_o = 30^\circ$) were anomalous, exhibiting little deviation from simple shear.

At 105°C and 120°C, specimens lost their 'stress whitened' opacity and became rather transparent before the onset of deformation. On deforming specimens at 105°C and 120°C, certain unusual phenomena were observed. For low angle specimens, a fibrous texture along the edge was noticed after shear strains of about 0.8, and one such example is shown in Figure 4.13 where $\lambda_o = 32^\circ$, and test temperature 105°C. The fibrous 'notches' gradually opened out on further deformation until slip-off fracture occurred in approximately the grid direction. A micrograph of a typical slip-off fracture edge at 105°C is illustrated in Figure 4.14, where the fracture edge is indicated by an arrow. Above $\lambda_o$ values of about 40°, where the fibrous texture at the edge of specimens was on a finer scale, data was rather inconsistent. In most cases during deformation, $\delta$ became positive (i.e. $\lambda > \lambda_o$) as shown in Figure 4.15. However, for a few specimens tested at 105°C and 120°C, $\delta$ became negative, even though simple shear in the c direction was the mode of deformation, thus $\frac{h}{h_o}$ would be expected to decrease in terms of the shear reorientation model. Although these specimens were an exception to the rule, it is considered of interest to report the results which are shown in Figure 4.16 together with results of specimens showing normal behaviour at 105°C. In Figure 4.16, the low angle specimen ($\lambda_o = 32^\circ$) is of the fibrous edge type, whilst specimens with $\lambda_o$ values of 61.5° and 46° were anomalous, with $\delta$ negative. A comparison between the shear reorientation model when fitted to the 90°C data ($\theta = 0.03^\circ$),
and the normal 105°C data, shows little difference in deformation behaviour between the two test temperatures.

During deformation, thickness measurements at elevated temperatures were impossible with the simple technique used, thus measurements were taken at room temperature before and after deformation, the specimen having been rapidly cooled to room temperature at the end of the test. Results showed that after deformation there had been an increase in thickness of specimens tested at 90°C and above. By comparison with specimens annealed (see section 4.4.3) at various test temperatures but not subsequently deformed, the change in specimen thickness was shown to be primarily due to the effect of annealing compared with the effect of tensile deformation. For example, for a specimen tested at 90°C, the change in thickness was accounted for by a 2% increase due to annealing, and a 1.5% decrease due to tensile deformation. These changes in thickness were only just within the 1.5% error of measurement. Although the results shown in Figure 4.12 indicate that \( \frac{h}{h_0} \) does not remain constant for high shear strains, the product \( \frac{a}{a_0} \times \frac{h}{h_0} \) does, indicating approximately plane strain deformation as suggested above. This behaviour is illustrated by the results in Table 4.2 for a typical specimen \( (\lambda_0 = 67°) \) tested at 90°C. It can, however, be seen by comparing Tables 4.2 and 4.1 that at 90°C there is possibly a slight trend towards an increase in area, associated with a slight decrease in thickness discussed above due to tensile deformation, resulting in approximately constant volume deformation. This was also exhibited in the case of the anomalous behaviour of specimens tested at 105°C and 120°C, in which \( h \) decreased and \( a \) increased, such that the product \( \frac{a}{a_0} \times \frac{h}{h_0} \) remained approximately constant.
At 0°C and -10°C, behaviour of specimens was rather variable. For all specimens, deformation was initially relatively uniform, but in some cases after a shear strain of about 0.5, localised slip-off fracture occurred (c.f. results of Keller and Rider (1966)). A typical fracture in a specimen ($\lambda_0 = 71^\circ$) at -10°C is shown in its late stages in Figure 4.17, where the fracture edge is indicated by an arrow. At 0°C certain specimens did, however, exhibit uniform deformation up to large shear strains, and the results for a typical specimen ($\lambda_0 = 48^\circ$) are illustrated in Figure 4.18, where the straight line is obtained from the expression for simple shear (equation 4.10). It can be seen that there is relatively good agreement between simple shear and experimental data.

4.4.3 Annealed Specimens

The aims behind a series of tests performed on annealed specimens were twofold. First, to compare the change in dimensions between controlled annealed specimens, and those specimens at the elevated temperatures prior to deformation. Secondly, to compare the differences in deformation between annealed specimens tested at room temperature, and specimens tested at the elevated temperature.

Changes in specimen dimensions were found to be identical in both specimens annealed for half-an-hour (measurements taken at 22°C) and specimens at the elevated temperatures (measurements taken after 2 minutes) awaiting deformation. Thus, macroscopic changes were independent of annealing conditions and time (over the range of 2-30 minutes). The most significant effect of annealing was a contraction along the c direction with no change in $h_0$. Table 4.3 lists the percentage contraction in the c direction for temperatures
between 70°C and 120°C. As a result of contraction, the grid direction rotated away from the tensile axis by a few degrees. There was also an increase in thickness (see Table 4.3) in specimens, although this was insufficient to maintain constant volume during annealing, resulting in an increase in density. The increase in density for specimens annealed at 105°C was measured using density gradient columns, and indicated an increase of 4.4%, compared with an increase in density obtained from data in Table 4.3 of 4.2%. This increase in density is possibly attributed to partial void closure within the material, which is discussed further in section 6.3.4.

Birefringence measurements suggested a small gradual disorientation in the chain distribution with annealing temperature, since at 70°C, 90°C, and 105°C the decrease in birefringence was about 2.5%, 3.5%, and 4.5% respectively.

There were, however, considerable differences in deformation behaviour between specimens tested at the elevated temperatures, and specimens annealed at the same temperature but tested at room temperature. Some typical results are shown in Figure 4.19 which indicate a constant value of h within experimental error. This contrasts with data shown in Figures 4.12 and 4.16 for specimens tested at the corresponding temperatures. The last experimental point for each specimen annealed at 105°C and 120°C indicates the end of uniform deformation (γ = 1) beyond which there was localised slip in a narrow region of the specimen, as shown in Figure 4.20 by the broken line. Such bands, however, had no well defined boundaries, in contrast to the slip bands reported by Keller and Rider (1966). Formation of such bands therefore prevented the continuation of uniform strain measurements being taken. For annealed specimens
with low values of \( \lambda_o \) a 'fibrous edge' also developed, similar to that associated with unannealed specimens tested at high temperatures.

For specimens annealed at 120°C and tested at 22°C, the grid dimension, \( a \), was found to increase by about 3.8\% for a shear strain of about 1, which contrasts with unannealed specimens where a decrease of about 3\% would be expected. This increase in \( a \), associated with no change in \( h \), leads to an increase in the grid area. Thus, the deformation was not exactly plane strain. However, a thickness decrease of 3.7\% was measured which indicated a constant volume deformation. For specimens annealed at 105°C and below, scatter in the values of \( \frac{a}{a_c} \times \frac{h}{h_o} \) and thickness measurements were within the experimental error of 2\%.

Variation of \( \frac{h}{h_o} \) with \( \gamma \) for specimens annealed at 70° and 50°C is shown in Figure 4.21, and it can be seen that there is no significant difference between this data and that in Figure 4.9 for unannealed material tested at 22°C. The curve in Figure 4.21 superimposed on the data is the shear reorientation model when fitted to the room temperature data in Figure 4.9 (\( \theta = 0.01^\circ \)).

4.5 Discussion

Tensile deformation of specimens with \( \lambda_o \) values of 90° and 0° resulted in fracture, without the characteristic uniform slip associated with intermediate angles. When the tensile stress is resolved along the c direction for specimens with \( \lambda_o \) values of either 90° or 0°, the stress conditions would favour chain separation and chain extension respectively. Thus, when considering the tensile deformation of such specimens, the crystal lattice strain has to
be taken into account. By using the stress data at fracture (see Chapter 5), and published crystalline lattice modulus data by Sakurda et al. (1966), it would appear that the crystal lattice strain at fracture for specimens with $\lambda_0$ values of 90° and 0° would be approximately 0.6% and 0.1% respectively. By comparison with the observed macroscopic strain at fracture (6% and 30% respectively) it is therefore most likely that most of the strain has been accommodated in the amorphous intercrystalline regions.

Various models have been suggested (see Peterlin (1971(a)) and Kuksenko and Slutsker (1968)) in order to account for the observed macroscopic strain in specimens ($\lambda_0 = 0°$), in terms of amorphous strain, where fracture is assumed to be the result of over strained tie molecules. For specimens with $\lambda_0$ values of 90°, deformation may have been by a reorientation process. However, this was not the case since there was uniform extension (6%) perpendicular to the c direction until fracture. A simple mechanism involving the straining of amorphous material is again suggested. Both models for fracture are further discussed in Chapter 6, when considering the strain in amorphous regions.

Kink band formation in polyethylene tensile test specimens has been studied in detail by Seto and Tajima (1966), who thought that the kink boundary was the point where slip in the c direction varied discontinuously, and within the band large amounts of slip occurred. However, little work has been reported on a detailed strain analysis within a kink band in oriented polyethylene. For specimens that exhibited uniform deformation within the kink band, a shear reorientation process (discussed below) occurred, which was unaffected by the presence of kink boundaries. This reorientation mechanism was
in fact applied by Brown et al. (1968) in order to predict the band angle in oriented polyethylene terephthalate. Kurokawa et al. (1967) reported that above the redrawing temperature of 70°C, no clear kink bands formed unless $\lambda_o$ was nearly 90°. This was certainly not the case in this work, since kink bands still formed in specimens with $\lambda_o = 70^\circ$, at temperatures of up to 120°C.

It was found that during deformation at 22°C of specimens with $\lambda_o$ values between 70° and 40°, the grid parameter $h$ increased by about 10% after a shear strain of 3, consistent with that predicted by the shear reorientation model with $\theta = 0.01^\circ$. By plotting the parameters $h$ and $a$ against shear strain it was, therefore, possible to compare data directly, from specimens with different values of $\lambda_o$. This would not have been the case if tensile strain ($\xi^{(0)}$) had been used as the abscissa (see Hinton and Rider (1968)).

In order to determine the magnitude of the shear reorientation effect on the chain distribution, a simple distribution function arising from the affine deformation of polyethylene when cold drawn, was adopted by Hinton and Rider (1968). The distribution function used was related to a strain ellipse in which the major and minor semi-axes $a'$ and $b'$ respectively were proportional to the two draw ratios of the oriented polymer in the plane of the sheet. If such an ellipse is sheared by 1%, as illustrated in Figure 4.22, the magnitude of $\theta$ is dependent upon the ratio of $a'/b'$. Thus, the empirical fitting parameter, $\theta$, is a function of the chain distribution. In Table 4.4 there are some calculated values of $\theta$ for various values of $a'/b'$, and it can be seen that if the affine model for cold drawing was correct, $a'/b' = 15$ (see Table 2.1), and therefore $\theta = 0.003^\circ$ would be expected. In Figure 4.9 the shear reorientation
prediction with $\theta = 0.003^\circ$ is compared with the room temperature data. However, this value of $\theta$ is unsatisfactory, since a value of $\theta = 0.01^\circ$ ($a'/b' = 8$) gave the best fit, which was comparable with that found by Hinton and Rider (1968) where $\theta = 0.02^\circ$. The distribution function of crystalline chains as obtained from the (002) reflection (see Chapter 6) does, however, agree relatively well with the affine prediction. Thus, it appears that non-crystalline chains (amorphous regions) play a vital role in the reorientation process. Further evidence to indicate the importance of the amorphous fraction is discussed in Chapter 6, where crosslinking is introduced into the amorphous regions, and considerable changes in the deformation behaviour are observed.

Deformation data from specimens with low values of $\lambda_0$ ($\lambda_0 < 30^\circ$) was not, however, in agreement with the shear reorientation model. This could be due to the unfavourably low shear stress conditions, since at low angles reorientation would result in the slip plane rotating towards the tensile axis where the resolved shear stress component is decreasing rapidly. Consequently, such reorientation is not favoured.

