The thermomechanical properties of aromatic polymers

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BLDSC no: DX 186922
THE THERMOMECHANICAL PROPERTIES OF AROMATIC POLYMERS

by

SININ BIN HAMDAN

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

June 1994

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Supervisor: Dr G M Swallowe
Department of Physics
DEDICATION

This thesis is dedicated to my son Saifuliwan Ezzedin, my daughter Aaliyawani Ezzerin and especially to my wife Dayang Maryani for all her sacrifices as a mother who also sought a degree at the same time.
ACKNOWLEDGEMENT

I would like to thank the Malaysian Government for funding me throughout the work. I would like to express my great appreciation to my supervisor Dr.G.M.Swallowe for his constructive comment and advice, for all his help and encouragement. Discussions with Dr.D.J.Parry are greatly appreciated. Special thanks go to Dr.P.C.Dawson whose comments on PEEK properties were of invaluable interest. Thanks are also due to Noori Al-Maliky for all his help on the earlier stage of the work, Farag Al-Hazmi and Mark Ashton who have help in any way. I am indebted to Mr.P.Newman for his help in the equipment construction and Mr.N.Miller of IPTME who helped with the hydraulic machine.

The company of Dr.T.A.Rafik, Zazli Chik, Razali Kadir, Ahmad Borhan, Mohammad Babateen, Adwan Hameed and Nadhum Zayer are also appreciated.
ABSTRACT

High performance aromatic polymers such as PEEK and PEK are widely used in composite and related applications. However, their high rate thermomechanical properties are not well understood. This thesis describes a series of investigations into their mechanical behaviour over a large range of strain rates ($10^{-3} - 10^{3} \text{s}^{-1}$) and temperatures (20-200°C) which were carried out in order to more fully understand their properties and to assess the applicability of standard polymer property models to their behaviour. The experiments involved the design and construction of two novel sets of high rate test apparatus. These were a cross-bow based system which enabled high strains to be obtained at strain rates of $10^{3} \text{s}^{-1}$ and a drop-weight system based around a high speed camera which enabled direct measurements of radial strain and observation of sample behaviour to take place. The cross-bow apparatus incorporated a laser-photodiode system to enable direct strain measurements to be made and thus had an advantage over conventional Hopkinson bars of direct, rather than derived, strain measurements with a sufficiently energetic projectile to produce large deformations. These systems were used in addition to standard hydraulic ram and dropweight equipment. A heater unit to enable tests to be carried out over the desired temperature range was also designed and constructed and used with all the above systems.

A comprehensive set of Differential Scanning Calorimetry and X-ray tests were carried out on samples before and after mechanical testing in order to provide structural data to aid the interpretation of the mechanical tests results.
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Notations

$A$ - area of sample (m$^2$)
$A_0$ - initial area of sample
$A(t)$ - area of sample at time $t$
$a$ - acceleration (ms$^{-2}$)
$C$ - speed of elastic wave (ms$^{-1}$)
$d_o$ - initial diameter of sample
$d(t)$ - diameter of sample at time $t$
$D_o$ - diameter of sample from film projection before impact
$D(t)$ - diameter of sample from film projection at time $t$
$E$ - Young's Modulus (Nm$^{-2}$)
$\varepsilon$ - natural strain or true strain
$\dot{\varepsilon}$ - strain rate (s$^{-1}$)
$\varepsilon$ - engineering strain
$F$ - force (N)
$f$ - degree of orientation
$\sigma$ - stress (Nm$^{-2}$)
$\sigma_e$ - stress in elastic solid or region
$\sigma_v$ - stress in viscous liquid
$\sigma_Y$ - yield stress
$\sigma_i(\varepsilon)$ - internal stress
$\sigma^*(\dot{\varepsilon})$ - effective stress
$g$ - gravity 9.8 ms$^{-2}$
$H$ - heat of fusion (Jg$^{-1}$)
$H_i$ - heat of fusion of fully crystalline polymer
$H_d$ - height of dropweight from base (m)
$h$ - thickness of sample (m)
$h_0$ - initial thickness of sample
h(t) - thickness of sample at time t
I - intensity of X-ray film
I_{\min} - minimum intensity
I_{\max} - maximum intensity
K - acceleration calibration factor (ms^{-2}V^{-1})
k - Boltzmann Constant (1.381x10^{-23} J K^{-1})
k_L - load calibration factor (NV^{-1})
k_o - displacement calibration factor (mmV^{-1})
I - length of projectile or arrow (m)
M - mass (kg)
\eta - viscosity coefficient
\theta - Bragg angle of diffraction (°)
p - pressure
\rho - density (kgm^{-3})
R - gas constant (8.314 J K^{-1}Mol^{-1})
r - radius of sample (m)
S - strain rate sensitivity
s - radius of X-ray diffraction on film
T - temperature (°C)
t - time (second)
u(t) - displacement of sample at time t
u_1(t) - displacement of incident bar at time t
u_2(t) - displacement of transmitter or instrumented bar at time t
\mu - coefficient of friction
V - volume of sample (m^3)
V_A - apparent activation volume (nm^3)
V_L - load signal (V)
V_D - displacement signal (V)
v - velocity (ms^{-1})
ν - poisson’s ratio

υ - frequency of chain segment (vibration frequency)

w(t)-displacement of sample, incident and instrumented bars

χ - degree of crystallinity

λ - wave length of CuKα radiation (1.54 Å)

X-absissa axis for displacement

Y-ordinate axis for load

Z-enlargement factor for film projection
CHAPTER 1

INTRODUCTION
1.0 INTRODUCTION

1.1 GENERAL INTRODUCTION

The successful use of a material in specific applications such as a high performance composites requires knowledge of its mechanical and thermal property profile. In addition to the usual static properties obtained at very low testing speed, characterization of its impact performance under dynamic loading conditions (such as high speed impact) has become essential. In the absence of data at higher strain rates and temperatures it is probably not sensible to estimate values by extrapolating from the lower strain rates and temperatures data.

A distinctive feature of the mechanical behaviour of materials is the way in which their response to an applied stress or strain depends upon the rate or time period of loading. In the simplest case elastic materials obey Hooke's law, whereby the stress is proportional to strain. Viscous materials, such as liquids, obey Newton's law whereby the stress is proportional to strain rate and independent of the strain. The behaviour of many polymers can be thought of as being somewhere between that of elastic solids and liquids. At low temperatures and high rates of strain they display elastic behaviour whereas at high temperatures and low rates of strain they behave in a viscous manner flowing like a liquid. Depending on the temperature and time scale of the measurement polymers can be classify as glassy solid, or an elastic rubber, or a viscous liquid, they may be described as 'viscoelastic' materials [1].

The effect of strain rate on the relative brittleness or ductility of polymers is investigated by various testing machines namely a servohydraulic machine, a Conventional Dropweight system, an Improved Dropweight in
conjunction with a high speed camera and a direct impact testing machine using a cross bow.

In all the testing machines, inertial and frictional effect of the equipment, compression configuration, test geometry and condition are made as similar as possible. Because of the influence of the elastic deformation of the testing machine, the accuracy of each machine was, where possible, tested using annealed pure aluminium.

In order to better understand the variation of polymer strength with deformation and orientation, this research is directed towards the experimental and analytical investigations of the behaviour of semicrystalline polymers at various strain rates and different temperature. The work describe here is concerned entirely with Poly-ether-ether-ketone (PEEK), Poly-ether-ketone (PEK) and Poly-ether-sulphone (PES). These materials were chosen as they are widely used and available commercially [2].

The influence of the morphology of PEEK on the mechanical properties is well recognised [3-4]. Major efforts have been made to estimate the crystallinity of thermally treated PEEK, since the degree of crystallinity strongly influences mechanical properties [5-13]. In this work X-ray Diffraction and Differential Scanning Calorimetry are both used to study the crystallinity and orientation of PEEK.

1.1.1 Effect Of Strain Rate

The stress-strain curve of a polymeric material depends upon the speed
of testing or the rate at which the sample is deformed. Strain rate and temperature effects on amorphous polymers have been investigated by many workers [14-17]. Strain softening and strain hardening are normal phenomena which both occur during polymer flow. The degree of softening and hardening are found to depend strongly on the strain rate at which the polymer is being tested. The yield stress of a polymer generally decreases as the temperature is increased but increases with strain rate [1]. Walley et al. [18] shows that all the polymers they examined exhibited higher yield stresses at high strain rates of $10^3 - 10^4 \text{s}^{-1}$ than at the lower rates.

The wide range of strain rates data can be used by engineers in calculating the response of structures made from these materials. Also strain rate response can give information about deformation mechanisms at the molecular level. At high rates of strain, there is not enough time (in many cases) for stress relaxation to occur to prevent brittle fracture by relieving some of the stress at points of stress concentration.

Chou et al. [19] noticed that both amorphous and semicrystalline polymers showed a viscous effect at the beginning of the deformation and plastic flow followed thereafter. They showed that at the highest strain rate ($10^3 \text{s}^{-1}$) the stress in the materials decreases while the strain is increasing.

1.1.2 Effect Of Temperature

According to elasticity theory, a linear relationship between stress and strain as well as a reversible process between external work and strain
energy are traditionally accepted as basic concepts in solid mechanics. However, this is not strictly true when considering the "thermomechanical effect" of a material where the temperature of the sample changes. Heat transfer will occur during deformation. Thermomechanical behaviour deals with the coupling effect of thermal and mechanical behaviour during the deformation process. Thermoelasticity and thermoplasticity are the two major concerns.

It is to be noted that the material as a whole becomes more compliant with rise of temperature. Thus in absolute terms the stress required to achieve a given strain drops and the observed variation in deformation behaviour on raising the temperature must be due to relative changes in the compliances of the components within the gradually softening overall structure.

At low temperatures the Young's Modulus of polymers are of order $10^8 - 10^{10}\text{Nm}^{-2}$ and they fracture at strains $\approx 5\%$ whilst at high temperatures Young's Modulus are of the order $10^6 - 10^7\text{Nm}^{-2}$ and extensions of 100% are easily achieved before fracture [1]. At intermediate temperature, called the glass transition range, the polymer is neither glass nor rubber-like with an intermediate modulus. Figure 1.1 shows a whole range of phenomena that can be displayed by a single polymer as the temperature is change.

A knowledge of thermal properties is important when considering rapid (and hence adiabatic) deformation. When a test piece is compressed, some of the work done in producing the deformation will appear as heat. At low rates of deformation this heat will be lost to the atmosphere and compression will take place isothermally. At high rates of deformation the
FIGURE 1.1 A whole range of phenomena displayed by a single polymer as temperature is change [1].

FIGURE 1.2 Effect of temperature on the rigidity of PEK and PES [20].
heat will be generated too quickly to be lost [19]. Compression will therefore take place adiabatically, and the temperature of the test piece will increase as compression proceeds.

The mechanical work is provided by the deforming sample and by friction. This work appears as heat in the near vicinity of the sample. The temperature rise in the deformation zone is considerable due to both plastic work or deformation and unusual friction conditions. A high temperature will occur if:

(i) The polymer has a large value for the product $\sigma \varepsilon$ at failure i.e. both that the energy dissipated during flow will be large, and also the stored energy density will be high;

(ii) For materials which undergo a phase transition the latent heat of fusion is small. This results in more of the energy going into raising the temperature than into a phase change.

