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CRYSTALLINITY CHANGES IN PET AND NYLON 11 WITH STRAIN, STRAIN RATE AND TEMPERATURE

by

J.O. FERNANDEZ LORENCES

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

JANUARY 1999

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Department: Physics
Esta tesis esta dedicada a mi familia; mi padre: Oscar Luis Fernandez; mi madre: Maria Rosario Lorences; mi hermana: Maria Piedad Fernandez y mi hermano: Jesus Fernandez quienes siempre me acompañan en mi camino sin importar la distancia que nos separe.
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ABSTRACT

The mechanical properties of PET (widely used in bottles and synthetic fibres) and Nylon 11 (also used in the fabrication of synthetic fibres) were studied over several decades of strain rate at different temperatures in an effort to provide a more complete description of these materials' behaviour. Processing techniques can be improved if such information is available. Tests were carried out using a conventional Hounsfield machine and two "in house" developed dropweight and a cross bow systems from -10°C to 200°C. The three systems enable true stress vs. true strain curves to be calculated. Strain limited tests were carried out at all the strain rates and the temperature rises were estimated from the area under the stress vs. strain curves. A heater unit and a Peltier device were used to attain the desired temperatures. X-ray diffraction provided an insight of the microstructure developed after mechanical tests. The information extracted comprised the interatomic plane distances and the dimensions of crystallites perpendicular to one plane. Differential Scanning Calorimetry (DSC) was employed to estimate the degree of crystallinity of the materials and calculate the transition temperatures. Due to its amorphous character, PET was a suitable material to be used to study the kinetics of crystallisation using the cold crystallisation peak. This was done by running the DSC at different heating rates allowing the calculation of the activation energy and frequency factor. The results were used, together with the temperature rise values, to understand the crystallisation of PET during deformation. PET yield stress increased with strain rate with a sharp increase beyond $10^3$ s$^{-1}$ while Nylon 11 yield stress showed a decrease at such strain rates. PET crystallised into the triclinic form at rates above $10^3$ s$^{-1}$ beyond 140% strain. Increases of up to 40% in crystallinity content were found which were thermally induced after the test ended. Nylon 11 mixed triclinic-hexagonal structure transformed into the pseudohexagonal form at $10^3$ s$^{-1}$ with an small increase in the degree of crystallinity whilst the as-received structure was conserved at higher strain rates with a decrease of crystallinity content.
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LIST OF POLYMER ABBREVIATIONS

ABS: acrylonitrile butadiene styrene
CBA: cellulose acetate butyrate
HDPE: high density poly ethylene
PBT: poly butylene terephthalate
PC: poly carbonate
PCTFE: poly chloro trifluoro ethylene
PE: poly ethylene
PEEK: poly ether ether ketone
PES: poly ether sulphone
PEK-C: phenolphthalein poly ether ketone
PEN: poly ethylene naphthalate
PET: poly ethylene terephthalate
PMMA: poly methyl methacrylate
PMP41: poly 4-methyl pentene-1
PP: poly propylene
PTFE: poly tetrafluoro ethylene
PU: poly urethane
PVC: poly vinyl chloride
PVDF: poly vinyldene difluoride
PVF: poly vinyl fluoride
TPS: toughened poly styrene
UPVC: unplasticised poly vinyl chloride
CHAPTER 1

INTRODUCTION
1.1 GENERAL INTRODUCTION

A polymer is a long chain molecule that is composed of a large number of repeating units of identical structure. Its name derives from the Greek words *poly* which means many and *meres* which means parts. A plastic usually consists of one or more polymers in addition to various additives and filler, Ward (1993).

The use of plastics in many applications has grown during the last twenty years and it is expected to increase further. The properties of these materials including their strength, ductility and absorbency contribute to the increase in manufacture of new plastic products according to Fried (1995). There is also a tendency towards replacing metals by plastics where the large gain in lightness outweighs the small deterioration in performance.

However, the successful use of plastics in specific applications requires knowledge of their mechanical and thermal response. In addition to the widely studied static response, the plastic deformation under high rates of loading has become very important for applications such as machining operations, crash helmets, exposure to particle impact, shock absorbers, bullet proof windows (Andrews and Ward (1970)). Such data would provide the basic information for computer aided design of components.

Fried (1995) suggested that the exact nature of the response of a polymeric material depends upon its chemical structure, conditions of preparation, molecular weight, molecular weight distribution, crystallinity content and the extent of any crosslinking or branching. However, general patterns can be drawn:

- The stress versus strain curves generally depend on the rate of deformation. The yield stress and modulus usually increase with strain rate. Strain softening and hardening are normal phenomena which may occur during plastic flow. The degree of softening or hardening depends upon the heat generated and morphological changes during deformation.
Introduction

- The yield stress and modulus generally decrease as the temperature increases and the polymer behaviour changes from glass-like to rubber-like.

- Strain induced crystallisation of amorphous or semi-crystalline polymers usually appears beyond the yield point during a tension test. Annealing before the tests often increases the crystallinity content. On drawing, the yield stress and Young’s modulus normally increase with the initial degree of crystallinity.

A large number of results have been published concerning such factors as: the influence of morphology on the mechanical properties; stress induced crystallisation; changes in topology during deformation, and; the nature of the tests. Thus, the various findings, agreement between them and the present work are addressed in the following chapters.

1.2 AMORPHOUS AND SEMI-CRYSTALLINE POLYMERS

Amorphous polymers consist of chains either randomly oriented or oriented without long range order. Amorphous materials can be regarded as liquids of very great viscosity. Normally, amorphous polymers are obtained by rapid quenching from the melt, although they can be prepared from solutions. Polymers can only crystallise at temperatures between the glass transition temperature and the melting point and the rate of crystal formation depends on the temperature. Thus, if the molten material is quenched very rapidly below its glass transition temperature the polymer cannot crystallise and it remains in an amorphous state. Polymers with a slow rate of crystallisation such as PET are easily obtained in an almost amorphous form by normal quenching techniques. Others such as PE or PMP41 which have very high rates of crystallisation have been recently obtained in an almost completely amorphous state by an ultraquenching technique developed by Hsu and Geil (1986). Posterior crystallisation of an amorphous material may happen, for example, on drawing or annealing when the following conditions are met by the polymer: i) the polymer chain and its substituent groups posses stereoregularity, Alexander (1969); ii)
polymer molecules are characterised by a high degree of configurational regularity and they can assume conformational regularity as they pack in the crystal, Miller (1966). Crystallisation can be aided by orientation.

Semi-crystalline polymers can be treated as a mixture of crystalline and amorphous phases. In a long chain polymer, the whole of the material cannot be crystalline. the crystalline regions consist of relatively thick lamellae embedded in an amorphous matrix. Most of the chains fold forth and back within the lamellae although there are many chains which thread their way through the structure and provide continuity, Ward (1993). Crystals are a regular three dimensional distribution of atoms in space and these are arranged so that they form a series of parallel planes separated from one another by a distance d, characteristic of each family of planes. Further crystallisation in a semi-crystalline polymer is difficult to attain due to the small amount of amorphous material left and hindrance by the existing crystals.

1.3 MATERIALS

The materials used in this study were the polyester Polyethylene Terephthalate (PET) grade B73 obtained from ICI and the amide Nylon 11 obtained from Goodfellow Cambridge Ltd. Both are thermoplastics, i.e., they can be heated and processed into the desired form, unlike thermosets which cannot be thermally processed once they have been made.

The use of PET as a consumer fibre dates back to 1953. It is also used by the beverage bottle industry and other moulding applications, Turi (1981). It has high strength, toughness, abrasion resistance and good resistance to chemicals and grease. The repeating unit consists of one benzene ring, two ethers, two carbonyl groups and two methylene units. It is formed by the condensation of ethylene glycol and terephthalic acid, Ward (1993):

\[
n \text{(HO-CH}_2\text{-CH}_2\text{-OH)} + n \text{(HOOC-C}_6\text{H}_1\text{-COOH)} \rightarrow H[\text{O-CH}_2\text{-CH}_2\text{-O-}\text{CO-C}_6\text{H}_4\text{-CO}]_n + n \text{H}_2\text{O}
\]
Owing to the possibility of rotation of the glycol groups about the single bonds, PET presents two alternative conformational isomers, namely gauche and trans.

In addition to fibre applications, Nylon 11 is used for manufacturing fuel lines and compressed air brake tubing, Fried (1995). It is obtained by the ring opening polymerisation of 11-aminoundecanoid acid. The water absorption of Nylon 11 is low, 2.5%, compared to almost 10% for other Nylons. The repeating unit comprises ten methylene groups, one carbonyl group and one amide, Fried (1995):

\[ H \left[ \text{HN} - (\text{CH}_2)_{10} - \text{CO} \right]_n \text{ OH} \]

PET was supplied in plate form whereas Nylon 11 was received in a rod shape. The samples were machined on a lathe into cylinders of approximately 4 mm diameter by 2 mm height. The diameter to height ratio was the same for both materials, so any dimensional effect was similar for both polymers which allows comparison of data.

1.4 OBJECTIVES

The main aims of this work are:

- To obtain information about the mechanical behaviour of these two thermoplastics up to large values of strain at rates ranging from $10^{-3}$ to nearly $10^4$ s$^{-1}$. The effects of temperature are investigated from 263 to 453 K.

- To investigate the effect of structure on the mechanical behaviour and vice versa, i.e., changes in microstructure induced by the different test conditions.

- To employ the results to test phenomenological models and infer possible mechanisms of deformation.
1.5 PROGRAMME

The use of conventional testing machines at low rates to study the mechanical behaviour of materials was established several decades ago. However, the introduction of high rate testing machines has been a slower process. The data acquisition and interpretation has experienced a continuous improvement throughout the years but still is an issue of some controversy.

The work reported here comprises the use of two 'in house' built machines developed during the last ten years, namely a Cross Bow driven impact system and an instrumented Dropweight machine. Their main characteristic is that they allow direct measurement of load and displacement yielding true stress versus true strain curves in compression. The assumption of volume conservation is employed to estimate the change in area with time from the change in height.

Low strain rate tests, $10^{-3} \text{s}^{-1}$ were carried out in a conventional screw driven machine. Load is measured by means of a load cell connected in series with the sample. Displacement is measured as the movement of one platen relative to a second which is fixed. The Dropweight machine load signal is produced by two strain gauges connected in series and glued onto a steel roller. Displacement is directly measured by the movement of a flag across a laser beam targeted on a large area photodiode. The measurement of displacement in the Cross Bow is achieved by the change in the distance between two flags placed in a laser beam. Strain gauges provide the load in the sample. In this case they are mounted in a long steel bar.

Subambient temperatures were attained using a Peltier heat pump. When current flows across the system it pumps heat from one side, which is cooled, to the other side. The temperature decrease depends on heat leaks, the efficiency of cooling and the current and voltage supplied. High temperatures were achieved using two soldering iron elements inserted on a block and connected to a temperature controller.
Amorphous PET was mechanically tested using the machines available under different conditions. However, it was mainly chosen because of its ability to crystallise. Thus, it was studied to establish the conditions under which crystallisation is induced, the effect of strain rate and temperature on the extent of the crystallisation and the kinetics of crystal formation. Semi-crystalline Nylon 11 was chosen to study the influence that any changes in morphology may have on the mechanical response but without forgetting the mechanical behaviour of the as-received material. Thus, as-received Nylon was annealed at two different temperatures which gave rise to morphological changes. The annealed specimens were tested under the same conditions as the as-received samples.

1.6 ERRORS

The values given in the tables in the following chapters were calculated as the average of three numbers except the crystallinity content values which were averaged from six. Thus, as a general rule for a small number of values, the errors were estimated as one fourth of the range between the maximum and minimum value. It was thought that the error calculated in such a way was indicative of the scatter in the data. In order to avoid complex data tables all the errors were estimated and the largest one is given on the tables. In any case, it will be shown in the plots that the scatter, and consequently the errors, were small compared with the data values.

An exception to the previous method was the yield stress values of tests carried out in the Dropweight machine. In this case, the oscillations following the yield point led to a larger error. Thus, the error was chosen as half of the largest oscillation and included in the data tables for every value of yield stress.
CHAPTER 2

MECHANICAL TESTS
2.1. INTRODUCTION

To assess the suitability of plastics for certain applications it is important to understand the deformation mechanisms and be able to simulate them. The manner in which the mechanical properties vary with temperature or time must be determined before intelligent use of a plastic is possible. The information required for these purposes can be obtained from mechanical tests. The response of materials to various types of external stress or strain conditions results from both their unique macromolecular nature and their particular chemical and physical structure, i.e. interchain forces, entanglements, cross-links. The behaviour of solids in dynamic testing is different from that in static testing.

Among all the mechanical properties, which include: yield stress, Young’s modulus, maximum elongation, fracture stress and energy absorption, this work is mainly concerned with the first of these. Yield stress is an important property and defines the practical limit of behaviour for ductile materials. With external loading a typical polymer stress versus strain curve consists of three regions:

i) the stress increases steadily with strain up to the yield point. It is considered to be an elastic extension and it represents the amount of force required to move molecular segments from their positions of equilibrium. The ratio of stress over strain is the elastic Young’s modulus

ii) a flow plateau follows yielding. In this region large viscoelastic movements take place whilst simultaneously molecular chain segments rotating, translating and perhaps unfolding. The plateau region of an extension stress versus strain curve has been ascribed to the process of conformational transformation from the initial helix to the planar zigzag (or gauche-trans), Kanamoto and Ohtsu (1988). Orientation is thought to be formed in this region.

iii) strain hardening. At large deformations there is an upswing in stress associated with molecular processes which increase the resistance of the material to
Yield stress defines the beginning of plastic deformation and local motion of molecules. After yielding, molecular motions take place with little changes in stress and the deformation is irrecoverable. Phenomenological models of yielding regards it as an activated process in which the applied stress biases the activation energy in accordance with Eyring's theory of viscoelasticity, Ishikawa et al. (1996). Also, Hellinckx and Bauwens (1995) explained the yield process as being a result of stress induced melting followed by re-crystallisation. Molecular models include that of Briscoe and Nosker (1985) who proposed that stress induced molecular flow due to a decrease of internal viscosity and yielding is due to the increase of free volume under stress. Also, Andrews and Ward (1970) observed that the viscoelastic behaviour of several polymers seemed to fit an aggregate model of mechanical anisotropic units. Several other process have been attributed to happen at some stage of the deformation process. Ward (1984) suggested that, at the yield point, a polymer molecule begins to change from cis to trans conformation; Han et al. (1994) claimed that yield stress denoted the point at which the internal viscosity falls to the values where the plastic strain rate equals the applied strain rate; Chow (1987) and Lucas et al. (1995) argued that yield should occur when the product of the applied strain rate and the apparent relaxation time reaches a value of unity. At the moment, molecular theories seem to provide little information to describe the whole evolution of the yield behaviour, on the other hand phenomenological models seem to agree with the yield data. Nevertheless these models are based on completely different physical concepts: an activation volume greater or smaller than the volume of a polymeric unit; the presence of several mechanisms with different activation volumes acting simultaneously or independently; or, the co-operative motion of n identical units.

The aim of this work was to study the mechanical properties of PET and Nylon 11 over several decades of strain rate under different temperature conditions. As previously described the test equipment comprised a Hounsfield machine and 'in house' Dropweight and Cross Bow systems. This study was also concerned with the effects that the equipment may exert on the response of the material. Several sources
of errors will be analysed and their influence assessed. The data will be compared against literature models and the physical meaning of the molecular parameters will be explained.

It is interesting to know the energy put into the system and the amount which is used for deformation. The energy balance equation for a high strain rate test is given by equation 2.1, Heavens and Field (1974):

\[ W_o = mgh = W_{EL} + W_{PL} + W_X + W_S \]  

(2.1)

where \( W_o \) is the impact energy, \( m \) is the mass of the weight, \( g \) the gravity constant, \( h \) the distance travelled by the weight, \( W_{EL} \) is the energy restored to the weight on recoil, \( W_{PL} \) is the work done on plastic deformation of the machine components, \( W_X \) is the work done on the sample and \( W_S \) is related to a sharp drop in pressure. For an impactor of 3.85 kg dropped from a height of 0.3 m the energy available is approximately (if friction in the guiding bars is neglected) 11 J. Figure 2.1 shows a typical force versus displacement curve for the weight of the Dropweight system used in this work. The work done on the sample is \( W_X = \int Fdx \) where \( F \) is the force and \( x \) the displacement. Geometrical integration of Figure 2.1 up to a displacement of 1.7 mm yielded a value of 4.1 J. Thus, only about 35% of the energy was employed on the sample.

2.2. THEORY

The fundamental parameters by which a deformation can be characterised are stress and strain. Stress is the force per unit of area while strain is the fractional change in length.

2.2.1 ELASTIC AND VISCOELASTIC DEFORMATION

When a linear elastic solid is deformed it is assumed that the deformation is
Fig. 2.1 Load vs. Displacement for a typical Dropweight experiment

Fig. 2.2 Arrangement used for low temperature tests. The hatched area is the Melcor’s Peltier effect heat pump.
instantaneous, after which it remains constant until the load is removed when the recovery is total. Under this condition the stress and strain are always proportional at small strains and can be expressed as a matrix:

$$\sigma_{ij} = E_{ijkl}e_{kl} \quad (2.2)$$

where \(i\) is the direction of the normal to the plane on which the stress acts and \(j\) is the direction of the stress. \(E_{ijkl}\) is a four rank tensor so every component of the stress, \(\sigma_{ij}\), is proportional to all the components of strain \(e_{kl}\).

However, polymer behaviour departs from the elastic behaviour acting as a viscoelastic solid. Viscoelasticity implies that stress and strain vary with time and the material displays intermediate properties between the elastic solid with complete recovery after the force is removed, and a viscous liquid where there is irreversible flow under the action of a force. The deformation of polymers is usually called 'anelastic' because partial recover occurs if a sufficient time or high temperature is given. Linear viscoelasticity theory assumes that the results of changing stresses are simply additive and the total stress is the sum of one term proportional to strain, Hooke’s law, and one term proportional to the flow rate, Newton’s law. In one dimension:

**Kelvin element:**
$$\sigma = E\varepsilon + \eta \frac{d\varepsilon}{dt} \quad (2.3)$$

**Maxwell element:**
$$\frac{d\varepsilon}{dt} = \varepsilon = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{\eta}$$

where \(\sigma\) is the stress, \(E\) is the Young’s modulus, \(\varepsilon\) is the strain, \(\eta\) is the viscosity and \(t\)
is the time. The previous formulas are only valid at small strains and low flow rates. The modelling of the viscoelastic behaviour requires multielement (springs and dashpots) models. An extension of the theory leads obviously to non-linear viscoelastic behaviour.

The phenomenological model behind the theory was proposed by Ree and Eyring (1958) and assumed that the deformation of polymers was a thermally activated rate process involving the motion of segments of chain molecules over potential barriers. The potential barrier separates two positions of equilibrium. Thus:

$$\frac{de}{dt} = \dot{\varepsilon} = \varepsilon_0 \exp \left( -\frac{\Delta H}{RT} \right) \sinh \left( \frac{\nu \sigma}{RT} \right)$$

(2.4)

where $\Delta H$ is the activation energy and $\nu$ the activation volume. Rearranging equation 2.4 and for $\nu \sigma >> RT$ ($\sinh(x)=0.5\exp(x)$) the stress can be written as:

$$\frac{\sigma}{T} = \frac{\Delta H}{\nu T} + \frac{R}{\nu} \ln \left( \frac{2\dot{\varepsilon}}{\varepsilon_0} \right)$$

(2.5)

which states that at high stresses the stress is proportional to the natural logarithm of the strain rate at a given temperature.

### 2.2.2 STRESS, STRAIN AND STRAIN RATE

If a cylinder of diameter $d_0$ and height $h_0$ is subjected to a uniaxial external force, $F(t)$, the cylinder dimensions change to $d(t)$ and $h(t)$ at time $t$. The true stress at any time $t$ is:

$$\sigma(t) = \frac{F(t)}{A(t)}$$

(2.6)

where $F(t)$ is the force exerted on the sample. Assuming volume conservation during
plastic flow, Polsson’s ratio $v = 0.5$, the area $A(t)$ at time $t$ can be calculated as:

$$V(t) = V_o \Rightarrow A(t)h(t) = A_o h_o \Rightarrow A(t) = \frac{A_o h_o}{h(t)} \quad (2.7)$$

therefore:

$$\sigma(t) = \frac{F(t)h(t)}{A_o h_o} \quad (2.8)$$

where $h(t)$ is the height of the sample. Thus, if the force and height change with time are recorded the change of stress with time can be calculated.

If strain is defined as a fractional change of height over the whole deformation period then:

$$\text{strain} = \int_{h_o}^h \frac{dh}{h} \quad (2.9)$$

Thus, if the fractional change is calculated at any time $t$ the true strain is:

$$\varepsilon = \int_{h_o}^h \frac{dh}{h} = \ln \frac{h}{h_o} \quad (2.10)$$

However, if the fractional change is related to the constant initial height, $h_o$, the engineering strain is obtained as:

$$e = \int_{h_o}^h \frac{dh}{h} = \frac{\Delta h}{h_o} \quad (2.11)$$

Engineering and true strain are almost equal for small strains. However, it is more meaningful to use true strain for large deformations. Therefore, if the evolution of height with time is known the true strain can be calculated.

In an ideal test, uniform deformation under a velocity $v$ will give the strain rate:
\[ \dot{\varepsilon} = \frac{v}{h} = \frac{de}{dt} \quad (2.12) \]

Nevertheless, the velocity and height change with time. So, in the tests carried out in this work the strain rate was simply estimated from the slope of the true strain versus time plot.

2.3. EXPERIMENTAL

The following sections describe the different systems utilised to test the materials, the devices employed to attain high and low temperature conditions and the equipment for data acquisition and analysis. The systems enabled true stress versus true strain curves to be obtained, and these are the data which must be used if trying to correlate the mechanical stress with the response of the molecular chains during deformation. The use of nominal or engineering stress may lead to incorrect interpretation of the results because the shape of the true and engineering stress versus strain curves vary depending on whether the instantaneous or initial area is chosen.

2.3.1 THE HOUNSFIELD MACHINE

Plate 1 shows the Hounsfield H50KM Universal test machine. The sample is placed between the two platens. The upper platen is joined to a crosshead which is moved by a motor up to a displacement limit of 1 m. The crosshead incorporates a load cell capable of recording a maximum load of 50 kN. The crosshead velocity can be adjusted in steps of 0.1 mm/min up to a maximum of 1 m/min. The Hounsfield machine was used for low strain rate tests and the crosshead speed used was 0.1 mm/min.

2.3.2 THE DROPWEIGHT MACHINE

The Dropweight machine, which is shown in Plate 2, was built by Dawson (1993). The machine was constructed in order to achieve strain rates of about \(10^2\) s\(^{-1}\) and it is
Mechanical Tests

extensively described in the work by Hamdan (1994). In the present study samples were placed between two hardened steel rollers while a third one incorporated two semiconductor strain gauges made by Kulite Sensors Ltd type AFP-500-090 (gauge factor of 140± 5% at 297 K and resistance of 500 Ohms). The two major advantages of semiconductor gauges are that they produce a large output and are available in very small sizes resulting in a fast response time. The gauges were glued on two opposite flat surfaces which were grounded on one of the rollers. They were connected in series to cancel out any bending strains and were powered with 15 volts DC via a voltage stabiliser. In this system loading is achieved by dropping a weight onto the upper roller which loads the specimen sandwiched between the middle and lower roller. The basis of the detection is that the magnitude of the stress pulse transmitted to the lower roller will depend upon the physical properties of the specimen. The weight, which was guided by three bars, had a flag attached to one side which crossed a laser beam targeted on a silicon photodiode when impacting the upper roller. The photodiode was a Centronic Large Area 100 mm² supplied by RS. The photodiode was illuminated with the expanded beam of a laser (Imatronic LDM 135 Laser Diode Module) and powered with a stabilised 5 V supply. The displacement was calculated directly from the photodiode signal which has obvious advantages over the double integration method of the load signal, consisting of integrating the acceleration versus time signal to obtain velocity and a second integration to obtain displacement as a function of time, employed by many authors, Dawson (1993) and Heavens and Field (1974). The system rested on a cast iron workshop anvil of 80 kg which disperses the stress waves.

2.3.3 THE CROSS BOW SYSTEM

The cross bow system was built by Hamdan and it is extensively described in Hamdan (1994). Its objective was to achieve compression rates of the order of $10^3$ s⁻¹. Plate 3 shows the system. The impactor was a cylindrical arrow approximately 0.5 m long. When released from the cross bow it travelled inside a guiding tube and impacted an incident bar of about 0.1 m. The sample was held between the incident bar and the instrumented transmitter bar, which was approximately 1 m long. The instrumented bar had two semiconductor strain gauges glued on opposite sides at approximately
Plate 1

THE HOUNSFIELD MACHINE
Plate 2

THE DROPWEIGHT MACHINE
Plate 3

THE CROSS BOW SYSTEM
0.25 m from the sample, about 20 times the bar diameter, a distance sufficient to ensure that the recorded signals are largely unaffected by the changes in loaded area as the deformation proceeds, as described by Gorham et al. (1992). At the end of the transmitter bar a concrete block was used to absorb the impact. The incident and transmitter bars had two flags attached to the incident and transmitter bars which cut the expanded beam emitted by a Laser Diode Module targeted on a photodiode. The detection system is the same as in the Dropweight machine. The system is mounted on a steel frame and protected from vibrations by vibration absorbent cork.

2.3.4 HIGH AND LOW TEMPERATURE EXPERIMENTS

Mechanical tests were carried out in the range 263 to 453 K. For the elevated temperature tests the polymer sample was placed on a block which was heated by two soldering iron elements. The block temperature was controlled by a thermostat which operated in the range 298-673 K.

Low temperature tests were achieved by means of a Melcor's Peltier effect heat pump. It can work up to a maximum current of 14 A and 8.6 V with a maximum power of 67 W. The maximum temperature difference attainable across the device would be 340 K. The device, when supplied with a suitable electric current, absorbed heat at one end, cooling it, while heat was rejected at the other end. If an appropriate means of dissipation of heat is used low temperatures will be attained. The device needed to be mounted suitably to allow cooling on site. Figure 2.2 shows the arrangement. Two blocks of brass were assembled and a hole about 2.54 cm in diameter was bored to fit around the Dropweight rollers. The heat pump was clamped between the block, cooling side, and a “heat sink”, hot side. The heat sink was an hollow block of copper connected to mains water. Thus, heat was dissipated from the hot side by keeping a continuous flow of water through the block. The pump was supplied with 8 V and 11 A and was able to attain differences of approximately 35 K.

When using the heating or cooling systems, the system was heated/cooled to the required temperature and about 30 extra minutes were allowed to make sure that the temperature was constant over the whole sample. A probe sample was used for
Fig. 2.3 Temperature vs. Voltage for an Alumel-Chromel thermocouple

\[ y = 24.476x \]
\[ R^2 = 0.9999 \]

Fig. 2.4 Thermostat Temperature vs. Sample Temperature

\[ y = 1.1925x - 15.242 \]
\[ R^2 = 0.999 \]
calibration, in which a small hole was bored to approximately the sample centre and a Alumel-Chromel thermocouple placed inside. The thermostat temperature was calibrated against the thermocouple temperature. Figure 2.3 shows the temperature versus voltage curve of the thermocouple. Figure 2.4 shows the temperature at the centre of the sample versus thermostat scale. Thus, the thermostat knob could be adjusted to achieve any required temperature.

Elevated temperature tests in the Hounsfield were carried out by clamping the block to the static lower platen and heating the sample in situ. For low temperature tests, the sample was positioned between two rollers and surrounded by the cooling system. The whole system was covered with polystyrene to minimise heat leaks. Samples for high temperature tests in the Dropweight machine were heated separately together with two rollers which were used to compress the sample. Low temperatures were achieved by surrounding the holder the rollers and the sample with the system. Polystyrene was also used in this case.

2.3.5 DATA ACQUISITION AND FILTERING

The signals emitted by the load cell and the displacement of the crosshead of the Hounsfield machine were captured by means of a DSA (Digital Storage Adaptor). A typical test at low strain rates had a duration of more than 15 minutes, so the signals were recorded in roll mode. The DSA was linked to a personal computer which enabled the data to be stored for subsequent analysis. The original data were in ASCII format, so signals were translated into real time and voltage by the program DSA.BAS (see Appendix 1) written in Basic2 by Z. Xinwu (Physics Department internal report). A plotter was connected in parallel with the DSA so a load versus displacement chart was also obtained.

A Tektronix TDS 360 oscilloscope was used to capture the photodiode and strain gauges signals of tests carried out in the Dropweight machine and the Cross Bow system. The load signal triggered the data acquisition when the signal surpassed a threshold, thus some information from before the beginning of the test was available.
The oscilloscope was provided with a facility to allow data to be directly saved in spreadsheet format.

The signals recorded in the three experiments were distorted by extraneous vibration and/or electrical noise of unknown origin. Noise and vibration can obscure or exaggerate some features characteristic of the material, so success hinges upon the ability to identify what is genuine material response. Smoothing of the curves was performed with the program Peakfit v4 by Jandel. The program carried out a FFT (Fast Fourier Transform) of the data. Briefly, the data are converted to the frequency domain, the contribution of certain frequencies can be removed and data are converted to the time domain again. The method did not show any specific dominant frequency which could produce the vibrations, so it is believed that they may have a random origin. Thus, a cut point was chosen and the frequencies above were removed. The cut was chosen at frequencies at least ten times larger than the characteristic frequency of the whole experiment. For example, the duration of an experiment in the Dropweight machine was approximately 1 ms that is to say 1 kHz. The cut was done above 15 kHz. A frequency of 25 kHz was chosen for the Cross Bow experiments although the level of noise in this signals was small and filtering practically did not affect the signals but it was done for comparative purposes. Signals obtained from the Hounsfield machine were cut above 0.05 Hz. The advantage of this process lies in the ability to recall the original data if it was thought that the signals were oversmoothed. Figures 2.5-2.10 illustrate typical displacement and load signals for the three machines employed. The Figures also include the curves after smoothing. It can be seen that the level of vibrations vary for the different machines but the smoothed curve seems to take into account all the features. The shape of the signal in Figure 2.10 after 0.000117 s is probably due to interference between the transmitted signal and the signal reflecting back from the end of the bar.

2.3.6 DATA ANALYSIS

True stress versus true strain curves were obtained by converting the load cell, crosshead displacement, strain gauges and photodiode signals in volts versus time to
Fig. 2.5 Typical displacement signal for the Housfield machine before and after smoothing.

Fig. 2.6 Typical load signal for the Hounsfield machine before and after smoothing.
Fig. 2.7 Typical displacement signal for the Dropweight machine before and after smoothing

Fig. 2.8 Typical load signal for the Dropweight machine before and after smoothing
Fig. 2.9 Typical displacement signal for the Cross Bow machine before and after smoothing.

Fig. 2.10 Typical load signal for the Cross Bow machine before and after smoothing.
load and displacement versus time.

2.3.6.1 HOUNSFIELD MACHINE

The crosshead volts versus time signal was converted into displacement versus time by multiplying by a factor typically of 10 mm/volt. The load cell signal factor was 5 kN/volt. Conversion factors were fixed at the beginning of the experiment by choosing in the Hounsfeld display a maximum load and displacement. These limits corresponded to a 1 V signal. These factors varied depending upon the test temperature and material. If $K_c$, $K_l$, $V_c(t)$ and $V_l(t)$ are the displacement factor, the load factor, the crosshead signal and the load cell signal respectively the true stress, $\sigma(t)$, and true strain, $\varepsilon(t)$, were calculated as follows:

$$F(t) = K_l V_l(t)$$

$$D(t) = K_c V_c(t)$$

where $F(t)$ and $D(t)$ are the force and displacement in kN and mm respectively. In a compression test:

$$h(t) = h_o - (D(F) - C(F))$$

and

$$A(t) = \frac{A_o}{h(t)} = \frac{\pi (d_o / 2)^2 h_o}{h(t)}$$

therefore equations 2.8 and 2.10 are:

$$\sigma(t) = \frac{F(t)}{A(t)} = \frac{K_c V_c(t)}{\pi d_o^3 h_o} 4(h_o - D(F) + C(F))$$

$$\varepsilon(t) = \frac{\ln \left( \frac{h_o}{h(t)} \right)}{\ln \left( \frac{h_o}{h_o - D(F) - C(F)} \right) }$$

and

$$\varepsilon(t) = \frac{d\varepsilon}{d(t)}$$
Mechanical Tests

**Fig. 2.11** Displacement vs. Load for Hounsfield machine alone

\[ y = -0.0002x^4 + 0.0034x^3 - 0.0281x^2 + 0.1309x \]
\[ R^2 = 0.9989 \]

**Fig. 2.12** Dropweight photodiode calibration

\[ y = -1.434x^4 + 6.0151x^3 - 8.2001x^2 + 6.3009x + 0.9408 \]
\[ R^2 = 0.9995 \]
The load versus displacement curve, $C(F)$ for the machine alone is shown in Figure 2.11. The height of the sample was calculated by subtracting the machine compliance from the displacement of the crosshead at the same values of load. All the operations required to obtain true stress versus true strain curves were performed in Microsoft Excel v5.0. The same spreadsheet package was used in the calculations in the following sections.