Deformation behaviour of specimens at $22^\circ$C therefore appears to some extent to depend upon the value of $\lambda_0$, which was similarly found by Kurokawa and Ban (1964), who categorised the tensile behaviour of annealed polyethylene specimens into three angular regions - $\lambda_0 > 70^\circ$, $60^\circ > \lambda_0 > 40^\circ$, and $30^\circ > \lambda_0$ - where in the middle region, extension was described as plastic flow with eventual break, in contrast to specimens with $\lambda_0$ values below $30^\circ$ in which slip-off occurred.
As the test temperature increased, deviation from simple shear also increased. In terms of the shear reorientation model, a value of $\theta = 0.03^\circ$ was required, which indicated that the distribution function was less oriented in the c direction, and had an $a'/b'$ parameter of 4, compared with 8 at $22^\circ$C (see Table 4.4). Thus, in testing specimens at $90^\circ$C, there had been a 50% decrease in the parameter $a'/b'$. Again, there is considerable discrepancy in $a'/b'$ at $90^\circ$C, between the predicted shear reorientation value and that expected using the affine strain ellipse, where only a 5.5% contraction in $a'/b'$ would be expected (see Table 4.3). Further evidence of a decrease in orientation at $90^\circ$C was indicated by a 3.5% decrease in birefringence. Work by Crawford and Kolsky (1951) attempted to predict the birefringence of drawn polyethylene for a given draw ratio, and it was shown that:

$$\Delta_n = \Delta_{n_{\text{max}}} \left[ \frac{3}{2(1-k^2)} - \frac{3 k \cos^{-1} k}{2(1-k^2)^{3/2}} \frac{1}{2} \right]$$  \hspace{1cm} (4.13)

where $\Delta_n$ is the measured birefringence, $\Delta_{n_{\text{max}}}$ the birefringence for perfect orientation, and $k$ the strain ratio parameter $\left(\frac{a'}{b'}\right)^{-1}$. Thus, using equation (4.13), a decrease of 3.5% in $\Delta_n$ at $90^\circ$C would be expected to be the result of a 20% decrease in the affine strain parameter $a'/b'$ (15), compared with the measured 5.5% decrease. Although the parameter $a'/b'$ for the strain ellipse, obtained from the shear reorientation model and affine model differ, the trend with temperature is at least the same. Difficulty, however, arises in trying to explain why there is little difference in deformation behaviour between specimens tested at $90^\circ$C and $105^\circ$C, and also why the annealed material (see below), exhibits little reorientation, even though the disorientation introduced due to annealing is the same as
that in specimens at the elevated temperatures prior to deformation. In the case of the latter, a combination of temperature and straining must influence in some way the subsequent deformation behaviour.

At high temperatures (> 105°C), and especially low values of $\lambda_0$ (30°C), the fibrous texture along the specimen edge was highly predominant. However, on further inspection of deformed specimens with larger values of $\lambda_0$, and those tested at temperatures as low as 50°C, small serrations along the edge were observed. This probably indicates that inhomogeneous slip at a submicroscopic level has taken place. A reason for a predominance in the fibrous texture at high temperatures could be associated with molecular scission in the over strained material connecting adjacent slip planes, consequently the effect of temperature would be to cause a retraction in the fractured material. Thus, the material 'peels' back under such retractive forces, as shown in Figures 4.13 and 4.14.

Annealing depends upon many factors such as temperature, rate of cooling, the medium in which the material is annealed, and whether or not the material is constrained. Thus, when comparing results with reported work on annealed material, annealing conditions are of vital importance. It is, however, generally thought that annealing causes increased crystallite perfection at the expense of changes within the amorphous regions (see Geil (1963)).

The effect of annealing was investigated by comparing the behaviour of specimens deformed at 22°C, or at the annealing temperature, following annealing. From Figures 4.19 and 4.21 it can be seen that the temperature above which annealing had any measurable effect on the subsequent deformation at 22°C was about 70°C. This was also the temp-
erature at which the onset of contraction in the c direction began, and it was also found that this effect was independent of annealing time (between 2-30 minutes), in agreement with that found by Rider (1965), and Siegmann and Geil (1970). The most significant feature in the deformation behaviour of annealed specimens was that specimens tested at 22°C deformed in simple shear (within experimental error), whereas specimens deformed at the annealing temperature (90°C and 105°C) showed a reorientation effect with $\theta = 0.03^\circ$. For an annealing temperature of 120°C, the specimens deformed at 22°C showed a 3.7% contraction in thickness, no other specimens showing such effect. This compares with the results of Yamada et al. (1971) on annealed high density polyethylene (126°C in silicon oil), where specimen thickness decreased by as much as 20% for tensile strains in the c direction of about 50%.

Effects of annealing oriented polyethylene specimens have been reported by various workers (see Hay and Keller (1967)), and it appears that in the course of annealing, the oriented chains would be expected to progressively rotate away from the c direction, consequently there would be a decrease in the degree of orientation which would affect the distribution function. Further consideration is, therefore, given in Chapter 6 to the morphology of annealed material, and a structural model is proposed, following discussion of experimental results, into the fibrillar nature of the material.
Figure 4.1: Micrographs of a specimen (a) before and (b) after deformation. The various measurements taken throughout the deformation are indicated (dot spacing = 0.2 mm).
Figure 4.2: A square deformed by simple shear.

Figure 4.3: Schematic diagram of a test specimen that has deformed by simple shear.
Figure 4.4: Micrograph of a specimen ($\lambda = 90^\circ$) which fractured after tensile testing.

Figure 4.5: A typical kink band formed in a specimen with $\lambda_o = 81^\circ$. 
Figure 4.6: Expansion of the kink band after further deformation.

Figure 4.7: Results from a specimen tested at 22°C, showing experimental values as circles, and the values according to equation (4.10) as the straight line.
Figure 4.8: Typical variation of $\delta$ with extension ratio, for a specimen tested at 22°C.

Figure 4.9: Comparison between the predictions of the shear re-orientation model with $\theta = 0.01^\circ$ and $0.003^\circ$ (continuous curves), and experimental values of grid parameters $a/a_0$ and $h/h_0$ against shear strain, for various specimens.
Table 4.1: Variation of grid area ratio, obtained from a specimen ($\lambda = 61^\circ$) deformed up to a shear strain of about 2.4 at 22°C.

<table>
<thead>
<tr>
<th>$a/a_0$</th>
<th>$h/h_0$</th>
<th>$(a/a_0 \times h/h_0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>0.993</td>
<td>1.000</td>
<td>0.993</td>
</tr>
<tr>
<td>0.984</td>
<td>1.001</td>
<td>0.984</td>
</tr>
<tr>
<td>0.986</td>
<td>1.004</td>
<td>0.986</td>
</tr>
<tr>
<td>0.989</td>
<td>1.014</td>
<td>1.002</td>
</tr>
<tr>
<td>0.996</td>
<td>1.014</td>
<td>0.996</td>
</tr>
<tr>
<td>0.980</td>
<td>1.028</td>
<td>1.007</td>
</tr>
<tr>
<td>0.993</td>
<td>1.030</td>
<td>0.993</td>
</tr>
</tbody>
</table>

Figure 4.10: Micrograph of a specimen ($\lambda = 0^\circ$) which fractured after tensile testing.
Figure 4.11: Typical variation of the grid parameter $h/h_o$, with shear strain at 50°C.

Figure 4.12: Comparison between the predictions of the shear re-orientation model with $\theta = 0.03^\circ$ and the experimental values of $h/h_o$, against shear strain for various specimens. The test temperature is shown.
Figure 4.13: Micrograph illustrating the fibrous texture that was observed along the edge of a specimen ($\lambda_0 = 32^\circ$) tested at 105°C.

Figure 4.14: A slip-off fracture edge of a specimen ($\lambda_0 = 32^\circ$) deformed at 105°C.
Figure 4.15: Typical variation of $\delta$ with extension ratio. The test temperature is shown.

Figure 4.16: Results from various specimens showing how $h/h_0$ varies with shear strain. The shear re-orientation model, with $\theta = 0.03^\circ$, is compared with data from specimens exhibiting normal behaviour, in contrast to those specimens ($\lambda_0 = 62^\circ$ and $46^\circ$) that exhibited anomalous behaviour.
<table>
<thead>
<tr>
<th>$a/a_0$</th>
<th>$h/h_0$</th>
<th>$(a/a_0 \times h/h_0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>0.997</td>
<td>1.004</td>
<td>1.000</td>
</tr>
<tr>
<td>0.995</td>
<td>1.007</td>
<td>1.001</td>
</tr>
<tr>
<td>0.992</td>
<td>1.013</td>
<td>1.004</td>
</tr>
<tr>
<td>0.988</td>
<td>1.017</td>
<td>1.004</td>
</tr>
<tr>
<td>0.978</td>
<td>1.015</td>
<td>0.992</td>
</tr>
<tr>
<td>0.974</td>
<td>1.033</td>
<td>1.006</td>
</tr>
<tr>
<td>0.967</td>
<td>1.027</td>
<td>0.993</td>
</tr>
<tr>
<td>0.952</td>
<td>1.079</td>
<td>1.027</td>
</tr>
<tr>
<td>0.930</td>
<td>1.082</td>
<td>1.006</td>
</tr>
<tr>
<td>0.915</td>
<td>1.120</td>
<td>1.024</td>
</tr>
</tbody>
</table>

Table 4.2: Variation of grid area ratio, obtained from a specimen ($\lambda = 67^\circ$) deformed up to a shear strain of about 2, at 90°C.

Figure 4.17: A slip-off fracture in a specimen ($\lambda = 71^\circ$) tested at -10°C.
Table 4.3: Changes in specimen dimensions due to annealing.

<table>
<thead>
<tr>
<th>Annealing Temp, °C</th>
<th>% Contraction in c direction</th>
<th>% Increase in thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>14.0</td>
<td>10</td>
</tr>
<tr>
<td>105</td>
<td>9.5</td>
<td>6</td>
</tr>
<tr>
<td>90</td>
<td>5.5</td>
<td>2</td>
</tr>
<tr>
<td>70</td>
<td>3.5</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 4.18: Results from a specimen, showing experimental values as triangles, and values according to equation (4.10) as the straight line. The test temperature is shown.
Figure 4.19: Variation of $h/h_0$ with shear strain for various annealed specimens deformed at 22°C.
Figure 4.20: Micrograph of an annealed specimen exhibiting localised slip, during a tensile test.

Figure 4.21: Variation of $h/h_o$ with shear strain for specimens annealed at $50^\circ C$ and $70^\circ C$, and then tested at $22^\circ C$. 
Figure 4.22: Diagram of the strain ellipse sheared into a new ellipse, with angle $\theta$ between the major axes.

<table>
<thead>
<tr>
<th>$a'/b'$</th>
<th>4</th>
<th>8</th>
<th>15</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta$</td>
<td>0.03°</td>
<td>0.01°</td>
<td>0.003°</td>
<td>0.0006°</td>
</tr>
</tbody>
</table>

Table 4.4: Calculated values of the re-orientation angle, $\theta$, for various strain ratios, after a shear of 1%.
5.1 Introduction

A primary problem in polymers is deciding what is meant by yield point. It is well known that for many polymers tested in tension, the load-extension curve shows a sharp fall in load after a certain strain. This initial fall in load is generally associated with the formation of a neck in the specimen, which often develops from a deformation band. Yield is, therefore, conveniently defined as the point at which maximum load is observed. In compression tests, or tensile tests at elevated temperatures, a load drop does not often occur, and the yield point is then defined as the point of intersection of two tangent lines on the load-extension curve, as shown in Figure 5.1. However, the nominal stress-strain curve, equivalent to the load extension curve, gives a rather distorted view of the properties of a ductile polymer, because of changes in the cross-sectional area of the specimen, particularly at large strains. The change in area can, therefore, be accounted for by plotting true stress-strain curves. If there is a fall in true stress, then this might be of some significance. Work by Brown and Ward (1968) on the load drop at the upper yield point of polyethylene terephthalate (isotropic and oriented) tested in tension, compression, and shear, found in most cases a drop in true stress at yield. Consequently, they interpreted the yield point as having an intrinsic importance, and suggested that possibly the yield drop could be interpreted in terms of a molecular flow process. Although a deformation band, which
indicates that considerable plastic deformation has taken place, is often responsible for a load drop, it does not always necessarily form at maximum load. Studies on oriented polyethylene terephthalate by Parrish and Brown (1970), found that depending on the initial orientation angle of the specimen, yielding at maximum load was the result of a diffuse thinning of the specimen in a region where the deformation band finally formed. Great care has, therefore, to be taken before trying to associate any particular phenomenon with a yield point.