The stress-strain properties of polymers are sensitive to the temperature at which they are determined. The modulus, yield strength and ultimate strength generally increase as the temperature decrease.

The effect of temperature on the rigidity of PEK and PES is shown in figure 1.2 [20]. PEK (semicrystalline) shows the higher modulus at temperatures below the glass transition temperature $T_g$, but then loses rigidity rapidly on passing through $T_g$ at 145°C. At 220°C PES (amorphous) loses all mechanical strength as $T_g$ is approached but PEK retains some rigidity until significant melting of the crystallites occurs in the region of 300°C.
If there were changes in crystallization during compression an increase in crystallinity would liberate heat. Hall [21] concluded that the transition from isothermal to adiabatic process in oriented polymers will occur within two decades of strain rate from $0.04$ to $4s^{-1}$, and the temperature rise during adiabatic process will have a marked effect on the stress-strain curve. At $T_g$, an amorphous polymer changes from a rigid glass to a rubber-like material. Semicrystalline polymers are a mixture of amorphous and crystalline materials. Since the degree of crystallinity of semicrystalline polymer can vary depending on thermal history, the glass temperature can change over a range of temperatures. These changes in $T_g$ which occur when polymers are tested above room temperature for a period of time will affect the strength of polymer when tested mechanically.

1.1.3 Crystallization And Orientation

Crystallization of polymers can occur when the molecular chains are aligned by orientation during deformation which may lead to strain hardening. The orientation processes arranged the molecules into adequate juxtaposition for them to take up positions of three dimensional order. It was early recognized that the X-ray diffraction pattern of a semicrystalline polymer shows both discrete reflections from the crystallites and diffuse scattering attributed to the amorphous regions [1].

During the cold drawing process (in a tensile test) very great changes in molecular arrangement take place especially near the yield point and beyond. The molecules tend to become highly oriented parallel to the
stretching direction. The crystallites in crystalline polymers also become rearranged so that the molecules line up parallel to the stretching direction.

Not all polymers which have a yield point show cold drawing. For instance, some low molecular weight polymers break at or just beyond the yield point. The short molecules cannot become highly enough oriented to prevent breaking of the polymer.

In some cases the crystal may become broken up into smaller units during this orientation process; but in other cases a recrystallization takes place. The crystals melt and then recrystallize in an oriented condition. As the molecules get more oriented, the material become stronger.

The fringed micelle model (figure 1.3) assumed that molecular chains alternate between regions of order (the crystallites) and disorder (the amorphous regions). The lamellar or folded chain theory deduced that molecular chains are folded back and forth within the crystal (figure 1.4). Chain folding as well as the more conventional threading of the molecules through the crystalline regions may be vital to the understanding of mechanical properties. At present it is thought that chain folding occurs as well as the more conventional threading of molecules through the crystalline regions (figure 1.5).

Oriented polymers possess anisotropic properties. Although some polymers possess isotropic bulk mechanical properties i.e. unoriented in macroscopic sense, they are not homogeneous in the microscopic sense, containing a spherulitic structure (clusters of disoriented crystallites containing amorphous material).
FIGURE 1.3 Fringed Micelle model [1].

FIGURE 1.4 Lamellar (folded chain) model [1].

FIGURE 1.5 Diagram of Hosemann [1].
1.2 OBJECTIVES

The main objectives of this research are:

(i) To obtain an adequate macroscopic description of the investigated polymer mechanical behaviour which relate stress and strain at various strain rate ranging from \(10^{-3} - 10^3 \text{s}^{-1}\);

(ii) To study the effect of environment temperature i.e. from 20°C (room temperature) to 200°C (maximum continuous use temperature for PEEK [20]) on these polymer at all ranges of strain rate;

(iii) To investigate the effect of the crystallinity and orientation on the mechanical behaviour of these polymers;

(iv) To use the results of these tests to investigate possible constitutive models for these polymers.

1.3 MATERIALS

The materials used in this work is semicrystalline Poly-ether-ether-ketone (PEEK) grade 150G, Poly-ether-ketone (PEK) grade 220G. An amorphous Poly-ether-sulphone (PES) grade 4100G was tested to provide complementary information. All of these materials are obtained from Wilton Materials Research Centre, ICI plc.

PEEK is a thermoplastic resin of some interest to certain elements of the aerospace industry. It has a repeat unit of three aromatic rings separated
by two ethers and one carbonyl group in that order (figure 1.6) [2]. The structure has been extensively characterized [22-24]. The glass transition temperature $T_g$ and melting point $T_m$ are about 144°C and 335°C respectively. The crystal unit cell of PEEK has been discussed by many workers [25-32].

PEK has a remarkably high glass transition temperature about 162°C and the melting point is 373°C [2]. Its structure comprises two aromatic rings separated by an ether and a carbonyl group (figure 1.7). Bulk properties of a typical PEEK and PEK available commercially are listed in table 1.1 [25].

All polymers used were machined from a plate. The thickness of the plate limited the size of the cylindrical compression samples. The samples were machined on a lathe from a single plate to eliminate the wide variation of material properties. Their configuration is a short cylinder of ~7.0 mm diameter and ~3.5 mm thick (i.e. thickness of the plate). This sample geometry is recommended by many workers [18]. It is good practice, however, for diameter/height ratio to be the same for all samples tested because the values of coefficient of friction $\mu$ are different at different strain rates.

Sample size can be an important influence on friction, since larger samples deformed at the same strain rate involve longer radial displacements at higher velocities than in the case of small samples [33]. Gorham et al. [34] discusses some of the main sources of error associated with a very high strain rate (up to $10^5 \text{s}^{-1}$) direct impact compression test which include friction conditions at sample interface and inertial effects that takes into account the motion of both surfaces.
FIGURE 1.6 Repeat unit of PEEK \(^2\)

FIGURE 1.7 Repeat unit of PEK \(^2\)
<table>
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<tr>
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<tr>
<td>Lattice parameters (Å)</td>
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<td>7.75</td>
</tr>
<tr>
<td>(a)</td>
<td>5.96</td>
<td>5.86</td>
</tr>
<tr>
<td>(b)</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>(c)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystal density</td>
<td>1430</td>
<td>1400</td>
</tr>
<tr>
<td>Measured amorphous density (kg m(^{-3}))</td>
<td>1272</td>
<td>1265</td>
</tr>
<tr>
<td>Main chain bond angle</td>
<td>123°</td>
<td>125°</td>
</tr>
<tr>
<td>(T_g) (°C)</td>
<td>154</td>
<td>144</td>
</tr>
<tr>
<td>Crystal melting point (°C)</td>
<td>367</td>
<td>335</td>
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</table>

TABLE 1.1 Bulk properties of a typical PEEK and PEK [25].
1.4 RESEARCH PROGRAMME

In experimental investigations of the mechanical behaviour of material, a variety of testing machine has been established for testing at high strain rates. Unfortunately, most systems measure the parameters involved as an interpretation of another parameter rather than directly measuring the parameters of interest. Alternatively these parameters are evaluated by trying to interpret them through the use of the theory of propagation of elastic-plastic wave in an instrumented bar.

During the test event, the sample deforms and transmits stress that can be expressed in simplest terms as the force-time and displacement-time curves. These two curves yield the stress-strain curve and provide data on the effective dynamic modulus of the material under the conditions of test.

The work reported here was all conducted in the compression mode, and usually deformation was concluded at a true axial strain of 0.6. It is evident that the maximum strain rate obtainable with the hydraulic machine is of the order of $10^5 \text{s}^{-1}$. Due to this restriction the drop weight was introduced. The dropweight impact test has been used by a number of workers in the high strain rate region ($10^2 - 10^3 \text{s}^{-1}$) and the usual mode of deformation is also compression [35-37].

In an attempt to achieve a test at a strain rates of $10^4 \text{s}^{-1}$, the author has developed a simple impact machine using a cross bow. At its present stage of development this machine is only able to produce strain rates in the order of $10^3 \text{s}^{-1}$. Earlier attempt using an air gun proved unsuccessful due to the small weight of the pellet compared to the dimension of the sample.
At low strain rates, i.e. the quasi-static loading, stress and strain are both measured from force and displacement independently. Load is normally measured with a load cell connected in series with the sample. Displacement is measured as the movement of the moving platen between the jaw in the hydraulic machine. When operating in the dynamic loading i.e. $7 \text{s}^{-1}$, it is necessary to carefully consider the compliance of the testing machines especially as this may differ dramatically depending on whether the machines is operating in tension or compression.

In the dropweight system, the force-time pulse is again detected using a strain gauged anvil in series with the sample and is then converted to a stress-strain curve by applying Newton's laws and assuming the sample deforms at constant volume [35-37]. In this method the initial velocity prior to impact is very crucial in the strain calculation. This is discussed in detail in section 3.1.2.2 (Strain Analysis). It is more realistic to measure the displacement of the sample directly rather than through calculation.

In this work two direct measurements of the strain has been established for the dropweight systems. In the Conventional Dropweight system, displacement of the sample is measured from the movement of the dropweight and the force measured by a strain gauged anvil whilst in the Improved Dropweight system, the radial displacement of the sample is captured by a high speed camera and the force measured via an accelerometer. In both systems, wave propagation effects are neglected and uniform stress and strains are assumed in the test sample although any non-uniformity can be detected from the photographs.

The advantage of using these two dropweight systems were that:
(i) In the Conventional Dropweight system the initial velocity before impact is not important in the axial strain measurement. The axial displacement is monitored continuously throughout the impact;

(ii) In the Improved Dropweight system the radial displacement of the deforming sample was known and hence the radial strain and deforming area were determined. The radial strain can be converted to axial strain through the poisson's ratio relationship with the assumption of volume conservation (see section 3.1.4 Volume Conservation And Poisson's Ratio Measurement). In this system, the small amount of displacement due to the compression of the anvil performed by dropweight experiments on the anvil alone (no sample) need not be calculated.

The fourth system used in this research is a semi direct impact Cross Bow system. In an earlier attempt the arrow was impacted directly on a sample mounted on a calibrated strain gauged anvil. This method of force detection was thought to be very accurate by hindering the wave propagation effects. Unfortunately, the contact time of the arrow which depends on the double transit time of the stress wave created ringing oscillations on the force-time trace produced by the strain gauged anvil.

The system was improved so that the force was measured using an instrumented bar and displacement monitored with an intermediate bar in contact with the sample. This method of sample displacement measurement needs a separate displacement reading from the intermediate bar alone (no sample) which is then used in the same manner as in the quasi-static test as a correction applied for machine compliance (details in section 3.2.6.1).

Tested and annealed PEEK and PEK samples were examined using wide angle X-ray diffraction. X-ray photographs of PEEK samples were
also taken using a 'Unicam' camera (see section 4.3.1). These photographs were scanned through a CCD (close circuit display) camera where intensity variations in the photograph can be quantified by a computer via a software package called Rheed Vision. Differential scanning calorimetry has been used to investigate crystallization and melting endotherm of the tested and annealed PEEK and PEK samples.