### 2.3.6.2 DROPWEIGHT MACHINE

Strain gauges and photodiode were calibrated before mechanical tests were carried out. The photodiode was calibrated by cutting the laser beam with the blade of a digital Mitutoyo callipers (Digimatic model CD6). The output voltage was recorded with a digital voltmeter. Figure 2.12 shows the displacement versus voltage plot. The curve shows some curvature so the plot was fitted to a fourth order polynomial rather than to a linear fit. The laser intensity was usually adjusted so the photodiode output reproduced the calibration curve. The flag attached to the weight was adjusted to strike the roller when it was in the linear part of the photodiode response. Strain gauges were calibrated statically in the Hounsfield machine keeping the same test arrangement as in the Dropweight machine. The output was recorded with a voltmeter. Figure 2.13 shows the load versus voltage curve and the linear fit. The 'steps' in the Figure were caused by the limited accuracy of the voltmeter to two decimal Figures.

Stress and strain curves were calculated as for the Hounsfield machine except that the strain gauges calibration factor and the third order polynomial were used to convert voltage into load and displacement.

### 2.3.6.3 THE CROSS BOW SYSTEM

Owing to the length of the transmitter bar, strain gauges could not be directly calibrated using the Hounsfield machine. Instead a pair of the same type of strain gauges from the same production run were glued on a roller and calibrated statically.
**Mechanical Tests**

**Fig. 2.13** Dropweight strain gauges calibration

\[ y = 93.42x - 626.29 \]
\[ R^2 = 0.9993 \]

**Fig. 2.14** Cross Bow strain gauges calibration

\[ y = 124.79x - 834.05 \]
\[ R^2 = 0.9982 \]
Mechanical Tests

\[ y = -0.0085x^3 + 0.0539x^2 + 0.5297x - 0.2884 \]
\[ R^2 = 0.9984 \]

Fig. 2.15 Cross Bow photodiode calibration

\[ y = 7.907x^2 - 15.956x - 248.17 \]
\[ R^2 = 0.9994 \]

Fig. 2.16 Second order fit of strain gauges
The diameters of the roller and bar are the same, 12.69±0.01 mm, so the calibration factors were assumed to be the same. This is in accordance with Hamdan (1994) who found that the difference between direct calibration of the gauges glued in the transmitter bar using a Split Hopkinson Bar and calibration of gauges glued on a roller of the same diameter was about 0.02%. Figure 2.14 shows the load versus voltage curve and the linear fit. Thin pieces of aluminium, 0.13 mm thick, were used to calibrate the photodiode. The aluminium was placed between the impact and transmitter bar and the voltage corresponding to the gap between the two flags recorded with a voltmeter. The laser intensity was adjusted before every test to start from similar conditions. Figure 2.15 shows the flag separation versus voltage for the Cross Bow system. The data analysis was exactly the same as for the Dropweight machine except the conversion factors.

2.3.7 STRAIN LIMITED TESTS

Strain limited tests were carried out at four strain rates with the aid of metal rings. The rings were placed in the machines with the sample in the middle and the load was applied as usual. The thickness of those rings were 1.5, 1, 0.5 and 0.3 mm. Thus, for specimens 2 mm thick, the strains attained were 30, 70, 140 and 185% respectively. The internal diameter of the rings was such that the sample expansion was halted before the sample diameter was equal to the internal ring diameter. The purposes of these tests were to study the influence of strain in the deformation process and microstructure, see Chapters 3 and 4, and to estimate the temperature rise at different strains. Under the assumption that all the work was transformed into heat (no heat was generated due to crystallisation or any other process), the temperature rise was calculated by, see Appendix 2:

\[ \Delta T = \frac{\int \sigma \, d\varepsilon}{C_p \rho} \]  

(2.16)

where \( C_p \) is the specific heat and \( \rho \) the density of the sample. In the calculation of temperature rises the density of amorphous PET was chosen as 1.35 g/cm\(^3\) and the
specific heat was 1.315 \text{Jg}^{-1}\text{K}^{-1}. Integration of the curves was done geometrically. The error in the temperature rise was small, about 2 K because integration along the strain axis cancelled out the effect of vibrations.

2.4. ERRORS

Load and displacement measurements were subjected to several sources of error, such as deflection of bars and rollers, calibration, stress wave dispersion, friction restraints on the loaded surfaces, inertial effects by both radial and longitudinal particle acceleration, adiabatic heating, ejection of the sample and volume conservation assumption.

The steel rollers, although much harder than the materials used, are also subjected to compression. Thus, Heavens and Field (1974) claimed that the insertion of a sample will give rise to a non uniform strain near the surfaces of the steel rollers. The change in length of the rollers at the peak of the force curve can be calculated from Hooke’s law. A typical value of force at the yield point is approximately 2300 N, see Figure 2.1:

\[ \sigma = E \frac{\Delta h}{h_o} \Rightarrow \Delta h = h_o \frac{\sigma}{E} = h_o \frac{F/A}{E} = 1 \mu m \]

where \( h_o \) is the height of a roller equal to 12.69 mm which is equal to the diameter and \( E \) is the Young's modulus for steel equal to 200 GPa. At the peak of the Load versus Elongation curve the load is 20000 N which yields a deflection of about 10 \( \mu \)m. These values are even smaller than the error in measuring the sample dimensions which is approximately \( \pm 0.05 \) mm. Therefore, the compression of the rollers can be neglected.

Another source of error is the residual non-linearity in the overall system calibration where the force calibration factor is assumed to be the linear fit of the Force versus Voltage plot. The force applied to the rollers can be written as: \( F = kV(1+bV) \), Figure
2.16 shows that $b = \frac{7.907}{15.956} = 0.5V^{-1}$ and the second order fit is only 0.001 better than the linear fit, so it was discarded. The difference in the force value using both fits is smaller than 1\% for a voltage of, for example, 6.9 V, which is about the middle of the calibration range.

Any sudden contact between two bodies initiates vibrations and stress waves in both. The propagation of longitudinal stress pulses is dispersive for wavelengths that are of the same order of magnitude as the bar diameter, Gorham et al. (1992). Hence, for small diameter bars dispersion effects are only significant at high frequencies. The diameter of a roller or bar is approximately 12.69 mm. Thus, the frequencies affected by dispersion effects along the rollers or bars have frequencies greater than $f = \frac{c}{\lambda}$ where $f$ is the frequency and $c$ the sound speed in the bar, approximately equal to 5240 ms$^{-1}$, Hamdan (1994). Substituting into the previous equation the frequency is equal to 413 kHz. As can be seen from Figure 2.17 the frequency spectrum of a typical high rate experiment does not contain frequencies above 50 kHz, so dispersion effects are not important. Note that dispersion would be avoided if the bar had an infinite cross section.

Friction at the specimen ends is the most important quantity which is likely to cause significant deviation from the assumptions of uniaxial, homogeneous stress as well as the largest error in stress measurements. The interface introduces an effective hydrostatic term that makes the apparent flow stress of the polymer significantly greater than the true flow stress. The correction for friction at the yield point has been reported as $\Delta \sigma_y = \frac{2 \mu d}{3h}$ by Gorham et al. (1992) and $\mu = \frac{m}{2\sqrt{3}}$ or $\mu = \frac{m}{\sqrt{3}}$ where $\mu$ is the coefficient of friction and $m$ is the friction parameter. Samples were lubricated with high vacuum grease to reduce friction to low values. According to Walley et al. (1989), the lubricant that produces the most uniform deformation in a compression test is one that squeezes out in such a manner that the outwardly directed traction it exerts because of viscous drag exactly balances the inwardly directed traction due to shearing of the lubricant between the specimen surface of the anvil. Contrary to what
can be thought, Walley et al. found that frictional stress of unlubricated polymers is higher in the low rate tests than in high rate tests probably due to the absence of a rapidly shearing surface layer. These authors estimated the friction parameter for several materials and the values of \( m \) for lubricated specimens were below 0.05 for different lubricants. Therefore, in the worst case the correction to apply to a sample of 4 x 2 mm will be between 2 and 4% of the flow stress depending on which relationship between \( \mu \) and \( m \) is chosen.

The importance of friction in the machines used was tested by using PTFE without lubricant. This material has a very low friction coefficient and it is used as a lubricant itself. Thus, the true stress versus true strain curves should provide information about the behaviour of the lubricant during the deformation process. At low strain rates, Figure 2.18 the curve reveals the normal behaviour of PTFE. However, at medium strain rates Figure 2.19 the curve reveals some abnormal behaviour, it shows a sharp drop in stress about 20% and an increase in stress above 50% strain. Walley et al. (1989) reported yield stresses of 10 and 25 MPa at 10^{-2} and 10^{4} s^{-1} for PTFE which seems to agree with Figures 2.18 and 2.19. However, the same authors, Walley and Field (1994) reported that the yield stress between those strain rates did not follow a straight line with the logarithm of the strain rate, it increased and decreased and could not be fitted to Eyring's theory. The argument is that the yield stress of PTFE must increase with strain rate in accordance with viscoelasticity theory. Nevertheless, it is difficult to reach a conclusion with the present data, but it may be speculated that at low strain rates the lubricant may be efficient whereas at medium strain rates the efficiency may depend upon the strain.

As the rate of deformation increases so the force required to accelerate the material also increases. If the magnitude of this inertial force is significant compared with the deformation loads, the deformation is no longer uniform. According to Gorham (1989) quoting the results of Davis and Hunter (1963), the inertial stress component was cancelled if \( h = \frac{\sqrt{3}}{2} d \) whilst Samanta (1970) argued that cancellation occurred if \( h = \frac{\sqrt{3}}{4} d \). On the other hand, Gorham (1989) reported that those shape criterion are
**Mechanical Tests**

Fig. 2.17 Frequency Spectrum of typical Dropweight test

Fig. 2.18 PTFE tested at $10^{-3}$ s$^{-1}$ at 298 K
Mechanical Tests

Fig. 2.19 PTFE tested at 1230 s\(^{-1}\) at 298 K

Fig. 2.20 Strain vs. Time for the Hounsfield machine

\[ y = 0.0013x - 1.3753 \]
\[ R^2 = 0.9934 \]
not valid and no other suitable geometry was predicted. It is believed that this argument has not been resolved yet. The first order approximation of inertial force correction was reported by Gorham as:

\[
\rho \left( \frac{d^2}{16} + \frac{h^2}{6} \right) \dot{e}^2 - \rho \left( \frac{d^2}{8} - \frac{h^2}{6} \right) e^2 - \frac{\rho h v}{2}
\]

(2.17)

where \( \rho \) is the density, \( v \) the velocity of the lower specimen end and \( d \) and \( h \) are the specimen dimensions. The model assumes that the lower end of the specimen is moving with speed \( v \), as in the Cross Bow system. If the lower end is stationary, condition applicable to the Dropweight machine, the term proportional to \( v \) does not appear. Small samples and apparatus with small dimensions may minimise the inertial contributions. However, estimating first and second derivatives from calculated strain or velocity are usually unreliable, so the most appropriate use of the theory as it stands is simply as a check that inertial errors are negligible. Gorham et al. (1992) found that for copper the inertia forces were less than 2% the flow stress. Also, Gorham (1989) simulated the deformation of copper and reported that the inertial stress expressed as a percentage of the instantaneous flow stress goes from 1.2 to 0% with time. Sahraoui and Lataillade (1994) pointed out that the correction to apply for PMMA was less than 1.2%.

Adiabatic heating appears as a consequence of the heat developed due to the work done in producing the deformation. If the diffusion time of heat is much larger than the experiment time a rise of the temperature of the sample is expected which may affect the stress values. Plasticity theory asserts that deformation proceeds so as to maximise the dissipation of work. Chou et al. (1973) found that the computed and calculated temperature rise were equal and all the work was converted into heat. At low strain rates the heat developed during deformation will increase the sample temperature but an equilibrium temperature is reached rapidly compared to the experimental time, and the test will proceed in almost isothermal conditions. At high strain rates the work done on the sample will increase its temperature and the deformation proceeds adiabatically, i.e. without exchange of heat between the surroundings and the sample. However, the increase in temperature, see below, at the
yield point will not exceed 10 K owing to elastic behaviour but can be very large for large plastic deformations.

Experiments carried out using rollers or bars of 12.69 mm have an obvious limit of expansion after which sample is ejected out of the rollers and the strain measurement is no longer meaningful. Thus, assuming volume conservation if a sample of 4 mm diameter expanded until it reached the edge of the roller or bar, 12.69 mm diameter, the maximum strain was:

\[
h = \frac{h_o A_o}{A} = \frac{h_o \pi \left(\frac{d_o}{2}\right)^2}{\pi \left(\frac{d}{2}\right)^2} = \frac{h_o d_o^2}{d^2}
\]

so

\[
\varepsilon = \ln\left(\frac{h_o}{h}\right) = \ln\left(\frac{d^2}{d_o^2}\right) = 231\%
\]

Departure from the volume conservation assumption can lead to errors in the stress calculation. Effects such as barrelling which is due to friction and adiabatic heating could lead to volume changes. Walley et al. (1989) pointed out that plastic flow does not take place at constant volume but a volume change of 0.3% occurred after loading to 80 MPa. Nevertheless, these effects are very difficult to eliminate and volume conservation will be assumed throughout this work in accordance with other authors.

All the previous points emphasise the problems associated with measuring and comparing the mechanical performance of materials. Even further, Turner et al. (1984) remarked that each specimen type of a material has its own impact response characteristics and high precision cannot be expected. In order to make data comparable, exactly the same methodology has been followed for the experimental tests and the analysis of the signals. In addition, specimen dimensions were the same for all the materials tested. As a result of the previous discussion errors were expected to be about \(\pm 5\%\) at the highest strain rate, and since the errors are of the same order for different materials, this enabled us to compare the results with confidence.
2.5 RESULTS

Strain rates were calculated as the slope of the true strain versus time plots. The values were calculated as the average of ten tests at different temperatures. Figure 2.20 shows the plot for a typical experiment in the Hounsfield machine. The strain rate is approximately $10^3 \text{ s}^{-1}$ up to 50% strain. As a check of the validity of this value, an initial strain rate can be estimated by substituting into equation 2.12 the initial speed and height of the sample, thus: $\dot{\varepsilon} = \frac{0.1 \text{mm min}^{-1}}{2 \text{mm}} = 0.00083 \text{s}^{-1}$, which is close to the previous value. At higher velocities, strain does not fit to a straight line at large strains. Figure 2.21 shows a second order fit of true strain versus time for a medium strain rate test in the Dropweight and Figure 2.22 shows a linear fit up to 40%. The average value of the linear fits was $1230 \text{ s}^{-1}$. For this experiments the velocity was approximately equal to $2.2 \text{ m s}^{-1}$ which corresponds to a fall from 0.25 m if friction in the bars is ignored. In a similar way to before $\dot{\varepsilon} = \frac{2.2 \text{m} \cdot \text{s}^{-1}}{2 \text{mm}} = 1100 \text{s}^{-1}$, which is of the same order of magnitude as the average value. Figures 2.23 and 2.24 show the fits for a medium-high strain rate test in the Dropweight machine. The average value was $1940 \text{ s}^{-1}$. Likewise, for a fall of 0.6 m the strain rate estimation is $1700 \text{ s}^{-1}$. Figures 2.25 and 2.26 show the true strain versus time plots for the Cross Bow system. The strain rate up to 40% was as high as $8800 \text{ s}^{-1}$ on average. Both methods of calculating the strain rate yielded similar values.

2.5.1 POLYETHYLENE TEREPHTHALATE

Figures 2.27-2.30 illustrate the true stress versus true strain curves for PET at different temperatures and strain rates. The curves shown are the average curves of three tests. Figure 2.27 represents the curves at $10^3 \text{ s}^{-1}$. The yield stress was about 65 MPa at room temperature and decreased with increasing temperature. At temperatures of 363 K or above the material did not yield and the stress increased almost linearly up to large values of strain. At 263 and 298 K the curves show a drop in stress after
Mechanical Tests

Fig. 2.21 Second order fit of Strain vs. Time for Dropweight machine

\[ y = 8 \times 10^7 x^2 + 218244x + 133.14 \]
\[ R^2 = 0.9991 \]

Fig. 2.22 Linear fit of Strain vs. Time for Dropweight machine

\[ y = 1148.4x + 0.9865 \]
\[ R^2 = 0.9971 \]


Fig. 2.23 Second order fit of Strain vs. Time for Dropweight machine

\[ y = 2E+08x^2 + 550938x + 305.18 \]
\[ R^2 = 0.9989 \]

Fig. 2.24 Linear fit of Strain vs. Time for Dropweight machine

\[ y = 1891.4x + 1.6054 \]
\[ R^2 = 0.9959 \]
Mechanical Tests

Fig. 2.25 Second order fit of Strain vs. Time for Cross Bow machine

\[ y = 6 \times 10^9 x^2 + 2 \times 10^6 x + 112.11 \]
\[ R^2 = 0.9974 \]

Fig. 2.26 Linear fit of Strain vs. Time for Cross Bow machine

\[ y = 8639.7 x + 0.8213 \]
\[ R^2 = 0.993 \]
Fig. 2.27 PET tested at $10^3$ s$^{-1}$

Fig. 2.28 PET tested at 1230 s$^{-1}$
Fig. 2.29 PET tested at 1940 s⁻¹

Fig. 2.30 PET tested at 8800 s⁻¹ at 298 K
### TABLE 2.1

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### TABLE 2.3

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### TABLE 2.4

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Mechanical Tests

Fig. 2.31 PET Yield Stress vs. Strain Rate on a logarithmic scale

Fig. 2.32 PET Yield Stress vs. Temperature
Fig. 2.33 PET Flow Stress vs. Strain Rate on a logarithmic scale at 10% strain

Fig. 2.34 PET Flow Stress vs. Temperature at 10% strain
Mechanical Tests

Fig. 2.35 PET Flow Stress vs. Strain Rate on a logarithmic scale at 20% strain

Fig. 2.36 PET Flow Stress vs. Temperature at 20% strain
yielding, although this was not seen at higher temperatures. The nature of the yield drop has been a matter of controversy and will be discussed below.

Figure 2.28 represents the curves for PET tested at about 1230 s\(^{-1}\). The yield stress was about 140 MPa at room temperature and it decreased at higher temperatures. Unlike the results of the low rate tests the yield stress at 323 K, which is close to the glass transition temperature of PET, 353 K, was similar to the room temperature value. Figure 2.29 depicts the curves at 1940 s\(^{-1}\). The yield stress was about 160 MPa at 298 K. The trend of the curves was the same as for the medium strain rate, similar values of the yield point up to 323 K and lower values at higher temperatures. Both sets of curves display a tendency towards smaller values of stress after yielding.

The true stress versus true strain curve at room temperature and 8800 s\(^{-1}\) is shown in Figure 2.30. The stress increased linearly up to 203 MPa and it dropped afterwards. At strains of 95% there was an upswing in the curve which indicates that strain hardening phenomenon took place. Tests at higher temperatures were not carried out. The samples were very damaged after this test and were very difficult to use for subsequent analysis; see Chapters 3 and 4. At higher temperatures it was expected that no sample could be recovered.

The yield stress data together with the values of flow stress at 10% and 20% strain are tabulated in Tables 2.1, 2.2 and 2.3. Figure 2.31 shows the yield stress versus strain rate data for the different temperatures. The yield stress increased with strain rate at any temperature except at 453 K. Figures 2.33 and 2.35 display the flow stress at 10% and 20%. The curves resembled those of the yield stress. From Figure 2.35 and Table 2.3, it can be concluded that the values of stress at 20% are lower than the yield values which may indicate that some sort of strain softening occurred. Figure 2.32 depicts the yield stress versus temperature values. At low rate the yield stress decreased with temperature. However, it is remarkable that at higher rates the yield stress was almost constant up to 323 K and sharply dropped at higher temperatures. Figures 2.34 and 2.36 show the values at 10 and 20%. Curves are again similar to the yield stress one.
Fig. 2.37 PET Temperature Rise vs. Strain

\[ y = 1.1133x + 41.785 \]
\[ R^2 = 0.9894 \]

Fig. 2.38 PET fit to the Gaussian equation
The values of the temperature rise for the strain limited tests are tabulated in Table 2.4 and shown in Figure 2.37. It can be seen that at low strain rate the temperature rise increased linearly with strain. At higher rates, 1 and 10³ s⁻¹, the increase was linear up to 140% and slightly departure from linearity at larger strains. At 8800 s⁻¹ the temperature rise increased with strain. However, the four sets of data could be fit to fairly good straight lines. The latter agrees with Chou et al. (1973) who concluded that the temperature rise may be assumed to be linearly related to the strain after the specimen yielded.

It was first proposed by Argon (1973) that the plastic deformation of polymers could be described by an equation of the following type:

\[ \sigma_{\text{true}} = Y + G_p \left( \lambda^2 - \frac{1}{\lambda} \right) \]  

(2.19)

where \( \sigma_{\text{true}} \) is the true stress, \( Y \) the extrapolated yield stress, \( G_p \) the strain hardening modulus and \( \lambda \) the ratio of extension. This equation is called the Gaussian equation. The curve of PET tested at low rate and room temperature was fitted to this equation. This was done by taking points from the true stress curve in accordance with Haward (1987). The result is shown in Figure 2.38. The points display some scatter but they fitted fairly well to a straight line over a long range of extension between 65 and 115% true strain.

2.5.2 NYLON 11

True stress versus true strain curves of Nylon 11 are shown in Figures 2.39-2.43. Curves of Nylon 11 tested at 10³ s⁻¹ at 263 K and 298 K are shown in Figures 2.39 and 2.40 respectively. Yield stress always involves a change of slope in the true stress versus true strain curve. Thus, if a clear yield is not seen the yield stress can be estimated as the intersection of the tangents to the initial and final parts of the curves. In accordance with this, yield stress was about 50 MPa at 298 K while is approximately 35 MPa at 263 K. The stress continuously increased after yielding. The values of yield stress for different annealing treatments were very close, within about
Fig. 2.39 Nylon 11 tested at $10^{-3}$ s$^{-1}$ at 263 K

Fig. 2.40 Nylon 11 tested at $10^{-3}$ s$^{-1}$ at 298 K
Mechanical Tests

Fig. 2.41 Nylon 11 tested at 1230 s\(^{-1}\) at 298 K

Fig. 2.42 Nylon 11 tested at 1230 s\(^{-1}\) at 263 K
Mechanical Tests

Fig. 2.43 Nylon 11 tested at 8800 s^{-1} at 298 K

Fig. 2.44 Nylon 11 Yield Stress vs. Strain Rate on a logarithmic scale
5 MPa of the central value, which is within error.

Figures 2.41 and 2.42 show the curves at 1230 s\(^{-1}\). The yield stress was approximately 125 MPa at 298 K. Yield stress was taken as the maximum in the true stress versus true strain which corresponded to the maximum observed load, so the first peak or shoulder was ignored for practical purposes. The values of yield stress at 263 K are smaller than at 298 K again. After yielding, stress slightly decreased or remained constant up to large strains.

Figure 2.43 depicts the curves at 8800 s\(^{-1}\) and 298 K. The yield stress was about 110 MPa differing by about 5 MPa for different annealing treatments, again a very small amount. Yield drop was not seen for these tests, instead deformation seemed to evolve with little change of stress after yielding. The yield stress at high strain rates was smaller than the value at medium strain rates which will be analysed below.

The data are shown in Tables 2.5-2.7. Figure 2.44 shows the yield stress versus strain rate. The data showed an increase in yield stress from low to medium rate but it decreased for higher rates. Figures 2.46 and 2.48 show the flow stress values at 10% and 20% strain. The Figures are very alike to the yield stress one. Figure 2.45 depicts the values of yield stress versus annealing. The yield point seemed to be fairly constant with annealing treatment for the different strain rates. The same can be said for the flow stress at 10% and 20% in Figures 2.47 and 2.49.

Figure 2.50 depicts the data for Nylon 11 tested at 10\(^{-3}\) s\(^{-1}\) at room temperature and the best fit to the Gaussian equation. Again the points show some scatter but the confidence of the fit is reasonable. The stress values comply with the Gaussian equation between 15 and 65% strain, but it brakes down at larger strains.

2.6 DISCUSSION

The mechanical properties of PET and Nylon 11 were studied at different strain rates and temperatures by means of a conventional Hounsfield machine, a Dropweight
### TABLE 2.5

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<th>Rate (s(^{-1}))</th>
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### TABLE 2.6

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Mechanical Tests

**Fig. 2.45** Nylon 11 Yield Stress vs. Annealing Treatment. 1: as-received; 2: 15 min @ 170°C; 3: 30 min @ 190°C

**Fig. 2.46** Nylon 11 Flow Stress vs. Strain rate on a logarithmic scale at 10% strain
Fig. 2.47 Nylon11 Flow Stress vs. Annealing Treatment at 10% strain. 1: as-received; 2: 15min@170°C; 3: 30min@190°C

Fig. 2.48 Nylon 11 Flow Stress vs. Strain Rate on a logarithmic scale at 20% strain
Mechanical Tests

Fig. 2.49 Nylon 11 Flow Stress vs Annealing Treatment at 20% strain. 1: as-received; 2: 15min@170°C; 3: 30min@190°C

Fig. 2.50 Nylon 11 fit to the Gaussian equation

\[ y = 8.1047x + 53.227 \]

\[ R^2 = 0.9878 \]
mechanical and a Cross Bow system.

2.6.1 POLYETHYLENE TEREPTHALATE

The yield stress of PET at low rates, which are the most common type of experiment in the literature, was found approximately equal to 60 MPa by Walley and Field (1994) which compares fairly well with the value of 64 MPa found in this study.

The nature of the yield drop found in some polymers has been subjected to debate. Two explanations were given for a yield drop: i) localised heating during stretching causes softening; ii) geometrical effect due to the fact that the fall in cross sectional area during stretching is not compensated by and adequate degree of strain hardening. However, Brown and Ward (1968) suggested that the drop was intrinsic to the material after finding that it occurred after yielding in tension, shear and compression, although their stress calculations were based on the original cross section. Thus, they concluded that it was just the difference between conditions for the initiation of yielding and for the propagation of yielding that caused an intrinsic drop in the load.

G’Sell and Jonas (1991) used a pioneering system to stretch polymers at constant true strain rate which, they claimed, eliminated any geometrical effect. They found different post yield behaviours depending on the material tested. Therefore, the yield drop is material dependent and may not be exhibited by the same material, for example with a different molecular weight, let alone a different material.

Beyond the yield point, strain softening or hardening may take place. Chou et al. (1973) suggested that at strain rates above $10^3 \text{s}^{-1}$ the stress decreased while the strain increased possibly due to the heat developed. Walley et al. (1989) reported that the curves obtained at low strain rates, $10^2 \text{s}^{-1}$, invariably showed strain hardening once a critical strain characteristic of the polymer was exceeded, whereas curves obtained at higher strain rates usually showed either flow at nearly constant stress or strain softening. Hellinckx and Bauwens (1995) claimed that strain hardening was shown by engineering stress but not by true stress. The degree of strain softening exhibited by PE at the yield point increased as the temperature was reduced according to Brooks et
al. (1997) who quoted the results of Vincent (1960). Strain softening may be associated with a temperature rise in the material due to the heat developed. Viscous materials always exhibit stress relaxation during the process of deformation. Thus, due to relaxation the energy stored must decrease and it is dissipated as heat. The process of relaxation occurred continuously during the deformation. At small strains, the time required to deform the specimen is relatively short in comparison with the characteristic relaxation time of the material and the temperature rise is small. Chou et al. (1973) reported rises of 10 to 20 K at 20% strain and 1000 s\(^{-1}\) which are larger than the values tabulated in Table 2.4 for similar conditions.

Figures 2.27-2.30 show that stress dropped after yielding at any strain rate and temperature except at the lowest rate above 323 K. At the yield point, the temperature rise is smaller than 10 K for the highest strain rate, which is considered too small to produce any substantial softening. The fact that the drop was found under different conditions supports the idea that it is genuine to the material and not due to some effect in accordance with Brown and Ward (1968). Thus, after the chains were moved of their position of equilibrium to a new position and the material yielded, the stress required to continue deformation was smaller than at the yield point. Past the initial drop, the material experienced different behaviours. At low rates, the stress was constant after the drop and tended to increased at about 90% strain. These experiments followed isothermal conditions, i.e., the temperature of the sample reached a thermodynamic equilibrium rapidly compared with the time of the experiment. Strain hardening commenced when long movement of chains was initiated. In the \(10^3\) s\(^{-1}\) range, Figures 2.28 and 2.29, the stress at 100% strain and 323 K and below was smaller than after the yield drop. The experiments at this strains are adiabatic, i.e., the temperature of the sample increased in accordance with the temperature rise because the heat is not dissipated within the experiment time. Thus, it is thought that strain softening may have been caused by the heat developed which increased the temperature of the sample by approximately 40 K at 100% strain. At temperatures above room temperature, the heat developed and consequently the temperature rises are smaller, so strain softening is not very marked. At 8800 s\(^{-1}\), the material flowed at almost constant stress and exhibited a severe strain hardening above 90% strain. The
temperature rise for this type of experiment was estimated as 50 K, which should lead to strain softening as at lower rates. This may indicate that strain softening is not due to the heat developed. Nonetheless, the origin of this strain hardening is not understood and the following chapters will shed some light on the phenomenon.

Figure 2.32 shows that at high rates the yield stress did not decrease up to temperatures above 323 K. Contrary, Lee et al. (1988) reported that PEEK suffered a significant loss in its mechanical properties as the temperature approaches the glass transition temperature, the yield stress decreased by 30% for amorphous PEEK and 60% for semi-crystalline PEEK at rates of 20 mm/min. Truss et al. (1984) found a decrease of tensile yield stress with temperature of PE at strain rates of $10^{-2}$ s$^{-1}$ from 120 to 300 K. Fleck et al. (1990) reported a decrease on shear yield stress with temperature of PC up to 2000 s$^{-1}$ and 473 K. Andrews and Ward (1970) reported that yield stress of HDPE decreased with temperature at low strain rates (below $10^1$ s$^{-1}$).

Medellin and Phillips (1990) claimed that the yield stress of PEEK decreased monotonically with increasing temperature between 180 K to 333 K at 5 mm/min. Similar results were published by Jabarin (1992) on PET between 353 and 383 K at 127 mm/min However, he concluded (1991) that stretching around the glass transition temperature caused more amorphous chains orientation which resulted in higher mechanical properties than at higher temperatures Brooks et al. (1996), reported that the yield of PE increases approximately exponentially as the temperature is reduced. Lucas et al. (1995) found that the yield of PE decreased with temperature. Hartmann and Lee (1991) reported that the yield of PCTFE and PVF decreased with temperature with no effect at the glass transition temperature at rates of 2 min$^{-1}$. Han et al. (1994) reported a linear decrease with temperature of PEK-C. Bauwens-Crowet et al. (1972) found that the tensile yield stress of PC decreased linearly with temperature at a constant strain rate. The literature results seem to agree with the curve at $10^{-3}$ s$^{-1}$. However, at higher rates the data are not comparable. It is thought that the large yield stress found around the glass transition temperature must be related to changes associated with the glass transition and the viscoelastic character of the material which will be discussed in Chapter 6.
Another feature worth noticing is that the true stress versus true strain curves at low rate and temperatures of 363 and 453 K of Figure 2.27, did not show a yield point. It was reported by Hitt and Gilbert (1992) that UPVC above its glass transition temperature (353 K) behaved in a rubber like manner and showed no yield point, similar to Figure 2.27. It was suggested by Spruiell et al. (1972) quoting the results of Foster and Heap (1957) and Thompson (1959) that when amorphous PET is deformed above the glass transition temperature two deformation regimes could be distinguished. In one regime, occurring at relatively high strain rates, high stresses occurred; the second deformation regime, called flow deformation, was characterised by a low deformation stress. The curves above the glass transition temperature in Figures 2.27-2.29 seem to accord with this results, at low strain rates the material followed the flow deformation whereas at higher strain rates the material yielded at higher stresses.