In the previous two chapters, the approximately simple shear mode of deformation for oriented polyethylene was analysed in terms of resolved shear stress and normal stress after load maxima. From Figure 4.9 it is certainly apparent that deformation is approximately simple shear at very low strains (also see Darlington and Saunders (1970)), thus a correlation between the yield stress data and shear strain data could possibly indicate a molecular flow process at load maxima in terms of the onset of plastic deformation. It is, therefore, intended in this chapter to report an investigation into (a) the significance of load maxima in terms of both stress and strain, and (b) an analysis of the deformation regions before and after load maxima, paying special attention to the elastic region, i.e. recovery behaviour, of specimens. Finally, when considering stresses in a viscoelastic polymer such as polyethylene, strain rate effects are undoubtedly evident (see Kumar (1969) and Alfrey (1965)). It is not, however, intended to investigate such effects in detail, but only to make an allowance for the differences in shear strain rate between different specimens tested at the same crosshead speed, as suggested in section 3.5.4.
5.2  Experimental

All specimens were tested in the E-type Tensometer at a cross-head speed of 0.67 mm min\(^{-1}\). The majority of tests were carried out at 22°C, although a few were performed at elevated temperatures. The initial orientation angle (\(\lambda_0\)) for specimens was varied between 0° and 90°. Photographs were taken of the specimen during deformation and the event indicated on the load-extension curve. By knowing the ratio of chart paper to crosshead speed, the time at which each photograph was taken with respect to the onset of deformation could then be deduced, and hence the shear strain rate calculated.

All parameters used have been defined in previous chapters.

5.3  Results

5.3.1  Maximum Load Point

For most specimens tested at room temperature, the load-extension curve showed the familiar initial rise in load which was subsequently followed by a load drop. Specimens with \(\lambda_0\) values of 0° showed no load drop before fracture, and similarly for specimens with \(\lambda_0 = 90°\), although in this case there was a tendency for the load to level out before fracture occurred. In Figure 5.2 various load-extension curves are shown for specimens within the angular range of testing, noting that all the various axes are not to the same scale. If, however, true stress is considered, then depending on the value of \(\lambda_0\), a fall in true stress after maximum load point was not always evident. In Figure 5.3 the true tensile stress at load maxima, referred to as yield stress (\(\sigma_y\)), is plotted against
orientation angle at yield ($\lambda_y$). This presentation was similar to that used in Chapter 3 when describing post yield stress conditions in the form of a master curve. It was found that for specimens tested with $\lambda_o$ values less than $55^\circ$ there was no drop in true tensile stress after load maxima, whereas specimens with greater values of $\lambda_o$, showed a load drop. For example, a specimen with $\lambda_o = 67^\circ$ yielded at $\lambda_y = 59.5^\circ$, and a drop in true tensile stress subsequently followed. The paths taken by two typical specimens are indicated in Figure 5.3 by the broken lines, and the continuous line is a fit to the yield stress data using the Coulomb criterion, which was discussed in Chapter 3. The parameters $k$ and $\sigma_c$ had values of 0.08 and 6.4 N mm$^{-2}$ compared with those of 0.2 and 5.5 N mm$^{-2}$ respectively, found by Hinton and Rider (1968). The values of $k$ and $\sigma_c$ are, however, considerably lower than the values found for post yield deformation, reported in Chapter 3. It can also be seen from Figure 5.3 that the data from specimens with $\lambda_o = 90^\circ$ does not fit well to the Coulomb criterion. This is perhaps not surprising since the yielding process was unlike that of most specimens tested, since fracture rather than simple shear in the c direction occurred at load maxima. Also, for specimens with $\lambda_o = 0^\circ$ the deformation was not simple shear but of uniform extension in the c direction, and although no load drop existed, the yield point was determined as shown in Figure 5.1, and a value of 150 N mm$^{-2}$ was obtained for the yield stress (not shown in Figure 5.3).

If a molecular flow process at load maxima is envisaged for most specimens, then measurement of shear strain could possibly reveal a critical shear strain criterion for yield. The shear strain to yield, $\gamma_y$, is plotted in Figure 5.4 for various values of $\lambda_y$ and
test temperatures, and it can be seen that there is a marked
dependence in $\gamma_y$ upon $\lambda_y$. Thus, for specimens with $\lambda_o$ values
of $0^\circ$ and $90^\circ$ in which the mode of deformation is not simple shear,
as discussed in section 4.4.1, $\gamma_y = 0$. For all specimens in which
kink bands formed ($\lambda_o > 70^\circ$), the load-extension curve had a sharp
load peak (see Figure 5.2), consequently there was difficulty in
obtaining exact measurements of $\gamma_y$ because of the minimum time
between successive photographs (4 seconds). It was, however, found
that kink bands formed after load maxima, hence uniform measurements
of $\gamma_y$ were made without any interference from kink band formation.
For example, a specimen with $\lambda_o = 83^\circ$ tested at $22^\circ$C had a value of
$\gamma_y = 0.06$ when deformation was uniform (point A), whereas at point B
on the load-extension curve in Figure 5.2, a well defined kink band
was observed. It can also be seen from Figure 5.4 that temperatures
of up to $120^\circ$C had little effect in influencing the strain to yield.
This is consistent with the two definitions of yield mentioned in
section 5.1.

The yield point defined as load maxima is a convenient point on
the load-extension curve but as can be seen from Figure 5.4 is not a
criterion for the onset of molecular flow (in the case of oriented
polyethylene), since $\gamma_y$ is not independent of $\lambda_y$. Therefore, any
attempt to obtain a more satisfactory yield criterion requires a
detailed study of the deformation strains between 0 and $\gamma_y$.

5.3.2 Pre-Yield Stress-Strain Behaviour

The deformation behaviour at low strains for specimens tested at
$22^\circ$C was initially analysed using resolved shear stress and normal
stress. In Figure 5.5 the experimental data from three specimens
(\(\lambda_o = 55^\circ, 47^\circ,\) and \(36^\circ\)) illustrates the relationship between the resolved stresses. It was found that a transition in the resolved shear stress \((\sigma_s)\) occurred at a value of about 5.5 (± 0.2) N mm\(^{-2}\) in all specimens with \(\lambda_o\) values between \(26^\circ\) and \(67^\circ\) tested. Beyond this transition, deformation could be described in terms of the flow criterion used in Chapter 3, hence the characteristic straight lines of the form: \(\sigma_s = \sigma_c - k \sigma_n\), shown in Figure 5.5. The load maxima (yield point) when indicated on data plots such as illustrated in Figure 5.5, was found to be progressively closer to the transition point, as \(\lambda_o\) increased up to a value of \(67^\circ\), where they coincided. Alternatively, the transition point can be indicated on the load-extension curve as has been done in Figure 5.2 (see T), where it appears to be of no significance in its location, except that it progressively approaches the load maxima. If the transition point was of any significance in terms of a critical resolved shear stress for the onset of yield, and since deformation is principally the same for all specimens (simple shear), it would be expected that at the transition point, shear strain would be the same for all specimens. In Figure 5.6, variation of shear stress \((\sigma_s)\) with shear strain for the three specimens up to their transition points, shows that deformation is approximately independent of \(\lambda_o\), and that the shear strain values at the transition points are approximately the same.

Assuming that the shear strain rate \((\dot{\gamma})\) is the same for all three specimens, a fit to the data in Figure 5.6 using a simple empirical relationship of the form:

\[
\dot{\gamma} = a \sigma_s^b
\]  

(5.1)

was made, where \(a\) and \(b\) are fitting parameters. The continuous
curve in Figure 5.6 is a least squares fit to the data using equation (5.1) where \( a = 4.8 \) and \( b = 5.6 \). If deformation is simple shear at low strains, it follows from equation (4.10) that:

\[
\gamma = \cot \lambda - \cot \lambda_0
\]  

(5.2)

In order to relate this shear behaviour to the data in Figure 5.5 of \( \sigma_s \) against \( \sigma_n \), \( \gamma \) can be eliminated using equations (5.1) and (5.2), and the dependence of \( \sigma_n \) with \( \lambda \) obtained from equation (3.13) which is:

\[
\frac{\sigma_s}{\sigma_n} = \cot \lambda
\]  

(5.3)

Therefore, combining equations (5.1), (5.2), and (5.3) a relationship between \( \sigma_s \) and \( \sigma_n \) of the form:

\[
\sigma_n = \frac{\sigma_s}{a \sigma_s + \cot \lambda_0}
\]  

(5.4)

is obtained. Equation (5.4) therefore relates the dependence of \( \sigma_s \) and \( \sigma_n \) on \( \lambda_0 \). In determining the two fitting parameters, \( a \) and \( b \), only data up to the transition point was used as mentioned above, and the same values of \( a \) and \( b \) in equation (5.4) give rise to the three broken curves in Figure 5.5, and agree very well with the data up to the transition point.

5.3.3 Strain Rate Effects

In considering the relationship between shear stress and shear strain it is to be expected that the stress will depend to some extent upon strain rate. McLellan (1969) developed an expression similar to
that of equation (5.1) in order to predict the effects of strain rate on the stress-strain behaviour of certain metals and composites. A simple strain rate sensitive elastic component was added to a plastic component similar in form to equation (5.1), where parameter \(a\) was strain rate sensitive, and \(b\) a shape factor invariant with strain rate. McLellan (1969) showed that for an order of magnitude increase in strain rate, a 30% decrease in the \(a\) parameter for epoxy resins occurred.

From the tensile testing conditions in which the crosshead speed is constant, it is to be expected that there would be a change in shear strain rate due to the rotation of the shear direction during the test. Assuming the deformation is simple shear, one can combine equations (5.2) and (4.5), after differentiating with respect to time. Hence, the shear strain rate is:

\[
\dot{\gamma} = \frac{1}{\lambda_o \sin\lambda_o \cos\lambda} \frac{d\lambda}{dt}
\]  

(5.5)

where \(\frac{1}{\lambda_o} \frac{d\lambda}{dt}\), the extension rate, would be expected to be constant and equal in value to the crosshead strain rate. It can be seen from equation (5.5) that the initial value of \(\dot{\gamma}\) would be:

\[
\dot{\gamma}_o = \frac{2}{\lambda_o \sin2\lambda_o} \frac{d\lambda}{dt}
\]  

(5.6)

Hence, the initial shear strain rate \((\dot{\gamma}_o)\) is a function of \(\lambda_o\). Values of initial shear strain rate were obtained from measurements of shear strain and time from various specimens, and in Figure 5.7(a) the strain/time data shows that for shear strains of up to 0.4, \(\frac{d\dot{\gamma}}{dt} (\dot{\gamma}_o)\) is constant. This was also found in other specimens tested,
and in Table 5.1 the measured values of $\dot{\gamma}_0$ are listed. In the second two columns of Table 5.1 the measured and calculated (using equation (5.6)) ratios of initial shear strain rates with respect to the 55° specimen are compared, and it can be seen that there is good agreement. It is, therefore, apparent that there is little difference in the initial shear strain rate values for specimens with $\lambda_0$ values of 55°, 47°, and 36°, thus satisfying the condition for one value of $\alpha$ in equation (5.1) when fitted to the data in Figure 5.6.

On further inspection of equation (5.5) it can, however, be seen that for large strains, $\dot{\gamma}$ would be expected to decrease, since $\lambda$ would decrease considerably on testing. However, experimentally it is found that $\dot{\gamma}$ increases throughout the test, as can be seen in Figure 5.7(b). Thus, after a shear strain of about 2.3 for a specimen with $\lambda_0 = 47°$, $\dot{\gamma}$ had increased by a factor of about 2.5. A similar increase in shear strain rate was found for all specimens tested, and in most cases $\dot{\gamma}$ had increased by a factor of about 2 during the normal range of deformation studied. Although the cross-head speed is constant, $\frac{d\dot{\gamma}}{dt}$ in fact increases, consequently $\dot{\gamma}$ increases. This can only occur if the region deforming becomes relatively smaller, which could possibly be due to the constraining influence of the neck of the specimen.