1.5 CONCLUSION

In experimental investigations of the mechanical behaviour of solid polymer in our work, four different devices have been used: a commercial hydraulic machine (Dartec), a Conventional Dropweight, an Improved Dropweight in conjunction with a C4 camera and a Cross Bow system. Since the later three apparatus differed in their facilities for signal detection and processing, some disparities arise, constituting a timely warning against over facile interpretations of the data generated by the instrumented apparatus. Nevertheless, all the experimental techniques provide a method of obtaining directly stress-time and strain-time profile at speed well in excess of those attained by mechanical devices and without the disadvantage of having to undertake a wave analysis in the sample.
CHAPTER 2
THEORY
2.0 THEORY

In most general terms polymers change from glass-like to rubber-like behaviour as either the temperature is raised or the time scale of the experiment is increased. A simple constitutive relation for the behaviour of a linear viscoelastic solid is obtained by combining two laws:

(i) For elastic behaviour, Hooke's law for elastic solids;

\[ \sigma_e = E \varepsilon \] ........................(2.1)

(ii) For viscous behaviour, Newton's law for viscous liquids;

\[ \sigma_v = \eta \frac{de}{dt} \] ........................(2.2)

where \( \sigma, \varepsilon \) and \( E \) are the stress, strain and Young's modulus respectively. \( \eta \) is the viscosity constant and \( t \) is the time. A possible formulation of linear viscoelastic behaviour combines these two equations, thus:

\[ \sigma = \sigma_e + \sigma_v \] ........................(2.3)

This makes the simplest possible assumption that the stresses related to strain and strain rate are additive.

The Eyring treatment of an activated flow process requires that the whole of the applied stress acts on the activated deformation process and is dependent upon the strain after yield being permanent [1]. The
applied stress induces molecular flow. To gain a molecular understanding of the theory of thermally activated processes, the Eyring viscosity theory is considered.

Deformation of polymer usually involves the motion of chain molecules or parts of a chain molecule over potential energy barrier. The basic motion of chain molecules could be either intermolecular (e.g. chain sliding) or intramolecular (e.g. a change in the conformation of the chain). This situation is illustrated schematically in figure 2.1.

With no stress acting, a dynamic equilibrium exists, chain segments moving with a frequency $\nu$ over the potential barrier $\Delta H$ in each direction where:

$$\nu = \nu_o \exp \frac{-\Delta H}{RT} \hspace{1cm} (2.4)$$

where $R$ is the gas constant=8.314JK$^{-1}$mol$^{-1}$ and $T$ is the temperature in degree kelvin. This equation states that the frequency of molecular conformational changes depends on the barrier height and not on the free energy difference between the equilibrium sites.

The temperature effect on $\nu$ is primarily through the activation energy $\Delta H$. $\nu_o$ involves the fundamental vibration frequency and the entropy contribution to the free energy. It is assumed that the applied stress $\sigma$ produces linear shifts $\beta \sigma$ of the energy barriers in a symmetrical fashion. We then have a flow:

$$\nu_1 = \nu_o \exp \left( \frac{-(\Delta H - \beta \sigma)}{RT} \right) \hspace{1cm} (2.5)$$
in the forward direction (i.e. the direction of application of the stress) and:

\[ v_2 = v_0 \exp\left( -\frac{(\Delta H + \beta \sigma)}{RT} \right) \quad \text{(2.6)} \]

in the backward direction. This gives a net flow:

\[ v' = v_1 - v_2 = v_0 \left( \exp\left( -\frac{\Delta H}{RT} \right) \left( \exp\left( \frac{\beta \sigma}{RT} \right) - \exp\left( -\frac{\beta \sigma}{RT} \right) \right) \right) \quad \text{(2.7)} \]

in the forward direction. If we assume that the net flow in the forward direction is directly related to the rate of change of strain, we have:

\[ \frac{de}{dt} = \dot{\varepsilon} = \dot{\varepsilon}_0 \exp\left( -\frac{\Delta H}{RT} \right) \sinh \frac{VA \sigma}{RT} \quad \text{(2.8)} \]

where \( \dot{\varepsilon}_0 \) is a constant pre-exponential factor and the symbol \( \beta \) is replaced by \( VA \), which is termed the activation volume for the molecular event. \( \dot{\varepsilon}_0 \) includes the factor 2.

For high values of stress \( \sinh \chi = \frac{1}{2} \exp \chi \) and:

\[ \dot{\varepsilon} = \frac{\dot{\varepsilon}_0}{2} \exp\left( -\frac{(\Delta H - VA \sigma)}{RT} \right) \quad \text{(2.9)} \]

This gives the yield stress in terms of strain rate as:

\[ \frac{\sigma}{T} = \frac{\Delta H}{VA T} + \frac{R}{VA} \ln \left( \frac{2 \dot{\varepsilon}}{\dot{\varepsilon}_0} \right) \quad \text{(2.10)} \]
FIGURE 2.1 The Eyring model for creep [1].

FIGURE 2.2 Pictorial representation of the 'internal' stress $\sigma_1$ (which depends on strain) and 'effective' stress $\sigma^*$ (which depends on strain rate) [40].
This equation suggests that the plot of yield stress/temperature against log strain rate for a series of temperatures should give a series of parallel straight lines.

Most studies of polymer plasticity [38-40] have shown that over a large range of strains and strain rates, the experimental data are better fitted with an additive equation of the type:

\[ \sigma(\varepsilon, \dot{\varepsilon}) = \sigma_i(\varepsilon) + \sigma^*(\dot{\varepsilon}) \].............(2.11)

In such a representation, illustrated schematically in figure 2.2, stress-strain curves at different strain rates are separated by a simple vertical shift. \( \sigma_i(\varepsilon) \) represents the internal stress and measures the effect of the true plastic strain accumulated in the material during the previous mechanical history of the sample. \( \sigma^*(\dot{\varepsilon}) \) traditionally called the effective stress, reflect the strain rate sensitivity of the material.

\[ \sigma^*(\dot{\varepsilon}) = \frac{kT}{V_A} \ln \left( \frac{\dot{\varepsilon}}{\dot{\varepsilon}_0} \right) \].............(2.12)

\[ \dot{\varepsilon} = \dot{\varepsilon}_0 \exp \frac{\sigma V_A}{kT} \].............(2.13)

where \( k = 1.381 \times 10^{-23} \text{JK}^{-1} \) is the Boltzmann constant and \( V_A \) called the apparent activation volume. \( \dot{\varepsilon}_0 \) incorporates both the probability of thermally aided deformation (i.e. the activation energy term) and the dependence of the microstructure on temperature.
CHAPTER 3

THE RESPONSE OF POLYMERS AT VARIOUS STRAIN RATES AND TEMPERATURES
3.0 THE RESPONSE OF POLYMERS AT VARIOUS STRAIN RATES AND TEMPERATURES

3.1 INTRODUCTION

3.1.1 Background

In much of the polymer work reported, investigations have mainly been carried out in the quasi static and low strain rate regions ($10^{-4}$ – $10^{-2}$ s$^{-1}$ and $10^{-2}$ – 1 s$^{-1}$ respectively). In medium ($1$ – $10^{2}$ s$^{-1}$) and high ($10^{2}$ – $10^{4}$ s$^{-1}$) strain rate tests, inertia forces begin to become important and possible mechanical resonances must be taken into account.

The more recent investigation of mechanical properties of large number of polymers in compression test include those of Walley [18], whose work covers wide range of strain rates, Gorham [33,41,42] and Pope et al. [43] who offer an analysis of the measurement at high strain rate including the effect of sample size or inertia and friction.

More recently Gorham and coworkers [44] have developed an improved method for compressive stress and strain measurements at very high strain rates of up to about $10^{5}$ s$^{-1}$. They used a direct impact test in which a cylindrical projectile impacts a sample that is supported on an instrumented pressure bar. The pressure bar is 3 mm in diameter and samples are 1 to 2 mm in diameter and 0.5 to 1 mm thick. Nevertheless, account must be taken of the usual problems of friction, radial inertia, plastic wave propagation within the sample and adiabatic temperature rise due to the plastic work of deformation. In addition, interpretation of the results may be confused by dynamic ringing of the load measurement system.
Hydraulic testing machines are used routinely at low strain rates for a variety of tests. At high strain rates, techniques involving use of the Split Hopkinson Pressure Bar (SHPB) system are very common. Nevertheless, it can be commented that the SHPB is unable to deform samples at high strain rates to large values of strain (up to 40%). For large values of strain, the dropweight machine is the simplest machine and give a strain rate of about $10^3 \text{s}^{-1}$.

3.1.2 Stress, Strain And Strain Rate Analysis

All the samples studied in the mechanical tests were in the form of short cylinders. The following sections describe the techniques used to interpret the data obtained.

3.1.2.1 Stress Analysis

In compression, a circular sample of diameter $d_0$, height $h_0$ and area $A_0$ will eventually change their dimension to $d(t)$, $h(t)$ and $A(t)$ with time $t$. Stress is measured as force $F$ per area $A$. The true compressive stress at any time $t$ is thus:

$$\sigma(t) = \frac{F(t)}{A(t)} \ldots \ldots \text{(3.1)}$$

$F(t)$ is the force measured at time $t$ from the load cell or a strain gauged anvil or accelerometer or an instrumented bar. Assuming the deformation is homogeneous and the sample volume is conserved, the area $A(t)$ at time $t$ is calculated as:
\[ A(t) = \frac{A_0 h_0}{h(t)} \ldots \ldots (3.2) \]

where \( h(t) \) is the measured height. Alternatively \( A(t) \) can be calculated directly from the measured radial expansion obtained from the high speed camera photograph.

### 3.1.2.2 Strain Analysis

In dealing with large deformations, it will be more meaningful to use true strain \( \varepsilon \) in the data reduction. Because the yield stress is achieved at a comparatively low strain it is often adequate to use the engineering definition of the yield stress and note that for small strain, engineering strain \( \varepsilon \) is equal to \( \varepsilon \).

The engineering strain \( \varepsilon \), which is often used in the linear elastic analysis of polymers is defined as:

\[ \varepsilon = \frac{\Delta h}{h_0} \ldots \ldots \ldots (3.3) \]

and an increment of strain is:

\[ d\varepsilon = \frac{dh}{h_0} \ldots \ldots \ldots (3.4) \]

If in place of \( h_0 \) in equation (3.4) we write \( h \), then:

\[ d\varepsilon = \frac{dh}{h} \ldots \ldots \ldots (3.5) \]
and \(de\) is defined as an increment in natural or logarithmic strain (also called true axial strain). The true strain \(\varepsilon\) imposed is:

\[
\varepsilon = \int de = \int \frac{dh}{h} = \ln \left( \frac{h}{h_0} \right)
\]

Thus the true axial strain \(\varepsilon_A\) at any time \(t\) is calculated as logarithmic \((h(t)/h_0)\). One of the limitations of the Conventional Dropweight system [35-37] is that the axial strain is generally not measured but inferred from the acceleration of the dropweight. With the initial velocity of impact as \(v_0\) (measured by a velocity measuring unit), the velocity \(v(t)\) at any time \(t\) can be calculated as:

\[
v(t) = v_0 - \int a(t)dt
\]

where \(a(t)\) is the acceleration at time \(t\) and defined as:

\[
a(t) = \frac{F(t)}{M}
\]

\(F(t)\) is the force measured by the strain gauged anvil and \(M\) mass of the falling weight. The sample displacement \(u(t)\) is defined as:

\[
u(t) = \int v(t)dt = \int v_0 dt - \int \int (a(\tau)d\tau)dt
\]

The true axial strain of the sample at time \(t\) is:

\[
\varepsilon(t) = \ln \left( \frac{h(t)}{h_0} \right) = \ln \left( \frac{h_0 - u(t)}{h_0} \right)
\]
In this work the system is improved by calculating $\varepsilon_A$ directly from the measured displacement $u(t)$, except in the Improved Dropweight system where the axial strain is calculated from the radial strain obtained from the photograph. Both systems are fully described later in section 3.2.4 and 3.2.5 respectively.