Eyring’s theory of viscosity, see section 2.2, has been used to model the yielding behaviour of plastics with different success. The cornerstone of the theory is that the mechanical properties of a viscoelastic material should increase with the strain rate and the dependence must be linear with the natural logarithm of the strain rate. The review of the results contains the behaviour of stress with strain rate and the agreement with Eyring’s theory. Lee et al. (1988) reported that the yield stress of PEEK drawn at room temperature increased with the displacement rate. Truss et al. (1984) found a constant dependence of the yield stress on logarithm of strain rate at low rates and high temperatures which changed to a higher dependence at high rates and low rates in the range $10^{-4}$-$10^{-1}$ s$^{-1}$, i.e. two linear relationships with different parameters were needed to fit the data. Fleck et al. (1990) reported a very modest influence on the yield stress of PC in shear at high temperatures, with changes smaller than 20 MPa in the range $10^{-3}$-2000 s$^{-1}$. However, the data fitted a single stage Eyring equation. Chou et al. (1973) found increases in the yield stress of PMMA, CBA, PP and Nylon from 10 to 20 KSI in the range from $10^{-4}$ to 1000 s$^{-1}$. However, the yield stress did not increase linearly with the logarithm of strain rate for all the conditions and found a sharp increased beyond $10^{2}$ s$^{-1}$. Andrews and Ward (1970) reported that the yield stress fitted a linear relationship up to $10^{4}$ s$^{-1}$ for HDPE. Briscoe and Nosker
(1985) claimed that the Eyring type linear increase fitted the yield stress of HDPE up to $10^4$ s$^{-1}$, in contrast with Briscoe and Hutchings (1976) where a substantial enhancement in the room temperature flow stress of HDPE was reported. Jabarin (1992) found that the yield stress of PET increased with increasing speed of extension at 373 K. However, Spruiell et al. (1972) found that yield stress of PET was approximately independent of strain rate at 298 K while it increased logarithmically between 0.047 and 1.88 min$^{-1}$ at 333 K. Plummer et al. (1995) reported an increase of yield stress of POM with strain rate up to 1000 s$^{-1}$. Likewise, Hellinckx and Bauwens (1995) found that the yield stress of PVDF above 373 K was almost constant at low rates and increased at higher rates, exhibiting more than one linear relationship. The yield stress of PP was found to increase from 20 to 50 MPa on increasing the strain rate from 0.05 to 200 s$^{-1}$, Alberola et al. (1995). Povolo and Hermida (1995) reported that the yield curves of PMMA exhibited a definite curvature up to $10^1$ s$^{-1}$, so a simple Eyring equation did not fit all the data. Sjoerdsmma et al. (1982) found a linear relationship between the yield stress of TPS and logarithm of strain rate between $10^4$ and $10$ s$^{-1}$ up to 323 K. Sahraoui and Latallaide (1994) claimed that the yield stress of PMMA increased with strain rate up to $10^1$ s$^{-1}$. Walley and Field. (1994) found that PET yield stress increased from 83 to 193 MPa in the range $10^2$-2x$10^1$ s$^{-1}$ at 20% strain. Their study comprised a large number of materials behaving differently: ABS, PET, PP, PVC, and PVDF showed a bilinear relationship with a sharp increase at about 1000 s$^{-1}$; Noryl, dry Nylon 66, PC, PEEK and PES showed a decrease at about 1000 s$^{-1}$; while Acetal, Nylon 6, HDPE and PBT did not unambiguously a change of slope. Hartmann and Lee (1991) found that PCTFE and PVF followed a linear relationship up to 10 min$^{-1}$ and 383 K. Han et al. (1994) concluded that the yield stress of PEK-C complied with Eyring's equation at low rates. Alberola et al. (1997) found that the yield stress of PEEK showed to slopes up to 300 s$^{-1}$. Finally, Rao et al. (1997) reported that the yield stress of PU increased sharply beyond 100 s$^{-1}$.

Summarising, it is common to all the results that the yield stress increased with strain rate. This is due to the viscous character of polymers. The viscous behaviour arises because of the viscous resistance offered to motion of segmental units and molecular chains by the surrounding medium. Thus, the increase of yield stress with strain rate
Mechanical Tests

may be related to a slower segmental motion and/or rotation with increasing strain rate. However, whether the increase in yield stress is linear or not can not be inferred from the review.

Even though Eyring’s theory is based on viscoelasticity, the theory can not fit the data when a sharp increase in yield stress is found. In this case, two or more Eyring type equations should be used with different parameters for low and high rates. Thus, the yield stress behaviour have been associated with the mechanical relaxations (α, β and γ) and melting process, depending on the conditions. However, it is not clear whether the behaviour could be characterised by more than one set of parameters, which means that different mechanical processes would act independently under different conditions. Thus, Fotheringam and Cherry (1976) described the yield curves using a model based on n activated rate processes acting simultaneously, so the yield stress of a co-operative system has the strain rate dependence of a single activated rate process to the n"th power. The processes are thought to be related to the different degrees of freedom of a chain segment. Figure 2.51 shows the yield stress/temperature versus natural logarithm of the strain rate for PET at different temperatures. It can be seen that the yield stress of PET increased drastically at approximately 7, equivalent to $10^3$ s$^{-1}$. The data above $10^3$ s$^{-1}$ at 298 K followed a linear relationship with a factor of 0.97. Nevertheless, it can not be compared with data at other temperatures because there is insufficient data. Therefore, PET yield behaviour cannot be described by a single type of Eyring’s equation, so it is thought that PET was subjected to a strain rate enhancement above $10^3$ s$^{-1}$ due to some transition being activated. In terms of several processes, whether acting simultaneously or not, it is believed that they may have contributed differently to the yielding depending on the strain rate and temperature. The strain rate sensitivity can be estimated as the slope of the line between low rates and medium strain rates multiplied by the corresponding temperature. Thus, the strain rate sensitivities were, 5.0, 5.3 and 7.8 MPa/decade at 263, 298 and 323 K respectively. At room temperature and high rates the strain rate sensitivity was 31.5 MPa/decade.

However, whether two linear relationships or the more complicated relationship

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Fig. 2.51 PET Yield Stress/Temperature vs. ln Strain Rate

Fig. 2.52 Nylon 11 Yield Stress/Temperature vs. Ln Strain Rate
suggested by Fotheringham and Cherry (1976) are used, i.e., the activated processes act independently or simultaneously, the dependence of the yield behaviour on strain rate and temperature is useful to describe the mechanisms acting in a non-linear isotropic viscoelastic material. Both phenomenological and molecular models agree that a co-operative motion is responsible for yielding and plastic flow. The processes have been matched with different molecular phenomena. The melting-recrystallisation one has many followers. Hellinckx and Bauwens (1995) supported this idea and he found that the length of a chain segment melted would be equal to the lamellae thickness, so they concluded that the melting process affected a chain segment located between two folds. Andrews and Ward (1970) also supported this idea but evidence was not provided. This argument agrees with the idea that yield should be associated with the crystalline phase. Also, processes were associated with the transitions seen in the mechanical loss spectrum (or Differential Scanning Calorimetry), namely $\alpha$, $\beta$ and $\gamma$. These are the most common processes associated to the activation energies found.

However, several other processes have been reported to occur after yielding and the activation energy of those estimated and compared with the phenomenological activation energy. Truss et al. (1984) reported that plastic deformation involved pulling out of chains and suggested that it occurred with a substantial amount of chain scission of a weak point in the chain. Argon (1973) considered plastic deformation to occur by the kinking of molecular chains and estimated the energy associated with the formation of a kink. Thompson (1959) claimed that the simplest model in which the stretching of a linear polymer could be described involved two mechanisms. In the first the polymer slipped past each other bodily by relative movement of their centre of gravity, while in the second each randomly coiled chain tended to uncoil and straighten out in the direction of the tension. The first kind is not recoverable and it occurs as long as the stress remains, viscous extension. The second kind is recoverable for thermal agitation will restore the coiled state, rubber like extension. The kind of forces which may be overcome during deformation may be inter-molecular-elastic interaction between molecules or intra-molecular. Andrews and Ward (1970) pointed out that the sliding of molecules depended on short range intermolecular forces and was independent of entanglements. On the other hand Povolo and Hermida (1995)
quoting Robertson (1963) suggested that intra-molecular forces were the primary factor for deformation, its rate being a function of temperature. However, Yamamoto and Furukawa (1995) suggested that both forces were involved in the shear yield of polymers, this occurring by local motion of molecules. Thus, they concluded that shear yield consisted of intermolecular effects (cohesive energy density, chain sliding) and intra-molecular effects represented by the characteristic ratio (thought to be related to conformational or configurational changeability). Besides, Ishikawa et al. (1996) suggested a difference between plastic deformation and yielding claiming that the molecular process of plastic deformation was the rotation of small molecular segments, without the slip of molecular chains. However, craze yielding was accompanied by a slip between oriented molecular chains around voids resulting from high dilatational stress. Hartmann and Lee (1991) pointed out that whatever the yield process may be in detail, it occurred at a given average inter-molecular separation.

A proposed description of the deformation process is as follows: below the yield point the stress increased linearly with strain and the deformation was recoverable. The yield stress was a threshold, so below the yield there was not enough energy transferred to the system to overcome the energy barrier between the two equilibrium positions. Once the yield point was reached and chains started to move without recovery, intuitively, inter and intra-molecular forces should act. Intra-molecular forces act when changes in the chain were intended, whereas inter-molecular forces acted when two chains were brought close to each other. While all the movements were taking place the internal energy of the system increased because of chain movement. While the chains tended towards the new equilibrium position the energy began to decrease until the new positions were reached. This could explain the drop in stress if it is assumed that the equilibrium position was reached just after yielding. Beyond that, the viscous character of the material dominated the elastic behaviour. At low strains, the chains may have not change their position again and a fairly constant stress sufficed to produce conformational changes in the chain by rotation of molecules. At higher strain rates, the temperature rise could provide part of the energy required for such a changes to occur so the stress decreased. However, configurational changes are not discarded to occur which will be widely discussed in Chapter 6.
An understanding of plastic deformation in molecular terms is provided by the Gaussian equation. The equation was derived for low strain rate tests well below the glass transition temperature of the material. However, the model predicts that there could never be a peak in the true stress versus true strain curve and other beginning effects. Thus, due to the drop in stress seen for PET the agreement with the Gaussian theory began at strains beyond this point. The strain hardening modulus, $G_p$, is related to the molecular weight between entanglements, $M_e$, by $M_e = \frac{\rho RT}{G_p}$ where $\rho$ is the density. Thus, substituting the values for PET the molecular weight between entanglements was approximately 3000. This is approximately 15 repeating units of PET.

### 2.6.2 NYLON 11

The behaviour of Nylon 11 will be analysed much along the lines of the previous section, using the literature results already summarised. The yield stress of Nylon 11 at room temperature and low strain rates was found to be about 51 MPa which cannot be compared with any literature value. The curves for Nylon 11 seem different to those of PET, so some differences in their mechanical behaviour is expected.

Figures 2.39-2.43 show that the yield drop did not occur for Nylon under any conditions but some strain softening occurred in tests carried out at 1230 s$^{-1}$. As already suggested, the yield drop is intrinsic to a material and this results lend weight on the idea. Beyond the yield stress, stresses tend to be constant or increase. According to G'Sell (1979) true strain softening does not occur with crystalline polymers (Nylon 11 is a semi-crystalline, see Chapter 4). However, the temperature rise for Nylon 11 is expected to be slightly smaller than for PET, because both materials have similar density and specific heat values but the areas under the true stress versus true strain curves are in general smaller for Nylon. In any case the temperature rise is expected to be significant. Thus, the crystal structure may play some role in accounting for the absence of strain softening. Severe strain hardening at
8800 s\(^{-1}\) also occurred with Nylon 11 but at larger strains than for PET, approximately 130% and again it may be related to the crystal structure and will be discussed in Chapter 6.

It is worth mentioning that values of yield stress at room temperature were larger than at 263 K. The explanation for this could be the presence of water. It has been reported that the absorption of water (very high for Nylons) may act as a plasticiser, lowering the yield stress of the material in comparison with the yield stress of the dry material. For example Walley and Field (1994) reported that the yield stress of dry Nylon 66 is 80 MPa whereas is 50 MPa for the moist material. Thus, a larger absorbency of water while the material is cooled at 263 K would suffice to account for the lower values.

Figure 2.52 depicts the yield stress/temperature versus natural logarithm of strain rate. As for PET the data cannot be fitted to a single line. However, it was remarkable that the yield stress decreased for tests carried out at 8800 s\(^{-1}\) independently of the annealing treatment. This matched some of the results outlined above. The strain rate sensitivities can be estimated as above, giving 5.3 and 4.5 MPa/decade for as received Nylon at 298 and 263 K respectively. For samples annealed at 170°C for 15 minutes the strain rate sensitivities were 5.4 and 5.0 MPa/decade at the same temperatures. Finally, Nylon 11 annealed at 190°C for 30 minutes had sensitivities of 3.8 and 4.8 MPa/decade at those temperatures.

The possible molecular mechanisms outlined in the previous sections are valid for Nylon 11 as well. However, intuitively, in a semi-crystalline material deformation should be directly connected with the volume fraction of the crystalline phase; see below. Therefore, some extra consideration should be taken into account. Brooks et al. (1997) concluded that in the neck formed during tensile deformation the lamellae were destroyed by the process of shear along the polymer axis. Similarly, Hartmann and Lee (1991) citing Peterlin (1980) argued that the yield of semi-crystalline polymers started with a transformation from lamellar structure to a fibrous structure which was followed by the disruption of the crystallites. Jabarin (1991) pointed out that the deformation of crystallised PET involved the spherulitic deformation and
consequently the disruption of chain folded lamellae. Kennedy et al. (1994) proposed that a ductile deformation required that there be an adequate number of sequences of disordered chain units connecting the crystallites, i.e., the interlamellar region must possess elements or chains that display rubber-like behaviour.

Thus, any description of the deformation mechanisms must comprise considerations about the semi-crystalline character of this material. Nevertheless, an explanation of deformation in terms of the microstructure will be attempted in Chapter 6 when all the evidence is presented. Hence, Nylon 11 behaved similarly to PET up to the yield point. However, Nylon 11 did not show a drop in stress, then the mechanism involved must be different to that of PET. This could be related to the crystalline phase and the deformation of chains within the spherulites which have high cohesive energy. The relaxation of chains in the amorphous phase which may lead to a drop in stress may be compensated by the high energy required to deform the crystalline structure. Beyond the yield point the energy required to transmit the deformation seemed to increase constantly with strain and could be associated with the crystalline phase again. Thus, changes such as rotation of molecules and straightening of chains may not occur.

Figure 2.50 shows that the agreement between the Gaussian equation for Nylon 11 is restricted to small true strains. At large strains the stress flattened out and it did not comply with the equation. However, Haward (1993 and 1994) reported similar ranges for several materials. The molecular weight between entanglements for Nylon 11 was nearly 320 which corresponds to approximately one and a half repeating units of Nylon 11.

2.7. CONCLUSIONS

PET and Nylon 11 were tested using the same experimental methodology to make data comparable. Therefore, it can be concluded that:

i) the drop in stress after yielding is genuine to the material, which is supported by the idea that the drop was found for PET under different conditions whereas it did not
Mechanical Tests

occur for Nylon 11.

ii) the two materials behaved differently with strain rate. PET showed a sharp increase in flow stress at strain rates around $10^3$ s$^{-1}$. On the other hand, Nylon 11 yield stress increased almost linearly, although it did depart at the highest strain rate. The strain rate enhancement of PET and the opposite behaviour of Nylon 11 are believed to be intrinsic to the material and associated with the microstructure, see Chapter 6, contrary to Zhao (1998) who claimed that it was due to a thickness effect. The fact that the dimensions and the errors involved in measuring the deformation of both materials were almost identical but behaved completely different reinforces the veracity of the results against any dimensional effect. The departure of PET and Nylon 11 yield stress values from Eyring’s theory could be due to the assumption employed to apply the theory originally derived for solutions to the yield behaviour of solid polymers. Thus, the applied stress may not induce molecular flow much along the lines of the theory so the internal viscosity does not fall to a value such that the applied strain rate is equal to the plastic strain rate predicted by Eyring’s equation at high rates.

iii) PET yield stress decreased at low strain rates on passing the glass transition temperature. Nonetheless, at higher strain rates it was almost constant up to temperatures above the transition.

iv) two deformation mechanisms are envisaged for this materials. The deformation of PET involved the moving and rotation of molecular chains in the amorphous phase while the deformation of Nylon 11 must take into account the crystalline phase. Thus, the ways deformation is transmitted into the materials are different.

v) PET and Nylon 11 complied with the Gaussian equation in the case of compression, PET agreeing up to larger values than Nylon but departed from linearity at small values. The plots of true stress versus compression and the values of modulus agreed with data published by Haward (1993 and 1994). Polymers with a more extended chain configuration have higher values of the strain hardening modulus, $G_p$. Thus, the values of the modulus for PET and Nylon can be regarded as indicative of
the different behaviour shown by these materials. Nevertheless, large values of $G_p$
may lead to small unacceptable values of molecular weight between entanglements
according to the theory of rubber elasticity which may be the case of the value found
for Nylon 11 in this work.
CHAPTER 3

WIDE ANGLE X-RAY DIFFRACTION
3.1. INTRODUCTION

X-ray diffraction is recognised as one of the most powerful tools available for the study of solids and has been widely used in the study of polymer crystallinity. It has been extensively reported (see below) that PET crystallise during cold drawing. It is also believed that during compression molecular orientation and/or crystallisation may occur. X-ray diffraction was used to study the structure of PET and the possible structural changes with strain, strain rate and temperature. It is also the aim of the work described in this chapter to provide a more concrete structural basis for the interpretation of the mechanical properties reported in Chapter 2. As well as PET, the structure of Nylon 11 under different thermomechanical conditions was studied.

Regular crystallographic arrangement of molecules is needed to observe X-ray diffraction peaks. For any crystal, atomic planes exist in a number of different orientations each with its own specific d spacing. A single crystal can be characterised by its cell parameters a, b, c and the angles between them α, β and γ which form the unit vectors for a reference set of axis. The atomic planes can be indexed by the points at which the planes cross the axis. However, for mathematical reasons it is preferable to adopt the Miller indexes (hkℓ) which are obtained by taking the reciprocals of the intercepts and clearing of fractions.

When polymers are subjected to mechanical deformation the molecular chains either in the amorphous or crystalline phase tend to align themselves parallel to the direction of deformation. Both phases become oriented but the crystal structure is not destroyed. Readjustment within the unit cell can occur although, according to Miller (1966), the mechanism by which a crystal can change its orientation without losing its identity is not clear. Structural organisation in polymers has a determinant influence on the physical properties, particularly those correlated with mechanical behaviour. A structured material has mechanical properties vastly different from those of the corresponding random aggregate.
3.2 X-RAY DIFFRACTION

X-rays are generated when high energy electrons impinge on a metal target such as copper. The X-ray beam spectrum consists of two parts, a broad band of continuously varying wavelengths and another of sharp lines, $K_{\alpha}$ and $K_{\beta}$, the $K_{\alpha}$ being the more intense. Actually the $K_{\alpha}$ line is itself a doublet with the two components separated by a small wavelength increment.

When a beam of X-rays strikes a crystal in which the atoms are arranged in a three dimensional lattice, diffraction reinforcement occurs (from interference theory) only when the distance travelled by the X-rays reflected from successive planes, i.e. the path difference between two rays, differs by a complete number of wavelengths. The well known Bragg’s law, which is the basis of X-ray diffraction theory can be expressed as:

\[
\text{path difference} = 2d \sin \theta = n\lambda \quad (3.1)
\]

with $\theta$ the angle of diffraction, $n$ the diffraction order and $\lambda$ the wavelength. Also, the scattering of rays by atoms must be elastic, i.e. there is no energy loss, and the refracted rays have the same wavelength as the incident rays. For all the values of $\theta$ that do not satisfy equation 3.1, the diffracted rays will be out of phase with each other and no actual diffracted X-rays will be observed. By varying the angle $\theta$, the Bragg’s law conditions are satisfied by different $d$ spacings in polycrystalline materials. Plotting the angular positions and intensities of the resultant diffraction peaks produces a pattern which is characteristic of the sample and can be used to identify the material. The X-rays penetrate to a depth of several million layers before being appreciably absorbed. At each atomic plane a minute portion of the beam may be considered to be reflected.

A typical diffraction pattern of a semi-crystalline material comprises several peaks together with a diffuse background. The $d$ spacings for the different families of planes can be calculated from the angle at which the peaks occurs through Bragg’s law. The
relationship between the d spacing, the cell parameters and the Miller indexes for a triclinic cell is given by:

\[
d_{\text{hkl}} = \left| \begin{array}{ccc}
\frac{h}{a} \cos \gamma \cos \beta & 1 & \frac{h}{a} \cos \gamma \\
\frac{k}{b} & \frac{k}{b} \cos \alpha & 1 \\
\frac{l}{c} \cos \alpha & 1 & \frac{l}{c} \cos \alpha \\
\end{array} \right|^{-1/2}
\]

Thus, cell parameters can be adjusted and Miller indexes assigned to the reflections until the calculated d spacings fit the experimental pattern. However, this process is the most complicated for a triclinic cell because there are six parameters to calculate and the diffraction pattern must have at least seven peaks so the parameters can be estimated unambiguously.

Several contributions give rise to the diffuse background in accordance with Miller (1966) and Alexander (1969): i) the amorphous phase; ii) diffuse scattering due to defects in the lattice cell; iii) incoherent scattering and iv) the residual continuous spectrum of the X-rays. i) The amorphous phase presents a minimal kind of short range order consisting of most probable distances between neighbouring atoms. Thus, the distances between bonded atoms and second nearest neighbours within a polymer chain are subjected to little variation. These modes of quasi-short range order contribute to the background. Narten et al. (1991) estimated that the amorphous phase shows order up to 15 Å, contrary to what it is normally believed. ii) Part of the X-ray intensity scattered by the crystalline regions is lost from the peaks and appears as diffuse scattering in the background as a result of lattice imperfections. iii) The incoherent scattering has no consistent phase relationship to the incident X-rays, and, furthermore it consists of a band of wavelengths centred at a wavelength somewhat longer than that of the direct beam. It is the result of the shift in wavelength due to a loss of energy after an inelastic encounter between an X-ray photon with free electrons. iv) The residual X-ray spectrum. These X-rays will also be scattered by the
crystalline regions but the intensity is small and it contributes to the background.

The width of a peak in a particular phase pattern provides an indication of the average crystallite size. Hay et al. (1989) concluded that crystallite size is the dominant cause of line broadening. Large crystallites give rise to sharp peaks, while the peak width increases as crystallite size reduces. The size of crystallites perpendicular to the planes (hk\ell) can be estimated using Scherrer’s equation:

$$L_{\text{hk\ell}} = \frac{\lambda}{\beta \cos \theta}$$ (3.3)

where \(\lambda\) is the wavelength of the radiation and \(\beta\) is the width at half maximum in radians. The parameter \(L\) gives a weight average of the crystal size rather than the size of the largest crystals. Although the equation must be treated carefully Scherrer’s equation can be used as a measure of the order developed, and it is believed that the results will be representative of the real dimensions. Other authors, Alberola et al. (1995) and Natale et al. (1992) used \(1/\beta\) as a reliable parameter to evaluate the size of crystallites. The latter gives values with the same trend as Scherrer’s equation because for a fixed peak \(\cos \theta\) varies very little. Nevertheless the use of \(\cos \theta\) will take into account any lateral shift in the peak position produced by different treatment of the material prior to the scan.

3.3 EXPERIMENTAL

X-ray diffraction patterns were obtained using a Philips PW1050/25 diffractometer running at 40 kV and 20 mA. A nickel filter was used to select the copper \(K_{\alpha}\) radiation of wavelength 1.542 Å. The geometrical arrangement used is called symmetrical reflection in opposition to transmission mode. The X-ray beam passed a soller slits, which reduced the beam divergence, and a small divergence slit of 1° before it impinged on the sample at an angle \(\theta\). The reflected beam passed a receiving slit of 0.3° and entered the counter window. The advantages of the reflection mode over the transmission mode are that it increases the intensity and improves resolution.
However, if ideal optical conditions are not met, defocusing occurs which displaces the peak position, reduces the intensity and broadens the profiles. Richards (1995) reported in his book that if the specimen is 1 mm too high, for a typical diffractometer, a peak occurring, for instance, at 20° will shift 0.06° giving an error of 0.013 Å in the d spacing. Samples were held on an aluminium S shaped holder with glue. The samples were always aligned so as to present a flat surface at the focal point of the beam. There was the possibility that the surfaces were not completely flat but the roughness was always less than 1 mm.

The beam and counter movement was controlled via a personal computer using the Sietronics program Siehilt 122D v2.0. Slow scans were taken to improve resolution and intensity, the speed was usually set at 0.1 °/min and the step size at 0.05°. Scans were run between 10° and 50°, thus the whole experiment lasted for about 7 hours and a measurement was taken every 30 seconds. The patterns were analysed using the Sietronics program Traces v2.0. The program performed several routines on the scan, i) the contribution to diffraction of the Kα₂ line was stripped, the ratio of Kα₁/ Kα₂ used was 0.51; ii) the scan was smoothed by a weighted mean algorithm; iii) the program searched for the peaks and provided a list of the angles at which the peaks occurred and the corresponding d spacings. Background subtraction could have been performed but, within a good approximation, it only affects the intensity of the peaks not the positions and it was the examination of peak positions which was the aim of the work.

3.4 RESULTS

The accuracy of the diffractometer was tested using a silicon wafer. The pattern in Figure 3.1, taken at 0.2°/min between 10° and 100° shows the main reflection for silicon. The very sharp and intense peaks are typical of a very well structured material. The angles and d spacing values are tabulated in Table 3.1 together with the values from the literature. Table 3.1 shows that the two sets of values do not differ more than 0.002 Å indicating that the diffractometer was working perfectly and the procedure
Fig. 3.1 X-ray diffraction spectrum of a silicon wafer

Fig. 3.2 Aluminium holder and glue
followed to find the positions of the peaks was adequate. This indicates that X-ray diffraction of bulk materials can yield very accurate results, similar to powder diffraction. However, the polymer samples used had a range of dimensions after the strain rate tests were carried out and the surfaces after high strain deformation were irregular, which introduced an error in the peak positions. It is estimated that the polymer d spacings can be calculated with an accuracy of \( \pm 0.005 \) Å.

Owing to the thinness of some of the samples, especially those tested at high strain rates, there was the possibility that the X-rays were not absorbed before they reached the lower surface of the sample. Consequently, the holder or glue could give rise to diffraction peaks. This could happen if the X-ray beam impinged directly on the metal holder. In order to account for this effect a scan was recorded of the holder and glue without a sample. Figure 3.2 shows that several reflection peaks were obtained. The peaks at about 37° and 43° are very common in the X-ray pattern of samples used within this study; see Figures 3.3-3.11 and 3.15-3.20. These are in some instances very intense. Moreover the patterns of the samples tested at the highest strain rate, 8800 s\(^{-1}\) showed nearly all the peaks due to the holder and glue. The samples tested at such a rate were very thin and this may account for the appearance of all the reflections from the holder. Once the peaks were identified only those genuine to the sample were used in the calculations and the rest discarded.

### 3.4.1 POLYETHYLENE TEREPHTHALATE

The WAXS scans of PET are shown in Figures 3.3-3.11. Figures 3.3-3.6 show the PET diffraction patterns for the untested material heated for 30 minutes at different temperatures and tested at 10\(^3\), 1230 and 1940 s\(^{-1}\) respectively at different temperatures. The untested patterns show that the as-received material (at 298 K) was amorphous. However, when the sample was heated to 453 K, well above the glass transition temperature, the X-rays revealed some structure. Three peaks can be clearly distinguished, although they are very broad and the intensity is small. The latter means that some structure was developed on annealing but the crystals were very imperfect. It can be concluded that the PET chain possesses the stereoregularity necessary to
Fig. 3.3 PET untested, preconditioned at: (a) 263, (b) 298, (c) 323, (d) 363, (e) 453 K
Fig. 3.4 PET tested at $10^{-3} \text{ s}^{-1}$ and at: (a) 263, (b) 298, (c) 323, (d) 363, (e) 453 K
Fig. 3.5 PET tested at 1230 s⁻¹ and at: (a) 263, (b) 293, (c) 323, (d) 363, (e) 453 K
Fig. 3.6 PET tested at 1940 s⁻¹ and at: (a) 263, (b) 298, (c) 323, (d) 363, (e) 453 K
crystallise.

Mitchell et al. (1983) suggested that before crystallisation commences orientation of units must occur. Therefore, the patterns of untested samples between room temperature and 453 K should show some orientation. The only remarkable feature is the increase in intensity between 15° and 30° (Figures 3.3c,d) but with no sharp peaks appearing. When peaks appeared they are at 2θ values between 15° and 30° (see below) and the diffuse scattering was always present underneath. So, this deflection of the baseline could serve as a qualitative indication of orientation although no quantitative measurements were attempted. Measurements of orientation from one dimensional patterns have not been found in the literature and the qualitative method will be used for comparative purposes only. As support for the previous argument, Jabarin (1992) pointed out that a pattern like Figures 3c-d corresponds to an oriented amorphous sample.

The crystal structure of PET is triclinic with one chemical unit per cell. Daubeny et al. (1954) found that the cell parameters were: a = 4.56 Å; b = 5.94 Å; c = 10.75 Å; α = 98.5°; β = 118°; γ = 112°. These parameters were calculated for an amorphous film of PET highly stretched and it is regarded as the most reliable study on PET up to date. Jabarin (1992) reported that the main reflection occurred at 2θ equal to 17.35°, 22° and 25.75° corresponding to planes with Miller indexes (010), (110) and (100) respectively. The d spacings for those families are 5.11, 4.04 and 3.46 Å.

Figure 3.4 depicts the X-ray diffraction patterns of samples tested at 10³ s⁻¹ at different temperatures. The patterns display that the samples were oriented up to 363 K when very imperfect crystallites developed and some structure was revealed by the X-rays. Under slow compression the sample heated at 453 K for 30 minutes, before the test, Figure 3.4e, gave very intense and sharp peaks. By comparison with the untested sample, Figure 3.3e, it can be seen that the structure was more perfect after compression with d spacings similar to samples tested at higher strain rates, except that the (110) planes seemed to be a little closer together.
The samples tested at 1230 s\(^{-1}\), Figure 3.5, gave rise to a completely different pattern. At 263 K the sample did not have structure, Figure 3.5a, but the patterns of samples tested at room temperature and above revealed that the material crystallised into a fairly perfect structure of large crystals. The pattern for samples tested at 1940 s\(^{-1}\), Figure 3.6, are similar to those in Figure 3.5. The sample tested at 263 K, Figure 3.6a, had a more defined structure that its counterpart in Figure 3.5. In addition, peaks were much more intense and the structure seems to be more perfect for samples compressed at 1940 s\(^{-1}\). On increasing the strain rate to 8800 s\(^{-1}\) changes can be seen, Figure 3.7. The Figure reveals that the material did not show sharp peaks after compression at very high strain rates.

The peaks occurred at angles around those mentioned in the literature. Table 3.2 illustrates the \(d\) spacings corresponding to the tests illustrated in Figures 3.4-3.6 and are the average of three values. The data of Table 3.2 are plotted in Figure 3.12 for the different planes. Figure 3.12. reveals that the no major change occurred in the \(d\) spacing of a family of planes at a given strain rate. It also shows that the \(d\) spacing values almost superimposed for a family of planes at different strain rates, indicating that there was no change in \(d\) with strain rate. Furthermore, there is no change in structure with strain rate and all the samples seem to have crystallised into the triclinic cell. It is worth mentioning that all the values of Table 3.2 are below those reported by Jabarin (1992) who studied the X-ray diffraction of PET after slow strain rate tension and annealing.

Figures 3.8-3.11 show the X-ray diffraction of PET samples tested at different final strains in the machines. The purpose of these tests was explained in Chapter 2. At 10\(^{-3}\) and 1 s\(^{-1}\) the samples seemed to be oriented but there was no sign of structure formed due to compression. This is in accordance with Figure 3.4b which shows no crystallisation at all. At higher strain rates, Figures 3.10-3.11, the samples developed some structure. Samples gave patterns characteristic of oriented samples up to 140% strain when it is obvious that the material developed some structure. However, the final structure for samples tested up to 185% Figures 3.10d and 3.11d, was not as perfect as that of samples after “free” compression, Figures 3.6b and 3.7. The peaks
Fig. 3.7 PET tested at 8800 s$^{-1}$ at 298 K
### TABLE 3.1

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### TABLE 3.2

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Fig. 3.8 PET tested at $10^3$ s$^{-1}$ at 298 K, strain: (a) 35, (b) 70, (c) 140, (d) 185\%
Fig. 3.9 PET tested at $1\, \text{s}^{-1}$ at 298 K, strain: (a) 35, (b) 70, (c) 140, (d) 185%
Fig. 3.10 PET tested at 1230 s⁻¹ at 298 K, strain: (a) 35, (b) 70, (c) 140, (d) 185%
Fig. 3.11 PET tested at 8800 s\(^{-1}\) at 298 K, strain: (a) 70, (b) 140, (c) 185%
Fig. 3.12 PET d spacings vs. Temperature for the three main reflections. Continuous line 1230 s\(^{-1}\); discontinuous line, 1940 s\(^{-1}\). Error bars are too small to be shown.