5.3.4 Recovery Behaviour

If the critical shear stress transition point was of any significance, an investigation into the low strain region before transition in terms of elastic recovery behaviour, could possibly define a yield point in terms of the limit of elasticity. A series of cyclic tests on specimens in tension, with various values of $\lambda_0$ were therefore
performed at room temperature. Specimens were deformed by a certain amount of shear strain, after which the load was removed for an arbitrary time of 10 minutes, thus allowing the specimen to recover. The specimen was then deformed by a further increment of shear strain, and the same procedure as above repeated. In Figure 5.8 the path taken by a typical specimen with $\lambda_0 = 59.5^\circ$, during a series of such cyclic tests is illustrated. The measurements taken with specimen under load are indicated by circles, and when relaxed, (load removed) by triangles. Experimental data was represented in the way shown in Figure 5.8, because the path taken by a specimen that had undergone non-cyclic loading would have been approximately along the continuous line for simple shear, as shown in Figure 4.7. Because of the relatively large error involved in dot measurements at such low strains, it is therefore thought that the difference in deformation behaviour between the two types of test is not very significant. Although it was impossible to determine the actual path taken by the specimen during its recovery, it was possible to measure the recovered shear strain, and in the case of specimens deformed up to shear strains of 0.3, the maximum shear strain recovered was of the order of 0.04. From the data in Figure 5.8, it can also be seen that the elastic limit of reversibility occurs at a shear strain of about 0.03 ($\pm 0.01$).

It is realised that when the applied stress is removed from specimens, there is an instantaneous recovery, followed by a delayed elastic recovery (c.f. creep experiments). If there is any permanent set in the specimen, it could possibly be attributed to plastic flow. If, however, the time required for the delayed elasticity to decrease to zero is long, then difficulty arises in
differentiating between permanent set and delayed elasticity. For highly crystalline polyethylene (86%) used in this project, a long delayed elastic component would not be expected because of the small amorphous content, consequently it was assumed that 10 minutes (3 x test time for data in Figure 5.8), would most probably be sufficient time for complete recovery to occur. However, to ensure that 10 minutes was adequate time, a specimen ($\lambda_0 = 55^\circ$) was deformed up to a shear strain of 0.11, and the load removed. Shear strain measurements were then taken from the specimen at various time intervals of up to 500 hours. It was found that the shear strain had recovered by 0.025 after 10 minutes, and only 0.03 after 500 hours, confirming that within experimental error, 10 minutes was sufficient time to allow for recovery.

5.3.5 Post-Transition Point Stress-Strain Behaviour

It can be seen from Figure 5.5 that after the critical shear stress transition point, there is considerable deviation between data and equation (5.4), which predicts the shear stress and normal stress behaviour. However, the parameters a and b were obtained from a least squares fit of equation (5.1) to data up to the transition point. A fit was, therefore, made to the stress-strain data after transition, and in Figure 5.5, equation (5.4) is plotted (broken curves marked a) with the appropriate values of a (4.8) and b (5.6). It can be seen that there is better agreement between experimental data and theory, the behaviour of which was initially accounted for in terms of a flow criterion.

The question which now arises is that if the shear stress behaviour after the transition point is dependent upon the normal stress,
in the form expressed in equation (3.8) which is:

\[ \sigma_s = \sigma_c - k \sigma_n \]  \hspace{1cm} (5.7)

then how would this influence the stress-strain behaviour? By combining equations (5.2), (5.3), and (5.7) in order to eliminate \( \sigma_n \), one obtains the expression:

\[ \sigma_s = \frac{\sigma_c}{1 + \frac{k}{\cot \lambda_0 + \gamma}} \]  \hspace{1cm} (5.8)

Equation (5.8) therefore expresses the relationship between resolved shear stress and shear strain, assuming simple shear, and also assuming that the flow criterion is obeyed. Resolved shear stress-shear strain data after load maxima was, in fact, illustrated in Figure 3.8 where it was shown that for various specimens, the value of \( \lambda_0 \) had little effect in influencing such behaviour. This data is again shown in Figure 5.9, and it is compared with equation (5.8), which predicts an increase in \( \sigma_s \) for the two specimens with \( k \) values of 0.22 (\( \lambda_0 = 62^\circ \)) and 0.55 (\( \lambda_0 = 42.5^\circ \)). Thus, it can be seen from Figure 5.9 that there would be little difference in stress-strain data for different specimens if the flow criterion was obeyed.

In the early stages of deformation, equation (5.1) was used in order to obtain a fit to the stress-strain data, such that the shear stress, normal stress relationship could be predicted. A similar power law is discussed by Cottrell (1964) in order to describe strain hardening behaviour, where parameter \( b \) is inversely proportional to a strain hardening exponent. Superimposed on the data in Figure 5.9 is a least squares fit using equation (5.1), where \( a = 27.5 \) and \( b = 8.2 \) (continuous curve).
5.4 Discussion

The Coulomb yield criterion was satisfactorily fitted to the tensile stress data. However, it is apparent from the shear stress and shear strain data that maximum load has no intrinsic significance in terms of onset of plastic deformation in the form of simple shear. What is therefore the significance of maximum load for oriented polyethylene specimens? For specimens with large values of $\lambda_0$, maximum load point was well defined because specimens necked as a result of kinking, whereas specimens with lower values of $\lambda_0$ produced a rather ill defined maximum load point, beyond which there was only a gradual fall off in load as the specimen deformed relatively uniformly throughout its entire length. Thus, load maxima is probably influenced in some way by the physical necking of the specimen, which is attributed to its geometry. In Figure 5.10 the micrographs of two specimens ($\lambda_0 = 56^\circ$ and $83^\circ$) illustrates clearly the physical differences between the two types of neck. A fall in load after load maxima was explained by Vincent (1960) in terms of geometrical softening, which was due to the fact that a fall in cross-sectional area during stretching was not compensated by an adequate degree of strain hardening. If, however, there was a fall in true stress after load maxima, rather than just a fall in load, load maxima might be of some significance. As shown in Figure 5.3, a fall in true stress did occur for specimens with large angles, and this was also where the transition point occurred. However, for most specimens tested, a fall in true stress did not occur, contrary to that found by Brown and Ward (1968). Also, if deformation bands had formed at load maxima for all specimens, this might have been another factor to indicate that possibly load maxima was of some significance.
in terms of a molecular process, but this was not the case. It is, therefore, most likely that the geometry of the neck has affected the position of load maxima.

If specimen deformation is relatively independent of $\lambda_0$, then from the stress-strain data it is apparent that a critical shear stress criterion at the transition point is equivalent to a critical shear strain criterion, where the shear strain is of the order of 0.2 (± 0.03). This value is, of course, more acceptable in terms of the onset of plastic deformation, compared with a value of 0.9 at maximum load for a specimen with $\lambda_0 = 36^\circ$. Difficulty, however, arises in deciding whether or not the transition point is, in fact fortuitous, or has some intrinsic importance. The transition point certainly cannot be considered in terms of the elastic limit, since this occurred at a shear strain of about 0.03 (1.3% tensile strain, $\lambda_0 = 60^\circ$), and as can be seen from Figure 5.6, considerable simple shear had occurred between the elastic limit and the transition point. Accurate values of the elastic limit were difficult to determine because of the relatively large error of measurement at such low strains, consequently it was also impossible to analyse the deformation within the elastic region.

Darlington and Saunders (1970) made a detailed study into creep behaviour of oriented low density polyethylene at low strains in which deformation was dominated by a slip process, and reported that for tensile strains of up to at least 2%, specimens recovered by 98%. This value is comparable with that found in this work (1.3%), although for high density polyethylene, tensile recovery values might be expected to be even less than those for low density polyethylene, because of the smaller amorphous content. This is, of course, assuming that most of the recovery
behaviour is attributed to the relaxing of the constrained amorphous material between crystalline regions (see Zhurkov et al. (1965)). In the case of a two phase model postulated for high density polyethylene by Yamada et al. (1971), recoverability was attributed to the fact that there was sufficient energy in the amorphous region due to straining, to cause recovery of the crystalline regions. This indicated the presence of tie molecules in the amorphous regions, which is discussed further in Chapter 6.

If the normal stress component is considered in terms of its influence upon the resolved shear stress, then it must be emphasised that owing to the geometry of the resolved stresses, \( \sigma_s \) and \( \sigma_n \) are not independent of each other but related by equation (5.3). Consequently, it was shown in section 5.3.5 that if strain hardening was the only factor to cause an increase in \( \sigma_s \), and the resolved shear stress, shear strain data was unaffected by \( \sigma_n \), a variation of \( \sigma_s \) with \( \sigma_n \) could be predicted such that the trend after yield was similar to that found in Chapter 3, where the behaviour was analysed in terms of a flow criterion. It was conversely shown that by assuming the post yield stress behaviour could be described in terms of a flow criterion, the predicted shear stress, shear strain behaviour was similar to that expected of a material that underwent strain hardening. The problem is, therefore, to differentiate between the two effects. It certainly does appear that due to the geometrical conditions of the resolved stresses, analysis of the data presented on a \((\sigma_s, \sigma_n)\) plot can be rather ambiguous. This would also cast doubt on the significance of the critical shear stress transition point, since a turning point is also predicted by equation (5.4).
Figure 5.1: A typical load-extension curve obtained from a specimen tested at an elevated temperature, showing how yield point is determined when there is no load drop.
Figure 5.2: Load-extension curves obtained from various specimens tested at 22°C.
Figure 5.3: Variation of tensile yield stress with orientation angle at yield. The continuous curve is a plot of equation (3.11) with $k = 0.08$ and $\sigma_c = 6.4 \text{ N mm}^{-2}$.

Figure 5.4: Variation of shear strain at yield with orientation angle at yield, for various test temperatures. The broken curve indicates the general trend.
Figure 5.5: Variation of normal stress with shear stress for three specimens. The broken curves are plots of equation (5.4).
Figure 5.6: Typical pre-transition point shear stress-shear strain behaviour for three specimens. The continuous curve is a fit to the data using equation (5.1) where $a = 4.8$ and $b = 5.6$. 
Figure 5.7: Variation of shear strain with time for (a) small strain and (b) large strain specimen deformation. The broken curves indicate the general trend.
Table 5.1: Measured and calculated (using equation (5.6)) initial shear rates for various specimens.

<table>
<thead>
<tr>
<th>degrees</th>
<th>(sec)^{-1}</th>
<th>measured</th>
<th>calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>0.0019</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>47</td>
<td>0.0017</td>
<td>0.89</td>
<td>0.94</td>
</tr>
<tr>
<td>36</td>
<td>0.0020</td>
<td>1.05</td>
<td>0.99</td>
</tr>
<tr>
<td>26</td>
<td>0.0023</td>
<td>1.21</td>
<td>1.19</td>
</tr>
</tbody>
</table>

Figure 5.8: Cyclic loading and unloading of a specimen. The continuous line is a plot of equation (5.2), and the broken lines indicate the general path taken during loading.
Figure 5.9: Variation of shear stress with shear strain after yield. The continuous curve is a fit using equation (5.1) \((a = 27.5 \text{ and } b = 8.2)\) and the broken curves, plots of equation (5.8).
Figure 5.10: Micrographs of two specimens with (a) $\lambda = 56^\circ$ and (b) $\lambda = 83^\circ$, illustrating the difference between the types of neck formed in specimens tested (dot spacing = 0.2 mm).
CHAPTER 6

A Correlation between the Macroscopic and Structural Changes that occur in Oriented Polyethylene During Deformation

6.1 Introduction

When polyethylene is cold drawn, changes occur in the crystalline structure that subsequently influence the mode of deformation during redrawing. A study of the morphology of oriented polyethylene is therefore useful in order to understand the macroscopic deformation behaviour.