3.1.2.3 Strain Rate Analysis

Many low strain rate tests are carried out using a loading system consisting of a cross head moving with constant velocity. A constant displacement rate is admittedly not a constant strain rate. The deviation will be the difference between the engineering strain $\varepsilon$ and true strain $\varepsilon$ divided by the time. The relationship between the engineering and true strains is given by:

\[
\varepsilon = \ln \left( \frac{h}{h_0} \right) \quad \text{from (3.6)}
\]

\[
= \ln \left( 1 + \frac{\Delta h}{h_0} \right)
\]

\[
= \ln(1 + \varepsilon) \quad \text{(3.11)}
\]

In an ideal compression test, uniform deformation under a compression velocity $v$ will give a strain rate

\[
\dot{\varepsilon} = \frac{v}{h} \quad \text{(3.12)}
\]

at any point in the sample where $h$ is the current height of the sample. It is important to recognize that the strain rate during a dynamic test (i.e.
the hydraulic ram), particularly if large strains are involved, is not
constant. Owing to this inconsistency, the strain rate is simply measured
as a best fit gradient of the true axial strain against time over the plastic
region.

3.1.3 Inertial And Frictional Restraint In Compression Test

The most frequent objection to any form of compression test is that the
effects of friction are difficult to determine and eliminate. The further
problem of buckling encountered in simple compression of cylinders also
occurs. There is no sample geometry in direct impact for inertial stresses
to be zero. Further complications may arise from two effects which could
lead to volume changes. The first is adiabatic heating due to plastic work;
volume increase of ~2% at a strain of 0.8 if the polymer were
unconstrained. The second is compression due to the hydrostatic
pressure $\sigma/3$ of the uniaxial stress field of magnitude $\sigma$.

Inertial restraints imposed by both radial and longitudinal particle
acceleration in the sample could be reduce by using samples having
dimensions which satisfy the Davies-Hunter criterion:

$$h_0 = \sqrt[3]{\frac{3}{4} d_0 v} \ldots \ldots (3.13)$$

where Poisson's ratio $v$ is set equal to 0.5. Sample size can be an
important influence on friction, since larger sample deformed at the
same strain rate involve longer radial displacements at higher velocities
than in the case of small sample [33]. Davies and Hunter cite the analysis of Siebel which leads to the relation:

\[ p = \left( \frac{1 + 2 \mu r}{3h} \right) \sigma \] 

(3.14)

where \( p \) is the measured mean pressure, \( r \) and \( h \) the sample radius and height respectively, \( \sigma \) the material stress and \( \mu \) is a coefficient of friction that is assumed constant over the interfaces.

Walley et al. [18] decreased the size of the sample while maintaining the same aspect ratio of \( d_0/h_0 \) at the very highest strain rates \((10^4 \text{s}^{-1})\) to ensure that the contribution of inertial stresses to the measured yield pressure was minimal. In this work sample size was constant for all tests maintaining a constant \( d_0/h_0 \) ratio.

Interfacial friction plays a critical role and is unavoidable in compression test. To tackle the problem Walley et al. [18] searched for a way to reduce friction significantly, if possible to a sufficiently low level so as not to mask the essential features of the material behaviour. Lubrication, for instance helps reduce the interfacial friction. In this study, all samples ends were lubricated with petroleum jelly to reduce friction.

At low strain rate, the quasi-static test, friction at the lower and upper end on the sample are equal, hence deformation of the sample and eventually barrelling are uniformly distributed at the centre of the sample height. At high strain rate, friction is usually lower at the moving end (dynamic coefficient of friction) compared with the stationary end (static coefficient of friction).
To obtain uniform and equal radial movement at both ends of the sample in the high strain rate test, ideally both ends should move with the same velocity. Unfortunately, this creates problems with equipment design and the measurements of stress and strain.

3.1.4 Volume Conservation And Poisson Ratio Measurement

Frequently, in calculations concerning extensive plastic deformation, it is assumed that there is no change in volume of the material. For no change in volume, consider a cylindrical block of initial height $h_0$ and diameter $d_0$ uniformly compressed by a principal stress $\sigma$ to become a cylinder whose dimensions are $h$ and $d$. The equation for no volume change is then:

$$Ah = A_0h_0$$

$$\pi r^2h = \pi r^2h_0$$

$$\pi \left( \frac{d}{2} \right)^2 h = \pi \left( \frac{d_0}{2} \right)^2 h_0$$

$$\left( \frac{d}{d_0} \right)^2 = \frac{h_0}{h}$$

$$2 \ln \left( \frac{d}{d_0} \right) = \ln \left( \frac{h_0}{h} \right)$$

$$2 \ln \left( \frac{d}{d_0} \right) = -\ln \left( \frac{h}{h_0} \right)$$

$$2\varepsilon_R = \varepsilon_A$$
The expression \( \varepsilon_R \) and \( \varepsilon_A \) denote the true radial and axial strain respectively and \( \nu \) denotes poisson ratio. In this work the assumption of \( \nu = 0.5 \) for poisson's ratio is checked by measurement in the quasi-static test using an Instron machine.

The true radial strain \( \varepsilon_R \) is calculated as logarithmic \( \left( \frac{d(t)}{d_0} \right) \). The diameter of the deforming sample is viewed through a video camera and captured images are printed through a computer using software package called VIDI-PC. The video camera used was a Panasonic WVP-F10E with a Sony 'Super Beta hi-fi' video recorder, and using Sony Dynamicron PRO-X/L-250 tape. Figure 3.1 shows one typical printout of the sample diameter.

At the same time the height of the deforming sample is measured through a displacement transducer (TML UB5 Tokyo Sokki Kenkyuyo Co.Ltd. Ser. No. 012363). The technical data and calibration curve of this transducer is given in table 3.1 and figure 3.2 respectively. The height of the sample is monitored as voltage output from the transducer and the calibration factor of the transducer is 5.324mV(mm)\(^{-1}\). This measurement yields the true axial strain \( \varepsilon_A \).

Poisson ratio is calculated as the ratio of radial strain to axial strain using a program in Basic2 called Poisson.Bas (see appendix 1). Figure 3.3 shows the apparatus configuration in the poisson ratio measurement and figure 3.4-3.6 shows the plot of \( \varepsilon_R \) against \( \varepsilon_A \) for PEEK, PEK and PES respectively. Steps in plot are due to the camera resolution. Best line fits are used to calculate \( \nu \).
FIGURE 3.1 Typical printout of sample diameter from video.
### TABLE 3.1 Technical data for TML UB5 displacement transducer

<table>
<thead>
<tr>
<th>Capacity (Measuring range)</th>
<th>Date</th>
<th>Temperature</th>
<th>Humidity</th>
<th>Rated output (μV/V)</th>
<th>Sensitivity (μV/V)</th>
<th>Non-linearity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 (2.0-7) mm</td>
<td>1990.4.26</td>
<td>23°C</td>
<td>65%</td>
<td>2720</td>
<td>5440 × 10^-6</td>
<td>0.6%</td>
</tr>
</tbody>
</table>

**Bridge configuration**
- (Full bridge method)
- Input: Red (A) × Black (C)
- Output: Green (B) × White (D)

**Safe excitation**
- Input: 350 V (AC or DC)
- Output: 0.08 mm²

**Fitting Equation**
\[ Y = 5.324X - 11.27 \]
FIGURE 3.3 Apparatus configuration for poisson ratio measurement.
FIGURE 3.4
Plot Of Radial Strain Versus Axial Strain For PEEK
Poisson Ratio=Curve Gradient=0.48
FIGURE 3.5
Plot of Radial Strain Versus Axial Strain For PEK Poisson Ratio=Curve Gradient=0.53
FIGURE 3.6
Plot of Radial Strain Versus Axial Strain For PES Poisson Ratio=Curve Gradient=0.47.
All the three samples produced a poisson ratio of $-0.5$ for strain up to 30%. From this results it is concluded that there is no volume change in the sample with the geometry stated in equation (3.13) during quasi-static homogeneous compression. This conclusion is assumed to be true during dynamic (high strain rate) homogeneous compression so that the relation $\varepsilon_R/\varepsilon_A$ is always constant throughout the whole compression. This assumption has generally been accepted without question in the work of other investigators.

3.2 EXPERIMENTAL

The objective of this work was to investigate polymer response over a range of strain rates and temperatures. This involved using several different types of apparatus. The problem is that it is not possible to obtain from a single experimental technique a complete range of strain rates and thus several experimental techniques were involved in data collection.

With the hydraulic testing machine a range of strain rate from $10^{-4} - 10^{5}$ could be covered and with a Conventional Dropweight a range from $10^{2} - 10^{3}$ s$^{-1}$ was achieved. Two other experimental methods, an Improved Dropweight and Cross Bow systems have also been employed. The work to be described is concerned with the techniques and the testing of PEEK, PEK and PES under conditions of low and high strain rate at various temperature ranging from 20 to 200°C.
3.2.1 Data Transfer

In all the work described in this thesis, the Thurlby DSA 524 digital storage adaptor is used to capture signals from two channels. Most instrumental impact test systems have two selectable methods of triggering data collection, which are analogous to internal and external triggers on a digital oscilloscope. The former uses a rise in the load signal above a preset threshold value to trigger data collection, and the later generally uses the passage of a flag attached to the impactor through a light beam and photodetector to provide a trigger signal. An adequate number of data points collected prior to the trigger signal is saved as pretrigger information.

Immediately after a test, the digitized data from the DSA under DS-PC link software control are permanently stored in a floppy diskette. The permanently stored data is usually 4224 bytes from each recorded digitized memory. This large memory enables the complete signal from the test to be captured.

The signal captured consists of 4096 samples in compressed mode and in ordinary scan mode it only display 1028 samples. The signal from the scan mode can also be magnified ten times in the magnified mode. A suite of computer programs in Basic2 called DSA.BAS (see appendix 2) has been developed by Z.Xinwu (Physics Department internal report) for data translation. This program translates the ASCII format data to digital in real time and voltage.

3.2.2 Elevated Temperature Testings

Tests were carried out at room temperature and at elevated
temperatures. For the elevated temperature tests the polymer samples were mounted on a bar of mild steel which is heated by soldering iron elements. The heater temperature was controlled by a thermostat which has a range of 0-400°C.

The temperature of the sample immediately before testing was measured by means of a series of calibration experiments with a standard sample (see figure 3.7). The standard sample was drilled with a small hole and a thermocouple inserted into it. The hole was then covered with high temperature glue to ensure that the thermocouple reads the temperature inside the hole.

The rise time of the standard sample in achieving the required temperatures were less than 10 minutes. Nevertheless, in all experiments at elevated temperatures, the sample was allowed to reach thermal equilibrium (when a steady state temperature had been achieved) for 30 minutes prior to testing. It is estimated that with these precautions, the quoted temperature are accurate to ±2°C and that the maximum non uniformity of temperature is of similar order.