Fig. 3.13 PET x-ray diffraction scan fitted with PeakFit.
are broader and the first peak is not clear even at 185% strain. Thus, it can be implied that the samples tested “freely” attained strains larger than 185% and this gave rise to a more perfect structure. The spacing was only calculated for the samples compressed at a strain of 185% and for two peaks. The d spacings for the sample tested at 1230 s\(^{-1}\) were 3.92 and 3.49 Å whereas the d spacings for the sample tested at 8800 s\(^{-1}\) and 185% were 3.92 and 3.42 Å. These spacings were different to the interatomic spacing of samples tested without constraints but within error, as can be seen from Table 3.2.

It has been seen that the material crystallised under certain conditions. The X-ray traces reveal that the structure created in some samples was more perfect than for others, for example compare Figure 3.6a to Figure 3.6b. However, further information can be extracted from the X-ray data. The Scherrer’s equation can be used to estimate the size of the crystallites in a particular direction perpendicular to one of the crystallographic planes. The Jandel program PeakFit v4 was used to separate the peaks into individual peaks, in a similar way to Camkak and Kim (1997). The peaks were fitted to a Pearson VII function, after the background was subtracted by the deconvolution method and the FWHM (full width at half maximum) was then given by the program. All the fits were above \( r^2 = 0.99 \), see Figure 3.13 for an example. No correction for the peak positions were made as was also the case in the work by Camkak and Kim.

Only the patterns which showed sharp peaks were fitted. The (100) peak was chosen for the calculations of crystallite size because it appeared in all the patterns, was the most intense and any change in crystallite size should be more easily detected than for the other peaks. Table 3.3 shows the FWHM and the size of the crystallites perpendicular to the (100) planes. Figure 3.14 represents the data. The sizes of the crystallites are all around 6 nm. It can be seen that the crystal size followed a similar trend up to 323 K, there is no change in size with temperature or strain rate within errors. At higher temperatures the crystal size for the higher strain rate increased up to 8 nm. The size of crystallites of samples annealed at 453 K and slowly compressed was 4.14 nm.

3.4.2 NYLON 11
Fig. 3.14 Size of PET crystals vs. Temperature
The results of this work show that crystal structure of Nylon 11 varies with crystallisation temperature and testing conditions. Other workers have found Nylon 11 to have at least four polymorphic crystal forms: a triclinic \( \alpha \) form and three pseudohexagonal forms, \( \gamma, \delta \) and \( \delta' \). Solution cast Nylon 11 crystallised into the triclinic form, according to Chen et al. (1985). However, Chen et al. (1985) quoting the results of Schmidt and Stuart (1958) reported that isothermal crystallisation of Nylon 11 from the melt gave the \( \alpha \) modification while Kim et al. (1985) concluded on the basis of their results that the melt crystallised films did not have the \( \alpha \) form structure despite the general similarity of the diffraction patterns of melt and solution crystallised Nylon 11. Chen et al.(1985) reported that Nylon 11 crystallised at atmospheric pressure contained both the \( \alpha \) and one of the pseudohexagonal crystal forms \( \delta' \), different from the variation \( \delta \) observed when melted at high pressures.

Consequently, indexation and d spacings are not consistent. As mentioned above Kim et al. (1995) presented two different patterns; the solution crystallised had the \( \alpha \) form with d spacings of 11.33, 4.44 and 3.72 Å corresponding to the (001), (100) and (010) planes respectively. On the other hand the melt crystallised Nylon had d spacings of 11.95, 4.40 and 3.82 Å corresponding to the same families of planes. Nevertheless, Wu et al. (1996) quoted Hasegawa et al. (1974) who proposed a model based on a triclinic \( \alpha \) form with antiparallel chain packing for samples quenched from the melt. The peak positions of Nylon 11 uniaxially stretched at 20.9° and 23°, corresponded in accordance to his model to the (200) and (020) peaks the second one being the most intense. Nevertheless, the first set of Miller indexes seems to be more popular.

Figures 3.15-3.20 depict the diffraction patterns for Nylon 11 samples after different thermal and mechanical treatment. The as-received material was semi-crystalline with two clear peaks given by planes spaced 4.38 and 3.92 Å. The planes can be indexed as (100) and (010). On compressing the as-received material at low strain rate \( 10^{-3} \text{s}^{-1} \), Figure 3.15b, the (100) reflection decreased in intensity while the intensity of the
Fig. 3.15 Nylon 11 as-received tested at 298 K. (a) untested, (b) $10^{-3}$, (c) 1230, (d) 8800 s$^{-1}$
Fig. 3.16 Nylon11 annealed 15 min @ 170°C tested at 298 K.
(a): untested, (b) $10^{-3}$, (c) 1230 (d) 8800 s$^{-1}$
Fig. 3.17 Nylon 11 annealed 30 min @ 190°C tested at 298 K. 
(a): untested, (b) 10^{-3}, (c) 1230 (d) 8800 s^{-1}
Fig. 3.18 Nylon II as-received; tested at 263 K (a): untested, (b) $10^{-3}$, (c) 1230 s⁻¹
Fig. 3.19 Nylon 11 annealed 15 min @ 170°C tested at 263 K.
(a): untested, (b) $10^3$, (c) 1230 s$^{-1}$
Fig. 3.20 Nylon 11 annealed 30 min at 190°C tested at 263 K. 
(a): untested, (b) $10^{-3}$, (c) 1230 s$^{-1}$
Wide Angle X Ray Diffraction

(010) did not change and two peaks can still somehow be distinguished. At higher rates, 1230 s\(^{-1}\) only one broad, although very intense, reflection was produced. At 8800 s\(^{-1}\) the intensity of the reflection decreased and two peaks similar to the low rate samples were found. The annealed samples tested at room temperature showed a similar type of behaviour, Figures 3.16-3.17. Samples tested at 263 K presented some different features. The reflections of the untested samples, Figures 3.18a-3.20a, are shallow and the peaks are visible only in the samples annealed although they are very diffuse. On increasing the strain rate the patterns are similar to those tested at room temperature.

Despite the difficulty in obtaining d spacings for samples tested at low strain rates, values were obtained and all are tabulated in Table 3.4. Figure 3.21 represents the data of Table 3.4 only for the samples tested at room temperature. The data for the annealed samples are shifted one and two units respectively to present the data together. The most remarkable feature is that the peaks move towards each other and finally merge into a single peak characteristic of a pseudohexagonal structure at strain rates of 1230 s\(^{-1}\), but separate again at higher rates. The (100) family underwent a more drastic change in the d spacing and seems to be more sensitive to strain rate while the (010) planes d spacing remained almost constant. Figure 3.22. shows the d spacings for samples annealed for different times and the as-received material. The untested material experienced an overall increased in the (100) spacing while the (010) decreased. The latter seems to indicate that the volume remains almost constant, within errors. The unique peak at 1230 s\(^{-1}\) and the first and visible peak at 8800 s\(^{-1}\) did not vary with thermal treatment. But the Figure shows that the family planes (100) after compression at 8800 s\(^{-1}\) did not recover to the value of the untested or low rate tested sample. The d spacing was approximately 4.4 Å compared to 4.2 Å. The possible implications will be discussed later.

3.5. DISCUSSION

Wide angle X-ray diffraction was used to investigate the crystal structure of PET and Nylon 11 tested in compression. X-ray is a suitable technique because it mainly
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Fig. 3.21 Nylon 11 (100), continuous line, and (010), discontinuous line, d spacings vs. Strain Rate on a logarithmic scale for samples tested at rt. Top: annealed 30min@190°C; Middle: annealed 15min@170°C; Bottom: as-received. Middle and top figures are offset one and two units respectively. Error bars are too small to be shown.

Fig. 3.22 Nylon 11 d spacing vs. annealing for samples tested at room temperature. 1: as-received; 2: 15min@170°C; 3: 30min@190°C. Curves from top to bottom: untested (100) d spacing, tested at 10⁻³ s⁻¹ (100) d spacing, tested at 8800 s⁻¹ (100) d spacing, tested at 1200 s⁻¹, untested (010) d spacing.
detects the presence of order.

3.5.1 POLYETHYLENE TEREPHTHALATE

It can be concluded that the as-received material was amorphous. Polymers such as PES do not crystallise under any conditions. However, on annealing as-received PET crystallised into a very imperfect structure. The X-ray patterns produced from material tested under different conditions were used to assess the influence of testing conditions on the resultant structure.

The combined effect of temperature and strain rate had different effects on the material. At low strain rate the material changed from an oriented amorphous to a fairly perfect structure at the higher temperatures. Chang et al. (1993) pointed out that above the glass transition temperature and at low strain rates crystallisation did not depend upon strain rate but on temperature. This lack of dependency might have been caused by the competition between the time of crystallisation and the rate of crystallisation. On the other hand Jabarin (1992) reported that a faster speed of stretching (maximum stretching speed 127 mm/min) imparted a higher degree of crystallinity. Evstatiev et al. (1992) claimed that cold drawing led to the formation of small and imperfect crystallites. Figures 3.5 and 3.6 illustrate that on increasing the strain rate beyond 1230 s⁻¹, crystal structure was evident at any temperature except 263 K. Also, at strain rates of 1940 s⁻¹ the samples developed microscopic structure even at 263 K. At 8800 s⁻¹ structure was not developed. Consequently the strain rate seems to play an important role in the crystallisation of PET even at a fixed temperature. This can be seen at the same temperature if the sequence of Figures, for instance at room temperature, Figures 3.3b, 3.4b, 3.5b, 3.6b, 3.7 are compared. Misra and Stein (1979) and Spruiell et al. (1972) reported that below the glass transition cold drawing led to the creation of crystals. However, Figures 3.4a-c show that no crystallisation occurred in samples compressed at low strain rates except those which were tested at high temperatures.

Jabarin (1992) reported that samples of PET with low levels of orientation did not
crystallise on stretching with a stretching speed of 5 mm/min, and annealing while samples with intermediate degree of orientation crystallised after such conditioning. It is possible that the samples tested at 263 K did not develop a more perfect structure because of less mobility of the chains at low temperatures than at temperatures above room temperature; see Figures 3.5a and 3.6a. The temperature of the test did not allow chains to move relative to each other as freely as they would do at a higher temperature. Probably neither a high degree of orientation was induced during deformation nor a final strain as large as for samples tested at room temperature was attained. Nonetheless, it can be seen that some crystal structure was formed. This suggests that the orientation and/or final strain may have some influence in the crystallisation.

Thus, it was important to define the onset of the development of structure at high strain rates so the influence of strain could also be assessed. Chang et al. (1993) and He and Porter (1987) reported an increase in crystallisation with draw ratio (strain). Figures 3.8-3.11 reveal that no crystal formation occurred at low strain rates up to strains of 185%, as was expected. However, at high strain rates crystals developed at large compressive strains. At 1230 s\(^{-1}\), the material remained amorphous, although chains seem to be oriented, up to 140% strain when some indications of structure are evident. At higher strains the structure formed is more perfect but not as perfect as the samples “free” tested, compare Figures 3.5b and 3.10d. The latter only indicates that the samples may have attained slightly higher final strains than 185%. At 8800 s\(^{-1}\) the structure developed is not seen in “free” tested samples. This indicates that large strains and high strain rates may be a hindrance to the formation of the triclinic structure of PET. Jabarin (1992) concluded that strain induced crystallisation occurred when samples are stretched to amounts below the strain hardening region, i.e. medium amounts of strain. This disagrees with the results presented from the present study. In contradiction to Jabarin it was reported by Spruiell et al. (1972) that the stress appeared to be more important than the amount of strain. This is only true if the material strain hardens, otherwise, the stress is constant after the yield point and the constant stress does not exert any influence.

It seems that contradictions appear between data available in tension experiments and
the results presented so far. This seems to indicate that the mechanisms of crystal formation in compression may be different to those in tension. Alfonso et al. (1978) reported that orientation of the amorphous phase plays a very important role in crystallisation of PET in tension and it might be dependent on strain rate according to Spruiell et al. Also it is well known, Chang et al. (1993) that the mechanism of crystallisation of PET during stretching changes from a three dimensional spherulite shape to one dimensional fibrillar structure as the orientation increases. The latter is supported by the arrangement of a typical tension test, the sample is stretched in one direction, the chains tend to align in that direction and microscopically, spherulites are stretched to form fibrillar structures. However, in compression the sample is allowed to expand in two directions and spherulites may be squeezed but they might not change its morphology. That change of morphology during crystallisation in tension may not hold true in compression and the mechanisms could therefore be different.

Thus, PET developed structure under strain at different rates independent of temperature. The peaks corresponding to the main reflection were indexed as (010), (110) and (100) after Jabarin (1992). The d spacings remained nearly constant when the temperature was varied; see Figure 3.12. Changes in the unit cell dimension of polymers under certain conditions have been found. Blundell and D'Mello (1991) reported an increase in the cell dimensions of PEEK with temperature of annealing, although the dimensions recovered on cooling. Hay et al. (1989) reported a decrease in cell volume of PEEK with temperature of crystallisation. The effect of a change of cell dimensions is that some rearrangement of atoms within the cell must occur without being large enough as to give rise to another crystallographic system.

The crystallite size is another important feature which may account for any change in the mechanical properties of PET. Figure 3.14 shows the crystallite size perpendicular to the (100) direction. The crystallite size of samples tested at 1230 s\(^{-1}\) was almost constant at around 6 nm (Hay et al. (1989) reported values of 10 nm for PEEK) with a small decrease at 363 K which is within errors. But the samples tested at 1940 s\(^{-1}\) showed a steep increase in crystallite size at 363 K and then it remained almost constant with temperature. It seems that the combined action of strain and temperature
Wide Angle X Ray Diffraction

makes the crystals larger. The samples tested at 453 K at $10^3$ s$^{-1}$ had a crystal size of 4.14 nm, the smallest of all the values. The effect of the strain rate on the crystal size cannot be assessed at low temperatures but has a marked effect at high temperatures. The crystal size at 453 K increased from 4.14 to 8.06 between $10^3$ s$^{-1}$ and 1940 s$^{-1}$. Also, the temperature seemed to play an important role, at low strain rates an increase in temperature accounted for the formation of crystals while at high strain rates the crystals grew bigger above the glass transition temperature. Samples tested at 1230 s$^{-1}$ above the glass transition temperature were expected to have larger crystallites, but no change was found and the reason is not clear. Unlike the reported arguments about crystallite development the reported tendencies of crystal size seem to be more consistent. Natale et al. (1992), and Alberola et al. (1995), claimed that crystal size and perfection of PP increased with temperature of annealing as Misra and Stein (1979), and Spruiell et al. (1972) concluded the same for PET. Also, Evstatiev et al. (1992) proposed that cold drawing and thermal treatment grew more perfect crystallites. Spruiell et al reported an increase in crystallite size with strain rate at low strain rates. If the parameter L is a measurement of the crystal size perpendicular to a family of planes then it must be proportional to the d spacing of such a family

$$L_{hkl} = p d_{hkl} \quad (3.4)$$

where p is the number of planes within one crystal. The (100) family has a d spacing around 3.5 Å. Thus p is equal to 12 for crystals of 4 nm, 17 for crystals of 6 nm while it is 23 for 8 nm. Therefore, a family of planes within a thick crystal contains more atoms than the same family in an smaller crystal. Moreover, the FWHM (Full Width at Half Maximum) of the (100) plane is narrower than the FWHM of the other two planes so the crystals perpendicular to (100) are larger than perpendicular to (010) and (110). Therefore, atoms are expected to take positions preferentially in the (100) planes which means that the atoms stack preferentially in the (100) direction. The same conclusion could have been drawn comparing the intensities of the peaks because the position of atoms relative to a given set of planes is the most significant factor determining the intensity of the reflected beam and the (100) peak is the most intense.
Daubeny et al. (1954) carried out a thorough study to reveal the structure and position of atoms of highly stretched PET. They concluded that the unit cell contained one chemical unit. The length of the chain was slightly smaller than the c parameter, thus the molecule could not be completely planar. The O-C=O group appeared to be about 12° out of the plane of the benzene ring while the glycol group departed from planarity by about 20°. Chains adopted a zig-zag morphology. Cold drawing aligned the chains in the direction of stretching and the crystal structure was presumed to be formed of extended chain crystallites according to Spruiell et al. (1972), although annealing made the crystals become significantly chain folded according to Evstatiev et al. (1992) and Misra and Stein (1979).

It was found in this work that the chains packed forming the (010), (110) and (100) planes. Consequently, when PET crystallised atoms arranged so they formed very simple crystallographic planes; see Figure 3.23. There is no evidence to support the idea that compression extended the chains and crystals might be formed of folded chains brought together by the compression. Those three planes are parallel to the z axis, and thus, it can be concluded that the molecules stack in the x and y planes with the long chains running parallel to the z direction. This means that the z axis may be almost perpendicular to the direction of compression in the experiments. Also it was concluded that the atoms seem to prefer the (100) plane so the compression direction might be along the x axis. Unlike other polymers an almost planar molecule fits better with its neighbours than a very non planar type. Since the chains seem to align in the z direction, steric hindrance would restrict the growth of folded chains crystals in directions other than normal to the compression direction.

Thus, it is proposed that at low strain rates the molecules relax as fast as they are aligned, they recover to their initial positions before neighbouring chains are moved resulting in little crystallisation. However, at low strain rate and high temperatures, near or above the temperature of crystallisation, the material tends to crystallise by itself due to thermal motion and compression makes the crystals fairly perfect. At high strain rates the crystallisation observed may be the effect of stress, strain rate and
Fig. 3.23 Triclinic cell and atomic planes.
strain. The stress initially observed at high strain rates (120 MPa compared to 50 MPa at low strain rate) may be required to overcome the forces between chains and to give rise to the slippage and rotation necessary to align the molecules. Rapid straining is required to produce the molecular alignment necessary to induce crystallisation and avoid relaxation. Large amounts of strain are needed to induce a high degree of orientation which must occur before any crystallisation takes place. It must be borne in mind that larger strains means a longer duration of the experiment. Thus, shorter times might not suffice to induce orientation even when stress or strain rate are high. Elevated temperature at high rates only makes the structure more perfect. Therefore, if entropy is a measurement of the thermodynamic order of a system the adjunction and alignment of molecules increases the order of the system and hence reduces the entropy. A reduction of entropy is sufficient to account for crystallisation. Mandelkern (1964) claimed that the tendency towards crystallisation is greatly enhanced by deformation since chains are distorted from their most probable configuration and if the deformation is maintained less entropy remains to be sacrificed in going over to the crystalline state.

In conclusion, PET crystallised on compression at high rates. It is concluded that the data available from tension experiments carried out by previous workers did not match the findings of this work. The latter together with the lack of literature data for compression experiments led us to believe that there is no argument to support the premise that the two types of experiments should yield the same results.

3.5.2 NYLON 11

The as-received Nylon 11 was semi-crystalline. The two main peaks in Figure 3.15a corresponded to the (100) and (010) peaks with spacing 4.38 and 3.92 Å respectively. On compressing the material it behaved in the same manner as a function of strain rate independently of the annealing treatment. According to Chen et al. (1985), who constructed X-ray diffraction patterns for different compositions of the α and δ' forms, the as-received material corresponds to an approximately fifty-fifty mixture of triclinic α form and hexagonal δ' form. Low rates of compression decreased the
degree of preferred orientation and increase the amount of hexagonal crystallites (Chen et al. (1985) claimed that an X-ray scan similar to Figure 3.15b corresponds to about 30% triclinic) while the material change to a pseudohexagonal structure at strain rates of 1230 s⁻¹ and partially recovered the triclinic form at higher strain rates.

The as-received material seems to be preferentially oriented in the (100) direction because of the great intensity of the first peak. The (010) plane is likely to be in the plane of the sample and perpendicular to the compression direction because its spacing was affected very little by compression. Nylon 11 crystallises in sheets linked by hydrogen bonds. Ramesh et al.(1994) reported that for Nylon 66 the distance between the (100) planes is largely fixed by the hydrogen bonds and is less sensitive to temperature variation. However Figure 3.21 shows that the (100) plane is more sensitive to variation and the (010) contained the hydrogen bonded sheets in agreement with the Hasegawa model.

The transition triclinic-pseudohexagonal is considered to be due to the effect of conformational motion and is associated with a packing change within the crystal allowing a greater amount of rotational freedom about the chain axis. Ramesh et al. (1994) reported that the transition must be a first order transition and this was supported by the hysteresis seen on annealing and cooling of samples. Nonetheless, all the previous authors reported that the transition occurred on annealing. But Ramesh et al. (1994) found that for samples crystallised between 196° and 260°, Nylon crystallised initially in the pseudohexagonal form and partially transformed to the triclinic only on cooling to room temperature. On annealing, the reverse transition happens at temperatures above the crystallisation temperature. However, Figures 3.15c-3.20c show that the samples tested in the Dropweight machine showed a complete destruction of the α form whereas the samples tested at higher strain rates, 8800 s⁻¹ showed some triclinic form.

It is proposed that the oriented semi-crystalline material transforms into a less oriented material at low rates of compression accompanied by a reduction of the triclinic form present. At faster speeds the transition triclinic-pseudohexagonal is obvious and the
sample retained the almost complete hexagonal form even after cooling. The explanation for this is not clear and it is thought that the sample did not reach its temperature of crystallisation during the test and there is no argument supporting that it should recover the triclinic structure. The structural transition may be caused by the compression and not by annealing. At higher strain rates, 8800 s⁻¹ the temperature attained by the sample may well be above its crystallisation temperature, it is possible that some melting may have taken place, and the recovery of part of the triclinic form is evident. However, the structure shown after these tests is slightly different from the primitive form and may be due to a different percentage of triclinic form, Figures 3.15b and 3.15d.

In summary, Nylon 11 was seen to transform from a triclinic-hexagonal structure to a pseudohexagonal structure characterised by the merging of two peaks. The effects of annealing of the material prior to testing seem to have only a very small effect on the structure under different mechanical conditions, notwithstanding small variations were found in the cell dimensions.
CHAPTER 4

DIFFERENTIAL SCANNING CALORIMETRY
4.1. INTRODUCTION

The study of the effect of heat on materials has a long history. Thermal analysis is the measurement of changes in the physical properties of a substance as a function of temperature whilst the substance is subjected to a controlled temperature programme. The various thermal analysis techniques differ in the physical property that is measured. Among the thermal analysis techniques thermogravimetry, differential scanning calorimetry, differential thermal analysis and differential mechanical analysis are the most popular. These techniques measure any change in the mass, enthalpy, temperature change and mechanical properties of the material respectively. When a solid substance is heated in an inert atmosphere, the resultant increase in molecular or atomic motion may lead to changes in crystal structure or melting; Brown (1988). Those changes are related to thermal events in the sample, and although the principle of operation differs from one technique to another, any change is reflected as a deviation from a baseline in a thermogram.

Thermodynamic transitions that can be detected by thermal analysis are the glass transition, crystallisation and melting of substances and solid-solid phase changes. On increasing the temperature, a polymer may reach its glass transition temperature, $T_g$. According to Nielsen (1962), at this temperature the polymer expands to the extent that there is enough free volume available in the material and enough thermal energy for molecular motion to begin. This is detected as a change in the thermogram baseline. Above the glass transition temperature the polymer may crystallise as a result of movement of chain segments induced by heat and this “cold crystallisation” is seen as an exothermic peak. At higher temperatures, $T_m$, the crystals collapse and an endothermic peak is recorded. The area under the melting peak is the heat of fusion of the substance. Thermal analysis may also be used to calculate the specific heat of a substance, study relaxation phenomenon and estimate shrinkage.

Thus, thermal analysis is an accurate and conventional tool for monitoring the response of polymers to temperature and stress. Differential Scanning Calorimetry (DSC) is one of the most widely used technique in thermal analysis. In this work DSC
Thermal Analysis

was carried out on both PET and Nylon 11 samples. The experiments were performed to find a quantitative measurement of the degree of crystallinity developed in the samples after mechanical test and to investigate other thermal phenomenon associated with the materials. PET has a glass transition temperature of 343 K, crystallises at a maximum rate from the melt at 451 K and melts at approximately 533 K. The Nylon 11 glass transition temperature is about 318 K and it melts at approximately 468 K.

This chapter gives a broad view, not only for those materials but for polymeric materials in general, of the phenomenon of crystallisation, glass transition and fusion. Also, the advantages of thermal analysis by DSC will be noted and compared with other methods of measuring the degree of crystallinity.

4.2. DIFFERENTIAL SCANNING CALORIMETRY

There are three main techniques to estimate the degree of crystallinity of a substance, namely X-ray diffraction, density measurements and thermal analysis (DSC in particular). X-ray diffraction calculations are based on a peak separation of the X-ray pattern and the comparison of the area under the peaks to the total area. Its shortcoming are that it needs correction for absorption, size of the sample and the subtraction of the amorphous contribution is not straightforward. Crystallinity determination by density measurements is based on the comparison of the density of the sample with the density of the amorphous and crystalline phase. Nevertheless, the two phase model, which is the core of the density method, cannot account for crystal defects, crystal thickening, molecular weight effects or nonlinearity in the amorphous phase with temperature, see Hoffman et al. (1985). A four phase model, each with a different density, comprising oriented, unoriented and continuous amorphous phase and a crystalline phase should be adopted to yield more reliable values. DSC values of crystallinity are found by dividing the enthalpy of fusion of the substance by the enthalpy of fusion for crystallites in the absence of an amorphous fraction. Its disadvantages are: uncertainty in placing the baseline for area integration, further crystallisation prior to melting and the availability of uncontrovertible heat of fusion data on equilibrium crystals of a polymer. The latter is not important if the crystallinity
values do not need to be accurate because the heat of fusion and crystallinity content follow the same pattern. The crystallinity values reported in the literature by different methods are not consistent and there are various explanation for this: Lee et al. (1988) reported that the degree of crystallinity determined by the density method showed a drastic reduction for samples drawn under different conditions. However, the degree of crystallinity estimated by the DSC method followed the same trend but the drop was much smaller. They suggested that voids could lower the density but would not alter the amount of energy involved in the thermal transitions. Natale et al. (1992) reported that DSC determination of crystallinity was coincident with WAXD, but the values obtained from density measurements were higher. Muller et al. (1987) claimed that the degree of crystallinity from density measurements is smaller than DSC determination while Graham et al. (1997) argued that crystallinity determination by density is higher than from DSC because DSC measures the core crystallinity whereas density measurements led to determine the core crystallinity and the interfacial region. Spruiell and co-workers (1972) estimated that the X-ray determination gave higher degrees of crystallinity than the density method. The difference between both methods could be explained by a preordering process during drawing which increased the effective density of the amorphous fraction. Cakmak and Kim (1997) reported values from DSC which were higher than density estimations and it was assumed that either voids were present or baselines were not correct, giving credit to both methods. It is believed that the X-ray diffraction method and DSC give reliable values if care is taken in the analysis of results and no large error is introduced by the system. Obviously the X-ray diffraction peaks and the melting of a substance is due to crystallites. However, the variation of the density of a sample may be induced by phenomena other than crystallisation.

4.2.1 BACKGROUND

DSC is a non-equilibrium technique in which the difference in the heat flow supplied to a sample and reference is measured as some function of time or temperature. The heat flow is measured by keeping the sample and reference thermally balanced, at the same temperature. Thus, thermal events in the sample appear as deviations from the
DSC baseline in either an endothermic or exothermic direction, depending upon whether more or less energy has to be supply to the sample relative to the reference. In fact, any transition in the range of 173 K to 873 K which involves the absorption or liberation of heat is amenable to study by DSC.

Brown (1988) reported that the DSC response is proportional to the heat capacity of the sample and it has been established that the thermal resistance of the major heat flow paths in a DSC cell are crucial to the performance and response of this technique. Accordingly, the difference in heat flow between the reference and sample in a calorimeter, needed to keep both at the same temperature i.e. the calorimeter signal, is given by:

$$\frac{dq}{dt} = \frac{dT}{dt} (C_s - C_r)$$

(4.1)

where q is the heat, T is the temperature, t is the time and $C_s$ and $C_r$ are the heat capacity of the sample-pan and reference-pan systems. The DSC technique measures an average enthalpy throughout the sample thickness. When a sample is introduced in a DSC cell the baseline is displaced in the endothermic direction, and the displacement, h, is given by:

$$h = B\phi m C_p$$

(4.2)

where B is a calibration factor, $\phi$ is the heating rate, m is the mass of the sample and $C_p$ is the specific heat capacity. After a substance undergoes a transition, the baseline will not return to the original baseline if the thermal properties, for instance specific heat, of the high temperature form are different from those of the low temperature form. The enthalpy change of a transition, if any, is calculated according to:

$$\Delta H = \frac{AK}{m}$$

(4.3)

where A is the area under the curve associated with the transition, m the mass of the
sample and $K$ is the calibration factor. The calibration factor can be estimated by direct substitution in equation 4.3 providing that the heat of fusion of a substance is known and the melting endotherm of a certain amount of material is calculated. The calibration factor contains contributions from the geometry and thermal conductivity of the sample and reference material system and it is virtually independent of temperature.

Below the glass transition temperature, $T_g$, only short range motion of several contiguous chain segments occur. When $T_g$ is reached long range segmental motions are allowed, molecular segments occasionally have room enough to jump from one position to another with respect to their neighbours and sufficient mobility is imparted to the molecular chain segments for processes such as thermal shrinkage and crystallisation to occur. The movement of chains above the glass transition temperature is explained by the theory of reptation. In accordance with this theory, movement can be visualised as the motion of a chain within a virtual tube, which is defined by the entanglements with neighbouring molecules; Fried (1995). The glass transition marks the change from glassy to rubber like phase (or viscous liquid depending on the molecular weight) which have different specific heats and, accordingly to the DSC operation fundamental, the process is seen as a displacement in the slope although the enthalpy change is zero. The glass transition temperature does not occur at a single temperature in a polymer but is in fact a temperature range of 15-20 K in which the onset of motion on the scale of molecular displacements can be detected. A co-operative movement of 20-30 carbon backbone atoms is needed for a normal glass transition. The glass transition resembles a second order transition which is characterised by a discontinuity in the specific heat. Nevertheless, it is not a true thermodynamic transition because it is influence by the kinetics of glass formation and the discontinuity, as indicated, is more gradual. Thus, it is considered to be a pseudo-second order transition.

Polymers, specially amorphous ones, may undergo crystallisation on heating to just above the glass transition temperature, referred as "cold crystallisation". As the chains are heated a critical mobility for crystallisation is reached and the material organises
with an exothermic process. The introduction of an additional quantity of energy during thermal scanning causes the transition into a thermodynamically more stable state with the consequent decrease in energy. The excess of energy is lost by the sample which explains the exothermic origin of the process. The process occurs over a range of temperature and it is detected in the form of a peak with an associated change in enthalpy. This phenomenon has been found for different types of polymers, PEEK, PET, Nylons, PP, etc.

As the temperature rises the energy given to the material increases the vibrational energy of the system until it is not stable and the crystals collapse. Thereby, the less perfect crystals melt first while more perfect crystals need higher temperatures to melt. Therefore, melting of crystallites occurs over a range of temperature and it is detected as an endothermic peak which gives the change in enthalpy associated with the process, the heat of fusion. Melting is a first order transition in that there is a discontinuity in the volume. Like the glass transition, it is not a true transition for polymers because in a true thermodynamic transition the melting should be infinitely sharp and this requires almost perfect internal arrangement of the crystalline phase and large crystals to minimise the surface or junction effect. Disorder is introduced by the chain ends so if the chain ends are not tolerated by the lattice, melting cannot be absolutely sharp. Thus, deviations lead to broadening of the melting range and this shows the extent to which the idea of a uniform crystalline state is approached.