6.1.1 X-Ray Diffraction

In oriented polyethylene, the c axis of the unit cell is parallel to the draw direction whilst the other two crystal axes, a and b, are randomly oriented normal to the direction of draw (see Aggarwal et al. (1961)). Consequently, oriented polyethylene has cylindrical symmetry about the draw direction. When X-rays are passed through a specimen, reflections take place at various crystallographic \{h k l\} planes, that are inclined at different angles ($\theta_b$) with respect to the incident beam. The X-rays subsequently leave the specimen at angles of $2\theta_b$ to the incident beam, where $\theta_b$ satisfies the Bragg equation. In Figure 6.1 a typical wide angle X-ray diffraction pattern obtained from oriented polyethylene is shown, where the strongest reflections situated along the equator of the pattern are from (110) and (200) planes. Because polyethylene has an orthohombic unit cell, lines normal to either (110) or (200) planes are at right
angles to the [001] direction, i.e. c axis. Perfect alignment between the c axis of all unit cells and the draw direction is, however, not possible, consequently there is a small angular distribution in c axes about the draw direction which results in a finite size of the (110) and (200) reflections, as shown in Figure 6.1. The mean c axis is therefore taken to be perpendicular to the line joining the two (110) reflection peaks, and is referred to as the c direction.

In Figure 6.2 a photograph of a typical low angle diffraction pattern obtained from oriented polyethylene at room temperature, shows two discrete reflections normal to the meridian of the pattern (c direction), and one diffuse streak along the equator. The distance between the discrete reflections is interpreted as being due to a periodic spacing associated with a regular arrangement of crystalline and amorphous regions along the draw direction, whilst the diffuse streak is generally associated with microvoids that have formed during the cold drawing of polyethylene (see Alexander (1969)). The lateral extent of the streak is interpreted as being inversely proportional to the width of the scattering structure (void) which has its longest dimension in the draw direction (meridian), as shown schematically in Figure 6.3. The theoretical basis for the method used in analysing the diffuse streak was developed by Guinier (1952), and has since been used successfully in studying voids in fibres (see Alexander (1969)). It is shown by Guinier (1952) that the intensity distribution (I) of the diffuse reflection along the x axis (see Figure 6.3) is given by the following exponential relationship:

\[ I \propto \exp \left( -\frac{4\pi^2 b^2 \epsilon^2}{x} \right) \]  

(6.1)
where $\lambda$ is the wavelength of X-rays used (1.54 Å), $\epsilon$ the angle the X-rays are scattered through, and $b_x$ the semi-minor axis of the void. A plot of $\ln I$ against $\epsilon^2$ subsequently gives a straight line, from which the value of $b_x$ can be calculated. There is also a similar expression for the intensity distribution along the $y$ axis, from which $a_y$ (semi-major axis) can be calculated.

6.1.2 Structural Model

The model adopted for oriented polyethylene is similar to the one described in detail by Peterlin (1971), where the basic element is the long ($> 10 \mu$m) and thin ($100 \sim 200 \AA$) microfibril. In Figure 6.4 a schematic diagram of the model shows the microfibrils extending in the direction of draw, each one being composed of oriented folded chain crystal blocks (lamellae) connected in the $c$ direction by many extended tie molecules. It is the regular crystal block spacing, referred to as the long period ($L$), that gives rise to the discrete reflections on the low angle diffraction pattern. In Figure 6.4 all lamella surfaces are shown to be at right angles to the $c$ direction, however it is most likely that there is, in fact, a distribution in orientation of lamella surfaces about the $c$ direction, as shown in Figure 6.5, thus giving rise to a spread in the low angle reflections (see Corneliussen and Peterlin (1967)). All microfibrils are assumed to be interconnected by some interfibrillar tie molecules, and it is the space between the microfibrils that is associated with microvoids. The strength of the polymer in the draw direction is, therefore, dependent upon the microfibril, whereas in the transverse direction it is primarily dependent upon the interfibrillar tie molecules.
6.1.3 Shear Deformation Modes

There was sufficient evidence in the previous chapters to indicate that the macroscopic deformation of oriented polyethylene was slip in the c direction. Consequently, when a structure such as the one illustrated in Figure 6.4 is sheared in the c direction, two modes of slip are possible. The first is intracrystalline or chain slip, in which the oriented chains within each lamella slide past one another. This process results in the lamella normal \( n^\perp \) rotating away from the c direction such that the angle between the c direction and the newly formed lamella normal is the same as the shear angle, \( \omega \), as illustrated in Figure 6.6(a).

The other possible mode of slip is fibrillar slip, and this occurs when the microfibrils slide over each other, as shown in Figure 6.6(b), but in this case the lamella normal and c direction remain parallel during deformation. Thus, when macroscopic shear occurs in oriented polyethylene it could be due to either intracrystalline slip \( \gamma_c \), or fibrillar slip \( \gamma_F \), or both. In the case of the latter occurring, the total observed macroscopic shear strain \( \gamma \) would therefore be:

\[
\gamma = \gamma_c + \gamma_F = \cot \lambda_c - \cot \lambda_o
\]  

(6.2)

assuming simple shear.

In Figure 6.7 the two modes of deformation are illustrated, together with the appropriate changes that occur in wide and low angle patterns. The angle between the lamella normal and specimen edge is represented by \( \lambda_n \) in Figure 6.7, thus the intracrystalline shear
strain \( (\gamma_c) \) is defined as follows:

\[
\gamma_c = \tan(\lambda_n - \lambda_c)
\]  

(6.3)

6.1.4 Orientation

In a two-phase model that consists of crystalline and amorphous regions such as the one adopted, no single measurement is adequate in describing the alignment of all molecular chains within the oriented polymer. From X-ray diffraction data, only information about the crystalline (ordered) regions can be obtained. For example, in the wide angle diffraction patterns, the short reflection arcs from the (110) and (200) planes give some indication of the distribution of molecular chain axes about the c direction. Various people such as Kasai and Kakudo (1964) have, in fact, measured the azimuthal width at half maximum intensity \( (\psi) \) of the (110) reflections in order to give an indication of the degree of orientation of oriented polyethylene. However, if a careful study of c axis orientation is required, then measurement of the (002) distribution is necessary because of a possible ambiguity in interpreting the (002) distribution directly from the (110) distribution. Low angle X-ray diffraction patterns reveal the orientation of the ordered lamellae regions, thus by knowing the angular spread of the low angle reflections, it is possible to estimate the orientation of lamella surfaces (see Figure 6.5).

In contrast to X-ray diffraction, birefringence depends upon orientation of both crystalline and amorphous regions. Stein and Norris (1956) expressed the total birefringence of oriented polyethylene in terms of crystalline, amorphous, and form birefringence. By using X-ray and birefringence data, Stein and Norris (1956) then calculated
the birefringence of the amorphous fraction. X-ray and birefringence measurements are therefore required when studying orientation changes in a two-phase material. Other techniques can also be used for detecting orientation changes, and these are described in a review by Statton (1967).

6.1.5 Irradiation

In order to carry out further investigations into the two modes of deformation postulated, it was thought that crosslinking the molecular chains might possibly inhibit one of the modes of slip (intracrystalline). Thus, polyethylene was irradiated by γ-rays at relatively low doses. When polyethylene is irradiated in a vacuum, various effects are noticeable (see Charlesby (1960)), the main ones being: (a) the evolution of hydrogen, (b) the formation of c-c bonds between molecules (crosslinking), and (c) the destruction of crystallinity at high doses. For a certain dose of radiation, a transition point is reached at which the polyethylene becomes partly insoluble due to the formation of a three-dimensional network. This transition point, known as the gel point, corresponds to one crosslinked unit per weight average molecule. The radiation dose at gel point depends upon factors such as molecular weight of the polymer, and it was calculated to be about 6 M.rads from experimental data obtained by Dr. Fydelor (Royal Military College of Science) on high density polyethylene. Investigations into the location of crosslinks prior to and after gel point were performed in detail by Kawai et al. (1965) on both bulk and single crystals of high density polyethylene. The findings were: before gel point, solubility was probably associated with 'ineffective' crosslinks that formed intra-molecularly, whilst the insolubility after
gel point was attributed to 'effective' crosslinks that formed between different molecules. Consequently, Kawai et al. (1965) concluded that the 'ineffective' crosslinks most probably formed across the fold of a molecule, whereas the 'effective' crosslinks were between different lamellae.

6.2 Experimental

6.2.1 Procedure

The majority of specimens \( (\lambda_o = 60^\circ \sim 40^\circ) \) were tested at 22°C and 105°C, using the small tensile machine plus heating unit. All X-ray diffraction patterns were obtained from specimens at room temperature, consequently specimens deformed at 105°C were rapidly cooled down to room temperature. A check was made on the macroscopic dimensions and birefringence of specimens to ensure that no change had occurred due to this rapid cooling. Thus, in order to analyse the deformation behaviour of specimens at 105°C using X-rays, a number of specimens with identical values of \( \lambda_o \) were deformed up to various values of shear strain.

During deformation, the extinction direction with respect to the specimen edge was measured and this was assumed to coincide with the c direction. A check was necessary in order to verify this assumption, using the following procedure. With a specimen positioned in front of the collimator of the Unicam X-ray camera, one of the cross-wires of a telescope was rotated to be parallel to the measured extinction direction. A fine wire attached to the front of the film cassette was then rotated so that its direction was parallel to the crosswire. On passing X-rays through the specimen, a comparison between
the shadow cast onto the film by the wire (extinction direction) and the c direction was therefore made. For all stages of specimen deformation, extinction and c directions coincided to within 0.3°.

Using the normal flat film technique for wide angle diffraction, with the specimen (c direction) perpendicular to the incident X-ray beam, it is impossible to detect the (002) reflection, because the reciprocal lattice points that lie on the axis of rotation cannot intersect the sphere of reflection. Consequently, the (002) reflection was obtained by mounting the specimen with the c direction horizontal and perpendicular to the beam, and then rotating the c direction through the Bragg angle \( \theta_b \) (37.3°). The reflection was then detected on cylindrical film, as shown schematically in Figure 6.8.

A similar technique was applied when using a diffractometer in order to confirm the assumption made in section 6.1.1, which was that the (002) and (110) reflection maxima were perpendicular. A specimen was aligned in the goniometer with its c direction in the machine direction. The specimen was then tilted through the appropriate Bragg angle, and the counter placed at an angle of \( 2\theta_b \) with respect to the incident beam. Rotation of the specimen occurred about an axis normal to the specimen surface, subsequently the exact location of the reflection maxima with respect to the c direction (90°) could be determined from knowledge of the calibrated goniometer and chart recorder. It was found that maxima occurred at 90° for the (002) Bragg angle, and 0° and 180° for the (110) Bragg angle.
6.2.2 Measurements

The main angular measurement taken from the wide and low angle X-ray diffraction pattern was the angle between the lamella normal and c direction \((\lambda_n - \lambda_c)\), as shown in Figure 6.7. Error in determining \((\lambda_n - \lambda_c)\) was less than 2°. A number of other measurements were also taken, but these are discussed in the appropriate sections.

6.3 Results

6.3.1 Check on Fibre Symmetry

X-rays were initially passed through an undeformed specimen \((\lambda_o = 0^\circ)\) in three orthogonal directions: x, y, and z as shown in Figure 6.9. Wide angle diffraction patterns obtained from passing X-rays in the x and z directions were similar to the one in Figure 6.1, whilst in the y direction, the wide angle pattern confirmed that the (110) planes were randomly distributed about the c axis (see Figure 6.10(a)). In the x and z directions, low angle patterns were very similar to the one illustrated in Figure 6.2, where the long period \((L)\), calculated using Bragg's law, was about 175 À (± 5 À). There was, however, a difference in the lateral width of the discrete reflections, since in the low angle pattern obtained from X-rays in the z direction, the angle subtended by the extremities of the reflection \((2\alpha)\) at the centre of the diffraction pattern was 45°, whereas in the x direction, the angle was about 65°, indicating a larger lamella distribution about the c direction, in the (yz) plane. A low angle pattern obtained from X-rays in the y direction is shown in Figure 6.10(b) and clearly illustrates the strong diffuse streak, although there is no evidence for any discrete
reflections. Microdensitometer traces of the low angle reflections revealed a symmetrical intensity peak about the meridian, the direction of which was assumed to be parallel to the direction of the mean lamella normal.