In tests performed using the hydraulic ram, the heater was clamped onto the lower platen where it acted as an anvil for the sample to rest on. In the Conventional Dropweight system, the sample together with 2 roller steels (miniature platens) were heated instantaneously before testing. The sample in the Improved Dropweight system was heated separately from the anvil which was itself heated simultaneously by 4 soldering iron elements. In the Cross Bow system the sample and the bar ends were heated together.
FIGURE 3.7 THE HEATER CONFIGURATION
3.2.3 Static And Dynamic Test

(Quasi-static and low regions strain rates test)

This investigation was performed to study the effect of temperature at two different strain rates namely $3 \times 10^{-3} \text{s}^{-1}$ termed as quasi-static test and $7 \text{s}^{-1}$ termed as dynamic test. The compression test were carried out using the Dartec hydraulic machine.

3.2.3.1 The Dartec Hydraulic Machine

Figure 3.8 shows the M1000/RE-50/100 kN straining frame. Plate 1 shows the Dartec Hydraulic machine. This test frame is designed for static or fatigue testing. It is designed for mounting a Dartec 50/100 kN servo jack unit and load cell. This machine was able to perform compression tests with the crosshead speeds of up to $2 \text{ms}^{-1}$. The maximum load limit is 50 kN and the machine is capable of a maximum displacement of 100 mm.

Static mean or peak values of load and stroke signals may be observed on the meter i.e. the digital indicator on the control panel. Display of the load and stroke is in real units (kN, mm).

The variables (in volt) may be recorded or displayed on an oscilloscope or some other instrument by connecting it to the output sockets on the panel. For load signal, 1 volt represents 5 kN whilst the stroke signal, 1 volt is equivalent to 10 mm. All the tests were done on stroke control.

3.2.3.2 The DSA Unit Setting

(i) Quasi-static test signal

Figure 3.9 shows the typical load and stroke signals obtained in a static
FIGURE 3.8 Dartec M1000/RE-50/100 hydraulic machine straining frame
TIME BASE = 20S
CH1 V/DIV = 100mV  Displacement (mm)
CH2 V/DIV = 0.5V  Load (kilonewton)

FIGURE 3.9 Load and stroke signals from quasi static test
test. The DSA setting for this test is as follows:
Channel 1: 0.5 V/div
Channel 2: 100 mV/div
Time base: 20 s/div

The duration of the test is -200 seconds and the compression is done by the stroke control on a ramp wave function. The crosshead speed in this test is calculated by distance travel per time duration from the stroke signal. The speed is estimated as -0.01 mms⁻¹. Since the test is slow, the signals are recorded in the roll mode of the DSA.

(ii) Dynamic test signal
Figure 3.10 shows the typical load and stroke signals obtained in a dynamic test. The DSA setting for this test is as follows:
Channel 1: 1 V/div
Channel 2: 100 mV/div
Time base: 5 ms/div

The duration of the test is -100 ms and the compression is done by the stroke control on a saw tooth wave function. The crosshead speed is calculated by the same method in the static test and estimated as -20 mms⁻¹. Since the test is fast, the signals are recorded by single trigger when the load commences.

3.2.3.3 The Machine Compliance

The load and stroke signals of the machine alone is shown in figure 3.11. Figure 3.12 shows the load displacement curve for machine compliance, PEEK, PEK and PES from quasi-static test at room temperature, calculated using the LOADDISP.BAS program (appendix 3.3). It is
FIGURE 3.10 Load and stroke signals from dynamic test
TIME BASE = 10S
CH1 V/DIV = 20mV  Displacement (mm)
CH2 V/DIV = 1V    Load (kilonewton)

FIGURE 3.11 Load and stroke signals from machine only
FIGURE 3.12
Load And Displacement Curve From Machine, PEEK, PEK And PES
necessary to carefully consider the compliance of the testing machine, especially as this may differ dramatically depending on whether the machine is operating in tension or compression.

The machine compliance curve is calculated using a polynomial fitting obtained from the Grapher Golden software package. The machine compliance equation is \[ Y = 67.25X^2 + 39.24X \] where \( Y \) and \( X \) are the load in kilonewton and displacement in millimetre respectively. Figure 3.13 shows the curve obtained from the polynomial fitting. Considering the machine as hard, the machine compliance is assumed to be the same at all crosshead speeds.

In the stress-strain measurement, the sample displacement was calculated by subtraction of the compliance curve from the total load-displacement curve of the sample. Figure 3.14 shows the difference in stress-strain curve for PEK at room temperature static test when the machine compliance is taken into consideration.

3.2.3.4 Data Analysis

The stress and strain are calculated by a program IPTME.BAS (Appendix 3.4). This program reads data from the sample parameter file (specifies the diameter \( d_0 \) and height \( h_0 \) of the sample) and data from the load and displacement translation files.

The base value of the load signal is set as zero load in the program. The starting point for the displacement is assigned by the program to correspond to the starting point of the load. All calculations assumes the samples volume is conserved i.e. poisson's ratio equals 0.5.
FIGURE 3.13
Dartec Hydraulic Machine Compliance Curve
Fitting Equation: \( Y = 67.25X^2 + 39.24X \)
FIGURE 3.14
Stress Against Strain For PEK From Quasi Static Test At 20°C With And Without Machine Compliance
The true stress: \[ \sigma(t) = \frac{F(t)}{A(t)} \]

where \[ F(t) = k_L V_L(t) \]

\[ k_L = 5 \text{ kN}V^{-1} \text{ and} \]

\[ V_L(t) \text{ is the load signal in volts} \]

and \[ A(t) = \frac{A_0 h_0}{h(t)} \]

where \[ A_0 = \pi \left( \frac{d_o}{2} \right)^2 h_0 \]

\[ h(t) = h_0 - u(t) \]

\[ u(t) \text{ displacement at time } t \]

\[ u(t) = k_o V_o(t) \]

\[ k_o = 10 \text{ mm}V^{-1} \text{ and} \]

\[ V_o(t) \text{ the displacement signal in volts.} \]

True axial strain: \[ \varepsilon_A(t) = \ln \frac{h(t)}{h_0} = -\ln \frac{h_0 - u(t)}{h_0} \]

The strain rate: \[ \dot{\varepsilon}_A(t) = \frac{d\varepsilon_A}{dt} \]

3.2.3.5 Results

Figure 3.15-3.17 shows the plots of stress against strain for PEEK, PEK and PES respectively from the quasi static test for temperatures between 20 to 200°C. Figure 3.18-3.20 shows similar plots from dynamic tests.
FIGURE 3.15
True Stress Against True Axial Strain For PEEK From Quasi Static Test At 20°C To 200°C
FIGURE 3.16
True Stress Against True Axial Strain For PEK From Quasi Static Test At 20°C To 200°C
FIGURE 3.17
True Stress Against True Axial Strain For PES From Quasi Static Test At 20°C To 200°C
FIGURE 3.18
True Stress Against True Axial Strain For PEEK From Dynamic Test At 20°C to 200°C
FIGURE 3.19
True Stress Against True Axial Strain For PEK From Dynamic Test At 20°C to 200°C
FIGURE 3.20
True Stress Against True Axial Strain For PES From Dynamic Test At 20°C to 200°C
3.2.4 The Conventional Dropweight System (strain rate $10^2 \text{s}^{-1}$)

The instrumented impact tester in this study, which is functionally equivalent to that used by Field, Swallowe, Pope and Palmer [45], was initially built by Dawson [37] to establish an experimental facility to operate at a strain rate of $10^2 \text{s}^{-1}$. The free fall dropweight is positioned within 3 guide rods, as shown in figure 3.21. Plate 2 shows the Conventional Dropweight system with the laser-photodiode unit and velocity measuring unit attached to it.

The base was a cast iron workshop anvil of 80 kg mass resting on a concrete floor. The dropweight incorporated a hardened steel roller which impacted the sample assembly. The weight weighed 10 kg. Dawson used the system to measure stress via a strain gauged anvil and convert the force to strain through double integration of the acceleration and velocity (see equation 3.9) This calculation is highly dependent on the accurate knowledge of the impact velocity and is therefore prone to error.

An earlier attempt by the author was to make direct measurement using a two lever (jaw) displacement transducer. It created severe problems due to misalignment and initial compressive resistance from the lever itself. A second attempt was to use a piston type transducer. Although the problem of alignment was overcome shock during the initial impact gave an unpredictable overshoot to the signal. A method considered successful was the use of a photodiode targeted with a laser beam.

In our system, the stress is measured via a strain gauged anvil and the
FIGURE 3.21: CONVENTIONAL DROPWEIGHT SYSTEM CONFIGURATION
Plate 2  Conventional Dropweight System
strain is directly measured from the displacement of the dropweight when passing through a laser beam which is targeted to a large area photodiode.

The strain gauge used in the load measurement is from Kulite Sensors Ltd., type S/ULP-120-160 (gauge factor 55±5% at 75°F, resistance 120±10% ohms). The gauges are attached opposite to each other using a super glue on flat surfaces ground on roller r.".

These gauges are connected in series so that the resistance change induced by impact would be due to compressive stresses only. Any bending of the rollers causing an increase in the resistance of one gauge should be cancelled out by the decrease in the resistance of the gauge diametrically opposite.

The photodiode used to measure the displacement is an RS Medium Area 41.3 mm². Table 3.2 shows the technical data of this diode and figure 3.22 shows a simple circuit to operate the photodiode in a reverse bias. The laser used to illuminate the photodiode is Imatronic LDM 135 Laser Diode Module. Figure 3.23 shows the LDM 135 typical application.

3.2.4.1 Calibration

The strain gauged anvil was calibrated statically using an Instron machine up to a force of 5000 kg. The gauge was connected in series with a 330Ω resistor R1. A simple measuring circuit (figure 3.24) is used connected to a stabilised 15V constant supply voltage. The output voltage across R1 was recorded with a four figure Fluke 8050A digital
Medium Area 41.3mm²

**technical specification**

- Peak spectral response: 800 nm
- Peak responsivity: 0.5 A/W
- Active area: 41.3 mm²
- Dark current: 4 nA (Vₐ = 1 V)
- Capacitance: 325 pF (Vₑ = 0 V)
- Reverse breakdown voltage: 60 V
- Response time: 25 ns (Vₑ = 10 V, Rₑ = 1000)
- Operating temperature range: -40°C to +70°C

**TABLE 3.2** Technical data for RS Medium Area photodiode

---

**FIGURE 3.22** Circuit diagram for the photodiode

- 5 VOLT TTL
- LASER
- TO DSA
FIGURE 3.23 LDM 135 Typical Application

FIGURE 3.24 Circuit diagram for voltage stabiliser
voltmeter. The resulting plot of force versus voltage is given in figure 3.25, the gradient gives the calibration factor of 190,098 NV⁻¹.

The photodiode was calibrated statically by cutting the laser beam with the blade of a two figure digital vernier ("Digimatic Model CD-6" serial 7154796 Mitutoyo Corporation). The output voltage was recorded by digital voltmeter. Figure 3.26 shows the plot of the static calibration. The dynamic calibration was done by dropping a dropweight and recording the output voltage continuously when the dropweight passes through the laser beam. The pulse obtained is a trace of voltage against time (see figure 3.27).

To obtained a trace of voltage against displacement, the time axis of the output pulse is converted to displacement axis by multiplying with the velocity of the dropweight while crossing the laser beam. Since the displacement within the photodiode is small the velocity is assumed constant. The velocity is measured by the velocity measuring unit. Figure 3.28 shows the plot of the dynamic calibration. It can be commented that the curve is not linear at the beginning and at the end of the trace. Nevertheless the linear part between 2.4 to 4.4 mm (i.e. 2 mm displacement compare with 3.5 mm sample thickness) is sufficient to incorporate strain measurement in the sample which only consider strain up to 60%.