The exact determination of the melting point of a polymer by DSC is not only complicated by the fact that the melting occurs over a range of temperature but also the melting point of a semi-crystalline substance can be affected by the presence of the amorphous phase. This lends weight to the pseudo character of the transition, because theoretically the transformation temperature should be independent of the relative abundance of either of the phases being maintained in equilibrium. Thus, a new concept must be introduced which is thermodynamically correct. The equilibrium melting point, $T_m^\infty$, is defined as the temperature at which the crystalline and liquid phases are in equilibrium; Manderlkern (1964). Therefore, the free energy is zero and
the equilibrium temperature is equal to: \( T_0 = \frac{\Delta H_0}{\Delta S_0} \), where \( \Delta H_0 \) and \( \Delta S_0 \) are the enthalpy and entropy of fusion of the perfect crystal. The equilibrium temperature can also be defined as the temperature at which the last vestiges of crystallinity disappear, and it represents the temperature of the hypothetical macroscopic perfect crystal. According to Fried (1995), in general \( T_m \neq T_0 \) because of: i) the kinetic effect of a finite heating rate; ii) the crystallite size which can be influenced by the conditions of crystallisation or impurities present. Furthermore, the surface free energy increases with decreasing crystallite size and therefore, \( T_m \) decreases with decreasing size. The equilibrium melting point for PET is about 553 K, Fried (1995), and for Nylon 11 Fakirov et al. (1985) reported that the equilibrium melting point was at about 514 K.

4.2.2 THE SYSTEM

DSC was carried out in a Mettler DSC30 measuring cell connected to a Mettler Thermal Analysis system TA300 with a TC10A TA processor. The central unit of the system is the TA processor. It acquires the input data, controls the furnace temperature and calculates the final numerical results. The signal from the cell is \( H = \frac{\Delta U}{E} \) where \( \Delta U \) is proportional to the temperature difference between the reference and sample and \( E \) is the calorimetric sensitivity. It can be divided into a temperature, \( E_{rel} \), dependent term which is contained in the TA processor as a polynomial \( E_{rel} = A + BT + CT^2 \). This is the temperature dependence of a platinum resistance thermometer which is used to control the temperature of the furnace. The independent term, \( E_{in} \), is determined by calibration using the known heat of fusion of a substance. Figure 4.1 illustrates the DSC30 cell. The furnace temperature is controlled via a platinum thermometer while the sample and reference pan temperature are recorded by two thermocouples. The heat is transferred into the sample and reference pans by two probes and the difference in heat flow is the signal sent to the processor. The cell also has a gas inlet so experiments can be carried out in other type of atmosphere rather than air.
The DSC system was subjected to heat flow and temperature calibration. The heat flow was calibrated using the heat of fusion, which is 28.45 J/g, of an exactly known quantity of indium. A pan containing indium, lead and zinc was used for the temperature calibration, the melting points are 156.6, 327.4 and 419.5°C respectively, Figure 4.2 shows the temperature calibration scan. The calibration method available calculated and transferred the values of A, B and C automatically into the system when the run was finished while the calorimetric sensitivity of indium, $E_{\text{m}}$, in points/mW had to be entered manually. Next, the heat of fusion of indium by integration of the melting peak was estimated and its value compared with the standard value. If the values did not compare well, the new value of $E_{\text{m}}$ was introduced and a new run and integration was carried out until the two values agreed reasonably well. Several runs were needed until the accuracy achieved was satisfactory, Figure 4.3 shows the last of those runs, the heat of fusion was 28.98 J/g and the temperature of melting was 157.0°C. The value of E for indium was 39. The internal calibration of the system implies that the calibration factor in equation 4.3, K, is 1. Thus, the processor estimates the heat of fusion of a substance by dividing the area under the baseline over the mass of the sample.

4.3. EXPERIMENTAL

PET and Nylon 11 samples were tested in the temperature ranges 0-623 K and 0-548 K respectively at a heating rate of 10 K/min using an empty pan as reference. The cell was purged with argon, at a rate of approximately 80 cm$^3$/min, to avoid any reaction between the sample and atmospheric oxygen at high temperatures. Samples were weighted in a Sartorious balance, model R180D. Precise weighing is very important in enthalpy determination so, two independent measurements were taken and the results averaged. Approximately 5-10 mg of sample were put inside a standard aluminium pan and sealed. The pans were pierced so the air trapped in the pan before sealing or any gas produced during heating could be evacuated. The purpose of sample preparation is to reduce the thermal resistances, crucial to the performance of the system as already mentioned. Consequently, at the same time that the lid of the pan was pierced it was bent slightly downwards so the lid kept the sample in contact with
Fig. 4.1 Sectional view of the DSC measuring cell
Fig. 4.2 Temperature calibration.

Fig. 4.3 Heat flow calibration
the bottom of the pan.

Several runs were made to reduce errors and check for reproducibility. When enough material was available two runs were made for each individual sample. Moreover, as indicated in Chapter 2 every mechanical test was carried out on three samples under the same conditions, so, each point in the graphs is an average of six measurements. The degree of crystallinity is equal to

\[ X_c = \frac{\Delta H}{\Delta H_m^\circ} \]

where \( \Delta H \) is the heat of fusion of the material obtained by integration of the DSC curve and \( \Delta H_m^\circ \) is the heat of fusion of 100% crystalline material. The value reported in the literature in the absence of amorphous phase is 115 J/g for PET, Mettler Manual and Mandelkern (1964) (a value of 140 J/g was also reported by Turi (1981) quoting the results of Wunderlich (1980)). The Encyclopedia of Polymer Science and Technology suggests a value of 206 J/g for Nylon 11.

Perhaps, the main error of DSC analysis comes from baseline placement for integration. The selection of the baseline starting and ending points must be based on some theoretical considerations, however, theory does not cover all the possibilities and it is the shape of the curve and the displacement from the blank baseline that determines the correct baseline for integration. Khanna and Kuhn (1997) argued that for amorphous polymers (based on their findings on Nylon 6) a baseline should be drawn between the state of equilibrium which occurs just above the glass transition temperature and the post-melting equilibrium temperature. They detected that the baseline did not return to the original value after the cold crystallisation (equilibrium was not re-established) and they named the process occurring between cold crystallisation and melting, "silent crystallisation" The author pointed out that the shorter the temperature difference between cold crystallisation and melting the smaller the influence of silent crystallisation in the result. For crystallinities larger than 25% the integration between a pre-melting and post-melting point temperature is correct as long as moisture content of the sample is low. Moreover, peak separation in PET is easier than for Nylons because PET has a low crystallisation rate, which allows the cold crystallisation to be easily identifiable while Nylons have a high crystallisation.
Thermal Analysis

rate and the cold crystallisation occurs very close to the glass transition making the identification more difficult. PET integration was done separately for the cold crystallisation and melting for simplicity. Besides, silent crystallisation can only occur in a range of about 30 K in PET while this range is about 170 K for Nylons, so the error introduced in the measurements due to independent integration is estimated to be about 2%. Owing to its high initial degree of crystallinity, see below, Nylon 11 was integrated between the pre-melting and post-melting points with an error of approximately 2% as well.

The melting temperature was taken as the maximum deflection of the peak. Slade (1970) pointed out that the increase in slope in Figure 4.3 leading to the maximum deflection is due to the time required for the equilibration between the furnace and the sensor, the thermal lag. He recommended that the melting point of another substance should be estimated by drawing a line parallel to the calibration slope and extrapolate it to the baseline. The intersection of these two lines marks the temperature sought. Consequently, if there was no thermal lag and the slope in Figure 4.3 was completely vertical, the maximum deflection would be equal to the melting temperature. The melting points would be about 2 K smaller if the method was used.

Calibration was carried out every six months. At the same time, a blank experiment with two empty pans, was run. The blank experiment should provide a straight line, otherwise it would have indicated that there is a problem with the sensor, thermocouples or the holders are dirty. Dirtiness reduces the thermal resistance between the sample and the holder, which is very important in temperature determinations, while the dependence of heat of fusion on thermal resistance is minimised by integration.

4.4 RESULTS

The as-received materials Figures 4.4b and 4.17a had the following features: i) PET: glass transition at 353.1 K, cold crystallisation at 416.6 K and melting at 528.2 K. The total crystallinity was 11.8%, almost amorphous.; ii) Nylon 11: melted at 464.5 K with
an enthalpy of fusion of 57.2 J/g, i.e. 27.8% crystallinity. It did not cold crystallise and the glass transition temperature was 315.5 K. Both materials followed the relationship for polymers with unsymmetrical chain units, which states that the glass temperature is approximately two thirds of the melting point, $T_g / T_m = 2/3 = 0.66$. The ratio for symmetrical polymers should be about 0.5. The values were 0.66 for PET and 0.68 for Nylon 11.

4.4.1 POLYETHYLENE TEREPTHALATE

The DSC scans for PET untested, tested at $10^3$, 1230, 1940 and 8800 s$^{-1}$ and heated for 30 minutes at different temperatures before the test are shown in Figures 4.4-4.8. The glass transition of untested samples, Figure 4.4, is very sharp up to annealing temperatures of 323 K, at higher annealing temperatures the glass transition broadens and it is barely visible on samples annealed at 453 K. The glass transition temperature drops by 8 K, from 353 to 345 K on increasing the annealing temperature. Likewise, cold crystallisation was seen only up to annealing temperatures of 363 K and the peak intensity decreased as the temperature increased. The cold crystallisation temperature is very difficult to assess because of the asymmetry of the peaks obtained, see Figures 4.4a and 4.e. However, the cold crystallisation temperature between the samples tested at room temperature and 363 K decreased by about 5 K, from 416 to 411 K, not a very large change. It is worth mentioning at this stage that the melting temperature did not vary by more than $\pm$ 3 K for any of the samples compared to the as-received sample, and it will be regarded as constant under any conditions. Samples tested at low strain rate showed thermograms, Figure 4.5, very similar to the untested material. The glass transition and cold crystallisation are measurable up to 363 K and the thermal deflection of both transitions decreased in intensity with increasing test temperature. The cold crystallisation peaks were fairly symmetric and the corresponding temperatures were almost constant at around 393 K. At strain rates of 1230 s$^{-1}$, Figure 4.6, there seems to be a transition in the material behaviour. The glass transition was not observed while cold crystallisation, although it was not distinguishable in the figures, it was present but it represented a small percentage of the overall crystallinity content compared to the contribution of the melting endotherm. The samples tested at
Fig. 4.4 PET untested, preconditioned at: (a) 263, (b) 298, (c) 323, (d) 363, (e) 453 K
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Fig. 4.5 PET tested at $10^{-3}$ s$^{-1}$ and at: (a) 263, (b) 298 (c) 323, (d) 363, (e) 453 K
Thermal Analysis

Fig. 4.6 PET tested at 1230 s⁻¹ and at: (a) 263, (b) 298, (c) 323, (d) 363, (e) 453 K
Fig. 4.7 PET tested at 1940 s\(^{-1}\) and at: (a) 263, (b) 298 (c) 323, (d) 363, (e) 453 K
Fig. 4.8 PET tested at 8800 s\(^{-1}\) at 298 K
263 K were an exception and the transitions are clear. The cold crystallisation peak occurred at approximately 392 K. Samples tested at 1940 s\(^{-1}\), Figure 4.7, behave in a similar manner to those tested at 1230 s\(^{-1}\) but the absence of glass transition and cold crystallisation occurred at any temperature. At the highest strain rate, 8800 s\(^{-1}\), the sample showed a very broad cold crystallisation peak and glass transition, Figure 4.8.

The scans of samples compressed at different amounts of strains are displayed in Figures 4.9-4.12 for rates of 10\(^{-3}\), 1, 1230 and 8800 s\(^{-1}\) respectively. At low strain rates, 10\(^{-3}\) and 1 s\(^{-1}\) the material underwent sharp glass transition and cold crystallisation. At 1230 s\(^{-1}\), the samples underwent glass transition and cold crystallisation up to 140% strain, while at 185% strain, transitions were not seen. It is worth noting the variation of the cold crystallisation temperatures. At 10\(^{-3}\) s\(^{-1}\), the cold crystallisation temperature for samples tested up to 30% strain is 418 K (close to the untested value) and it decreases with strain up to 392 K very similar to the value of 393 K reported above for samples tested without constraints. At 1 s\(^{-1}\) the cold crystallisation temperature decreases from 415 K to 394 K. At 1230 s\(^{-1}\) the temperature drops from 414 to 394 K, comparable to 392 K for free samples, before it disappeared at higher strains. At 8800 s\(^{-1}\), Figure 4.12, the glass transition and cold crystallisation were visible up to 140% when it disappeared, the cold crystallisation temperature also decreased, from 405 to 396 K, but there is no possible comparison with a free tested sample. The changes of the glass transition and cold crystallisation under different conditions might shed some light on the behaviour of the material and it will be discussed below.

Samples annealed at 453 K did not undergo either glass transition or cold crystallisation as already mentioned. Nevertheless, the samples showed other interesting features. i) the as-received PET was transparent, but visual inspection of the sample in the hot stage revealed that the material turned white and opaque above the cold crystallisation temperature, a process named whitening. It is possible that whitening is produced by the movement of chains before the formation of crystals. It was reported by Gupta and Salovey (1990) that the similar material PEEK also changed to white and opaque on heating above the cold crystallisation temperature; ii)
Fig. 4.9 PET tested at $10^3$ s$^{-1}$ at 298 K, strain: (a) 35, (b) 70 (c) 140, (d) 185%
Fig. 4.10 PET tested at 1 s\(^{-1}\) at 298 K, strain: (a) 35, (b) 70, (c) 140, (d) 185\%
Fig. 4.11 PET tested at 1230 s⁻¹ at 298 K, strain: (a) 35, (b) 70, (c) 140, (d) 185%
Thermal Analysis

Fig. 4.12 PET tested at 8800 s\(^{-1}\) at 298 K, strain: (a) 70, (b) 140, (c) 185%
the samples tested at 453 K at 1230 s⁻¹ showed two melting peaks, a major one around the usual temperature and a minor one at a higher temperature, Figure 4.6e. It was also observed for samples heated at 363 K and 453 K tested at 1940 s⁻¹, Figures 4.7d and e. It is not very clear in the figures so an insertion with the melting peak is included. The difference in quality between the insertion and the whole scans is due to the resolution of the scanner used to create the figures. The two melting peaks may indicate the presence of two species of crystallites, one more perfect than the other.

The area of the cold crystallisation peak and the heat of fusion are tabulated in Tables 4.1 and 4.3 while the total crystallinity obtained by subtracting the previous values and dividing it by 115 J/g for PET is tabulated in Tables 4.2 and 4.4. The crystallinity values against temperature, strain and strain rate are illustrated in Figures 4.13-4.16. Figure 4.13 reveals that the degree of crystallinity tended to increase with strain rate up to 1940 s⁻¹, at any temperature except at 453 K when it was approximately constant. It seems that the degree of crystallinity at this temperature does not depend on strain rate. At 8800 s⁻¹ the crystallinity content decreased, probably as a result of melting during impact. Moreover, the samples tested at low strain rates needed higher annealing temperatures to reach a high degree of crystallinity. At low temperatures and low strain rate the crystallinity content remains almost constant and then it turns upwards at higher strain rates while at high temperatures the crystallinity increase occurred at low strain rates, Figure 4.14. Figures 4.15 and 4.16 show that the degree of crystallinity increased with strain rate and strain. At low strain rates or small amount of strain the level of crystallinity increased by a small amount. The largest increases occurred on samples compressed to 185% strain at 1230 and 1940 s⁻¹.

### 4.4.2 NYLON 11

Figures 4.17-4.22 depict the DSC scans of Nylon 11 samples tested at various strain rates and temperatures after different thermal treatment. All the samples underwent glass transition on heating and the glass transition temperature did not vary by more than ± 3 K, without any apparent tendency, around the value of 316 K estimated for the as-received material. Likewise, the melting temperature did not vary by more than
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Fig. 4.13 PET Crystallinity Content vs. Strain Rate on a logarithmic scale

Fig. 4.14 PET Crystallinity Content vs. Temperature
Thermal Analysis

Fig. 4.15 PET Crystallinity Content vs. Strain Rate on a logarithmic scale.

Fig. 4.16 PET Crystallinity Content vs. Strain.
± 2 K around the value of 464 K. The shape of the melting peak varied depending upon the thermal treatment. As-received samples showed two melting points, the low temperature peak being smaller than the high temperature. Under compression at any strain rate the low temperature melting peak disappeared. Likewise, samples annealed at 170°C for 15 minutes showed two melting peaks but on compressing the material showed only one broad melting point. Nevertheless, as-received or annealed at 170°C samples of Nylon 11 and tested at 263 K showed a shoulder even after compression as a reminiscence of the low melting peak, Figures 4.20b and 4.21b. Samples annealed at 190°C for 30 minutes showed only one melting peak. Chen et al. (1985) reported that Nylons showed the presence of two distinct melting peaks. It seems that two species of crystals are present and one of them underwent a phase transition under some test conditions.

Nylon samples seemed to undergo an endothermic relaxation, i.e. the equilibrium was not re-established after the glass transition. After the glass transition temperature, 323 K, the thermogram baseline turned upwards again, reaching similar values to pre-glass transition values and then it continue normally until melting occurred. The relaxation did not show any consistent tendency with temperature or strain rate, although it seems to be less important, although present, at high strain rates, Figures 4.17d-4.19d, or untested samples, Figures 4.17a-4.22a. On the other hand, samples tested at $10^{-3}$ s$^{-1}$ seemed to undergo large relaxation phenomenon and samples tested at 1230 s$^{-1}$ showed the relaxation on as-received samples but not on annealed samples. Thus, a pattern of occurrence cannot be extracted from the data. It could be that the sample did not undergo cold or silent crystallisation above the glass transition but the exothermic turn is due to water which was lost exothermically when the temperature surpassed 323 K. The latter is based on the fact that moisture regain of Nylons is high, the order of several per cent. Nylon 11 equilibrium water absorbance is about 2.5%, one of the smallest among the amides. The water absorption increases with the amide group concentration in the polymer backbone reaching values of 9% for Nylon 66.

A measurement of the water absorption of as-received Nylon 11 was attempted by weighing the mass of two samples before and after drying them. Thus, two samples of
Fig. 4.17 Nylon 11 as-received tested at 298 K: (a) untested, (b) $10^{-3}$, (c) 1230, (d) 8800 s$^{-1}$. 
Fig. 4.18 Nylon 11 annealed 15min@170°C tested at 298 K:
(a) untested, (b) 10³, (c) 1250, (d) 8800 s⁻¹
Fig. 4.19 Nylon 11 annealed 30 min @ 190°C tested at 298 K:
(a) untested, (b) $10^{-3}$, (c) 1230, (d) 8800 s$^{-1}$
Fig. 4.20 Nylon 11 as received tested at 263 K: (a) untested. (b) $10^3$. (c) 1230 $s^{-1}$
Fig. 4.21 Nylon 11 annealed 15 min @ 170°C tested at 263 K:
(a) untested, (b) 10⁻³, (c) 1230 s⁻¹
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a) Temperature ('C)

Fig. 4.22 Nylon 11 annealed 30 min @ 190°C tested at 263 K:
(a) untested, (b) 10^3, (c) 1230 s^-1
20.88 and 26.49 mg (five measurement were taken) where left on a dissecator for four weeks. The weights after that period were 20.77 and 26.36 mg. The values are averages of five measurements and the standard deviation was 0.01 in all the cases. The loss of mass was approximately 0.5%, this indicates that the water content of the Nylon was small.

Figures 4.23-4.24 depicts the degree of crystallinity for Nylon 11 samples under different conditions. Table 4.5 represents the heat of fusion values and the crystallinity values are tabulated in Table 4.6. Figure 4.23 shows that the crystallinity content increased with strain rate up to 1230 s\(^{-1}\) and then it decreased at the highest strain rate. It also shows that, in general, the samples tested at 263 K had a higher degree of crystallinity than samples tested at room temperature. Figure 4.24 represents the crystallinity data against annealing treatment. The Figure reveals that the crystallinity increased with heat treatment and strain rate except at the highest rate, 8800 s\(^{-1}\), where a small, but not significant, decrease can be seen.

4.5 DISCUSSION

The thermal behaviour of PET and Nylon 11 was studied by DSC. The samples studied were subjected to different thermomechanical treatments before the scan. Samples were tested in closed pans without any constraints, i.e. free to shrink, under an argon atmosphere.

4.5.1 POLYETHYLENE TEREPTHALATE

As received PET underwent glass transition, cold crystallisation and fusion in the range 273-623 K. The material was almost amorphous, crystallinity content 11%, which indicates that it was quenched from the melt prior to testing. On heating the material showed a strong tendency to crystallise from the supercooled glass.

It has been reported that crystallisation of PEEK from the glass produced spherulites an order of magnitude smaller, and smaller and thinner lamellae than those in melt
### TABLE 4.5

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<tr>
<th>Rate (S(^{-1}))</th>
<th>T (K)</th>
<th>As Received</th>
<th>15min@170°C</th>
<th>30min@190°C</th>
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### TABLE 4.6

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<th>Rate (S(^{-1}))</th>
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<th>As Received</th>
<th>15min@170°C</th>
<th>30min@190°C</th>
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Fig. 4.23 Nylon 11 Crystallinity Content vs. Strain Rate on a logarithmic scale

Fig. 4.24 Nylon 11 Crystallinity Content vs. Annealing for samples tested at 298 K.
1: as-received; 2: 15min@170°C; 3: 30min@190°C
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crystallised material. A higher nucleation density was cited by Gupta and Salovey (1990) as the reason for the reduction in spherulite and lamellar size. Thus, crystallisation from the melt produces larger and more perfect crystals than cold crystallisation which involves crystallisation in constrained regions and crystallisation on annealing before melting. An increase in crystallinity might involve an increase in the total number of crystallites and/or the average perfection of existing ones.

The as-received material was annealed up to 453 K. The crystallinity content was nearly constant up to 323 K and then it increased rapidly up to values of 50%. The increases may be associated with crystallisation above the glass transition temperature. At temperatures of 363 K which is lower than the maximum crystallisation rate temperature, the crystallisation occurred slowly but was not zero. So, annealing for 30 minutes increased the crystallinity by a small percentage, 18% compared to 12%, and it shows that the material crystallised at low temperatures at a very slow rate. It is well established that the degree of crystallinity of polymers increases on annealing. Natale et al. (1992) found an increase of crystallinity on increasing the annealing temperature of PP. Alberola et al. (1995) claimed that the crystallinity of PP was almost constant up to 363 K and then, it increased at higher temperatures. Pillon et al. (1987) reported an increase of the crystallinity content of PET with temperature of annealing. However, Muller et al. (1987) claimed that the degree of crystallinity of PET was independent of annealing and it could be explained by structural changes occurring in the calorimeter. The optical phenomenon of whitening is likely to be caused by the formation of crystallites. The new arrangement of the polymer chains scattered the light while disordered material transmitted the light.

On increasing the strain rate, the degree of crystallinity is higher independently of the temperature; see Figure 4.14. Figure 4.13 shows that at temperatures up to the glass transition temperature, the development of a significant amount of crystallinity requires high strain rates, while above the glass transition temperature the increment of crystallinity is significant at low strain rates. Thus, the crystallinity content of PET increases with strain rate and temperature of deformation. Two cases require a special
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attention: i) samples tested at $10^3 \text{ s}^{-1}$ and 363 K have a high content of crystallinity, about 20% higher than the untested. As already mentioned, at 363 K crystallisation may occur during annealing forming metastable polymer crystals which may experience a perfecting process on compression, increasing the heat of fusion even at slow rates, although new crystallites may have been induced by compression as well; ii) samples tested at 8800 s$^{-1}$ showed a significant decrease in the crystallinity content and it is possible that the samples melted during mechanical test and re-crystallised after completion of the test.

The sharp glass transition showed by the as-received sample, is not detected at high temperatures around 453 K, it broadened at low strain rate at any temperature, it was barely perceptible at 1230 s$^{-1}$ and was not detected at 1940 s$^{-1}$. Cheng et al. (1986) reported that any crystallisation broadened the glass transition range, Slade (1970) claimed that the glass transition temperature decreased in magnitude and broadened with increasing crystallinity and Turi (1981) cited Ito and co-workers (1973) who argued that the glass transition temperature is primarily determined by the local oscillations in the amorphous region. Therefore, the increase in crystallinity at high strain rates restricts the glass transition. Thus, the absence of the change of the baseline characteristic of the glass transition at high strain rates may be due to physical crosslink induced in the amorphous phase by the crystalline entities. Consequently the crosslinking which resulted from the increase of crystallinity, may bring chains together reducing the free volume essential for backbone chains to move. Chain molecular motion is intense at low strain rates (low crystallinity) which may give rise to orientation but motion decreases with increasing strain rates restricting orientation. Finally, the glass transition temperature is accompanied by a configurational entropy increase. At low strain rates, chain movements are allowed accompanied by an increase in volume and the formation of unstable chain configurations which increased the entropy; at high strain rates the crosslinking held large movement and the increase of entropy and glass transition did not occur.

The cold crystallisation peak temperature decreased by about 20 K at all strain rates compared to untested samples. It also decreases in intensity with strain rate until is
barely perceptible above the baseline. The cold crystallisation peak disappeared at annealing temperatures above the cold crystallisation temperature. Lin and Koenig (1984) pointed out that the cold crystallisation peak disappearance was associated with a transition in the physical properties such as density which increases with crystallinity content. Thus, the increase in crystallinity during heating or mechanical testing before the DSC run produced a decrease in the amount of chains cold crystallised during the DSC scan. On annealing the as-received material the temperature decreased by 5 K. Turi (1981) quoted Song et al. (1989) who claimed that the cold crystallisation temperature decreased obviously due to a nucleation effect with increasing crystallinity, but it seems to occur with no increase in crystallinity content, for instance untested and tested at $10^{-3}$ s$^{-1}$ at 298. However, the melting endotherm for all the samples, independently of heating or strain rate was very similar between 50 and 60 J/g and it was the reduction of the cold crystallisation peak which brought about the increase in the overall crystallinity content. It seems that the material cannot be obtained with a crystallinity content higher than approximately 50% as a result of entanglements and crosslinking. Therefore, for a combination of strain, strain rate and temperature there was a maximum degree of crystallinity that could be achieved. When the crystallinity increased there was less material to incorporate into the crystalline phase and the amorphous regions were very much surrounded by crystals. Thus, the movement of the material left was more restricted and crystallisation became very difficult above those percentages. As about half of the material crystallised, the other half could not organise regularly.

Upon annealing a minor melting peak has been found by different authors and they offer different explanations for the phenomenon. Lee et al. (1998) found that upon annealing a minor melting peak was generated about 10 K above the annealing temperature. It was proposed that the minor peak could be due to the melting of regions of crystallites of low degree of order, which could possibly exist in the amorphous phase, and the major melting peak could be due to the melting of large, stable spherulites, consisting of well formed lamellae in the crystalline phase. However, Blundell and Osborn (1983) proposed that the minor melting point was associated with the melting of the crystallites formed during the previous
crystallisation process and the large melting peak at higher temperatures was due to melting and recrystallisation into more perfect crystals during the heating run. Cheng and co-workers (1986) also found a minor melting peak for PEEK isothermally crystallised, at about 15 K above the crystallisation temperature. Natale et al. (1992) and Alberola et al. (1995) found that PP showed a small melting peak at about 20 K higher than the annealing temperature, and proposed that it could be due to the melting of crystalline entities of small size and/or low degree of perfection. Two melting peaks have also been reported for PET samples annealed above 423 K by Pillon and Lara (1987). Muller et al. (1987) reported the presence of two melting peaks and suggested a similar explanation to Blundell's quoting the results of Holdsworth and Turner-Jones (1971) who argued that although the reorganisation process is not seen in the thermogram it happened. Lin and Koenig (1984) reported two melting points and they preferred the melting and recrystallisation explanation to the two different morphological crystalline or one form differing in size and perfection explanation. The same effect was found in PEN, Cakmak and Lim (1997), suggested that the minor melting peak was due to crystals produced during annealing which melted approximately 10 K above the annealing temperature. But, the results presented above did not show a second melting peak at a lower temperature for PET, probably because it overlapped with the major melting peak. Nonetheless, it is very remarkable that, in this work, a second melting peak was observed at approximately 15 K above the major peak under certain conditions, 453 K at 1230 s\(^{-1}\) and 363 and 453 K at 1940 s\(^{-1}\). The origin of this peak is not clear and it could be due to melting of very small highly ordered regions as described by Alberola et al. (1995) and Cakmak and Lim (1997) who claimed that high melting points are due to crystalline perfection. Thus, the high melting point could have a true microstructural origin. Nonetheless, the heat of fusion associated with the high temperature melting is smaller than the low temperature and it is not only different to all those quoted above but nothing similar has been found by the author in the literature. Consequently, if the melting peaks are due to two species of crystals, the more perfect crystals were a minority which indicates that the perfecting process is not very efficient.

The major melting point remained almost constant for all the samples. Perhaps the
melting point should have varied under different testing conditions, however shrinkage could prevent changes and the peak occurred at the same temperature. Variations in the melting point could be seen when samples were held constrained because constraining retards the relaxation of previously imposed molecular orientation, this tends to slow crystallisation and crystal perfecting processes which may lead to changes in the melting endotherm. On the one hand, Turi (1981) quoted Illers (1970) amongst others, who found the melting point changed for samples constrained, Smook and Pennings who (1984) attributed the difference between constrained and unconstrained melting point to the development of a partially ordered melt in the constrained state experiments and Yubayashi (1966) who claimed that the melting point remained unchanged under any conditions even for constrained experiments.

The behaviour of PET at different strains is displayed in Figures 4.15 and 4.16 and Tables 4.3 and 4.4. It can be seen that large amounts, 185%, of strain and high rates are required to obtained high crystallinity content, although at 140% the increase is noticeable. Again, the increase in crystallinity content is detected as a reduction of the cold crystallisation exotherm. Melting points are nearly constant, in accordance with Turi (1981) quoting the result of Song et al. (1989) who reported that the melting point of PEEK was constant with draw ratios while Alberola et al. (1995) could not explain the increase of the melting point by 7 K on increasing the draw ratio. However, the cold crystallisation temperature was approximately 413 K at 35% strain, similar to as-received samples, it slightly decreased for samples tested up to 70% strain and then it decreased to 393 K, the value measured for tested samples. Cakmak and Lim (1997) reported that the cold crystallisation temperature moved to lower temperatures and was directly related to the reduction of entropy with preferential orientation. Thus, if highly orientated specimens were obtained at large amounts of strain, the chains required lower energy to crystallise. As the energy transferred into the system is proportional to the temperature, crystallisation occurred at a lower temperature. The value of crystallinity at 8800 s⁻¹ and 185% strain was 47.4% which is much higher than the “free” tested sample, 25%. This lends weight on the idea that the material reached temperatures near the melting point and it did not fully re-
crystallise during cooling after the impact.

An experiment was carried out on as-received PET in an attempt to confirm that idea. A sample was heated up to 543 K, which is the end of the melting peak, in the DSC. A normal scan was then run on the same sample yielding a crystallinity degree of 23%. This shows that when PET is heated above the melting point and slowly cooled the degree of crystallinity is larger than in the as-received material but much smaller than the crystallinity content of samples tested in the $10^3$ s$^{-1}$ range. The similarity between the crystallinity content after heating to 543 K and the degree of crystallinity of “free” tested samples at 8800 s$^{-1}$ re-reinforces the previous statement. Nevertheless, the temperature increase needed to melt the samples would require approximately an extra 100 K above the temperature rise estimated at 185% strain which seems very large.

Results reported in the literature on the dependence of the degree of crystallinity with strain or strain rate are now discussed. Lee et al. (1988) reported that annealing as-received amorphous PEEK increased the crystallinity content. Samples drawn at 20 mm/min at room temperature showed an increase in crystallinity content for the as-received samples but the crystallinity of annealed samples tested at room temperature decreased on drawing possibly because of interference between the ether and ketone linkages. Only the as-received sample drawn at room temperature is comparable with the results presented here and both found an increase. Jabarin (1992) reported an increase of the degree of crystallinity of PET with strain rate (maximum stretching rate 127 mm/min) at stretching temperatures above the glass transition temperature with crystallisation occurring during the stretching process for those samples stretched at high speed and at a high extension ratios. This is similar to the increase seen on samples tested at 363 K and $10^3$ s$^{-1}$. Misra and Stein (1979) reported an increase in crystallinity of 15% in PET samples tested below and above the glass transition temperature at a speed of 10% min$^{-1}$. Further annealing after stretching increased the crystallinity up to 40%. Spruiell et al. (1972) found a slight trend toward increased crystallinity below the glass transition temperature with increasing strain rate (maximum strain rate 1.88 min$^{-1}$) while the crystallinity, above the glass transition
temperature but below the cold crystallisation temperature, decreased with increasing deformation temperature at a given strain rate. Alberola et al. (1995) reported that the crystallinity of PP increased with draw ratio at 0.05 s\(^{-1}\) by about 7%. This agrees with the two first columns of Table 4.4. This authors also reported that at strain rates of 100 s\(^{-1}\) the crystallinity decreased and then it increases to values near the as-received materials at 300 s\(^{-1}\). Chang et al. (1993) found that above the glass transition temperature i) the crystallinity induced is clearly dependant on temperature but no so clearly on strain rate (maximum of 0.17 s\(^{-1}\)); ii) the start of crystallisation shifted to lower draw ratios when the strain rate increased; iii) at a given draw ratio the crystallinity is slightly higher for higher strain rates and iv) the crystallinity and orientation followed a linear relationship. Turi (1981) cited Smith and Lemstra (1980) who reported increases in crystallinity of HDPE with draw ratio. The same author quoted that Koenig and Mele (1968) found that when the draw ratio is less than 160% no crystallisation takes place in PET because of small uncoiling and elongation. Table 4.4 shows that the onset of crystallisation in this work is about 140% for PET.