X-rays were then passed through specimens that had been annealed at various temperatures, and it was found that as the temperature increased, the discrete reflections increased in intensity by 200% at 105°C, and the long period, revealed by X-rays in the z direction had increased up to 225 Å (± 5 Å). At 105°C and above there was no evidence of a diffuse streak as revealed by X-rays in the z direction, although at 90°C the streak was still evident. There was some indication of crystal disorientation at 105°C, since there was an increase in the lateral width of the low angle reflections, and also an increase in the azimuthal width (ψ) of the (110) reflections (see section 6.3.3). However, at 105°C and above, a four point pattern of the type shown in Figure 6.11 was revealed by X-rays in the x direction, and it can be seen that the diffuse streak is still present. The four point pattern has been interpreted by workers such as Hay and Keller (1967), and Cowking et al. (1968), in terms of lamellae tilt, where the angle α in Figure 6.11 represents the inclination of the lamellae normals with respect to the y axis. The lamella structure which gives rise to a four point pattern is shown schematically in Figure 6.12, where L_y is the long period in the y direction. The values of L_y, L, and α were determined from the four point pattern at 105°C, and found to be 226 Å, 173 Å, and 42.5° respectively. It can be seen that there is good agreement with the long period values from both four and two point patterns, indicating that the effect of annealing had
caused a rotation of the lamella surface. However, this lamella surface rotation did not significantly influence the c axis alignment since from wide angle patterns, the increase in \( \psi \) was comparable to that shown in Figure 6.20. Consequently, at 105°C a slight modification to the fibrillar model is needed, such that in the \((yz)\) plane of the microfibril there is discrete lamella tilt.

The main study is that of changes in orientation of lamellae whose surface normals lie in the \((xy)\) plane, consequently X-rays were passed in the \(z\) direction during specimen deformation.

### 6.3.2 Deformation

Macroscopic deformation of oriented polyethylene has been discussed in detail in Chapter 4, where it is apparent that the mode of deformation is approximately simple shear, and consequently obeys a simple relationship of the form expressed in equation (6.2). Changes in the crystalline structure of oriented polyethylene during shear can be analysed in terms of chain orientation, obtained from wide angle diffraction patterns, and lamella orientation obtained from low angle diffraction patterns. From these observations the deformation of lamellae can be inferred applying the simple fibrillar model shown in Figure 6.7. Figure 6.13 shows two typical low angle patterns obtained from specimens deformed at 22°C \((\lambda_0 = 31^\circ)\) and 105°C \((\lambda_0 = 40^\circ)\) up to shear strains of 1.8 and 1 respectively, from which the intracrystalline shear strains were measured. Macroscopic shear strain \((\gamma)\) was therefore compared with the intracrystalline shear strain \((\gamma_c)\), and in Figure 6.14 two plots of \(\gamma\) against \(\cot \lambda\) for two specimens \((\lambda_0 = 40^\circ \text{ and } 51^\circ)\) deformed at
$22^\circ C$, clearly illustrates the good fit between simple shear (continuous line) and macroscopic data. Superimposed on the two plots in Figure 6.14 are plots of intracrystalline shear strain against $\cot \lambda_c$, and it can be seen that after a shear strain of about 0.9, data associated with macroscopic and intracrystalline shear modes deviate. This deviation was, in fact, found to occur in all specimens tested ($29^\circ > \lambda_o > 68^\circ$) at a constant shear strain of about 0.9, indicating the importance of shear strain as a parameter in describing the deformation behaviour of all specimens.

Associated with this deviation was a gradual decrease in intensity of up to 50% in the low angle reflections, suggesting some form of crystal disorientation. However, at $105^\circ C$ results showed that from the onset of deformation there was deviation between macroscopic and intracrystalline shear strains, as shown in Figure 6.15. Limited data obtained from specimens deformed at $120^\circ C$ and $90^\circ C$ showed no significant difference from the $105^\circ C$ data, whereas data from specimens tested at $50^\circ C$ coincided with the $22^\circ C$ data.

In order to account for the deviation between macroscopic shear strain and intracrystalline shear strain, a second mode of shear in the c direction, referred to as fibrillar slip, is assumed to be occurring. Assuming the principle of superposition of shear strains, an approximate value for the fibrillar shear strain component ($\gamma_F$) can therefore be calculated using equation (6.2), thus:

$$\gamma_F = (\cot \lambda_c - \cot \lambda_o) - \gamma_c \quad (6.4)$$

Figure 6.16 shows a plot of calculated fibrillar shear strain ($\gamma_F$)
against observed intracrystalline shear strain ($\gamma_c$) at 22°C and 105°C for all $\lambda_o$ values, where it can be seen that the contribution of fibrillar shear and intracrystalline shear components are temperature sensitive. Also from Figure 6.16 it can be seen that the onset of fibrillar slip occurs at lower strains with increase in temperature, consequently at 105°C the 'coarser' mode of slip (fibrillar) is taking place at low strains. Evidence for this mechanism was discussed in section 4.5, where a fibrous texture along the edge of specimens tested at 105°C and above was highly predominant, and was attributed to possible scission of interfibrillar tie molecules. Slip-off fracture also occurred at relatively low strains in a few specimens tested at high and low temperatures (see Chapter 4), where primarily fibrillar slip and intracrystalline slip would be occurring respectively. Thus, scanning electron micrographs were obtained of the slip-off fracture surfaces, hoping that the surface texture would be representative of the deformation mechanisms at high and low temperatures. In Figure 6.17 there are two micrographs obtained from the fracture surface of a specimen deformed at -10°C ($\gamma_c = 0.6$, $\gamma_f = 0$), and a specimen deformed at 120°C ($\gamma_c = 0.75$, $\gamma_f = 0.5$), where the shear strain values were obtained at the onset of slip-off. In the case of the 120°C specimen, the fibrillar slip component has apparently been the over-riding factor in influencing the surface texture of the fracture surface which is highly fibrous, compared with the smooth fracture surface obtained from the low temperature specimen that had undergone only intracrystalline slip.

6.3.3 Orientation Changes

The (002) pole density distribution was initially considered in the undeformed oriented polyethylene, and in Figure 6.18 there is
a typical (002) reflection obtained on cylindrical film using the technique described in section 6.2.1. From the intensity distribution of the (002) reflection, the density of (002) plane normals, or number of poles per unit solid angle \( \frac{dN}{d\Omega} \), can be determined as a function of the inclination (\( \chi \)) of plane normals to the c direction, such that for perfect alignment all plane normals would be expected to be parallel to the c direction (\( \chi = 90^\circ \)). This symmetric distribution about the c direction is shown in Figure 6.19, from which the azimuthal width at half maximum intensity was measured and found to be about 6.8°, comparable with that found for the (110) reflections discussed below.

Modlen (1969) developed a simple model in order to calculate the distribution of fibre axes after a matrix, which contained fibres that were initially randomly oriented, had been deformed. It was shown by Modlen (1969) that the density of fibre axes \( \frac{dN}{d\Omega} \) was proportional to the cube of the length of the radius vector (r) from the origin to the surface of the strain ellipsoid, i.e.

\[
\frac{dN}{d\Omega} = \frac{r^3}{2\pi} \tag{6.5}
\]

It has been shown that this is, in fact, identical to the Kuhn and Grün (1942) affine model.

Using the same notation for axes as shown in Figures 6.9 and 6.3, the equation of a strain ellipsoid is:

\[
\frac{x^2}{b^2} + \frac{y^2}{a^2} + \frac{z^2}{c^2} = 1 \tag{6.6}
\]

where \( a \), \( b \), and \( c \) are the appropriate major and minor semi-axes of the ellipsoid. Considering only the \((xy)\) plane, and using
polar co-ordinates, it can be shown that for a strain ellipse with axes $a$ and $b$:

$$r^2 = \frac{b^2}{\cos^2\chi + \frac{\sin^2\chi}{a^2/b^2}}$$  \hspace{1cm} (6.7)

where

$$r = \frac{y}{\sin\chi} = \frac{x}{\cos\chi}.$$

It follows from equations (6.5) and (6.7) that:

$$\frac{dN}{d\theta} = \frac{b^3}{2\pi \left(\cos^2\chi + \frac{\sin^2\chi}{a^2/b^2}\right)^{3/2}}$$  \hspace{1cm} (6.8)

In Figure 6.19 the symmetric continuous curve plotted over half the angular range, is obtained from equation (6.8), where $a/b = 13$. This value is in fairly good agreement with that obtained using the affine strain ellipse model discussed in Chapter 4, where $a/b = 15$. It can be seen that there is good agreement between experimental data and theory for angles close to $90^\circ$, although for larger angles deviation occurs, which would be expected, since the distribution function used in the model assumes that there are always some fibre axes at right angles to the major axis ($\chi = 0^\circ$ and $180^\circ$). However, it must be emphasised that the measured distribution is only approximate, since errors may arise as a result of broadening of the (002) reflection due to instrumental causes and sample alignment.

The azimuthal width at half-maximum intensity ($\psi$) of the (110) reflections, was used to indicate the changes in the degree of orientation of the crystalline regions during subsequent deform-
ation, where a decrease in $\psi$ represents an increase in the degree of orientation. Changes in $\psi$ are plotted against macroscopic shear strain in Figure 6.20, obtained from two specimens ($\lambda_o = 60^\circ$) deformed at 22°C and 105°C, and two factors are evident: (a) the effect of increasing temperature from 22°C to 105°C was to cause an increase in $\psi$, and (b) the effect of shear deformation at both 22°C and 105°C was to cause a decrease in $\psi$, the rate of which was temperature dependent.

Assuming that the percentage change in $\psi$ of the (110) reflection is equal to the percentage change in the azimuthal width at half maximum intensity of the (002) reflection ($\psi^H$), the new value of the strain ratio parameter $a^H/b^H$ due to shear can be predicted using equation (6.8). If $\psi_o^H$ is the initial value of $\psi^H$, then it can be shown from equation (6.8) that:

$$\left[\frac{a^H}{b^H}\right]^2 = \frac{\cos^2 \frac{\psi_o^H}{2} + \left[\frac{a}{b}\right]^2 \sin^2 \frac{\psi_o^H}{2} - \cos^2 \frac{\psi^H}{2}}{\sin^2 \frac{\psi^H}{2}}$$

(6.9)

where $a/b = 13$. Hence, assuming that $\psi_o^H$ decreases from $6.8^\circ$ to $5^\circ$ after a shear of about 3, then from equation (6.9) it follows that $a^H/b^H = 17.6$. Using the Crawford and Kolsky (1951) model (equation (4.13)), the change in birefringence ($\Delta_n$) can be predicted, and it was found by using the above data that an increase in $\Delta_n$ of about 4.8% would be expected. Birefringence measurements were made on specimens deformed at 22°C, and it was found that the maximum increase in birefringence was about 3% after a shear strain of 3. Since the calculated birefringence contribution is from the crystalline regions, and the measured, from both crystalline and
amorphous, it can therefore be seen that within experimental error the difference is not very significant, indicating that the increase in birefringence is attributed to an increase in the orientation of the crystalline regions. However, Kurokawa et al. (1966) found that there was no increase in birefringence within a deformation band formed in oriented polyethylene, although no values of the shear strain within the band were reported.

From the 105°C data, equations (6.9) and (4.13) can be similarly used in order to predict the change in birefringence due to annealing. Hence, using the values of $\psi^*(6.8^\circ)$ at 22°C and $\psi^*(8.6^\circ)$ at 105°C, a decrease of 4.5% in $\Delta n$ was calculated which was, in fact, experimentally measured (see section 4.4.3), indicating that the decrease in the degree of orientation is attributed to the crystalline regions.

6.3.4 Changes in Void Size During Deformation

Various workers (see Hargreaves (1970)) have reported that during the deformation of slip bands in oriented polyethylene, the bands lost their stress whitened opacity and became rather transparent. One possible explanation for this phenomenon, is that closure of microvoids within the band occur owing to the large shear strain. This effect was initially proposed by McClintock et al. (1966), where the closure of holes in a viscous body was considered in terms of normal ($\sigma_n$) and shear ($\sigma_s$) stresses. It was found that depending on the ratio of $\sigma_n/\sigma_s$, the voids either completely closed ($\sigma_n/\sigma_s = 0$), or increased in eccentricity until a steady-state was attained ($\sigma_n/\sigma_s > 1$). Owing to the experimental
conditions of testing specimens in this project, \( \sigma_n/\sigma_s \to 0 \) as deformation continues (\( \lambda \to 0 \)), thus gradual void closure would be expected. From the structural model discussed in section 6.1.2, it can be seen that void closure would be expected to occur when fibrillar slip was taking place, since the microvoids that are positioned between the microfibrils would then be subjected to a shear strain. However, it was found by using an optical microdensitometer, that for specimen deformation of up to shear strains of about 2, between the temperatures of 22°C and 90°C, there was no change in specimen transparency, indicating little void closure. Although the optical tests indicated little change in void structure, the detected dimensions of which would be of the order of 2,500 Å, there might possibly be changes in the smaller void dimensions, as detected by using X-rays.