3.2.4.2 Velocity Measuring Unit

If the weight and guided rod friction are neglected, the velocity just before impact is:

\[ v = \sqrt{2gh_d} \] ..........................(3.16)
FIGURE 3.25
Load Versus Voltage For Strain Gauged Anvil
Fitting Equation: $Y = 190.10X - 276.66$
FIGURE 3.26
Static Calibration For Medium Area Photodiode
Fitting Equation: $Y = 0.04284X + 1.808$
FIGURE 3.27
Voltage Against Time For Dynamic Calibration of Medium Area Photodiode
FIGURE 3.28
Dynamic Calibration For Medium Area Photodiode
Fitting Equation: \( Y = 42.74X + 0.567 \)
where \( g = 9.8 \text{ms}^{-2} \) and \( H_d \) the height of the weight from the base. Since the velocity is very crucial in calibration of the photodiode, a velocity measuring unit was employed. It consisted of two photodiodes and a laser beam with beam splitters (figure 3.29). The position of the measuring unit is located at the same height as the large area photodiode to be calibrated.

The beams shone onto two BPX 65 photodiodes 1.3 cm apart, and the time taken for the dropweight to fall between the two diodes was measured using a Gould (DSO) 400 dual beam storage oscilloscope. The velocity was taken as the distance between the diodes divided by the time taken to fall between them. The time was measured at the start of the voltage-time peaks for the diodes as shown in figure 3.30.

### 3.2.4.3 Accuracy of the measuring technique

Figure 3.31 shows a typical load and displacement signals obtained by impacting pure aluminium which had been annealed at 400°C for 4 hours. Figure 3.32 shows the stress-strain curve obtained from these signals. Aluminium was used because of its low yield stress and virtually all of the sample deformation on impact is permanent. Hence the final strain from analysis of figure 3.32 should be equal to the calculated strain from initial and final height of the sample after impact using equation 3.6.

The final strain measured from figure 3.32 was 134% while the final strain calculated using equation 3.6 was 123% (initial and final height are 2.93 and 0.85 mm respectively). This big error ~10% at the maximum
FIGURE 3.29 Velocity measuring unit

FIGURE 3.30 Pulse obtained from velocity measuring unit
FIGURE 3.31 Load-displacement signal for pure annealed aluminium
FIGURE 3.32
Stress against strain for aluminium annealed at 400°C for 4 hours.
strain can be argued as due to the nonlinear response of the photodiode at large displacement (see section 3.2.4.1) and also the thickness variation of the aluminium sample due to cutting processes.

Compression of rollers (also called the machine compliance) might also contribute to the final strain. Load-displacement measurements of the compliance have also been subtracted from the load-displacement sample results, but make no significant difference when testing the soft polymer. Assuming the deformation is homogeneous, at 40% strain considering only the linear part of the voltage-displacement curve, the error in the strain measurement is only 3% (i.e., $\frac{40\%\varepsilon}{134\%\varepsilon} \times 10\%\text{error}$).

3.2.4.4 Data Analysis

The true stress and strain are calculated by a program DROP.BAS (appendix 3.5). This program operate similar to IPTME.BAS except that the force calibration factor is:

$$k_L = 190,098 \, \text{N}^{-1}$$

while the displacement calibration factor:

$$k_D = 0.043 \, \text{mm(mV)}^{-1}.$$  

3.2.4.5 Results

Figure 3.33-3.34 shows the plot of true stress against true strain for PEEK and PEK for the whole range of temperatures (20-200°C) investigated.
FIGURE 3.33
True Stress Against True Axial Strain For PEEK From Dropweight Test ($10^2$ s$^{-1}$) At 20°C To 200°C
FIGURE 3.34
True Stress Against True Axial Strain For PEK
From Dropweight Test ($10^2$ s$^{-1}$) At 20°C To 200°C
3.2.5 The Improved Dropweight And C4 Camera

A dropweight apparatus that allows high speed photography of the deforming sample viewed along the impact axis through transparent anvils has also been developed (see figure 3.35). Plate 3 shows the Improved Dropweight machine. The fundamental apparatus for the Improved Dropweight system consists of an instrumented dropweight machine and high speed Atomic Weapon Research Establishment (A.W.R.E) C4 camera.

The film used was Ilford HP5 aerial film which was available in a roll. It was developed in Ilford ID-11 developer to produce negatives of a reasonably fine grain and adequate contrast.

Force-time curve for the impact process was obtained with the aid of a Bruel and Kjaer type 4343 accelerometer fixed to the falling weight (see figure 3.35). The output from the accelerometer was connected to a Bruel and Kjaer type 2626 conditioning amplifier linked to a digital storage adaptor DSA 524.

The high speed photographic experiment was undertaken in order to provide detailed visual information in the behaviour of a sample under impact. The photographic sequences show the sample before impact and then reveal several phenomena: elastic deformation, plastic flow and fracture. The radial expansion of the sample gives the strain and strain rate data.

Since two separate instrument are involved in the system, synchronization of the measuring apparatus is extremely important in
FIGURE 3.35: IMPROVED DROPWEIGHT SYSTEM CONFIGURATION
Plate 3 Improved Dropweight Machine
any study with this improved system. Special precautions are therefore taken in designing and synchronizing the dropweight with the camera.

The objectives of this improved system are:

(i) To provide an impact loading on a cylindrical sample, with the requirement that the deformation be uniaxial along the axis of the cylinder and symmetric about this axis.

(ii) To measure the force history of the applied force on the sample. The stress can be derived from simultaneous measurements of the impact force-time profile and area expansion of the sample from the photograph.

(iii) To measure the response of the sample to the aforementioned loading. This was a direct measurement of the radial expansion of the sample to avoid introducing any unnecessary assumptions. This measurement provide the true radial strain of the sample. The axial strain was derived from the radial strain through the Poisson ratio relationship ($\varepsilon_r/\varepsilon_A = 0.5$).

3.2.5.1 The Dropweight

Impact energy is transferred to a sample by the free, but guided, fall of a dropweight coupled to an accelerometer. The accelerometer measures the acceleration of the dropweight during impact. The dropweight was dropped from a specified height with a spring assisted catch. The impactor attached to the dropweight and the anvil are made of pilkington
armour plate glass discs and the impact process was photographed in transmitted light.

The dropweight was hollowed out to allow light to pass through it (see figure 3.35). Light was reflected from the mirror through the anvil to the prism from which it went to the camera. The upper glass disc was held in a recess in the weight with plasticine. The dropweight triggers the flash just prior to striking the sample by means of an electrical contact between a brass pin screwed into the falling weight and a piece of spring steel (near the anvil) connected to the flash.

3.2.5.2 The Accelerometer: Principle Of Operation

Figure 3.36 shows the configuration of the Bruel and Kjaer type 4343 accelerometer. The crystal is preloaded to about 2 MPa stress by screwing down the cap on the hemispherical spring. This prestressing puts the piezoelectric material at a more linear part of its stress charge curve. It also allows measurement of acceleration in both directions without the crystal going into tension. When the preload is applied, a voltage of certain polarity is developed but this soon leaks off to zero. Any further deflection (due to acceleration forces) gives a plus or minus charge, depending on the direction of the motion. Table 3.3 shows the technical data of the accelerometer used.

3.2.5.3 Calibration Methods:

(i) The Sinusoidal Motion Calibration Methods

The accelerometer was calibrated by a Bruel and Kjaer Vibration Pick-up
TABLE 3.3 Technical data for Bruel and Kjaer accelerometer type 4343
FIGURE 3.36 Brul and Kjaer Type 4343 accelerometer

FIGURE 3.37 Plot of voltage produced from accelerometer

acceleration ~1g
Preamplifier type 1606. It is mounted on a built-in shaker table of the preamplifier. The sinusoidal motion method is exemplified by the calibration facility of the National Bureau of Standard [46]. This consists of a modified electrodynamic vibration shaker which has been carefully designed to provide uniaxial pure sinusoidal motion and which is equipped with an accurately calibrated moving coil velocity pickup to measure its table motion.

Figure 3.37 shows the plot of the voltage produced from the accelerometer when the acceleration is equivalent to $g$ ($9.8 \text{ms}^{-2}$). The calibration factor $K$ is calculated as following:

Conditioning Amplifier Setting = $0.01g^{-1} \text{Vm}^{-1}\text{s}^{2}$

Peak to peak voltage of the signal at $1g = 21.2 \text{mV}$

\[
9.8 \text{ms}^{-2} = \frac{21.2}{2} \text{mV}
\]

\[
K = \frac{9.8}{10.6 \times 10^{-3}} = 925 \text{ V}^{-1}\text{ms}^{-2}
\]

(II) Transient Motion Calibration Method

The drop test method is of great interest. It employ the concept that the velocity change $dv$ during a time interval $dt = t_2 - t_1$ is given by:

\[
dv = \int_{t_1}^{t_2} adt ...................(3.17)
\]

where $a$ is the acceleration. The procedure involves measurement by some independent means, of the velocity change $dv$ of a rigid body to
which the pickup is attached and simultaneously recording of the output voltage $V_o$ of the pickup. This output voltage is given by:

$$V_o = K'a \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3.18)$$

$$a = \frac{V_o}{K'} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3.19)$$

where $K'$ is the unknown sensitivity $Vm^{-1}s^2$ of the pickup. Thus we may write:

$$dv = \int_{t_1}^{t_2} \frac{V_o dt}{K'} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3.20)$$

$$K' = \int_{t_1}^{t_2} \frac{V_o dt}{dv} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3.21)$$

The main usefulness of the above transient techniques lies in their ability to provide high acceleration values (up to several thousand g's) with large high frequency content (short pulse duration). For accurate calibration of the accelerometer, and to avoid ambiguity in interpreting the force-time curves, it was essential that the impact without a sample should be predominantly elastic in character. This was achieved by using a cast iron workshop anvil of mass 80 kg for the base plate (using the Conventional Dropweight in Section 3.2.4).

The accelerometer was calibrated by equating the impulse measured by the accelerometer (attached to the dropweight) to the momentum change suffered by the dropweight. The impact and rebound velocity were measured by timing the interruption of two light beams crossing the
dropweight using the velocity measuring unit.

One typical pulse from this dynamic calibration is shown in figure 3.38. The integral of area under the curve (found graphically from the impulse trace) is:

\[ \int_{t_1}^{t_2} V_0 dt = 6.15 \times 10^{-4} \text{Vs} \]

The velocity change during this impact is calculated from the velocity measuring unit and the pulse obtained is shown in figure 3.39.

Velocity before impact:

\[ v_1 = \frac{11.36 \text{mm}}{3.6 \text{ms}} = 3.16 \text{ms}^{-1} \]

and velocity of rebound:

\[ v_2 = \frac{11.36 \text{mm}}{4.0 \text{ms}} = 2.84 \text{ms}^{-1} \]

Therefore the change in velocity is thus:

\[ dv = v_1 - (-v_2) = 6 \text{ms}^{-1} \]

The calibration factor (with conditioning amplifier setting= 0.001g\(^{-1}\) Vm\(^{-1}\)s\(^2\)) is thus:

\[ K' = \frac{6.15 \times 10^{-4} \text{Vs}}{6 \text{ms}^{-1}} \]

\[ K' = 1.0257 \times 10^{-4} \text{Vm}^{-1}\text{s}^2 \]
FIGURE 3.38 Pulse of dynamic calibration from accelerometer

FIGURE 3.39 Pulse for impact and rebounce velocity measurement
\[
K = \frac{1}{K} = 9749 \text{ V}^{-1}\text{ms}^{-2}
\]

Therefore at 0.01g\(^{-1}\) Vm\(^{-1}\)s\(^2\) sensitivity, \(K = 974.9 \text{ V}^{-1}\text{ms}^{-2}\) and this value is very near to the value obtained from the sinusoidal motion calibration method which is 925 V\(^{-1}\)ms\(^{-2}\).