In view of the results presented it can be concluded that PET crystallised when the temperature, strain or strain rate, or a combination of those, is increased. The crystallinity increase is a genuine phenomenon and it is supported by XRD (Chapter 3). Thus, the reduction or absence of the cold crystallisation peak indicates that some of the chains crystallised before the DSC run. At high crystalline contents the material comprises an amorphous phase reinforced by crystallites, the crystals are closely tied to the oriented amorphous structure and the material is highly crosslinked. The crystallisation is accompanied by an increase in density. Among the factors which may give rise to crystallisation, orientation is probably the main one. Orientation reduces the barriers (it can induce nuclei which are stable enough to grow) to crystallisation, i.e., the molecules are much closer to the crystalline configuration and it may give rise to a energy driven crystallisation phenomenon. Uncoiling could be a second factor helping crystals to be formed, it is very common during tension tests that the material uncoils while chains are brought through the neck but it is very unlikely that uncoiling occurs during a compression test. It has been reported by Fried (1995) and Turi (1981) quoting results of Meinel and Peterlin (1967) that trans
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isomers with a lower energy content crystallise more easily than gauche isomers. Therefore, a trans-gauche transition may be induced by stress and strain while at the same time large strains help to lower the entropy of the amorphous regions favouring the trans configuration.

4.5.2 NYLON 11

It is known that polyamides exhibit a complex behaviour with temperature and Nylon 11 is not an exception. The as-received material was 28% crystalline; the DSC pattern is very similar to a pattern reported by Khanna and Kuhn (1997) for Nylon 6 of 35% crystallinity and it did not undergo cold crystallisation. Consequently, silent crystallisation should be almost negligible according to Khanna and Kuhn (1997). However, the absorption of moisture by Nylons is very high, several per cent compared to less than 1% for PET, and it occurs within the time scale of DSC sample preparation. The moisture is lost endothermically above the glass transition temperature and it should be seen as an increase of enthalpy. Moreover, moisture acts as a plasticiser because of the hydrogen bonding of water with the amide linkage, and lowers the glass transition to about 293 K. However, the glass transition temperature did not vary too much around the value of 316 K which is very close to the ultradry glass transition temperature, which is supported by the low water content found in the as-received material. Therefore, the origin of the enthalpic relaxation after the glass transition temperature seen in some samples (without any particular pattern) is not clear and it cannot be attributed unambiguously to silent crystallisation or moisture. Since silent crystallisation was not observed and moisture (whether present or not) was not considered in the heat of fusion calculations, the crystallinity was estimated by drawing a straight line between the pre-melting and post-melting temperature.

The crystallinity did not vary very much under different conditions, and it seems to increment up to 1230 s⁻¹ and slightly decreases at 8800 s⁻¹ but with very small percentage changes. Crystallinity seemed to decrease with the temperature test, although with only two test temperatures used a clear pattern could not be obtained. Turi (1981) quoting Chuah and Porter (1986) reported that the crystallinity of Nylon 6
decreased continuously with draw ratio and no explanation could be given. The melting point remained around the value of 464 K. Nevertheless the crystallinity index was complicated to obtain. The DSC scans show some other features which are worth analysing. The as-received sample showed two peaks. It is feasible that two species of crystals are involved in the melting of Nylon 11 according to Chen et al. (1985), namely lamellae and fibrillar crystals. However, if the material was crystallised from the melt a peak would appeared about 15 K above the crystallisation temperature but since the history of the material is not known the discussion will follow Chen’s argument. After compression, at any rate, the as-received material showed one broad peak. After annealing at 170°C the samples still seemed to be formed by two species of crystallites although the melting appeared to be very complex. Under compression the low temperature crystals underwent a transition to the high temperature form. After annealing at 190°C the DSC only recorded one peak. The annealing temperature was above the low melting peak, therefore, it can be concluded that annealing induced a transition in the low melting crystals and the two melting peaks merged. Nylon 11 tested at 263 K behaved very similarly. It is remarkable that the samples tested at 10^3 s^-1 showed a shoulder as a reminiscence of the low melting peak which implies that at low temperature the transition did not occur completely and low melting species are present. Chen et al. (1985) also reported that samples which showed two melting points at atmospheric pressure exhibit only the low melting temperature peak under 4 kbar. Likewise, Nylon 11 crystallised at 4 kbar showed only the low melting point while the two melting points were present when crystallised at atmospheric pressure. This effect seems to be strange but is not comparable with my results.

It can be concluded that the percentage of crystallites which gave rise to the low melting temperature change its morphology shifting its melting point to higher temperatures. However, the distinctive peak disappeared, the crystallites melted over a broad range of temperatures indicating that although the peak is not seen there is an ample range of crystal sizes. The low melting crystals might be a kind of metastable phase which could change its structure easily. On the one hand, the transition of the low melting crystallites obviously occurred when the material was annealed above the crystallites melting temperature and the low melting peak was then not observed. On
the other hand, compression brought about the same effect. It is thought that stress, strain and/or strain rate can modify the structure of the low melting crystals inducing a phase transition to the more stable high melting species.

The changes of the crystallinity index must be considered cautiously because the maximum changes of 4% are close to the estimated error in the measurement. DSC scans disclosed another features such as the double character of the crystals present in the as-received material and the conditions under which the crystals characterised by a low melting peak transformed into the high melting class of crystals.
CHAPTER 5

KINETIC ANALYSIS OF CRYSTALLISATION AND GEL PERMEATION CHROMATOGRAPHY
5.1 KINETIC OF CRYSTALLISATION

5.1.1 INTRODUCTION

It was considered possible that the crystallisation observed in high rate tests could be due to thermally induced cold crystallisation during a test and a set of thermodynamic experiments were carried out to investigate this possibility. The former can be concluded from the fact that a cold crystallisation peak at approximately 403 K did not appear in samples tested at high rate. Thus the sample must have cold crystallised at some stage during the test. Therefore several samples were cold crystallised to study the behaviour of the material around the cold crystallisation temperature.

Above the glass transition temperature large scale mobility of segments may occur. The increase in available thermal energy increases the number of possible spatial conformations. Under certain conditions the chains can organise into regular crystalline structures and the total crystallinity of the polymer increase.

DSC can be used to calculate the kinetic parameters of the crystallisation of amorphous polymers; see Chapter 4. The process of crystallisation in amorphous polymers can be treated in the same way as a chemical reaction where part of the amorphous phase is transformed into crystals. The rate of evolution of heat during the reaction, in this case heat of crystallisation, is measured directly in terms of power as a function of temperature. The change in heat content and in the thermal properties of the sample is indicated by a deflection or peak in a thermogram, see Figure 5.1. Borchardt and Daniels (1957) cited Spiel (1944) as the first to conclude that the area under the curve is directly proportional to the heat transferred in the reaction. If the reaction proceeds at a rate which varies with temperature the position of the peak varies with the heating rate and this variation can be used to determine the transformation reaction kinetic constants.

The two basic approaches to kinetic analysis are isothermal methods and non-
isothermal (dynamic) methods. In an isothermal method the sample reaction evolution is monitored as a function of time at a constant temperature. Non-isothermal methods record the response of the sample as a function of temperature. Hatakeyama and Quinn (1994) pointed out that non isothermal methods are preferred, the reasons being: i) the preliminary heating stage of an isothermal experiment can change the morphology and structure of polymers; ii) the reaction process can be followed over a wide temperature range; iii) several reaction steps can be observed in a single experiment; iv) reaction kinetic parameters can be estimated from a single run.

The non-isothermal analysis methods may be divided into two groups. On the one hand, Ozawa (1965) and Kissinger (1957) among others proposed methods to calculate the reaction kinetic parameters based on the shift of the crystallisation peak at different heating rates. Therefore several runs are needed. On the other hand, Borchardt and Daniels (1957) suggested calculations based on direct measurements of the system signal, that is to say measurements are taken directly from the thermogram, under the assumption that the reaction constant, $k$, is proportional to the area under the peak.

The cold crystallisation of PET was studied in order to understand the kinetics of crystallisation of the material, its evolution with time and temperature and the possible relationship with the hardening process described earlier; see Chapter 2. The kinetic parameters were derived from the data and used to estimate the evolution of the degree of crystallinity during a typical high strain rate compression test.

5.1.2. THEORY

A reaction can be characterised by a rate constant, $k$. The rate constant dependence on temperature is given by the Arrhenius equation:

$$k = Ae^{-E/RT} \quad (5.1)$$

where $E$ is the activation energy, $R$ is the gas constant and $A$ is called the frequency
factor. If natural logarithms are taken:

$$\ln k = \ln A - \frac{E}{RT} \quad (5.2)$$

Therefore, a plot of $\ln k$ versus $1/T$ should yield a straight line, allowing the activation energy, $E$, and the frequency factor, $A$, to be calculated. Although the Arrhenius equation was developed for isothermal reactions it can be applied to non-isothermal reactions providing that valid integration limits are chosen in accordance with Hatakeyama and Quinn (1994).

The progress of a reaction has to be measured in some way. Normally, in thermal analysis of a reaction, the fraction reacted is defined as: $\alpha = \frac{\Delta H}{\Delta H_{\text{tot}}}$ i.e. the ratio of the area under the thermogram deflection up to a temperature or time to the total area. A kinetic study involves attempting to relate the experimental $\alpha$-time or $\alpha$-temperature values with values predicted by theoretical models. The equations describing the models can be written in integral forms:

$$f(\alpha) = k(t - t_0) \quad \text{(at constant } T) \quad (5.3)$$

or differential forms:

$$\frac{d\alpha}{dt} = k(\alpha) \quad \text{or} \quad \frac{d\alpha}{dT} = \frac{k}{\phi} g(\alpha) \quad (5.4)$$

where $\phi$ is the heating rate. The assumption that the experimental heating rate $\phi = \frac{dT}{dt}$ corresponds to a constant sample heating rate is a point of controversy but a constant relationship is accepted in most treatments. The form of the functions $f(\alpha)$ or $g(\alpha)$ depends upon the process considered although they are not independent.
The forms of \( f(\alpha) \) and \( g(\alpha) \) can be seen on Table 5.1. The different forms arise from different treatments of the reaction kinetics. The function \( P1 \) and \( E1 \) are general functions and are a result of a very simplified model. The Avrami-Erofe'ev functions are based on a nucleation and growth of spherulites in one dimension \( A1 \), two dimensions \( A2 \) and three dimensions \( A3 \). \( R2 \) and \( R3 \) are based on geometrical considerations in two and three dimensions respectively. The functions based on diffusion mechanisms are thought to be very complicated and seldom used. The final functions based on order of reaction are commonly used under the assumption that the reaction under study is of first, second or third order.

The analysis methods are subdivided into differential methods based on use of equation 5.3 and integral methods based on equation 5.4. Three methods are outlined below, together with their main assumptions and validity. The Kissinger (1957) and Ozawa (1965) methods are integral whereas Borchardt and Daniels (1957) is differential. These are commonly used and sometimes incorporated into software packages.

The Kissinger (1957) treatment was derived for Differential Thermal Analysis (DTA), the difference in temperature between the sample and a reference is recorded as a function of the temperature. Nevertheless the DTA instrument signal can be directly substituted by its DSC equivalent. The main assumption of the Kissinger approach is that the peak deflection occurs when the reaction rate is a maximum, this is only true when the heating rate is a constant. It is also assumed in Kissinger's derivation that \( g(\alpha)=(1-\alpha)^n \), where \( n \) is the order of reaction. Accordingly, the maximum occurs at a temperature \( T_m \) defined by \( \frac{d}{dt}\left( \frac{d\alpha}{dt} \right) = 0 \), substituting the form of \( g(\alpha) \) into equation 5.4 and differentiating yields:
\[
\frac{E \phi}{RT_m^2} = A n (1 - \alpha)^{n-1} e^{\frac{-E}{RT_m}} \tag{5.6}
\]

It is also shown that:

\[
n(1 - \alpha)^{n-1} = 1 + (n - 1) \frac{2RT_m}{E} \tag{5.7}
\]

hence the left side of equation 5.7 is not only independent of the heating rate but nearly equal to unity since \(E >> RT_m\). Thus, substituting equation 5.7 into equation 5.6, neglecting small quantities and differentiating:

\[
\frac{d}{d\left(\frac{1}{T}\right)} \left( \frac{\ln \frac{\phi}{T_m^2}}{\beta}\right) = -\frac{E}{R} \tag{5.8}
\]

equation 5.8 makes possible the determination of the activation energy, \(E\), regardless of reaction order by making DSC scans at a number of heating rates.

Ozawa (1965) derived his method for analysis of thermogravimetric data. Thermogravimetry records the weight change of a sample as it is heated at constant rate. Like the Kissinger approach, the Ozawa method can be applied to DSC and Ozawa suggested that if the property measured by other types of thermal analysis is a function of \(\alpha\) only, the change in the property can be treated in a similar way to the change in weight. The method makes use of equation 5.4 rearranged:

\[
\frac{d\alpha}{g(\alpha)} = A e^{\frac{-E}{RT}} dT \Rightarrow \int_{\alpha_0}^{\alpha} \frac{d\alpha}{g(\alpha)} = \int_{\alpha_0}^{\alpha} \exp \left(\frac{-E}{RT}\right) dT \tag{5.9}
\]

Ozawa (1965) quoting the results of Doyle (1961) expressed the right hand side of equation 5.9 as a function of
and proposed that $p$ can be approximated if $E/RT > 20$ as

$$\log p\left(\frac{E}{RT}\right) = -2.315 - 0.4567 \frac{E}{RT} \quad (5.11)$$

Now, for a given value of $g(\alpha)$, the left side of equation 5.9 is a constant which does not depend on the heating rate. Therefore if the reaction proceeds to a given value at the temperature $T_1$ for the heating rate $\phi_1$, it will do so at $T_2$ for $\phi_2$, and so on and the following linear relations can be derived

$$\frac{AE}{\phi_1 R} p\left(\frac{E}{RT_1}\right) = \frac{AE}{\phi_2 R} p\left(\frac{E}{RT_2}\right) = ... \quad (5.12)$$

Thus, the following linear relations can be derived using equation 5.10:

$$-\log \phi_1 - 0.4567 \frac{E}{RT_1} = -\log \phi_2 - 0.4567 \frac{E}{RT_2} = ... \quad (5.13)$$

therefore, a plot of $\log \phi$ versus the reciprocal temperature for a given value of $g(\alpha)$ must give a straight line, the slope of which gives the activation energy. Several runs at different heating rates are again needed.

As pointed out before a different approach can be followed. Borchardt and Daniels (1957) derived a formula to calculate the reaction rate, $k$, for DTA of solutions. The main assumption is that the heat evolved is directly proportional to the number of moles reacting. Uniform temperature of the sample is also assumed and this cannot be met exactly by solids. They found based on thermodynamic reactions that for the case of first order reaction:
\[ k = \frac{C_p \frac{d\Delta T}{dt} + K\Delta T}{K(S-s) - C_p \Delta T} \]  

(5.14)

where \( S \) is the total area under the curve, \( s \) is the area up to a certain temperature and \( K \) the heat transfer coefficient. Under the assumption that the magnitudes \( C_p \frac{d\Delta T}{dt} \) and \( C_p \Delta T \) are an order of magnitude smaller than the quantities to which they are added and that for DSC \( \Delta T = \frac{dH}{dt} \), then:

\[ k = \frac{dH / dt}{S-s} \]  

(5.15)

Formulas to calculate the frequency factor, \( A \), are proposed by the previous authors though the reaction order or the form of \( g(\alpha) \) would be needed. An easy method to estimate the value of \( A \) from DSC or DTA curves was proposed by Rogers and Smith (1967) based on the following considerations. The deflection of the DSC curve from the baseline is given by \( b = -h \alpha \) where \( b \) is the deflection, \( h \) is the heat of reaction per unit weight of the sample divided by the sensitivity of the instrument and \( \alpha = Ae^{\frac{-E}{RT}} \) for a first order rate law. The maximum occurs when \( \frac{db}{dt} = 0 \). Thus, differentiating with respect to time:

\[ \frac{db}{dt} = 0 = h \frac{d\alpha}{dt} A e^{\frac{-E}{RT}} + h \alpha A e^{\frac{-E}{RT}} \frac{E}{RT^2} \frac{dT}{dt} = -b A e^{\frac{-E}{RT}} + \frac{b E}{RT^2} \frac{dT}{dt} \]  

(5.16)

and solving for \( A \):

\[ A = \frac{\phi E e^{\frac{RT_{\text{max}}}{RT_{\text{max}}}}}{RT_{\text{max}}^2} \]  

(5.16)

Hence only the activation energy, the maximum temperature and heating rate are
required. The authors found excellent agreement between the values calculated this way and the literature values for several materials.

5.1.3. RESULTS

Approximately 10 mg samples of PET were used for each DSC scan. The procedure for running the DSC and sample handling were exactly as before; see Chapter 4. PET samples were heated up from 273 to 623 K at heating rates from 1 to 20 Kmin⁻¹. Several samples were heated at the same heating rate and the results averaged. Samples underwent glass transition, cold crystallisation and melting in the temperature range. The peak temperatures and the area under the cold crystallisation and melting peaks were measured. The DSC thermograms at different heating rates are shown in Figures 5.1(a) - (e). It is clear that the curves are very asymmetric.

The DSC curves show different features depending on the heating rate. At 1 K/min the peak was small and not very well defined whereas at faster heating rates the maximum deflection appears clear in the thermograms. However, at heating rates of 2 K/min or faster a second peak developed and its intensity varied with the heating rate. Kissinger (1957) found a double peak on the curve accompanying decomposition. He found that the reaction order of the reaction changed at some stage of the process. The cause of the shape of the curve in Figure 5.1 was not identified. However, two parallel analysis were carried out based on the two sets of different peaks. Results are summarised in Table 5.2. It can be seen that the temperature of the maximums increased with heating rate because the temperature increased more during the time it took for the chains to crystallise.

The data shown in Table 5.2 were plotted using Microsoft Excel v6.0. The program is also able to perform a least square fit of the data. Figure 5.2 shows the data fitted to a straight line using Ozawa and Kissinger methods for the high temperature peak. Figure 5.3 shows the data for the low temperature peak. The same Figures also include the fitting equation and the correlation coefficient. The points seem to fit well to straight line although it seems that the data would be fitted best by and arc between
Kinetic Analysis of Crystallisation and GPC

Fig. 5.1a: DSC scan at 1 K/min

Fig. 5.1b: DSC scan at 2 K/min
Fig. 5.1c: DSC scan at 5 K/min

Fig. 5.1d: DSC scan at 10 K/min
Fig. 5.1e: DSC scan at 20 K/min
TABLE 5.1 (from Brown (1988))

<table>
<thead>
<tr>
<th>Acceleratory $\alpha$-time curves</th>
<th>( f(\alpha) = k_t )</th>
<th>( g(\alpha) = \frac{1}{k} \frac{d\alpha}{dt} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1 power law</td>
<td>( \alpha^{1/n} )</td>
<td>( n(\alpha)^{(n-1)/n} )</td>
</tr>
<tr>
<td>E1 exponential law</td>
<td>( \ln \alpha )</td>
<td>( \alpha )</td>
</tr>
</tbody>
</table>

2. Sigmoid $\alpha$-time curves

| A2 Avrami-Erofe'ev                | \( [-\ln(1-\alpha)]^{1/2} \) | \( 2(1-\alpha)[-\ln(1-\alpha)]^{1/2} \) |
| A3 Avrami-Erofe'ev                | \( [-\ln(1-\alpha)]^{1/3} \) | \( 3(1-\alpha)[-\ln(1-\alpha)]^{2/3} \) |
| A4 Avrami-Erofe'ev                | \( [-\ln(1-\alpha)]^{1/4} \) | \( 4(1-\alpha)[-\ln(1-\alpha)]^{3/4} \) |
| B1 Prout-Tompkins                 | \( \ln[\alpha/(1-\alpha)] \) | \( \alpha(1-\alpha) \) |

3. Deceleratory $\alpha$-time curves

3.1 based on geometrical models

| R2 contracting area               | \( 1-(1-\alpha)^{1/2} \)   | \( 2(1-\alpha)^{1/2} \)   |
| R3 contracting volume             | \( 1-(1-\alpha)^{1/3} \)   | \( 2(1-\alpha)^{2/3} \)   |

3.2 based on diffusion mechanisms

| D1 one dimensional                | \( \alpha^2 \)            | \( 1/2 \alpha \)           |
| D2 two dimensional                | \( (1-\alpha)\ln(1-\alpha)+\alpha \) | \( [-\ln(1-\alpha)]^{-1} \) |
| D3 three dimensional              | \( [1-(1-\alpha)]^{1/3} \) | \( 3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1} \) |
| D4 Ginstling-Brounshtein          | \( (1-2\alpha/3)-(1-\alpha)^{2/3} \) | \( 3/2[(1-\alpha)^{1/3}-1]^{-1} \) |

3.3 based on order of reaction

| F1 first order                    | \( -\ln(1-\alpha) \)     | \( 1-\alpha \)             |
| F2 second order                   | \( 1/(1-\alpha) \)       | \( (1-\alpha)^2 \)         |
| F3 third order                    | \( [1/(1-\alpha)]^2 \)   | \( (1-\alpha)^3 \)         |

TABLE 5.2

<table>
<thead>
<tr>
<th>RATE (K/min)</th>
<th>FIRST PEAK (K)</th>
<th>SECOND PEAK (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>383.0</td>
<td>399.4</td>
</tr>
<tr>
<td>2</td>
<td>387.3</td>
<td>405.6</td>
</tr>
<tr>
<td>5</td>
<td>394.5</td>
<td>416.9</td>
</tr>
<tr>
<td>10</td>
<td>405.5</td>
<td>428.9</td>
</tr>
<tr>
<td>20</td>
<td>414.8</td>
<td>443.6</td>
</tr>
</tbody>
</table>
Kinetic Analysis of Crystallisation and GPC

\[ y = -11866x + 29.89 \quad R^2 = 0.9833 \]

\[ y = -11025x + 15.805 \quad R^2 = 0.9804 \]

Inverse Temperature (K\(^{-1}\))

Fig.5.2 High temperature peak. Top: linear fit by Ozawa's method. Bottom: linear fit by Kissinger's method.

\[ y = -14513x + 38.087 \quad R^2 = 0.9824 \]

\[ y = -13716x + 24.112 \quad R^2 = 0.9802 \]

Inverse Temperature (K\(^{-1}\))

Fig.5.3 Low temperature peak. Top: linear fit by Ozawa's method. Bottom: linear fit by Kissinger's method.
the two extremes. The cause may be attributed to experimental errors and/or failing to meet all the assumptions.

Figure 5.4 shows the data according to Borchardt and Daniels (1957) treatment. The authors pointed out that a straight line would be only obtained if the correct value of the reaction order was assumed. Figure 5.4 shows the data for a first order process. As the Arrhenius plot gave a good linear correlation this can lead to the conclusion that crystallisation is a first order process. In this case, the deviation from a straight line may be due to applying the theory developed for solutions to solids.

All the assumptions of any particular fitting method can seldom be met and the shape of the curves are strongly influenced by experimental conditions. Moreover, if a linear plot is obtained using a particular method this does not signify that the assumptions of the derivation are satisfied as many methods are insensitive to error. Accordingly, the data presented should be treated carefully but it is expected to be representative of the crystallisation rate process and was used for further analysis.

Table 5.3 illustrates the results. An activation energy for subsequent calculations was obtained as an average of the various methods. The activation energy for crystallisation is the minimum energy that one mole of amorphous segments must possess for crystallisation. Sun et al. (1984) reported activation energies of crystallisation of undrawn PET between 159 and 246 kJ/mole. The same authors quoted values of previous investigators between 155 and 264 kJ/mole. The values found in this work are smaller than reported values except in the case of Cobbs and Burton (1953) who found an energy of 84 kJ/mole. Table 5.4 shows the values of the frequency factor according to Roger and Smith (1967). The latter reported a decrease in the frequency factor with increase in the heating rate although the source of the unexpected effect was not identified. It can be seen in Table 5.4 that the frequency factor increases with heating rate and then decreases. The trend resembles that of Figures 5.2 and 5.3. This is in accordance with Roger and Smith's argument that the values of A appear to be quite sensitive to errors in E and T_{max}. Table 5.4 also shows an average frequency factor used for the remaining calculations.
Fig. 5.4 Linear fit according to Borchardt and Daniels method.

\[ y = 14362x - 29.693 \]
\[ R^2 = 0.9859 \]

Fig. 5.5 Voltage vs. Time
Kinetic Analysis of Crystallisation and GPC

TABLE 5.3

<table>
<thead>
<tr>
<th>Magnitude</th>
<th>LOW T PEAK</th>
<th></th>
<th>HIGH T PEAK</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ozawa</td>
<td>Kissinger</td>
<td>Ozawa</td>
<td>Kissinger</td>
</tr>
<tr>
<td>Gradient E/R</td>
<td>14513</td>
<td>13716</td>
<td>11866</td>
<td>11025</td>
</tr>
<tr>
<td>Activation Energy</td>
<td>120603</td>
<td>113980</td>
<td>98606</td>
<td>91618</td>
</tr>
<tr>
<td>(J/mole)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Averaged Energy</td>
<td>117±3</td>
<td></td>
<td>103±7</td>
<td></td>
</tr>
<tr>
<td>(kJ/mole)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE 5.4

<table>
<thead>
<tr>
<th>HEATING RATE</th>
<th>$A_{LOW}$ (min$^{-1}$)</th>
<th>$A_{HIGH}$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$9.7 \times 10^{14}$</td>
<td>$2.5 \times 10^{12}$</td>
</tr>
<tr>
<td>2</td>
<td>$1.3 \times 10^{15}$</td>
<td>$3.0 \times 10^{12}$</td>
</tr>
<tr>
<td>5</td>
<td>$1.4 \times 10^{15}$</td>
<td>$3.1 \times 10^{12}$</td>
</tr>
<tr>
<td>10</td>
<td>$1.1 \times 10^{15}$</td>
<td>$2.5 \times 10^{12}$</td>
</tr>
<tr>
<td>20</td>
<td>$9.8 \times 10^{14}$</td>
<td>$1.8 \times 10^{12}$</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>$1.2 \times 10^{15}$</td>
<td>$2.6 \times 10^{12}$</td>
</tr>
</tbody>
</table>
Ideally $E$, $A$ and $g(\alpha)$ should be calculated. We have seen how the different authors dealt with $g(\alpha)$ either by assuming a form proposed in the literature or eliminating it. If $g(\alpha)$ were known the evolution of crystallisation at any time and heating rate could be calculated, and this was the objective of the work carried out. According to the theory

$$g(\alpha) = \frac{d\alpha}{dT} \phi$$

The right side of the equation was plotted versus $\alpha$ and fitted using MathSoft Mathcad v5.0 to a general form of $g(\alpha)$ suggested by Brown (1988)

$$g(\alpha) = \alpha^{w}(1-\alpha)^{y}(-\ln(1-\alpha))^{w} \quad (5.17)$$

It was found that the whole function could not be fitted to a single curve of this form. Once again the shapes of the curves seen in Figure 5.1 gave rise to problems. Hence, the early stages of the process were neglected and data above $\alpha=20\%$ was fitted. The results obtained for $u$, $v$ and $w$ were too large compared with the values proposed in the literature for such parameters and the method was abandoned.

Therefore, a different approach was pursued. During a compression test the temperature on the sample rises by 100 K in approximately 1.3 ms. It is estimated that the sample reaches the temperature for onset of crystallisation approximately 1 ms after the compression begins, that is to say when the increase in temperature is about 80 K; see Chapter 2. Thus, cold crystallisation may happen during the last 0.3 ms of a test. Assuming that the temperature is 373 K and $\alpha$ is equal 0 at the temperature at which cold crystallisation commences, an increase in $\alpha$ over a period of 0.3 ms was calculated using equation 5.4 rearranged:

$$d\alpha = A e^{rac{-E}{RT}} g(\alpha) dt \quad (5.18)$$

The calculation could only be done under the assumption that the temperature was constant since the rate constant $k$, is used. The value calculated can be interpreted as the isothermal increase in $\alpha$ in 0.3 ms. It reasonable to conclude that the values
obtained were an underestimation for at higher temperatures $\alpha$ can only increase. Table 5.5 summarises the results for the different activation energies, frequency factors and several forms of $g(\alpha)$. Among the different forms proposed for $g(\alpha)$, only those different from zero for $\alpha$ equal zero were suitable, the reason being that if $g(\alpha)$ was equal to zero then no change in $\alpha$ would ever occur. The results show that no significant amount of crystallisation occurred during a compression test due to heating of the sample. However, since the temperature of the sample is increasing during that 0.3 ms and the increase in $\alpha$ would be expected to be larger although it would still be very small. The conclusions that can be drawn is that no significant crystallisation can occur due to cold crystallisation during the deformation process.

When the end of a typical compression test was reached the sample temperature was at least 405 K. Then the sample cooled down much more slowly than it was heated. It is obvious that the sample temperature remained above the onset of cold crystallisation for a period of time. Therefore an increase in the degree of crystallinity might occur and it would be possible to estimate if the cooling rate was known. The best procedure would be to record the temperature history of the sample on site after a test. However, previous attempts by Dawson (1993) were unsuccessful because of damage of the thermocouple during impact. The procedure followed here tried to resemble the conditions after a compression test finished as faithfully as possible. A bore of approximately 0.5 mm was made in a sample and a Aluminium-Chromel thermocouple placed inside. The sample was heated up to 403 K in a hot plate with the thermocouple inserted to record the temperature. After 30 minutes at the desired temperature thermal equilibrium in the sample was reached. Then, the sample was taken off the heater and placed between two metal plates. Although two small plates are used instead of rollers the conduction effect should be similar. It is intended to avoid cooling in air because the rate would be slower than between metal anvils. The thermocouple output was recorded using a Tektronix TDS 360 oscilloscope; see Chapter 2. The thermocouple signal can be seen in Figure 5.5.

Figure 5.5 shows that the time taken by the sample to cool down from 405 K to 373 K is approximately 4 s. Using equation 5.18 similar calculations were carried out with
TABLE 5.5

Middle column, $E=117 \text{ kJ/mol}$, $A=1.2 \times 10^{15} \text{ min}^{-1}$. Right column, $E=103$, $A=2.6 \times 10^{12}$

<table>
<thead>
<tr>
<th>$g(\alpha)$</th>
<th>$d\alpha_1$</th>
<th>$d\alpha_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1-\alpha$</td>
<td>$2.2 \times 10^{-7}$</td>
<td>$4.5 \times 10^{-8}$</td>
</tr>
<tr>
<td>$2(1-\alpha)^{1/2}$</td>
<td>$4.4 \times 10^{-7}$</td>
<td>$9.0 \times 10^{-8}$</td>
</tr>
<tr>
<td>$3(1-\alpha)^{2/3}$</td>
<td>$6.6 \times 10^{-7}$</td>
<td>$1.4 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

TABLE 5.6

<table>
<thead>
<tr>
<th>$g(\alpha)$</th>
<th>$d\alpha_1$</th>
<th>$d\alpha_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1-\alpha$</td>
<td>$0.05$</td>
<td>$1.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>$2(1-\alpha)^{1/2}$</td>
<td>$0.10$</td>
<td>$0.02$</td>
</tr>
<tr>
<td>$3(1-\alpha)^{2/3}$</td>
<td>$0.15$</td>
<td>$0.03$</td>
</tr>
</tbody>
</table>

TABLE 5.7

<table>
<thead>
<tr>
<th>RATE</th>
<th>$M_w$</th>
<th>$M_n$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20900</td>
<td>8815</td>
<td>2.35</td>
</tr>
<tr>
<td>0.001</td>
<td>22450</td>
<td>9330</td>
<td>2.4</td>
</tr>
<tr>
<td>1230</td>
<td>21200</td>
<td>9005</td>
<td>2.4</td>
</tr>
</tbody>
</table>
the difference that the time is taken as 4 s. In this case the isothermal temperature is taken as 405 K so the calculated values indicate the amount of material converted in 4 s if the temperature were held at 403 K. Table 5.6 summarises the results. It can be seen that the degree of conversion ranges from 1 to 15 %. A close look at the thermograms in Figure 5.1 shows that at a temperature of 403 K the reaction is still at an early stage. The partial area under the curve to the total area is small, the degree of crystallinity or reaction conversion is low. The latter is in accordance with Table 5.6.