The diffuse streak on the low angle diffraction pattern was analysed using the Guinier (1952) plot discussed in section 6.1.1. With reference to Figure 6.3, only the parameter \( b_x \) was calculated, since in the \( y \) direction the diffuse streak was within the beam stop, thus making it impossible to calculate \( a_y \). Low angle patterns were obtained from specimens that had been deformed by various increments of shear strain, and in Figure 6.21 there are plots of \( \ln I \) against \( \varepsilon^2 \), for two specimens deformed at 22°C and 90°C, where 90°C was the limiting test temperature at which the diffuse streak still existed. It can be seen from the plots that a linear relationship is not obtained, suggesting that there is a distribution in void size (\( b_x \)). The limiting gradients at both ends of the curve (22°C) were measured, from which the values of \( b_x \) were calculated, and found to vary between about 100 Å to 170 Å.
It can also be seen from Figure 6.21 that for macroscopic shear strains of up to 1.6 \( \gamma_F = 0.45 \) at 22°C, there had been no change in the distribution of \( b_x \) values, implying that there had been no void closure. Also, an increase in temperature (up to 90°C) had not altered the actual overall void size distribution significantly, although it had caused a gradual decrease in the intensity of the diffuse reflection. It is shown by Guinier (1952) that the intensity of the scattered X-rays is a function of the number of voids, and the differences in electron density between voids and surrounding material. A decrease in intensity at elevated temperatures is, therefore, possibly the result of a reduction in void density by selective void closure.

6.3.5 Deformation of Slightly Crosslinked Oriented Polyethylene

Oriented polyethylene samples were given radiation doses of 2 Mrads, 5 Mrads, 8 Mrads and 15 Mrads. Before irradiation, infra-red spectra of the oriented samples were obtained, and a typical spectrum is shown in Figure 6.22, where the main absorption band (1,475 cm\(^{-1}\)) is attributed to C-H bending of \( CH_2 \) groups. For further interpretation of such a spectrum see Ritchie (1965). When polyethylene is irradiated, various factors such as oxidation and unsaturation (c=c) reduce the degree of crosslinking (see Charlesby (1960)), and although samples were irradiated in a vacuum, there was still the possibility of small traces of oxygen that would react readily with radicals, to form carbonyl compounds such as aldehydes (-CH\(_2\)-CHO) and ketones (-CH\(_2\)-CO-CH\(_2\)-) that are relatively unstable at high temperatures, compared with polyethylene. Up to 8 Mrads there was no indication of oxidation. However, some oxidation appeared to
have occurred in the 15 Mrad specimens, since the infra-red spectrum, as illustrated in Figure 6.23, showed an absorption band at 1700 cm$^{-1}$, which is attributed to carbonyl groups. A few tests were still carried out on the 15 Mrad specimens, although it was realised that there would be more degraded molecular chains in the polyethylene specimens, compared with the lower dose specimens.

A series of continuous test were initially carried out on irradiated specimens at 22°C and 105°C, and the macroscopic deformation analysed in a similar way to that described in Chapter 4. In all cases at room temperature, deformation was uniform up to shear strains of about 1.5, after which there was considerable non-uniform deformation in the form of localised slip (c.f. tests on annealed and low temperature specimens), that eventually resulted in the narrow deformed region becoming transparent. This effect was more predominant in the 8 and 15 Mrad specimens, and a typical photomicrograph illustrating such a localised region is shown in Figure 6.24, where the specimen ($\lambda = 63^{\circ}$) had been irradiated to a dose of 8 Mrads. Consequently, it was only possible to analyse deformation up to the onset of localised slip, and in Figure 6.25 a plot of $h/h_0$ against $\gamma$, obtained from specimens with $\lambda$ values of about 60$^{\circ}$, shows how an increase in irradiation affects the deviation from simple shear. Up to 5 Mrads (6 Mrads - gel point) crosslinking had little effect on the deformation geometry, and this is indicated in Figure 6.25 by the fact that there is good agreement between data and predictions of the shear reorientation model, when fitted to unirradiated room temperature deformation data (see Figure 4.9) where $\theta = 0.01^{\circ}$. However, for doses beyond gel point (8 and 15 Mrads), deviation from simple shear was considerably greater,
although there was little difference between the 8 and 15 Mrad data, which may be attributed to the fact that the degree of crosslinking in the 15 Mrad specimen was not significantly greater than in the 8 Mrad specimen, due to oxidation in the case of the former. A fit to the 8 and 15 Mrad data, using the shear reorientation model, was made, and this is shown in Figure 6.25 with $\theta = 0.035^\circ$.

The effect of irradiation on the shear behaviour of specimens at 22°C, as indicated by a plot of $h/h_0$ against $\gamma$ is, therefore, apparently independent of irradiation up to the gel point. This is further indicated in Figure 6.26 for data obtained from specimens tested at 105°C, where the continuous curve is a fit to unirradiated deformation data at 105°C (see Figure 4.16), where $\theta = 0.03^\circ$.

Above the gel point (8 Mrads), deviation from simple shear was again considerably greater than pre-gel point specimens, and this is shown in Figure 6.26 by the broken curve. In the case of irradiated specimens tested at 105°C, deformation was uniform, unlike that of the room temperature specimens where localised slip was predominant. However, for the 15 Mrad specimen, the annealing effect of testing at 105°C produced a surface texture, as shown in Figure 6.27, where it appears that there are fine cracks perpendicular to the c direction, consequently, deformation studies were not carried out on such specimens.

Specimen deformation was also analysed using wide and low angle X-ray diffraction, in order to investigate the intracrystalline and fibrillar modes of slip. It was thought that if crosslinking had formed intermolecularly, then possibly intracrystalline slip would be inhibited, consequently, fibrillar slip would occur earlier on in
the deformation process. Intracrystalline and fibrillar shear strain values were determined using the same procedure as described in section 6.3.2, but it was found that for all irradiation doses, the intracrystalline slip component was not significantly effected. In Figure 6.28, a plot of $\gamma_{F}$ against $\gamma_{C}$ at 22°C and 105°C for 8 Mrad specimens, shows there is good agreement with data obtained from unirradiated specimens, which is shown in Figure 6.16. The last experimental point in the 22°C data in Figure 6.28 marked the onset of localised slip, as illustrated in Figure 6.24, beyond which it was impossible to determine accurately the amount of intracrystalline shear within the region. For all irradiated specimens, it was in fact found that the onset of localised slip occurred during the early stages of fibrillar slip.

6.4 Discussion

When a two-phase structure such as that associated with oriented polyethylene is deformed in tension, deformation can be analysed primarily in terms of three mechanisms: (a) intracrystalline slip, (b) fibrillar slip, and (c) intercrystalline slip. The last mode of deformation which involves the slipping of adjacent lamellae has, in fact, been an important mode of deformation for oriented polyethylene under certain conditions, and it has been reported by various workers such as Keller and Pope (1971), Yamada et al. (1969), and Cowking et al. (1968). However, intercrystalline slip would result in the lamella normal and c direction rotating away from the tensile axis, thus macroscopic deformation would certainly not be simple shear in the c direction. Also, if one considers the model suggested by Peterlin (1971(a)), in which there are relatively few
tie molecules between microfibrils, compared with intercrystalline
tie molecules, then intercrystalline slip would be an unfavourable
mode of shear. Thus, on the assumption that macroscopic deformation
can be accounted for in terms of structural changes (see
Kukšenko and Slutsker (1968)), two modes of slip in the c direction,
intracrystalline and fibrillar slip, are postulated.

From the structural analysis performed on oriented polyethylene
during deformation at 22°C, it is apparent that the critical shear
stress required to cause intracrystalline slip is less than the shear
stress required to produce slip between microfibrils, since intra-
crystalline slip was the initial mode of shear. If this is the
case, then why is there a transition from intracrystalline slip to
fibrillar slip after shear strains of about 0.9? The answer is that
the transition is probably associated with crystal strain hardening,
which is due in part to the strained intercrystalline tie molecules.
Thus, assuming that the tie molecules are of varying length and
distribution, the effect of intracrystalline slip would be to over-
strain certain tie molecules, with the result that fibrillar slip
would become the easier slip mechanism. An estimate in the amount
of $\gamma_F$ can be made from fracture data from specimens with $\lambda_o = 90^\circ$,
in which fracture occurred at tensile strains of about 6%.
Assuming that the strain to fracture is mainly attributed to the inter-
fibrillar tie molecules, it would then mean that on shearing the
microfibrils, only shear strains ($\gamma_F$) of about 0.35 would be
attained before fracture. In fact, values of 1.4 were recorded for
$\gamma_F$ (see Figure 6.16), consequently some mechanism is occurring
between the microfibrils so as to allow large shear strains to be
attained. When interfibrillar tie molecules are strained to their
limit, after a shear strain of about 0.35, two possibilities can occur: (a) there is tie scission (see Peterlin (1971(a))), and (b) the interfibrillar tie molecules are pulled out of the crystalline regions, consequently there is disorientation of the crystalline regions because of the random nature of the tie molecules. The latter idea agrees well with X-ray results, since during fibrillar slip there was a gradual decrease in intensity of the low angle reflections, indicating a decrease in order within the crystalline regions. Becht (1971) was also in favour of some form of disintegration of the crystalline regions of oriented polyethylene, although in this case polyethylene was strained along the c direction. However, because of the simple techniques used in analysing the deformation, it is impossible to say that only one particular mechanism was in fact occurring during fibrillar slip.

At elevated temperatures, the important changes that occurred in specimens prior to deformation were shrinkage along the c direction, increase in long period, increase in intensity of low angle reflections, and a slight reduction in the degree of orientation. All these phenomena that occur on annealing oriented polyethylene, are discussed by Peterlin (1971) and Cornelissen and Peterlin (1967), where it is apparent that the important effect due to annealing is shrinkage of tie molecules, that exert strong moments on the folded chain blocks, with the result of crystal rotation. It is, therefore, the relatively temperature sensitive interfibrillar tie molecular regions, compared with the crystalline regions, that could account for the increased compliance in fibrillar slip at 105°C. Keller and Pope (1971) considered deformation of oriented low density polyethylene in terms of mainly intracrystalline and intercrystalline
slip, in which at 22°C, deformation was accounted for by intracrystalline slip, but as the test temperature increased, it was found that intracrystalline slip was completely suppressed. This was not found in high density polyethylene used in this project, although there was a smaller contribution of shear strain from the intracrystalline shear at elevated temperatures.

During fibrillar slip, no evidence was found to indicate void closure in unirradiated polyethylene. It could be, however, that larger shear strains ($\gamma_f > 1$) are required before there is any significant change in the void size.

The effect of shear strain on the degree of orientation is greater at 105°C than 22°C, which is possibly due to the operation of the fibrillar mode of slip at 105°C. Fibrillar slip would, however, only result in an increase in the degree of orientation if there was an angular distribution of microfibrils about the shear direction. Sakaoku and Peterlin (1967) reported that the effect of annealing oriented polyethylene was to cause a rotation in the microfibrils away from the draw direction, which would result in a distribution of microfibrils. The concept of fibrillar slip producing an increase in the degree of orientation would, therefore, be in agreement with the above findings. The effect of intracrystalline slip on the degree of orientation is also significant, especially at 22°C, since as illustrated in Figure 6.20, the rate of increase in the degree of orientation decreases in the strain region, where the intracrystalline slip component is rapidly decreasing. By using the simple model developed by Modlen (1969) and the changes in $\psi$ during deformation, the increase in birefringence was satisfactorily accounted for. It is, however, apparent that during the redrawing
of oriented polyethylene, the increase in birefringence is only very small.