3.2.5.4 The Conditioning Amplifier

The amplifier used is Bruel and Kjaer type 2626. The output from the accelerometer is fed directly to a conditioning amplifier. The charge sensitivity of the amplifier is set according to the accelerometer sensitivity i.e. 9.8g\(^{-1}\) pCm\(^{-1}\)s\(^2\). The voltage sensitivity is set at the lowest value i.e. 0.001g\(^{-1}\) Vm\(^{-1}\)s\(^2\). The conditioning amplifier has built in filter circuits and several test were performed at different frequency ranges before eventually selecting the widest frequency range possible with this amplifier i.e. from 0.3Hz to 30 kHz.

3.2.5.5 Accelerometer And Flash Synchronization

The entire success of the analysis of the force-time histories and the photographic records to yield a dynamic stress-strain curve depends on being able to relate them accurately in time. Precise timing is a fundamental requirement in the use of photography to assign the sequence of events, which occur during impact to features of the force against time graph. This was accomplished experimentally by using a
twin channel transient recorder (DSA524). The falling weight triggers the DSA just prior to striking the sample. Synchronization of the flash which is also triggered by the falling weight and the impact commencement is done by adjusting the height of a spring steel connected to a trigger box. Figure 3.40 shows a typical signal obtain from the accelerometer and flash.

Since all the samples used in this work are machine from a flat plate, the height of the sample and thus the height of the spring steel is constant. Care must be taken in adjusting this spring steel, too high means too many frames taken before impact. Too low means impact commences earlier than the flash and the first frame of impact cannot be defined. The optimum height of the spring steel should include a few frames before impact that are illuminated during the rise time of the flash intensity.

The DSA determined the time when the photograph was taken by means of a photodiode connected to the first channel. This enabled the start, intensity and duration of the flash to be measured during impact. The acceleration values are captured on the second channel in the usual manner.

The last frame (the n-th frame) with the sample stationary was assumed to coincide with the initial rise of the force-time curve. This n-th frame is thus the first frame of impact. Since the accelerometer is mounted at the top of the dropweight, there is a significant time delay for the stress wave to travel along the dropweight.

Theoretically, the time delay can be calculated using the velocity of sound in both pilkington glass impactor and the carbon steel dropweight. Velocity of sound in the glass and steel are 5334 and 5151 ms$^{-1}$
TIME BASE = 200μS
CH1 V/DIV = 0.2V  ACCELEROMETER
CH2 V/DIV = 5V  FLASH

FIGURE 3.40 Accelerometer and flash signals

TIME BASE = 200μS
CH1 V/DIV = 0.2V  ACCELEROMETER
CH2 V/DIV = 1V  STRAIN GAUGE

FIGURE 3.41 Time delay measurement signals
respectively. Time duration in 2.5 cm glass is thus 4.8 \( \mu s \) while in the 9.5 cm steel the time duration is 18.5 \( \mu s \). The total time for the wave to travel from the point of impact to reach the accelerometer is thus 23.3 \( \mu s \).

The time delay between the point of impact and accelerometer mountings was measured by impacting a roller steel with attached strain gauge. The time delay is thus the time difference between the accelerometer and strain gauge signals. In this work the time delay is 24 \( \mu s \) (see figure 3.41).

If \( \Delta t \) is the time difference between the flash and impact, \( dt \) the time delay and \( \delta t \) is the interframe time (see section 3.2.5.6 below) therefore the first frame of impact i.e. the n-th frame in the photographic records is:

\[
n = \frac{\Delta t - dt}{\delta t} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3.22)
\]

3.2.5.6 The A.W.R.E. C4 Camera And The Flash

The operation of the camera is shown in figure 3.42. Plate 4 shows the A.W.R.E. (Atomic Weapon Research Establishment) C4 camera. This camera takes 140 frames in 2 films tracks, 70 frames in each track. The film is specially cut into a curve strips with radius of curvature of 5.3 m. In an impact experiment, the whole event can be recorded continuously by all the frames in one exposure. In each exposure care must be taken to ensure that the duration of the light source is optimum to avoid double exposure. Since the duration of the flash is fixed, the recorded time for exposure is varied by the rotation speed of the camera.

The rotating mirror is driven by an electric motor, via a belt. The rotation
FIGURE 3.42 A.W.R.E. C4 Camera configuration

KEYS
Fv framing lenses for frame 1 to 70
Fw framing lenses for frame 71 to 140
H shutter
I1, I2, I3 image
J collimator
K focussing len
Lv, Lw focussing lenses for beam V & W respectively
M rotating mirror
N beam splitter
Pv, Pw plane mirror for reflecting V & W respectively
Tv, Tw film track for beam V & W respectively
of the motor was controlled by a variac thus controls the rotation speed. In this work the rotation speed of the mirror is fixed for all experiments. With flash duration of 2616 µs (68 µs rise time) and impact duration of ~1170 µs the recording time (i.e. the time for one full rotation of the rotating mirror) is chosen as 1180 µs giving framing interval as ~ 8.43 µs i.e.1180µs/140 frame.

The rotation speed is measured by a light pulse reflected by a silvered portion of the mirror shaft to a silicon photodiode with integrated amplifier. Figure 3.43 and 3.44 shows the configuration of the rotation speed measurement and the circuit diagram of the integrated amplifier. This diode is fed to a single shot oscilloscope. Figure 3.45 shows the typical rotation speed used in this work. The same type of photodiode is also used to measure the flash duration.

The flash used in this work is an Elevam MFT 218 Xenon flash tube. The characteristics of this flash is shown in figure 3.46. It is charged to 1 kV. Triggering of the flash is done by means of an electrical contact between a brass pin screwed into the dropweight and a piece of spring steel (at the anvil) connected to a trigger box. Figure 3.47 shows the circuit diagram of the trigger box.

It is important that the flash is triggered earlier than the impact. This is to make sure that the event captured by the camera before impact is within the rise time of the flash intensity, which is not instantaneously bright enough. At the same time the event before impact can be used in the enlargement factor calculation (see below).

The duration of the flash is long enough to capture the whole event (140 frames) in one exposure. To avoid double exposure of the event, the speed of the rotating mirror is adjusted to capture the whole event in one
SMALL TORCH
LIGHT
PHOTODIODE
SILVERED SURFACE
ROTATED VIA A BELT

FIGURE 3.43: CONFIGURATION OF THE ROTATION SPEED MEASURING UNIT

FIGURE 3.44: CIRCUIT DIAGRAM OF THE INTEGRATED AMPLIFIER
FIGURE 3.45 Rotation speed signal. Time difference between two peaks (full rotation) = 2.36 ms. Half rotation = 1.18 ms.

Design Flash Voltage 900
Maximum Flash Voltage 1050
Minimum Starting Voltage With Minimum 4.0 KV Trigger 800
Maximum Energy Input (Watt.sec = \(\frac{cv^2}{2}\)) Per Flash 200
Nominal Life in Flashes At Maximum Input 10,000

FIGURE 3.46 Elevam MFT 218 Xenon flash tube characteristic
Figure 3.47 Circuit Diagram of the Trigger Box
exposure. Too fast a speed might expose some of the frame twice and too slow speed might lack the important intermediate event. This exposure time is critical because the shutter of the camera is of the continuous access type.

3.2.5.7 Load Record And Filtering

It is necessary to ensure that the accelerometer and mounting (the dropweight) are sufficiently stiff, so that oscillations on the load record do not obscure the results. Uniaxial loading can be achieved by adjusting the lower anvil (with the glass impactor resting on the glass anvil) in the absence of a sample until Newton's ring are seen in the middle. If this is done, the sample deforms about its centre, if not it might slip off to one side.

The signal derived from an impact test on the glass anvil is distorted by extraneous vibrations. This may be removed by filtering. Electronic smoothing of the curve can dilute the resolution in important areas of the response curve. It is likely that electronic filtering can transform a peak into minor change of slope. It could also be argued that lack of filtering overcomplicates the response curve.

Briefly, in these experiments, the transient stress pulses, which may contain contributions from the measuring systems, are transformed to the frequency domain where a correction for these dynamic effects is performed. Digital filtering is used on the original unfiltered data. Inverse transformation then yield the true stress pulse. This is carried out using the MATHCAD Numerical Analysis package on a personal computer.

Fast Fourier Transform and on line data acquisition methods are used. In this way the filtered data can be compared with the original data,
allowing the effect of the filtering to be easily seen. If the resultant data are judged to be overfiltered, the original can be recalled and a lesser degree of filtering used. This has a major advantage over electronic filtering in which the original data can never be recovered.

Fourier transforming the data showed that a reproducible resonance between 20 and 26 kHz was produced for all samples. This indicate that it is the resonance frequency characteristic of the equipment. However due to a natural vibrational frequency of the sample, the cut off filtering frequency could not be less than 20 kHz. Setting the critical filtering frequency is important to avoid removing the sample response information. Figure 3.48 shows a typical signal before and after filtering.

3.2.5.8 Data Acquisition

The data acquisition system is outlined in schematic form in figure 3.49. The flash signal captured via a photodiode is used to trigger the DSA on channel 1. The signal records the start of the flash prior to impact, flash duration and intensity.

The accelerometer signal which is required to define the impact acceleration (thus force and stress) is transferred in analogous form, i.e. volts to the DSA on channel 2 through the conditioning amplifier.

3.2.5.9 The DSA unit setting

The flash and accelerometer signals are connected to channel 1 and 2 input of the DSA respectively. The principal setting of the DSA are
\[ i := 0..1023 \]
\[ v_i := \text{READ(peek2c)} \]
\[ f := \text{fft}(v) \]
\[ n := \text{last}(f) \]
\[ j := 0..n \]
\[ g_j := f_j \cdot \Phi(30-j) \]
\[ h := \text{ifft}(g) \]
\[ n2 := \text{last}(h) \]
\[ k := 0..n2 \]

**FIGURE 3.48** Signals before and after filtering by Fast Fourier Transform (FFT)
FIGURE 3.49 SCHEMATIC DIAGRAM OF DATA ACQUISITION SYSTEM
indicated below:

Channel 1: 5 V/div in ac coupling
Channel 2: 0.2 V/div in ac coupling
Timebase: 200 µs/div

3.2.5.10 Data Analysis

Having translated and filtered the data, the data are then correlated with the interframe time intervals of the photographic record. These interframe data should correspond to the diameter reading of the photographic record. The program STRESS.SAS (see appendix 3.6) written for stress-strain measurement reads initial diameter and height of the sample, number of frame, initial diameter from photographic record after enlargement through a slide projector and the baseline voltage of the acceleration signal. This program permits the result of the analysis to be listed as true stress and true axial strain.