5.1.4. DISCUSSION

Kinetic parameters were calculated according to different methods, namely Ozawa, Kissinger and Borchardt and Daniels. They developed their theories for different analysis systems but all are valid for DSC. The results show that no significant crystallisation takes places during the duration of a high rate test. When cooling after a test it was shown that the crystallinity level could increase significantly when the temperature of the sample is raised to or above that of the onset of crystallisation.

However, the predicted crystallinity increase was not as large as the actual measurements on tested samples; see Chapter 4. The DSC measurements on tested samples showed that after a high strain rate test nearly all the cold crystallisation possible had occurred. There is one main factor which may account for a larger value of $\alpha$: the temperature attained during a compression test may be larger than 405 K. The maximum temperature used in the calculations was reached at 185% strain but the samples probably attained larger strains; see Chapter 2. Thus, if a higher temperature was reached it would lead to more crystallisation as can be seen from Figure 5.1. This would be reflected in the calculation and therefore the values of the degree of conversion would be larger.

In conclusion, the kinetic analysis of PET seems to suggest that some of the crystallinity observed by DSC occurs due to heating of the sample but after the high strain rate test comes to an end. The results obtained shed light on the crystallisation process and its dependence on time during a high strain rate test.
5.2. GEL PERMEATION CHROMATOGRAPHY

5.2.1 INTRODUCTION

Intuitively, smaller chains can crystallise easily than longer chains. Thus, if chains were broken during the impact process, this could ease the process of crystallisation. Any breakage of a significant amount of chains should be reflected on the average molecular weight. So, the molecular weights of samples of as-received PET, tested at $10^{-3}$ and $1230$ s$^{-1}$ were estimated by chromatography. Gel Permeation Chromatography (GPC) is one of the most widely used methods for the routine determination of molecular weight distribution and is based on the principle of size exclusion, i.e., the different permeability of gels to molecules of different sizes.

Each sample of a polymer contains molecular chains of varying length with a distribution which is seldom symmetric. For a discrete distribution of molecular weights, an average molecular weight is defined as:

$$
\bar{M} = \frac{\sum N_i M_i^\alpha}{\sum N_i M_i^{\alpha-1}} \quad \quad (5.19)
$$

where $N_i$ indicates the number of moles of molecules with a molecular weight of $M_i$. The molecular weight averages that are important in determining polymer properties are the number average, $\bar{M}_n (\alpha = 1)$, and the weight average, $\bar{M}_w (\alpha = 2)$. The ratio $\bar{M}_w / \bar{M}_n$ is called the polydispersity index (PDI).

5.2.2 EXPERIMENTAL

A typical chromatographer consists of injection pumps, a glass column filled with gel and a detector. During GPC operation, pure prefiltered solvent is continuously
pumped through the column at a constant flow rate. Then, a small amount of dilute polymer solution is injected by syringe into the solvent stream and carried through the column. Polymer molecules can then diffuse from this mobile phase into the stationary phase composed of solvent molecules occupying the pore volumes. The smallest polymer molecules are able to penetrate deeply into the interior of the pores, but the largest molecules may be completely excluded from the smaller pores or only partially penetrate the larger ones. As pure solvent elutes the columns after injection, the largest polymer molecules pass through and finally out of the packed columns. These are followed by the next largest molecules and so on, until all the polymer molecules have been eluted out of the column in increasing order of molecular weight.

The concentration of polymer molecules in each eluting fraction can be monitored usually by means of a differential refractometer, which can detect small differences in refractive index between pure solvent and polymer solution. A signal from the detector is recorded as a function of time, which for a fixed flow rate is directly proportional to the elution volume, \( V_e \). The elution volume is the quantity of solvent passing through the gel bead up to the appearance of a separate fraction. For substances polymerised from the same monomer, the logarithm of their elution volume and either the molecular weight or the number of units will yield a linear relationship in the range of applicability of the gel. With standard substances of known molecular weight a calibration curve can be plotted in the linear part of which, knowing the elution volume of a sample of unknown molecular weight, the unit number or the molecular weight can be established. In addition, the value read on the calibration curve must be multiplied by a factor which depends on the polymer used for calibration and the material of the sample. The use of the calibration curve and the concentration, which is proportional to \( N_\text{av} M_w \), allows a computation (by commercially available software) of the molecular weight distribution and illustrates the number of molecules in each molecular weight component; from Determann (1969) and Kremmer and Boros (1979).

The experiments were carried out at RAPRA Technology Ltd. The chromatographer was a Polymer Laboratories GPC-210. The column contained PL gel 2 x mixed bed-
B, solvent was flushed at 1 ml/min at 120°C. The detection was by refractive index. The solution was prepared by adding 8 ml of solvent (1,3-cresol with antioxidant) to 14 mg of sample. The solutions were warmed for thirty minutes at 303 K to aid polymer dissolution. Prior to the chromatography, the solutions were filtered through a 0.2 micron PTFE membrane. All the samples appeared to be fully soluble. The GPC system was calibrated with polystyrene and a mathematical procedure involving the use of literature viscosity constants was applied to the calibration to allow for the difference in chemical type between the sample and the calibrants. The data were analysed using Polymer Laboratories ‘Caliber’ software.

5.2.3 RESULTS

The weight average, weight number and polydispersity index are given in Table 5.7. The data are an average of two runs. Figure 5.6 shows the calculated molecular weight distribution for duplicate runs of each sample. The plot was normalised with respect to area, the y axis being a function of weight fraction.

The long term reproducibility of a particular GPC system may not be good so the technique is best regarded in a comparative manner, with the emphasis being placed on any observed differences between samples and not simply on the numerical values of the results themselves. The results suggest that there are no significant molecular weight differences between the samples.

Thus, it can be concluded that plastic deformation or crazing will account for the bulk of energy dissipated during tests of PET, as opposed to the breakage of chains.
Fig. 5.6 Weight fraction vs. Molecular weight
CHAPTER 6

ANALYSIS AND DISCUSSION
6.1. INTRODUCTION

It is intended in this chapter to discuss the results of mechanical tests, X-ray diffraction and DSC and relate them to each other since this may reveal some features not obvious in the individual discussions. Any changes in morphology will aid in the understanding and interpretation of the mechanical response of the materials and vice versa.

Yield stress, strain softening and strain hardening will be compared against atomic planes separation, crystal size, strain induced crystallisation and thermodynamic transitions in a search for any correlation. However, it must be emphasised that the information extracted from XRD and DSC gave an insight into the microstructure of the material after the deformation ended at large values of strain. Only the strain limited tests gave information at several intermediate microstructural states and all were at or above 30% strain. Thus, all the information was obtained beyond the yield point and consequently, molecular mechanisms associated with yielding can only be conjectured with no solid basis.

Extreme care was taken in the experimental part to allow for reproducibility. Thus, specimens were lubricated in both ends prior to tests. The photodiode and strain gauges were calibrated consistently throughout the work by straightforward but accurate means whereas the X-ray diffractometer and calorimeter were calibrated with standard materials.

This chapter first presents the evidences found in this study and likely explanations for the phenomena encountered such as absence of yielding or yield stress enhancement, possible explanations of the deformation mechanisms are discussed next and finally two mathematical models of polymer behaviour are reviewed.
6.2. DISCUSSION

6.2.1 YIELD DROP

G'sell and Jonas (1981) explained deformation as a thermally activated nucleation and propagation of waves. They carried out experiments in which the strain rate was changed during the deformation. Two sorts of behaviour were found: i) the stress changed gradually, normal transients; ii) the stress increase (peak) and decreased, inverse transients. Owing to the similarity between the shape of the yield drop and the inverse transients, they concluded that there was some evidence that the initial stress drop in PVC was associated with inverse stress transients when rapid strain rate changes were performed. The abrupt true peak of inverse transients could be attributed to the supplement of stress necessary to overactivate the existing plastic waves while a sufficient number of new ones could be nucleated; this was modelled by elastic and plastic contributions only. By contrast, the absence of a yield drop in HDPE is linked with the presence of normal stress transients. The yield response was rounded off due to their smaller elastic moduli and their large viscoelastic compliances. The contribution of the viscoelastic strain rate becomes very important when the test temperature is above the glass transition temperature. Thus, the viscoelastic strain rate could accommodate part of the total strain rate at the critical moment when the density of the plastic waves had to increase. Thereby, polymers with subambient glass transition should not show a drop in stress whereas glassy polymers should. Nylons are an exception because of the absorption of water which acts as a plasticiser. Thus, plasticisers make possible the movement of viscoelastic chains in this otherwise glassy polymers. Therefore, their findings agree with the idea that a yield drop is intrinsic to the material.

A requirement to observed a true yield drop is homogenous deformation. Thus, compression tests, in which necking does not occur, are thought to produce homogeneous deformation across the cross section of the specimens. The results of PET found in this work completely agree with G'Sell and Jonas' conclusions. Thus,
PET which is a glassy polymer experienced a yield drop when tested at temperatures below the glass transition. The Nylon results agree with the observations of G'Sell and Jonas in that they show no yield drop. G'Sell and Jonas explained this observation in terms of the plasticising effect of water in Nylon. However it is doubtful if the approximately 0.5% water content in the samples used could be sufficient to avoid a yield drop and another factor may be involved. The interpretation of the yield drop in terms of waves is in agreement with the earlier suggestion that the yield drop could be due to the difference in conditions for the initiation of yielding and the propagation of flow; see Chapter 2.

6.2.2 HIGH TEMPERATURE TESTS

Low strain rate: the stress vs. strain curves above the glass transition temperature, see Figure 2.27 of Chapter 2, revealed that PET did not show a yield point but the stress increased monotonically up to large values of strain. It has been reported that yielding involves similar molecular motions to those that produce the $\alpha$ relaxation. This relaxation occurs for PET at approximately 353 K. So, samples tested above the glass transition underwent such a transition before the deformation commenced. Above the glass transition temperature the molecules have more mobility, thus at low rates, the molecules relaxed as fast as they were extended resulting in little internal stress. Therefore, it could be argued that when the tests began the $\alpha$ relaxation involving cooperative molecular motions had taken place and deformation happened by short, slow and independent movement of chains. This could be a consequence of only elastic and viscoelastic strains being involved in the deformation which are completely and partially recoverable respectively. This could described what has been called the flow deformation regime. This regime was accompanied by the development of some structure before and during deformation, in the case of the highest temperature the structure was fairly perfect, with a high final degree of crystallinity content. Thus, at low strain rates the deformation proceeded without major movements of chains and crystallites induced by the deformation (in the case of 453 K almost all the crystallisation is formed before the test) developed by short rearrangements of chains. This rubber like deformation seems to be associated only with
changes in the molecular conformations.

Medium and medium-high strain rates: however, the same argument cannot be used at higher strain rates because the material showed a very clear yield point. Above the glass transition, the degree of orientation achieved is markedly dependent on strain rate. It is thought that at these strain rates molecular movements occurred because the strain rate surpassed the thermal relaxation rate. Thus, the stress may have induced a further co-operative movement of chains which led to yielding. Perhaps, plastic strain was also involved in the deformation and the molecules slipped under the action of stress in the plastically deformed regions. In this range of strain rates and at 363 K the material showed an increase in yield stress, 78 MPa compared to 65 MPa which induced an increase in crystal size from 6 to 8 nm and crystallinity content, 42% compared to 48% at the higher rate. At 453 K, the yield stress and degree of crystallinity were very similar at both strain rates, 41 MPa for 50% and 42 MPa for 50%, both showing a second small melting peak. However, the crystal sizes were different, 6 and 8 nm. This disparity was not expected. The combination of high stresses and temperature may have led to the formation of a kind of very highly perfect crystals which melted at a higher temperature. Figure 6.1 shows the crystal size versus yield stress at 298 K at 1230 and 1940 s⁻¹.

Thus, whether at low or high strain rates, above the glass transition temperature structure was developed and the crystallinity content was high. Therefore, the increase in configurational entropy at the glass transition had to be decreased afterwards by means of strain and/or stress and/or thermal movement to account for crystallisation. When the test temperature was below the cold crystallisation temperature the strain and/or stress induced further crystallisation whereas on tests carried out at 453 K only thermal energy was needed to overcome the crystallisation barrier.

6.2.3 LOW TEMPERATURE TESTS

Up to the glass transition temperature two types of behaviour can be distinguished. At low strain rates the yield stress steadily decreased with temperature, in agreement with
many authors. These experiments led to some orientation of the chains and a very small increase in the crystallinity content. A large cold crystallisation peak and glass transition were observed. However, the yield stress is almost constant at strain rates in the $10^3$ s$^{-1}$ range. The final structure contained a high degree of crystallinity (nearly complete absence of cold crystallisation), absence of glass transition and fairly well developed structure.

Intuitively, the yield stress enhancement around the glass transition temperature should be related to the nature of this transition, the viscoelastic behaviour of polymers and the entropy (mobility) increase happening around the transition. Again, at low rates it can be said that the rate of thermal relaxation acting against the applied stress exceeded the rate of strain, so the yield stress decreased compared to the room temperature value, although some degree of orientation was attained. However, at higher strain rates thermal relaxation was avoided.

Bearing in mind that PET was almost amorphous, yield stress was governed by the molecular mobility of the amorphous phase. On increasing the tests temperature close to the glass transition temperature it is expected that chains oriented more easily, so small strains at high rates may have led to a very high degree of orientation. Thus, a high degree of orientation counterbalanced the temperature effect and can account for the high values of yield stress just below the glass transition. Beyond the glass transition temperature, owing to the increase in the polymer chain mobility, orientation was probably lost which together with the rubber-like character yielded a decrease in yield stress.

The comparison of tests carried out at different temperatures with Nylon 11 is difficult. While the yield stress values are higher at room temperature, the structure developed is less clear at 263 K and the crystallinity content is higher for the low temperature tests. The moisture absorption which forms hydrogen bonds with the amide linkage can account for this. While the absorption of moisture, which can be higher at lower temperatures, led to softening the material and a smaller yield stress, it can obscure the DSC measurements leading to erroneous values of the crystallinity
content. In any case the changes are only about 2%.

6.2.4 STRAIN LIMITED TESTS, KINETICS AND GEL PERMEATION

The strain limited tests provided very useful information. Low strain rate tests showed that samples were oriented up to 185% strain with an increase in crystallinity of about 6% for a temperature rise of approximately 63 K. At higher strain rates, $10^3$ s$^{-1}$, structure was developed in samples tested above 140% strain, with crystallinity increases of 20-30% for the highest strains with temperature rises above 100 K. The comparison of tests limited at 185% strain and free tests showed that free tested samples gave rise to a more defined X-ray scan, although the degree of crystallinity of both tests was almost the same. This indicates that the strain attained by free tested samples was slightly above 185%. The conditions for the onset of crystallisation can be obtained from these experiments. At 1230 s$^{-1}$ the structure was seen to developed at strains of 140% with crystallinity increase of 7% for a temperature increase of about 70 K. Therefore, it is clear that the structure developed and the crystallinity experienced a significant increase above 5% when the temperature rise was about 65-70 K, i.e. the temperature on the sample was approximately 363 K. However, the initial increase between the untested value and the 5% increase occurred a few degrees below this, and so it seems that under stress, crystallisation begins to take place just above the glass transition temperature but at a very small rate.

The cold crystallisation peak temperature decreased with strain at any strain rate. Thus, in accordance with the argument of Chapters 3 and 4, it is thought that large strains at any strain rate induced orientation of the chains along the z axis. However, the degree of orientation is expected to be rate dependent, i.e., the degree of orientation should be higher at higher strain rates. Crystallisation is usually described in terms of a nucleation and growth model. The growth of the new partly crystalline structure in an initially amorphous polymer is expected to be a nucleated process. Smith and Steward (1974) assumed that nuclei of ordered material are formed as a result of thermal fluctuations, and that some of these nuclei grow by the addition of more material to form crystallites. The main effect of orientation was to reduce the
induction or nucleation time. Mechanical orientation of the molecules assisted the production of nuclei by bringing molecular segments into favourable juxtaposition, leading to a reduction in the configurational arrangements of chains with respect to each other, entropy change needed for nucleus formation. This led in turn to lower the temperature of onset of crystallisation. A decrease in conformational, arrangement of molecules with respect to each other, entropy could also lead to lower the onset temperature. Thus, the more extended amorphous chains may contain more trans conformational isomer which could be packed into the crystal lattice much more easily than an undrawn sample containing more of the gauche isomer.

The structure growth and crystallinity increase were dependent on the deformation conditions, strain, stress and strain rate but the kinetic study indicated that the morphological changes occurred after the experiment was finished. Moreover, GPC showed that whatever the conditions for crystallisation are, it was not induced by the breakage of chains.

Unlike crystallisation under quiescent conditions, crystallisation under the application of forces has not been comprehensively studied. It is expected that the application of forces affected the crystallisation kinetics to a certain extent as already mentioned. It is clear that crystallisation only occurred, except in high temperature tests, when a high strain and strain rate was applied. Nevertheless, it is reasonable to be cautious about the onset of crystallisation with time. It must be borne in mind that the kinetics study was carried out on untested samples whereas when samples which have undergone 140% strain are likely to be oriented. Molecular alignment can increase the nucleation rate of crystallites in agreement with the previous argument, so, the crystallisation in oriented samples may happen in a much shorter time than in unoriented specimens of the order of milliseconds compared to seconds according to Smith and Steward (1974). Nonetheless, crystallisation would only take place at a very late stage in the deformation process towards the end of the experiment, when temperatures above the glass transition are reached, and it will not affect the following discussion of the deformation mechanisms.
Figure 6.2 shows the crystallinity content versus temperature rise at different strain rates and Figure 6.3 shows the same at different strains. It is clear that the higher the temperature rise the higher the final crystallinity content was. It can be seen that the crystallinity content is almost linear with the temperature rise at low rates and departs at higher rates. Figure 6.3 shows that the crystallinity basically increased at high temperature rises.

The fact that d spacing was almost independent of strain rate also supports the postulate that the structure was developed after the tests. Thus, when structure was formed it did not depend on the conditions and the cells were always equal, higher strain rates or stresses did not induced smaller cells or interatomic distances.

6.2.5 UNTESTED STRUCTURE

The discussion of the deformation mechanisms, see below, requires a little description of the morphology of the material tested. XRD and DSC revealed that the structure of as-received PET was almost amorphous. It is likely that the material was nearly isotropic, see Figure 3.3b of Chapter 3, i.e., it was not oriented. The supermolecular organisation could be regarded as a composite like material built up of two phases - a small crystalline phase, about 10% in accordance with DSC, randomly dispersed in the prevailing amorphous matrix. A two phase model would be adequate to describe it. The amorphous phase is not likely to be highly crosslinked by the small crystalline regions but as any other polymer was possibly highly entangled. The chains probably were on a more or less extended configuration because of the difficulty that PET has in forming folded structures compared to other polymers with a much more flexible chain. The average molecular weight was about 20,000. Thus, the deformation of PET possible involved movements such as slippage, rotation and straightening of chains.

As received Nylon 11 showed structure which corresponded with an approximately fifty-fifty mix of triclinic and pseudo-hexagonal systems. The percentage of crystalline phase was about 28%. Generally in semi-crystalline polymers when referring to molecular bridges between crystalline regions one uses the term "tie molecules".
Fig. 6.1 PET Crystal Size vs. Yield Stress

Fig. 6.2 PET Crystallinity Content vs. Temperature Rise
Fig. 6.3 PET Crystallinity Content vs. Temperature Rise

Fig. 6.4 PET isomers; (a) trans; (b) gauche (after Brown (1993))
Chains are usually not regularly folded, the beginning and end of the chains belong to different crystallites and the larger molecules bind the structure together by forming interlamellar ties between crystallites. Thus, the structure of Nylon 11 is supposed to be formed of crystalline regions (lamellae), the isotropic conformationally disordered, liquid like amorphous regions and the interfacial regions that connect the two consisting of tie molecules. The interfacial regions can be regarded as a rigid amorphous phase between the crystals. The trajectory of many of the chains probably passed through all three regions. The three phases are of the same chemical composition but differed in morphology, thus contributing differently to the properties; the amorphous phase has a smaller modulus than the crystalline phase. The morphology may fit a parallel-series model consisting of crystalline and amorphous regions in series connected in parallel with the rigid amorphous phase. Therefore, deformation of semi-crystalline Nylon 11 also involved the deformation and consequently the disruption of chain folded lamellae (crystallites).

The deformation of PET tested at 453 K should also be explained in terms of the semi-crystalline nature as for Nylon. The crystallinity before the test was as high as 47%. However, the XRD revealed that the structure was very imperfect, so it is thought that the crystalline phase consisted of highly defectuous lamellae. The latter together with the temperature involved in the test, which is close to the onset of melting, made the deformation similar to a purely viscous material. Thus, the deformation mechanisms explained above, section 6.2.2, are likely to be more accurate than the pattern which will be followed for Nylon.

6.2.6 DEFORMATION AT LOW STRAIN RATE

Beyond the yield stress and the stress drop, PET flowed at an almost constant stress with a slight upswing at large strains. This material showed some degree of orientation in the amorphous phase, a very small, but real, increase in crystallinity and a temperature rise (although the test notionally proceeded isothermally) of about 65 K. At test temperatures up to the glass transition, the glass transitions are clearly seen on the subsequent DSC trace, so neither glass transition nor cold crystallisation
Analysis and Discussion

occurred before or during testing. Thus, the temperature rise did not affect the level of stress and the deformation proceeded as to move the chains which led to orientation with the hardening occurring when further movements were hindered by inter- and intra-molecular forces. It seems that molecular segments were nucleated but low strain rates, which allow relaxation of the chains, and the isothermal conditions were not enough to induce further growth of crystallites by bringing chains into adequate positions, or more importantly, nucleate a high number of chains which could have led to a large increase in crystallinity when tested below the glass transition temperature.

However, above the glass transition temperature, the material crystallised before the test, and deformation increased the degree of crystallinity. At the highest test temperature almost all the crystallinity was induced thermally but at 363 K a high number of chains seemed to be nucleated prior to deformation which acted as nuclei for further growth of crystals bringing about an increase in crystallinity of approximately 19%.

Thus, up to the yield point only elastic strain acted which is associated with the deformation of intra-molecular bonds and is completely recoverable. Beyond the yield point and below the glass transition temperature the strain is mainly plastic causing permanent deformation. The propagation of the deformation between the yield drop and the onset of strain hardening occurred at almost constant stress. No increase in stress was required to produce the molecular movements. Strain hardening was due to a resistance to further deformation of the polymer network. On the other hand, near the glass transition, the viscoelastic component of strain, which is associated with the limited retarded movement of amorphous chains and is partially recoverable, played an important role and can explain the almost absence of strain hardening. Above the glass transition temperature, viscoelastic deformation was probably more important than plastic.

Chain movements induced by stress, as opposed to temperature, below the glass transition temperature are expected to be more important than above. Chain slippage is expected to occur which involves two phases: the short term wriggling motions that
correspond to the migration of a molecular kink along the chain and a second movement with a much longer time associated to the movement of the chain as a whole through the polymer. This may lead to reduce the entanglement degree of the network. Slipping can account for high deformations of the sample. Chain scission is not likely to occur. C-H wagging vibration and aromatic C-H bending mode contributed to the overall orientation in accordance with Dulmage and Geddes (1958).

Above the glass transition, the crystals formed prior to deformation may retard or inhibit some of the movements. However, at 453K it is clear that on applying stress the structure was perfected as indicated by the better definition of the X-ray peaks. The process of crystal perfection possibly occurred through the pulling of defects from the crystallites into the amorphous phase. Thus, knots, loops and entanglements were relegated to interlamellar regions increasing the density of the crystalline phase.

Nylon 11 yielded gradually without any sharp transition between the elastic and plastic regions. Strain hardening started just after yielding, the stress increased steadily and tended to flatten at about 100% strain. This was followed by an increase in the (010) peak intensity, compared to the untested material, until the two peaks nearly merged. This is a consequence of loss of preferential orientation in the (100) direction, so movements within the lamellae were likely to occur. The final structure was made up of approximately 30% crystals of triclinic nature but only one class of crystals which gave rise to solely one melting peak. Thus, slow deformation could perfect the low melting species. When tested at 263 K a shoulder could be seen on the DSC trace indicative of the two phases present. This may indicate that low temperatures prevented the transition of low temperature melting crystals to the high temperature class. The crystallinity content increased by an small percentage, about 3% compared to untested samples. It is thought that the increase is real, at least for samples tested at room temperature.

As already mentioned the deformation mechanisms are expected to be different for semi-crystalline polymers. According to Lee et al. (1988), plastic deformation of structures generally involves rotation and sliding of stacked lamellae and chain tilt and
slip inside each lamellae. Therefore, it is possible that in Nylon the mechanism of plastic deformation involved both, those for a combination of glassy amorphous and crystalline phases. Uncoiling and translational motion of molecular chain segments in the amorphous component may have coupled with the spherulite deformation in the crystalline state. The presence of tie molecules must also be taken into account. Assuming that Nylon is a composite consisting of an amorphous phase reinforced with a crystalline phase and all assembled by tie molecules, then on compression, whatever the strain rate, the amorphous phase first deformed under the applied stress owing to its more disordered and softer character. Then, the amorphous phase imparted stress to the crystalline entities whose plastic deformation was governed by the defect concentration.

The continuous strain hardening could be associated with the orientation of crystallites, which are much harder to orient than the amorphous phase. Thus, up to the yield point only the amorphous and interfacial regions were involved in the deformation but the stress was applied to crystals just beyond the yield stress. The mass fraction of interfibrillar tie molecules may have increased with drawing and hence the resistance to further deformation increased which also contributed to strain harden the material.

The main morphological changes at high strains could be the tilt and slip of segments within the lamellae which led to a simple change in the orientation of the structural units giving rise to a more intense (010) peak. The overall deformation was largely governed by the plastic deformation of the crystalline phase which was greater than the effect of moisture causing plasticisation of the polymer.

The increase in crystallinity detected by DSC can be due to an increase of the lamellae structure. Thus, large deformation also oriented the amorphous phases which may have induced a slow accretion of molecular segments, perhaps tie molecules (which increased in length with strain) to the crystallites, yielding an enlarged lamellae size, longitudinally and laterally.
Nevertheless, it must be noticed that the melting-re-crystallisation process may have also occurred in Nylon. The process would have evolved so as to melt a molecular segment and re-crystallise it in a direction perpendicular to the applied stress. It was pointed out by Kennedy et al. (1994) that there was no need for a temperature rise for a partial or complete melting process to occur in order to account for the melting re-crystallisation phenomenon.

6.2.7 DEFORMATION AT MEDIUM AND MEDIUM-HIGH STRAIN RATES

At higher strain rates, in the $10^3$ s$^{-1}$ range, PET samples showed strain softening, development of structure, an increase in crystallinity of almost 40% and absence of glass transitions when the test temperature was 298 K or above. Strain softening began at small temperature rises at approximately 10 K (estimation of maximum temperature rise at the yield point). It was as large as 50-75 MPa for test temperatures up to the glass transition and it decreased in magnitude with increasing test temperature.

It seems that even a small amount of heat, which due to the adiabatic condition could not be dissipated, decreased the stress required to produce the deformation. However, the level of stress was enough to orient the chains and induce the formation of structure afterwards. The question arising is why low strain rates oriented the chains which did not crystallise, while higher strain rates induced crystallisation which mainly occurred during the cooling stage. The tests carried out at 263 K in the $10^3$ s$^{-1}$ range may provide information in this area. These tests showed that the crystallinity content was smaller than tests conducted at higher temperature, cold crystallisation was present and the structure formed was not very perfect. Strain softening is significant but the temperature attained in the sample during the test was some 30 K below that attained in the room temperature tests. Thus, at the maximum strain the temperature rise may have increased the temperature of the sample to a value below 373 K, so crystallisation occurred, in accordance with the previous argument that crystallisation begins when the temperature of the sample exceeded the glass transition temperature, but the increase was much smaller due to a lower final
temperature. Therefore, it seems that temperatures in the sample approaching the cold crystallisation temperature are needed for a large increase in the crystallinity content.

It has been discussed that at these strains the deformation proceeded with rotation, slippage and orientation of the chains, in a similar way to low strain rate tests. Slippage was likely to occur along the z axis, perpendicular to the applied stress. It is also expected that below the glass transition the deformation consisted of elastic deformation up to the yield point changing to plastic at larger deformation. Near and above the glass transition, a large component of viscoelastic deformation is expected to occur, which together with the temperature, may account for the strain softening and temperature rises. However, even at temperatures below the glass transition, the conditions for crystallisation were favourable, orientation, slippage and rotation lowered the energy barrier. Thus, a higher degree of orientation due to higher yield stresses, no relaxation of chains before neighbouring chains were aligned due to the high rate and the temperatures attained in the sample led to a lowering of the configurational entropy change needed to surpass the barrier for crystallisation and heavy nucleation occurred. Therefore, high strain rate conditions induced nuclei which later served as sites for further crystallisation.

It seems to be compulsory that a gauche-trans transition occurs in order to account for large crystallisation. According to Pereira and Porter (1983), the gauche conformation is found only in the amorphous regions as it cannot occupy normal lattice positions, and is isomerised under certain conditions to the trans form, which in turn can exist in both amorphous and crystalline regions. Gauche-trans isomerism occurs in the ethylene glycol units. But, to pass from one rotational isomeric form to another required an energy barrier to be surmounted, so that the possibility of the chain molecules changing their conformations depended on the relative magnitude of the energy barrier compared with thermal energies and the perturbing effect of applied stress. Therefore, conditions under low rates probably did not induce trans isomer and the crystalline structure could not be developed very much whereas high rates isomerised a large number of gauche segments which in turn led to a large extent of crystallisation. Figure 6.4 shows the trans and gauche conformations.
At a strain rate of 1230 s\(^{-1}\), Nylon 11 yielded and showed slight strain softening which was smaller when tested below room temperature. The strain softening was much less steep in the case of Nylon 11 compared to PET, about 20 MPa for strains of about 100% and almost zero for tests carried out below room temperature. However, the material crystallised into the pseudohexagonal form and showed only one peak in the DSC scan. The crystallinity content of samples tested at medium rates was higher than specimens tested at low strain rates.

The events followed the natural course and higher rates induced a transition from triclinic to pseudohexagonal characterised by the merging of the (100) and (010) peaks. The (100) d spacing seemed to be more sensitive to strain rate, i.e., this plane spacing underwent a greater change than the (010) to allow the crystallographic transition to occur. The crystallite planes (100) were probably rotated to lie perpendicular to the direction of the acting stress and consequently gave rise to a textured sample. Bearing in mind that a hexagonal cell can be formed from three triclinic cells, the change from triclinic to pseudohexagonal was likely to occur by both a small change of the \( \gamma \) angle from 112 to 120° but mainly by the straightening of chains along the \( z \) axis tilting the \( \alpha \) and \( \beta \) angles from 98.5 and 118 degrees to 90 degrees. At this strain rate the increase in crystallinity content could be associated with the pulling out of chains at large tilted angles which hindered the movement of lamellae and with the accretion of more oriented amorphous chains as the new cell was being formed. The hexagonal cell has one of the largest density packing of all the crystallographic cells, so an increase in density should be expected. The transition is considered to be due to the effect of conformational motion and is associated with a packing change within the crystal, allowing a greater amount of rotational freedom about the chain axis. The idea that conformational changes took place in Nylon at this rates supports the argument in favour of similar changes in PET.

The temperature rise for PET and Nylon was expected to be almost the same because of their similar yield stress, density and specific heat. However, Appendix 2 shows that the work done is equal to the heat only if the change in internal energy is zero.
This was not the case of Nylon, because the crystallographic transition used part of the thermal energy generated in the sample, so the temperature developed was possibly smaller than for PET which led to a decrease of the strain softening phenomenon.

The overall deformation was connected with the volume fraction of the hard component and arguably proceeded by large and rapid disruption of the lamellae structure. The molecular chains, preferentially those in the (100) planes slipped within the lamellae whereas the hydrogen bonds prevented major movements of the segments contained in the (010) planes to give rise to a new structure. It is thought that the (100) family was almost aligned with the (010) plane which gave rise to only one peak.