The macroscopic deformation behaviour of irradiated oriented polyethylene illustrates how significant the amorphous fraction is in governing the amount of deviation from simple shear, since for only small doses of radiation above the gel point, sufficient disorder was introduced into the amorphous regions, in the form of crosslinks, to cause considerable deviation from simple shear. There was, however, little difference in the shear strain contributions ($\gamma_c$ and $\gamma_p$) between irradiated and unirradiated polyethylene during deformation, but this could be attributed to the fact that 8 Mrads was insufficient radiation to produce adequate crosslinking, so as to affect the onset of fibrillar slip. Specimens irradiated up to 15 Mrads were not comparable, due to oxidation effects. It could, therefore, be that larger doses of radiation are required in order to produce significant changes in the deformation mechanism.

One phenomenon which was common to irradiated and annealed specimens, in which crosslinking and shrinkage had occurred in the amorphous regions respectively, was localised slip which occurred during the early stages of fibrillar slip. If localised slip is associated with inhomogeneous fibrillar slip, then this mechanism could be characteristic of two planes of weakness between microfibrils. Thus, if there had been inhomogeneous crosslinking in the interfibrillar regions, which is possible because of the few interfibrillar tie molecules, then slip between the microfibrils would result in non uniform constraints on the interfibrillar tie molecules, consequently leading to inhomogeneous fibrillar slip, as shown
in Figure 6.24. If slip-off fracture also occurs, which was the case, then this indicates that possibly interfibrillar tie scission is occurring, but it was discussed above, for unirradiated specimens, that during fibrillar slip, tie molecules are probably pulled out of the crystalline regions, thereby preventing considerable tie scission. However, for irradiated specimens, the interfibrillar tie molecules are less easily pulled out of the crystalline regions because of the intermolecular and intramolecular crosslinks, consequently tie scission with subsequent slip-off fracture would be highly predominant. The occurrence of localised slip in annealed specimens may be attributed to the fact that annealing produced non-uniform shrinkage, together with folding of the interfibrillar tie molecules, consequently deforming the specimens at 22°C would result in non-uniform fibrillar slip.
Figure 6.1: A typical wide angle X-ray diffraction pattern obtained from oriented polyethylene.

Figure 6.2: A typical low angle X-ray diffraction pattern obtained from oriented polyethylene.
Figure 6.3: (a) Low angle X-ray diffraction pattern illustrating the strong diffuse streak, and (b) the associated void structure of which the major and minor semi-axes are represented by $a_y$ and $b_x$ respectively.

Figure 6.4: Microfibrillar model adopted for oriented polyethylene.
Figure 6.5: A distribution of lamellae surfaces about the c direction which gives rise to a spread in the low angle reflections.

\[ \gamma_C = \tan \omega \]

(a)

\[ \gamma_F = \tan \omega \]

(b)

Figure 6.6: Changes in the lamella surface for shear in the c direction, during (a) intracrystalline slip and (b) fibrillar slip.
Figure 6.7: Diagram illustrating the changes in wide and low angle X-ray diffraction patterns when, structure (a) deforms by (b) intracrystalline slip and (c) fibrillar slip.
Figure 6.8: Plan view of the experimental arrangement used for detecting the (002) reflection.

Figure 6.9: Diagram illustrating the directions of the axes $x$, $y$, and $z$ with respect to the specimen.
Figure 6.10: Wide angle (a) and low angle (b) X-ray diffraction patterns revealed by X-rays in the y direction.

Figure 6.11: A low angle four point pattern obtained by passing X-rays in the x direction through oriented polyethylene annealed at 105°C.
Figure 6.12: Schematic diagram of lamellae orientation which would give rise to a four point pattern.

Figure 6.13: Low angle patterns revealed by X-rays in the z direction, from specimens deformed at (a) 22°C ($\gamma = 1.8$) and (b) 105°C ($\gamma = 1$).
Figure 6.14: Comparison between macroscopic ($\gamma$) and intracrystalline ($\gamma_c$) shear strain values obtained from two specimens deformed at 22°C. The continuous line is a plot of equation (6.2) for simple shear.
Figure 6.15: Comparison between macroscopic ($\gamma$) and intracrystalline ($\gamma_c$) shear strain values during the deformation of a specimen at 105°C. The continuous line is a plot of equation (6.2).

Figure 6.16: The relationship between intracrystalline and fibrillar shear strain contributions during specimen deformation, at 22°C and 105°C.
Figure 6.17: Scanning electron micrographs of two slip-off fracture surfaces, obtained from (a) a specimen deformed at -10°C, and (b) a specimen deformed at 120°C.
Figure 6.18: A typical wide angle X-ray diffraction pattern obtained on cylindrical film illustrating the (002) reflection.

Figure 6.19: Distribution of (002) poles per unit solid angle in oriented polyethylene. The continuous line is a fit to the distribution, using equation (6.8).
Figure 6.20: Variation of the azimuthal width at half maximum intensity of the (110) reflection with macroscopic shear strain at (a) 22°C, and (b) 105°C.
Figure 6.21: Guinier plots obtained from the low angle diffuse streak for a specimen deformed by various amounts of shear strain at 22°C, and for a specimen deformed at 90°C.
Figure 6.22: A typical infra-red spectrum obtained from oriented polyethylene.
Figure 6.23: An infra-red spectrum obtained from oriented polyethylene after it was irradiated up to a dose of 15 Mrads.
Figure 6.24: A micrograph illustrating typical localised slip in a deformed polyethylene specimen that was irradiated up to a dose of 8 Mrads (dot spacing = 0.2 mm).
Figure 6.25: Variation of $h/h_0$ with macroscopic shear strain, for specimens irradiated up to various doses and deformed at 22°C. The continuous lines are the predictions of the shear re-orientation model.

Figure 6.26: Variation of $h/h_0$ with macroscopic shear strain, for specimens irradiated up to 5 and 8 Mrads and deformed at 105°C. The continuous line is the prediction of the shear re-orientation model for unirradiated polyethylene.
Figure 6.27: A micrograph of an irradiated specimen (15 Mrads) at 105°C illustrating a surface cracking phenomena.

Figure 6.28: The relationship between intracrystalline and fibrillar shear strain contributions during the deformation of irradiated specimens at 22°C and 105°C.
Summary and Suggestions for Further Work

The most important results which have been presented in this thesis are summarised as follows:

When oriented polyethylene was tested in tension, deformation was to a first approximation simple shear parallel to the c direction. However, there was in fact a gradual deviation from simple shear which was only readily observable at large shear strains, and this deviation could be accounted for by the shear reorientation model suggested by Hinton and Rider (1968). It was assumed that the distribution function for oriented polyethylene was directly related to a strain ellipsoid, although there was some discrepancy in the strain ratio parameter $a/b$, between that obtained from the reorientation model and that from the affine model. The magnitude of the reorientation effect depends upon the degree of orientation of the polyethylene, consequently deformation at elevated temperatures indicated that there was a decrease in the degree of orientation of the polyethylene, although it did not agree exactly with the decrease in orientation calculated from the decrease in birefringence. It did, however, appear that the amorphous material in oriented polyethylene played a vital role in influencing the deviation from simple shear.

Analysis of the resolved shear stress and normal stress after yield, revealed a flow criterion of a form similar to the Coulomb criterion, the parameters of which were sensitive to temperature and initial orientation angle ($\lambda_0$). However, because of the
nature of resolving both shear and normal stresses from the tensile stress, they were dependent upon each other, thus making it difficult in deciding whether or not the normal stress component affects the flow stress behaviour. Resolved shear stress-shear strain behaviour was apparently independent of $\lambda_0$ and exhibited strain hardening. Consequently, from the stress-strain data, the relationship between the resolved shear stress and normal stress was predicted, and found to be similar in form to that expressed by the flow criterion, for shear stresses greater than a critical shear stress, referred to as a transition point. It was, therefore, most likely that strain hardening was the important factor which influenced the flow stress behaviour, rather than a decrease in the normal stress component during deformation, which was really a consequence of the testing geometry.

An attempt was made to analyse the significance of load maxima in the load-extension curve, which is normally referred to as yield point, in terms of the elastic limit or onset of plastic flow. It was, however, found that shear strain at load maxima was a function of $\lambda_0$, and since simple shear was the primary mode of deformation for most specimens tested, it seemed that a critical shear strain criterion for yield could be appropriate. The onset of plastic flow was, in fact, found to occur in all specimens tested, at shear strains of about 0.03, the value of which was much smaller than that found at load maxima. In addition, a transition point, as mentioned above, was found to occur in the resolved shear stress and normal stress relationship, beyond which the deformation was analysed in terms of the flow criterion. Since the resolved shear stress-shear strain behaviour was independent of $\lambda_0$, the transition point which occurred
at a critical shear stress, corresponded to a critical shear
strain, the value of which was about 0.2.

Studies of changes in the morphology of oriented polyethylene
during shear revealed two modes of slip parallel to the c direction.
One mode occurred on a fine scale and was referred to as intra-
crystalline slip, whereas the second mode occurred on a relatively
coarser scale and was referred to as fibrillar slip. Both
components were found to be temperature sensitive.

From wide angle X-ray diffraction, changes in the degree of
orientation during deformation were obtained, and by using a simple
model suggested by Modlen (1969) in order to determine the distrib-
ution of chain axes, the increase in the degree of orientation was
satisfactorily accounted for in terms of the increase in bire-
fringence.

The following suggestions are made for possible further work
on deformation of oriented polyethylene:–

(a) The deformation of oriented polyethylene appears to
be related to its molecular structure in so far as
the amorphous fraction plays an important role in
affecting the macroscopic shear behaviour. Hot
drawn polyethylene compared with cold drawn poly-
ethylene is supposedly relatively free of crystal
defects, and contains a reduced number of tie mole-
cules (see Peterlin (1971)), consequently it would
be expected that the increased perfection would
result in less deviation from simple shear, and a
decrease in the strain hardening.
(b) It would be of interest to perform a series of tests in order to study the effect of temperature and strain rate upon the resolved shear stress-shear strain relationship, and the subsequent effect upon the parameters in the flow criterion. This could also be carried out on specimens with \( \lambda_o = 0^\circ \), using a shear testing jig, with \( \sigma_n = 0 \).

(c) The temperature range of testing could be expanded especially to find out what changes occurred in the deformation when temperatures close to the melt were used.

(d) Further structural changes during deformation could possibly be analysed using electron microscopy in the hope of detecting two types of slip lines on different scales. However, there would be difficulty in specimen preparation.

(e) Measurement of changes in void structure, if any, during fibrillar slip can also be made, although large shear strains (>3) would be required, necessitating an alternative testing technique.

(f) If, during fibrillar slip, interfibrillar tie scission did occur, which was suggested especially in the case of irradiated polyethylene, then the radicals formed might be observed under favourable conditions, using electron spin resonance.
ACKNOWLEDGEMENTS

I would like to thank -

My supervisor, Dr. T. Hinton, for suggesting the programme of research carried out, and for his encouragement and interest throughout the past three years.

B.P. Chemicals Ltd., and the Science Research Council for a co-operative award in pure sciences (CAPS).

My industrial supervisor, Dr. K. Lawrence, for his assistance at B.P. Chemicals Ltd., Epsom Division.

Dr. J. G. Rider for many helpful discussions.

Mrs. Gillian Smith for writing some of the computer programs.

All technical staff, especially Mr. D. Leong and Mr. C. White.

Miss Caroline Bate for reading the draft of this thesis.

Miss M. Nicholson for typing this thesis.
REFERENCES


Cullity, B. D., 1956, Elements of X-ray Diffraction, Addison-Wesley, Reading, Massachusetts.


Hinton, T., 1972, Unpublished data.


Kawai, T., Keller, A., Charlesby, A., and Omerod, M. G., 1965,
Phil. Mag., 12, 657.


Kuhn, W., and Grün, F., 1942, Kolloidzeitschrift, 101, 248.


Kurokawa, M., Konishi, T., Sakano, H., and Kondo, M., 1967,
Sen-i Gakkaishi, 23, 95.


Robertson, R. E., and Jolyson, C. W., 1968, J. Polymer Sc., A-2, 6, 1673.


Stein, R. S., and Norris, F. H., 1956, J. Polymer Sc., 21, 381.
Vincent, P. I., 1960, Polymer, 1, 7.