6.2.8 DEFORMATION AT HIGH STRAIN RATE

At 8800 s\(^{-1}\) PET showed its highest yield stress, a yield drop, constant flow (no strain softening) and a severe strain hardening. But XRD revealed that structure was hardly formed and the crystallinity content was smaller in comparison with tests at medium strain rate.

The strain hardening cannot be related to the destruction of structure because, as the strain limited tests showed, structure was not developed until approximately 140% strain. Thus, the cold crystallisation peak was clear in the DSC and hence only a small percentage of chains crystallised. Moreover, if the strain limited test at 185% and the test without restraints are compared, the former was halted at 185% strain and afterwards induced an increment of approximately 35% crystallinity, while the latter stopped at a higher strains and induced only a 15% increase. Consequently, under the assumption that crystallisation occurred after the test, conditions up to 185% favoured crystallisation whereas further deformation did not, but structure was not destroyed.

It is believed that the absence of strain softening, the strain hardening and the small increase in crystallinity should have the same origin. Orientation, slipping and rotation of chains had to occur during the deformation process, in a similar way to that occurring in lower rate deformation. However, it is possible that at these strain rates
strain softening was counterbalanced by a large stress required to defy a very high plastic resistance to deformation. The network was opposed to very high changes in the microstructure formation. At a strain of around 90% (the temperature increase was about 75 K) the resistance to further movements increased markedly due to the short time given to the segments to accommodate themselves. PET molecules are known to be very stiff and therefore do no easily re-align. In addition, the temperature continuously increased, at a very high rate indicated by the large area under the stress versus strain curve, and the sample probably reached temperatures near the onset of melting, if not higher. This may have destroyed part if not most of the nucleated nuclei and relieved the effect of stress, so that on cooling the crystallisation could have evolved in a similar way to crystallisation from the melt in air which may give rise to a smaller degree of crystallinity. The experiment carried out on as-received PET in an attempt to disclose the origin of the decrease of crystallinity content, see Chapter 4, is not conclusive. However, it indicates that melting and subsequent crystallisation on cooling yields a value of crystallinity content similar to that found in samples tested at 8800 s⁻¹.

At 8800 s⁻¹ the yield stress of Nylon 11 was smaller than for tests at 1230 s⁻¹. The stress profile after yielding resembles that of low rate tests. The structure shown was partially triclinic, as the structure shown by samples tested at low strain rates, but X-ray peaks occurred at different angles to those found for low rate tests. DSC revealed only one broad melting peak, so the low melting species were again perfected.

The strain hardening may be due to two of the phenomena explained before acting together. On the one hand the disruption of lamellae and on the other hand the resistance to plastic deformation required high stresses at this strain rate. In this case, the plastic resistance was not governed by the stiffness of the individual molecular chains but by the crystalline and tie molecules structure. Changes in morphology may have accompanied the strain hardening in this case.

Although different to the structure shown by untested samples or samples tested at low rates, the material showed the triclinic-pseudohexagonal structure. It is not known
whether the triclinic structure disappeared and then crystallised again on cooling or it was always present. If the transition did not happen during the test the cell was probably disrupted, changing the interatomic distances. If the transition occurred during the test, it is thought that the high strain rates involved finally disrupted or partially destroyed the pseudohexagonal structure perhaps during strain hardening. In both cases, it seems that the reduction in crystallinity may be associated with the disruption of the structure.

6.2.9 DEGREE OF CRYSTALLINITY VERSUS YIELD STRESS

It has been extensively reported that yield stress increased with crystallinity content, thus, specimens with an initially higher crystallinity content yielded at higher values. However, despite this, it has been emphasised that the crystallisation occurring during the tests cannot be related to the yield stress. It is worth noticing that the degree of crystallinity and the yield stress correlated well for both materials.

Figure 6.5 shows that the yield stress and the crystallinity content up to the glass transition temperature followed a linear relationship for PET. At higher temperatures there are insufficient points to judge. It therefore seems that the level of stress is related to the structure induced afterwards. Thus, high yield stresses induced more crystallisation than low stresses. Crystallisation seems to be initiated by a critical stress level which may be established within the PET when the strain rate exceeded some critical value, which seems to be more important than the strain. Large strain did not induce crystallisation unless the stress was high. Strain rate plays an important role because the increase in yield stress is a direct consequence of the increase in strain rate. However, the relationship failed at 8800 s$^{-1}$ and the enhancement at 1230 s$^{-1}$ cannot be explained in terms of the crystallinity content but it is clear that up to 1940 s$^{-1}$ the higher the yield stress, the higher the crystallinity content.

Figure 6.6 shows that as received Nylon 11 yield stress and crystallinity content also followed a linear relationship at room temperature, although departure at lower temperatures and on annealing. Despite the fact that yield stress and crystallinity both
Fig. 6.5 PET Crystallinity Content vs. Yield Stress

\[
y = 0.2795x + 6.473 \\
R^2 = 0.9978
\]

\[
y = 0.3665x - 7.5031 \\
R^2 = 0.9996
\]

\[
y = 0.2438x - 1.5226 \\
R^2 = 0.9289
\]

Fig. 6.6 Nylon 11 Crystallinity Content vs Yield Stress

\[
y = 0.0213x + 29.766 \\
R^2 = 0.953
\]
decreased at 8800 s\(^{-1}\), a critical value of stress cannot be established because the decrease in crystallinity (as explained above) may have a different origin that the decrease of yield stress. Further, in general the variation of crystallinity content in Nylon 11 is believed to have a different origin to PET due to crystallisation.

In this work there is no direct correlation between the yield stress and the crystallite size, perfection or degree of crystallinity induced in the samples. Such a relationship could be expected between the orientation of the molecular structure and the mechanical properties because, in accordance with the results, orientation is the only phenomenon which could act up to the yield point. It can be supposed that the initial mechanical properties are predetermined by the structure of the amorphous phase and, more particularly, by the amount of maximally extended chains bearing the stress.

The comparison of Nylon 11 samples annealed at different temperatures caused difficulties. The yield stress did not follow any specific pattern, it tended to be smaller for the longest annealing time whereas the crystallinity content tended to increase with annealing time, with maximum changes around 4%. No major conclusion can be extracted from this. It would be expected that the thicker the lamellae the higher the yield strength of the material. However, according to Lee et al. (1988) quoting the results of Starkweather (1959) reported that the yield stress of Nylon decreased with the spherulite size. Samples annealed at 190\(^\circ\)C are expected to have larger crystallites, so the smaller yield stress agrees with the finding of the present author. The loss of the minor melting may play some role in affecting the yield stress.

**6.2.10 MODELS**

It was shown that the yield stress behaviour of PET failed to comply with the Eyring theory at high strain rates. The curvature of the yield stress versus logarithm strain rate is too large to fit it to a two process equation comprising a logarithm and a hyperbolic dependence and parameters could not be calculated. The nature of the yield stress is not clear but if orientational process occurred at the early stages of the plastic deformation, then the degree of orientation could be directly related to the yield stress.
Thus, the higher the orientation due to a higher strain rate, the higher the yield stress (energy) required to induce the movement of chains from their equilibrium position due to a higher cohesive energy between aligned chains.

Nylon 11 also failed to comply with the Eyring’s theory. Contrary to PET, Nylon 11 showed a decrease in yield stress with strain rate which cannot be explained in terms of Eyring’s theory. However, it is thought that the elastic behaviour up to the yield is similar for PET and Nylon, the eventual changes in the chain conformations and/or the magnitude of interaction between chains induced by the crystalline phase could not affect the molecular mechanisms implied at the beginning of the plastic deformation. It is also known that the amorphous phase deformed first due to its softer character. Therefore, it can be said that yielding of Nylon 11 occurred after orientation of the amorphous phase. However, the decrease in yield stress at high rates is not fully understood and whereas the medium rate values can be explained as before it is unlikely that at 8800 s\(^{-1}\) a disorientation phenomenon happened to account for a smaller yield stress.

If the viscoelastic contribution to flow stress for glassy polymers can be neglected past the yield regime, which is a very good approximation, the effective stress and plastic strain follows a relationship like:

\[
\sigma^* (\varepsilon) = \frac{kT}{V_a} \ln \left( \frac{\varepsilon}{\varepsilon_0} \right)
\]

Thus, the strain rate sensitivity, which is the slope of the stress versus logarithm strain rate plot is equal to \(\frac{kT}{V_a}\). For low rate tests, Figure 6.7:

\[
V_a = \frac{kT}{S} = \frac{1.3810^{-23} \times 298}{5.410^6} = 0.76\text{nm}^3
\]

The strain rate sensitivity of Nylon 11 between low and medium rates was 5.3, Figure
6.8, which yields an activation volume for Nylon of 0.77 nm$^3$.

The volume of the PET triclinic cell, using the parameters reported by Daubeney et al. (1954) is 0.267 nm$^3$ which is associated with one unit. In view of these results, although they must be treated very careful, the activation volume to yield at low strain rates involved approximately three units. The cell volume of the mixed structure of Nylon 11 is very difficult to calculate. However, the relationship given by Hellinckx and Bauwens (1995) can be used to estimate the number of carbons associated with the activation volume. Also, the calculations can be carried out for PET and the two values compared. According to these authors, the weight of a segment of n carbons is approximately $\frac{nM}{N}$ where $M$ is the molecular weight of the repeating unit and $N$ the number of carbons per repeating unit. Therefore, the activation volume can be expressed by:

$$V_a = \frac{nM}{\rho}$$  \hspace{1cm} (6.3)

where $\rho$ denotes the density of the polymer. The previous expression assumes that only the amorphous phase is involved in yielding. Thus, using the values found for PET, the number of carbons involved were 33. Thus, 33 carbons are equivalent to approximately 3 units, in complete agreement with the value found above. This supports the idea that the small crystalline phase in PET did not intervene during yielding. Following the same procedure and under the same assumption the number of carbons involved in the yielding of Nylon 11 were 29 which represents about 2.5 repeating units.

The activation volume is the volume swept out by the co-operative displacement involved in yielding through the crystal. It is not clear the magnitude of the activation volume for polymers. Darras and Seguela (1993), among others, reported activation volumes between 1 and 5 nm. However, G'Sell and Jonas (1981) quoted that Escaig (1978) claimed that activation volumes larger than a few tenths of nm because would
Fig. 6.7 PET Yield Stress vs. ln Strain Rate

Fig. 6.8 Nylon 11 Yield Stress vs. ln Strain Rate
signify that changes in microstructure could even completely screen the single mechanism activated process. The similar strain sensitivity for Nylon gave a similar activation volume to PET. The crystalline phase did not modify either the molecular mechanisms or the length of the backbone chain segments involved in the mechanical behaviour. This phase only induced a reinforcement effect of the amorphous phase.

The pre-exponential factor can be estimated by equating $\frac{kT}{V_a}$ to the $y$ intersection at a strain rate equal to 0, i.e., $\ln \varepsilon_o = 1$. For PET at low rates it is $6.7 \times 10^{-9}$ s$^{-1}$ and it is $6.4 \times 10^{-8}$ s$^{-1}$ for Nylon 11. The activation energy can be estimated from the intersection of yield stress/temperature versus logarithm strain rate:

$$\Delta H = V_a T \left( y_{\text{int}} + \frac{R}{V_a} \ln \varepsilon_o \right)$$

where $V_a$ is the activation volume in cubic meter per mole, and $R$ is the gas constant equal to 8.31 Jmole$^{-1}$K$^{-1}$. The values are, 94.8 kJmole$^{-1}$ for PET at low rates and 83.3 kJmole$^{-1}$ for Nylon 11. The $y$ intersections can be seen in Figures 6.9 and 6.10.

It is worth mentioning the outcome of the estimations if an independent second logarithm relationship is assumed above medium rates for PET. The activation volume would be 0.13 nm which would be associated with half a unit. Estimation using the formula suggested by Hellinckx and Bauwens (1995) would yield about 5.5 carbons, approximately half a unit again. The exponential factor would be 0.08 s$^{-1}$ and the activation energy approximately 15 kJmole$^{-1}$. The activation energy would be smaller than for low rates which contradicts the higher levels of stress found.

The activation energy at low rates is slightly smaller than the energy required to initiate crystallisation. Moreover, part of the activation energy for yielding should be used in providing a momentary increase $\Delta V_a$ associated with the formation of an empty site according to Ree and Eyring (1958). Thus, crystallisation (already suggested by other experiments) did not occur during yielding at low rates.
Analysis and Discussion

Fig. 6.9 PET Yield Stress/Temperature vs. $\ln$ Strain Rate

$$y = 0.0179x + 0.3372$$
$$R^2 = 1$$

Fig. 6.10 Nylon 11 Yield Stress/Temperature vs. $\ln$ Strain Rate

$$y = 0.0178x + 0.2941$$
$$R^2 = 1$$
process which could be related to yielding of Nylon 11 would be the melting and re-crystallisation of segments in the direction of the applied stress. Hellinckx and Bauwens (1995) reported that the heat needed to melt the segments associated with the activation volume is:

\[ W_m = \chi h \rho V_o \]

where \( \chi \) is the crystallinity content, \( h \) the specific melting enthalpy and \( \rho \) the density. Substituting the values gives 27 kJmole\(^{-1}\) for Nylon 11. This value is significantly smaller than the activation energy for yielding. Nonetheless, in accordance with the previous argument, only part of the activation energy would be used for the yielding process and as already mentioned the melting-recrystallisation process would not need a complete melting process. Thus, the calculations are crude but if this process was involved in yielding it would have two consequences: i) amorphous and semi-crystalline mechanisms of yielding would be different; ii) the crystalline phase would be involved in yielding which contradicts the previous discussion.

The yielding behaviour of PET can be separated in two according to the yield stress values, whatever the processes involved were: i) low strain rate up to the glass transition temperature; ii) above medium rates up to the glass transition temperature; the similar values between (i) and tests carried out at and above medium rates at temperatures beyond the glass transition suggests that the processes could be similar to (i).

Nevertheless, flow stress of PET complied with the Gaussian equation up to large values of strain. The Gaussian equation assumes a coiled configuration which was believed to remain throughout the whole deformation process; a fully stretched configuration was not approached. The fact that PET complied with the Gaussian equation reinforced the argument in favour of no crystallisation during the duration of the test. The strain hardening modulus is determined by the sum of the restraints imposed by a mesh of uncrossable polymer chains, so a larger modulus implies a more difficult deformation of the network; it is also determined by the decrease in
configurational entropy as a polymer chains assume a less random form, that is to say, orientation. The number of chains between entanglements was approximately equal to 15 repeating units. Considering that the length of a unit was almost equal to the c parameter (10.75 Å), the length between entanglements was about 16 nm. The number of units between entanglement was larger than the number of units involved in the initial part of the deformation which was expected because entanglements restricted the movements of segments of molecular weight well above the chain entanglement value.

The fit of the flow stress of Nylon 11 to the Gaussian equation was not as good as for PET. The stress flattened at high strains, it deviated from a linear fit and the strain hardening modulus was therefore meaningless. The low molecular weight between entanglements corresponding to 1.5 molecular segments is unrealistic which was supported by the fact that two and a half units were involved in yielding.

According to Haward (1987) the applicability of the equation is out of question. But interpretation needs more experimental evidence. Thus, the strain hardening modulus has been used as an empirical constant defining strain hardening behaviour. If the origin of the Gaussian equation and the results on thermoplastics are combined, it could be argued that there could be a mathematical analogy between rubber elasticity and the strain hardening process.
CHAPTER 7

CONCLUSIONS AND FUTURE STUDIES
7.1 CONCLUSIONS

The thermomechanical properties of PET and Nylon 11 were studied by means of a Hounsfield machine, a Dropweight machine and a Cross Bow system. The mechanical machines were used to produce true stress versus true strain curves by direct measurement. Stress measurement was determined by recording the output of strain gauges while the strain measurement was accomplished by an optical laser-photodiode system, which yielded the displacement of the sample without the need for estimating it from other measurements.

The resulting microstructure was studied by X-Ray Diffraction and Differential Scanning Calorimetry. X-ray diffraction was carried out using the whole sample after the mechanical tests. Accurate diffractograms were produced which revealed the atomic structure. Calorimetry was carried out on small parts of the samples, about 10 mg, which gave information about the different transitions and crystallinity content.

The mechanical response and structure changes of PET and Nylon 11 have been investigated in compression over nearly seven decades of strain rate, $0.001 - 10^4$ s$^{-1}$, at temperatures from 263 to 453 K. The form of the PET and Nylon 11 stress versus strain curves are different which can be attributed to the completely different structures and morphology, although some common features were found.

The shape of the stress versus strain curves varied depending on the strain rate and temperature. PET curves showed an increase in yield stress with strain rate at any temperature except near the onset of melting. However, the variation of yield stress with temperature differed at different strain rates. It decreased steadily at low strain rates but around the glass transition at medium rates it was enhanced. Flow stress was almost constant at low rates with a hardening effect at large strains. Nevertheless, strain softening was very pronounced at medium-high rates due to the adiabatic character of these tests. At high rates the softening was compensated by the strain hardening due to plastic resistance to deformation and the material strain hardened at high strains. The mechanical properties of PET mainly depended on the molecular
As-received Nylon 11 yield stress increased with strain rate except at high rates where the material showed a decrease in strength. Flow stress at low rates constantly increased up to large strains. At medium strain rates, a low degree of strain softening was shown by the material and although the test was adiabatic, perhaps not all the heat was used to increase the temperature of the sample. At high rates, the material strain hardened, slowly at small strains but severely at large strains. At temperatures below ambient, stress versus strain curves were similar but showed smaller yield stresses for the same rates. The changes with annealing were not very marked. The flow stress past the yield point and the trend in yield stress were almost the same as for the as-received material.

As-received PET exhibited no crystalline structure. It displayed orientation when tested at low strain rates and low temperatures whereas it partly developed structure at high temperatures before the tests which was perfected by the deformation. At medium and medium-high rates, structure was developed at any temperature (at subambient temperatures it was less defined) showing three diffraction peaks in agreement with the literature reports. The crystal size perpendicular to the (100) planes showed a little variation at 1230 s⁻¹ but increased markedly at 1940 s⁻¹ above the glass transition temperature. Thus, under this conditions large crystals were grown. Structure was hardly defined at high rates due to a less favourable conditions to grow crystals.

Nylon 11 was a very interesting material to investigate, it comprised a mixed triclinic-pseudohexagonal structure which may completely transform to the latter one under certain conditions, which makes it interesting for further investigation. As-received material consisted of both crystal structures showing two main peaks. On compression at low rates, the diffraction peaks tended towards equalisation of intensity and merging as a premonition of a crystallographic transition. The latter occurred at medium rates whereas the mixed structure was again detected at high rates.
The DSC measurements backed up the X-ray measurements. The crystallinity content slightly increased when compressed at low rates but showed a large increased after medium rates were applied. The glass transition and cold crystallisation were clear on the DSC scan after low rate tests but completely disappeared after medium rate tests due to crystallisation after the mechanical tests. The specimens with the largest crystal size showed two melting peaks, which confirmed the fact that larger crystallites needed higher temperatures to be melted. At high rates, the crystallinity content decreased compared to lower rates in agreement with the X-ray pattern. The increase in crystallinity was, most probably, thermally induced. When the temperature rise increased the temperature in the sample above the glass transition temperature, nucleation took place and crystallisation occurred by addition to the nuclei.

As received Nylon 11 was semi-crystalline, with almost 30% of the material in the crystallised state. The DSC scans revealed that two species were present the higher melting ones being more abundant. Compression transformed almost completely all the crystals to the high melting class. In general the melting peak was very broad and sometimes a shoulder could be seen as a remainder of the double character of the as-received material. The degree of crystallinity increased by a small percentage at low rates of compression. Medium rates induced a slightly higher crystallinity content whereas high rates destroyed part of the crystalline structure. The absence of cold crystallisation in Nylon 11 makes us believe that the crystallisation changes occurred by the addition or removal of chains to the existing lamellar structure without need for nucleation.

Strain limited tests revealed that high strain, strain rate and stress were required to nucleate and favour a significant growth of crystallites. It seems reasonable to conclude that a higher degree of orientation and temperatures within the sample above the glass transition temperature induced by these conditions with a very likely increase in the number of gauche isomers favoured crystallisation. However, the kinetic study proved that crystallisation had to happen during the cooling stage although not all the crystallinity content increase could be accounted for. The timing of formation or destruction of new crystal cells in Nylon 11 is not known. Besides, the degree of
crystallinity followed a fairly good linear relationship with yield stress. Thus, if the exact nature of the yield stress behaviour with strain rate is determined, this could lead to a better understanding of the induced crystallisation.

Two kinds of strength enhancements were found in this study. On the one hand, the yield stress near the glass transition temperature was found to be comparable to room temperature values. A higher ability to orient near the glass transition, of more importance than the temperature effect, could be the reason for the similar values of yield stress at room temperature and near the glass transition. On the other hand, yield stress beyond medium rates was larger than predicted by Eyring’s theory, if a hyperbolic sine relationship between strain rate and yield stress was expected due possibly to a higher degree of orientation. Thus, it seems that the degree of orientation increased with strain rate and further increased near the glass transition temperature.

Thus, the Eyring’s theory could not fit the data above medium rates for PET. The sharp increase is more likely to follow a double logarithm relationship. Nylon 11 did not follow the theory, in this case a decrease in yield stress at high rates could not be accounted for by the theory. However, crude calculations between low and medium rates led to the estimation of an activation volume for both materials. The agreement between the number of monomers corresponding to the activation volume of PET and the estimation using the formula reported by Hellinckx and Bauwens (1995) neglecting the crystallinity content suggests that only the amorphous phase was involved in yielding. The transmission of the deformation onto the crystalline phase occurred at a later stage.

PET and Nylon 11 flow stress was fitted to the semi-empirical equation proposed by Argon (1973) with different results. PET complied with the equation at strain from the yield drop up to large values whereas the flow of Nylon 11 only fitted the equation up to medium values of strain. However, it is remarkable that the equation could be applied to true stress curves in compression, which removes the problem of necking. This implies that uniform deformation was achieved throughout the cross section of the sample.
The different behaviour of Nylon 11 and PET past the yield stress, the different geometry of compression and tensile tests, for which the yield drop was attributed to necking, and the agreement with other authors supports the idea that the yield drop is a genuine phenomenon, dependent on the characteristics of the material.

7.2 FUTURE STUDIES

Firstly, other types of materials could be tested under similar conditions to search for reproducibility. These could be semi-crystalline and amorphous materials with special interest in those that can be obtained in both forms such as PET and PEEK which would reveal differences and similarities in their behaviour. Tests should be carried out at more strain rates which could be achieved by changing the initial velocity of compression or the sample dimensions, diameter and height. The latter also would yield information about the mechanical response dependence on dimensions which has been the issue of some controversy.

Secondly, as an outcome of more information available, Eyring’s theory could be checked more thoroughly at low rates. At high rates, the yield stress enhancement may claim a modification of the theory, taken into account that the theory was developed for viscous solutions. Activation energies could be estimated and compared against the energies required for process such as scission and kinking to occur.

Thirdly, X-ray diffraction patterns were taken in reflection but could be carried out in transmission when the thinness of the sample after deformation allows for it. Thus, perhaps more reflections could be found and studied. Values of the degree of orientation with strain and strain rate would be very interesting. For this, tests could be carried out at steps of 10% at different rates.

Fourthly, the kinetics of crystallisation of oriented samples but hardly crystalline, which can be achieved by slow compression, should be carried out. It is expected that a smaller activation energy would account for all the increase in the crystallinity
Finally, it would be desirable to obtain information about the supramolecular structure of the materials by Small Angle Scattering, which may change with orientation from a three dimensional growth to a fibrillar structure. Also, FTIR (Fourier Transform Infra Red) spectroscopy would provide information about the orientation mechanisms and the conformational changes in the chain.
Appendix 1

REM *****************************************************
REM * DSA.BAS *
REM *****************************************************

REM *****************************************************
REM * This program read and retreat the data from "dsa" *
REM * the result is stored in file of *.ZXW *
REM *****************************************************

REM *** define dimension and visual screen ***

DIM header$(128), result(4100), vt(5)
CLS
CLS #1
WINDOW #1 FULL ON
WINDOW #2 CLOSE
CLOSE WINDOW 3
CLOSE WINDOW 4
OPEN #3 WINDOW 4
xd=XACTUAL(#3)*0.01
yd=YACTUAL(#3)*0.1
WINDOW #3 SIZE xd, yd
WINDOW #3 CLOSE
CLS #1
CLS

REM *** read the original record from *.DSC ***
REM  decide the read format and read the headlind

PRINT "  please input the name of data file"
INPUT filename$
ext$=".dsc"
datafile$=filename$+ext$
fileinno=5
reclength=1

RECORD n; dsa$ FIXED I
OPEN #fileinno RANDOM datafile$ LENGTH reclength
FOR i=1 TO 128
header$(i)=" 
NEXT i

PRINT "  now the program is reading the data,"
PRINT "  waiting please ......"
datanumber=4096

REM read data from data file

i=1
WHILE NOT (EOF(#fileinno))
GET #fileinno, dsa$
IF i<129 THEN 200
nc=i-128
IF nc>datanumber THEN 250
k=i-128
result(k)=ASC(dsa$)
GOTO 210
200 header$(i)=dsa$
210 i=i+1
 POSITION #fileinno.NEXT
WEND
250 CLOSE #fileinno
    PRINT "data read have finished"
    CLS

REM *** reproduce graphic on screen ***

REM print header on screen

REM it iv itb are used for calculate tdiv and vdiv

v$=" "
t$=" "
datee$=" "
timee$=" "
namee$=" "
FOR i=2 TO 9
datee$=datee$+header$(i)
NEXT i
FOR i=14 TO 22
timee$=timee$+header$(i)
NEXT i
it=0
iv=0
itb=0
FOR i=26 TO 31
    IF header$(i)=" " THEN 300
    iv=iv+1
    v$=v$+header$(i)
NEXT i
300 FOR i=32 TO 48
    IF header$(i)="," OR header$(i)=" " THEN 310
    IF it=0 THEN itb=i
\[ t_s = t_s + \text{header}(i) \]
\[ \text{it} = \text{it} + 1 \]

IF header$\text{(i)}$ = "S" THEN 320

310 NEXT i

320 FOR i = 49 TO 100

namee$ = namee$ + header$\text{(i)}$

NEXT i

PRINT COLOUR(2); "test-name" = "namee$"

PRINT COLOUR(2); "test-date" = "datee$"; "test-time" = "timee$

PRINT COLOUR(2); "V/div" = "v$"; "T/div" = "t$

REM plot the grid and the curve

\[
x = 300 \\
y = 200 \\
\text{BOX } 300; 200, 4000, 3210 \\
\text{FOR } i = 1 \text{ TO 9} \\
x = x + 400 \\
\text{LINE } x; 200, x; 3400 \\
\text{NEXT i} \\
\text{FOR } i = 1 \text{ TO 7} \\
y = y + 400 \\
\text{LINE } 300; y, 4300; y \\
\text{NEXT i} \\
\text{FOR } i = 1 \text{ TO 4096 \text{ STEP 4}} \\
x = i + 300 \\
y = 1940 + ((\text{result}(i) - 128) \times 400) \div 30 \\
\text{PLOT } x; y \text{ COLOUR (2)} \\
\text{NEXT i}

REM *** cut the needed range from the curve ***
INPUT "Do you want copy the screen ? (Y/N)"; sd$  
IF LEFT$(sd$, 1) = "Y" OR LEFT$(sd$, 1) = "y" THEN GOSUB screen_dump  
PRINT "please input the begin and end data number (nub,nue)"
PRINT " 1 ";
FOR i = 3 TO 11 STEP 2
PRINT " ;400*(i - 1); " ;
NEXT i
INPUT nub, nue
number = nue - nub + 1
REM highlight the choised range
BOX 300 + nub; 200, nue - nub, 3210 FILL WITH 1
FOR i = nub TO nue STEP 4
x = i + 300; y = 1940 + ((result(i) - 128) * 400) \ 30
PLOT x; y COLOUR (7); NEXT i
INPUT "Is this the area you need ? (Y/N)"; are$
IF LEFT$(are$, 1) = "Y" OR LEFT$(are$, 1) = "y" THEN GOTO 4344
CLS: GOTO 320
REM input the result file name
4344 PRINT " please input the file name for storing the results"
INPUT re$
fileoutno = 6
filename$ = re$ + ".zxw"
REM *** calculate the value of v/div and t/div ***
FOR i = 26 TO 25 + iv

136
ii=i-25
vt(ii)=ASC(header$(i))-48
NEXT i
GOSUB translation
vdiv=tran
FOR i=1 TO 5
vt(i)=0
NEXT i
FOR i=itb TO itb+it-1
ii=i+1-itb
vt(ii)=ASC(header$(i))-48
NEXT i
GOSUB translation
tdiv=tran

REM *** calculate the value and stored data ***

OPEN #fileoutno OUTPUT filename$
REM PRINT #fileoutno namee$
REM PRINT #fileoutno datee$
REM PRINT #fileoutno timee$
REM PRINT #fileoutno number
FOR i=nub TO nue
  t=tdiv*i/100
  v=vdiv*(result(i)-128)/30
  PRINT #fileoutno t,v
NEXT i
CLOSE #fileoutno
CLS

REM *** give an instruction to read the data from the data file ***
please check following number,
they should be exact the same

The data have been stored in the file of ";filename$ 
When you want read data from ";filename$ 
please use following format"

open #fileno input 
";CHR$(34);filename$;CHR$(34) 
input #fileno namee$, datee$, timee$"
in #fileno number" 
for i= 1 to number" 
input #fileno t(i),v(i)"
next i"
close #fileno"

that's OK!"

CLOSE #fileinno

END

*** this subroutine calculate the units of divition ***

IF vt(1)=0 THEN 425
IF vt(2)>10 THEN 410
IF vt(3)>10 THEN 420
IF vt(4)=35 OR vt(4)=38 THEN k=1
IF vt(4)=61 THEN k=1.0e-3
IF vt(4)=62 THEN k=1.0e-9
IF vt(4)=69 THEN k=1.0e-6
tran=(vt(1)*100+vt(2)*10+vt(3))*k
GOTO 430
425 tran=vt(3)/10
GOTO 430
410 IF vt(2)=35 OR vt(2)=38 THEN k=1
IF vt(2)=61 THEN k=1.0e-3
IF vt(2)=62 THEN k=1.0e-9
IF vt(2)=69 THEN k=1.0e-6
tran=vt(1)*k
GOTO 430
420 IF vt(3)=35 OR vt(3)=38 THEN k=1
IF vt(3)=61 THEN k=1.0e-3
IF vt(3)=62 THEN k=1.0e-9
IF vt(3)=69 THEN k=1.0e-6
tran=(vt(1)*10+vt(2))*k
430 RETURN

LABEL screen_dump

REM *** DUMP THE SCREEN TO THE PRINTER ***

OPEN #5 DEVICE 21
x=300
y=200
BOX #5,300;200,4000,3210
FOR i=1 TO 9
x=x+400
LINE #5,x;200,x;3400
NEXT i
FOR i=1 TO 7
y=y+400
LINE #5,300;y,4300;y
NEXT i
FOR i=1 TO 4096
x=i+300
y=1940+((result(i)-128)*400)/30
PLOT #5,x;y
NEXT i
GRAPHICS #5 UPDATE NEW
RETURN
Appendixes

APPENDIX 2

The derivation of the temperature rise formula is as follow.

The first principle of thermodynamics states that:

\[ dU = \delta Q - \delta W \]

where \( U \) is the internal energy, \( Q \) the heat and \( W \) the work. If all the work is converted into heat, i.e. there is no other form of energy present such as energy released by crystallisation then:

\[ \delta Q = \delta W \quad (1) \]

According to thermodynamics the heat due to a temperature rise \( dT \) and the work done on a volume \( dV \) by a pressure \( p \) are:

\[ \delta Q = mC_pdT \]

and

\[ \delta W = Fdh = \sigma Adh \quad (2) \]

where \( C_p \) is the specific heat, \( A \) the area and \( h \) the height of the sample. Moreover, the relationship between the height and the strain is:

\[ \varepsilon = \ln \left( \frac{h}{h_o} \right) \Rightarrow d\varepsilon = \frac{dh}{h} \Rightarrow dh = h d\varepsilon \quad (3) \]

Using equations 1, 2 and 3, and substituting the pressure \( p \) by the stress \( \sigma \):

\[ mC_pdT = \sigma Ah d\varepsilon \Rightarrow dT = \frac{Ah}{mC_p} \sigma d\varepsilon \]
integration on both sides and substituting the density $\rho$ by $\frac{m}{Ah}$, the temperature rise is:

$$\Delta T = \int \frac{\sigma \Delta e}{\rho C_v}$$
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