The true compressive stress at any time t is:

\[ \sigma(t) = \frac{F(t)}{A(t)} \]

At any time t, \[ F(t) = Ma(t) \]

where M is the mass of the dropweight in kg and a(t) is the acceleration of impact measured from the accelerometer. a(t) is calculated from:

\[ a(t) = KV_a(t) \]

where \( V_a(t) \) is the voltage produced from the accelerometer during impact and K is the calibrated constant in V^{-1}ms^{-2}.
The enlargement factor is calculated as:

\[ Z = \frac{D_0}{d_0} \]

where \( d_0 \) is the original diameter of the sample before testing and \( D_0 \) is the sample diameter from the projected film before impact commencement. The sample diameter \( d(t) \) at time \( t \) is thus:

\[ d(t) = \frac{D(t)}{Z} \]

where \( D(t) \) is the sample diameter measured from the projected film of the event at time \( t \). Therefore the area \( A(t) \) at time \( t \) is calculated as:

\[ A(t) = \pi \left( \frac{D(t)}{2Z} \right)^2 \]

The radial strain is:

\[ \varepsilon_R = \ln \left( \frac{D(t)}{D_0} \right) \]

With the value of poisson ratio obtained from the quasi-static test, the true axial strain is given by:

\[ \varepsilon_A = \frac{\varepsilon_R}{\nu} \]

### 3.2.5.11 Results

Figure 3.50 to 3.52 shows the stress against strain curve for PEEK, PEK and PES respectively.
FIGURE 3.50
True Stress Against True Axial Strain For PEEK From Improved Dropweight Test ($10^3 \text{s}^{-1}$) At 20 to 180°C
FIGURE 3.51
True Stress Against True Axial Strain For PEK From Improved Dropweight Test (10³ s⁻¹) At 20 to 160°C
FIGURE 3.52
True Stress Against True Axial Strain For PES From Improved Dropweight Test ($10^3 s^{-1}$) At 20 to 120°C
3.2.6 The Cross Bow System

This investigation was undertaken with the object of determining the feasibility of obtaining a strain rate of the order of $10^4 \text{s}^{-1}$ in combination with the large strains that can be produced during a direct impact test.

When initially constructed, a direct impact configuration was adopted in which the arrow is a projectile which is fired directly against a sample resting on a strain gauged anvil. This method of transmitting energy to the sample is thought to be more efficient than using elastic-plastic wave propagation as in the Hopkinson bar. Nevertheless the long arrow creates a pulse of finite duration which causes oscillations in the load in the semiconductor strain gauged anvil.

Since the strain gauged anvil (the roller steel) is short compared with the arrow, the impact pulse is a mixture of transmitted and reflected pulses. A procedure was developed to remove the oscillation due to ringing in the anvil. In this procedure, an experimental record (voltage and time) is transformed to the frequency domain and then an appropriate frequency is filtered.

The use of a Fast Fourier Transform (FFT) algorithm on a personal computer is rapid enough for this procedure to be used on a routine basis for the correction of experimental results. Once the oscillations have been removed, the rise time is significantly improved and the yield point is very clearly determined. Since this oscillations frequency is not very high compared to the impact pulse, the filtered signal is distorted to an extent and the rise time of the signal is effected which causes the yield strain in the final stress-strain curve become unrealistic.
In order to overcome these difficulties, the strain gauged anvil was then replaced by an instrumented bar. The strain gauges were mounted on a pressure bar longer than the projectile (arrow) so that the time window is adequate for an experiment.

The final configuration of the system consists of two bars, incident and transmitter with a solid cylindrical sample placed between them (figure 3.53). Plate 5 shows the Cross Bow system. The short incident bar is essentially a mechanism for measuring plane impact on the sample and a base to carry a flag for strain measurement. The sample was deformed under the action of a compressive load induced into the free end of the incident bar by an arrow released from a cross bow.

The stress history was measured by instrumenting the transmitter bar with two semiconductor strain gauges (described earlier in the Conventional Dropweight system). These are bonded to opposite sides and electrically connected in series to cancel out unsymmetrical bending waves. The amplitude of the pulses is restricted within the elastic limit of the bar material. The gauges are fixed at a distance not less than five bar diameters down the bar from the sample.

Experimental measurements are made of the displacement-time profiles (obtained at the end of the incident bar in contact with the sample) using a square flag crossing a laser beam targeted on a large area photodiode (mentioned earlier in the Conventional Dropweight system). The strain and strain rate of the deforming sample is derived from an analysis of the displacement-time records.
Figure 3.53: Cross-Bow System Configuration (not to scale)
Plate 5  Cross-Bow System
3.2.6.1 The 'Compliance'

The usual configuration in the dropweight is that the upper surface of the sample is moving with velocity $v$ and the lower surface is stationary. In this system, the lower surface of the sample is also moving, typically at velocities up to $v/3$ and a more realistic analysis should take into account this movement.

In the determination of sample strain the displacement due to the incident and transmitter bars alone (no sample) is subtracted from the displacement of the sample and the bars. Figure 3.54 shows two displacement signals due to both the sample and the bars and due to the bars alone.

3.2.6.2 Elevated Temperature Testing

Earlier work was done by separately heating the sample up to the desired temperature and then bringing the pressure bars into contact with it. This method of heating yield results similar to those of the room temperature tests, indicating that the bar itself is an excellent heat conductor with the effect of rapidly cooling the sample.

This problem was overcome by designing the system so that the end faces of both bars were heated simultaneously with the sample. It is essential to ensure that the heat generated in the pressure bar does not alter the shape of the stress wave. The main concern is the effect of the increased temperature of the bar on the velocity and shape of the stress pulse.
FIGURE 3.54 Displacement signals from Cross Bow system with and without sample.
In the earlier (room temperature) work, the strain gauges were mounted at 10 times the bar diameter from the bar end. During high temperature tests, it was found that the resistance of the gauge fluctuated with heating, i.e. increased with temperature. With these changes in resistances, the signal produced obviously will have drastic changes compared to the baseline value. This problem of fluctuation was overcomed by mounting the gauge a half meter from the bar end.

Dixon and Ellwood [47,48] discovered no thermal effect of the bar on the shape of the incident, reflected and transmitted waveform in a Split Hopkinson Pressure Bar (SHPB) for sample heating up to 600°C using a similar heating technique to that employed here. The effect of heating temperature along the bar was monitored with a k-type thermocouple and it was found that the resistance of a strain gauge which is half meter away from the heater was not changed. These tests were carried out at 400°C and the maximum temperature used in this work was 200°C. It is therefore safe to assume that the system will be unaffected by the heating.

3.2.6.3 Calibration

A stress wave or pulse is transmitted through a body when the different parts of it are not in equilibrium; and because of the material properties of the body, a finite time is required for this equilibrium to be felt by other parts of the body. Elastic stress waves travel through a metal without causing any permanent disturbance to the location of the atoms within the metallic structure. The speed of longitudinal elastic waves, \( C_0 \), in a long rod, is given by:
\[ C_0 = \sqrt{\frac{E}{\rho}} \] ......................................(3.23)

where \( E \) is the Young's Modulus and \( \rho \) the density of the material. For 431 steel:

\[ \rho = 7800 \text{ kgm}^{-3} \]
\[ E = 212 \times 10^9 \text{ Nm}^{-2} \] and thus
\[ C_0 = 5240 \text{ ms}^{-1} \]

The intensity of stress propagated may be obtained by momentum considerations. After time \( t \), the compressed zone length is \( C_i t \) where \( C_i \) denotes the compressive wave front speed through the space occupied by the bar at time \( t=0 \). If the bar is originally stationary and the end face is caused to move with and maintain uniform speed \( v_0 \), then the whole length will be moving with uniform speed \( v_0 \) at time \( t \). Equating the change in momentum of this length \( C_i t \) to the impulse, (i.e. \( Mv = Ft \)) we have:

\[ (A_0 C_i t \rho_0) v_0 = (\sigma_0 A_0) t \] ..........................(3.24)

Thus

\[ \sigma_0 = \rho_0 C_i v_0 \] ..........................(3.25)

For a projectile of length \( l \), the duration of double transit time:

\[ t = \frac{2l}{C_i} \] ..........................(3.26)

\[ C_i = \frac{2l}{t} \] ..........................(3.27)
Therefore substituting $C_i$ in the equation above

$$\sigma_0 = \frac{\rho_o 2lv_o}{t} \quad (3.28)$$

$$\sigma_0 t = \rho_o 2lv_o \quad (3.29)$$

To convert the electrical signal into a force history, the instrumented pressure bar must be calibrated. A static calibration can be performed with an Instron mechanical testing machine, applying a known force to the bar ends. This is similar to the calibration used for the strain gauged anvil (see section 3.2.4.1). Since the bar is too long, bending and non-uniform compression exist which cause the static calibration method to be impracticable. Dynamic calibration of the bar gauges were done independently using SHPB system by Noori al-Maliky in the Physics Department, Loughborough University.

The impact between the projectile, incident and instrumented bar are considered through energy and momentum transmission [49]. At $t=0$, the projectile velocity before impacting the incident bar is $v_o$, while the velocity of the incident and instrumented bars are both zero. At

$$t = \tau = \frac{l_1}{C_1} = \frac{l_2}{C_2} = \frac{l_3}{C_3} \quad (3.30)$$

(where $l_1, C_1, l_2, C_2, l_3$ and $C_3$ are the length and speed of elastic wave in the projectile, incident and instrumented bar respectively) the velocity for both the projectile and incident bar are $v$. The compressive force and stress at the interface between the projectile and incident bar during the
period $0 < t < \tau$ is the same in both bars. Thus according to equation (3.25):

$$\sigma_1 = \rho_1 C_1 (v_0 - v) \quad \text{(3.31)}$$

$$\sigma_2 = \rho_2 C_2 v \quad \text{(3.32)}$$

Equating $\sigma_1 = \sigma_2$ we obtain:

$$\rho_1 C_1 (v_0 - v) = \rho_2 C_2 v \quad \text{(3.33)}$$

$$\rho_1 C_1 v_0 - \rho_1 C_1 v = \rho_2 C_2 v$$

$$v = \frac{\rho_1 C_1 v_0}{\rho_1 C_1 + \rho_2 C_2} \quad \text{(3.34)}$$

Since the same 431 steel is used for all the bars, therefore:

$$\rho_1 C_1 = \rho_2 C_2 \quad \text{(3.35)}$$

$$v = \frac{v_0}{2} \quad \text{(3.36)}$$

The change in momentum during impact is equal to the impulse delivered to the bar. This impulse must equal the area under the volts-time curve multiplied by the gauge calibration factor $k_L (NV^{-1})$. Thus the gauge calibration factor is then given by:

$$k_L \int V(t)dt = \sigma At \quad \text{(3.37)}$$

Using equation (3.29) i.e. $ct = \rho 2lv$ therefore:
\[ k_L \int V(t) dt = \rho 2 IvA \quad \text{(3.38)} \]

\[ k_L = \frac{2 \rho v l A}{\int V(t) dt} \quad \text{(3.39)} \]

The diameter of incident bar and instrumented bar =16.69 mm. The area of the bar \( A \) is thus 126.49x10^{-6} m^2. Projectile length \( l \)=25 cm and bar density \( \rho =7800 \) kgm^{-3}. In this work the velocity of the projectile used in SHPB \( v_0 \) is 15.33 ms^{-1}. Therefore the velocity \( v \) of the incident bar is 7.67 ms^{-1}. The integration of the impact pulse shown in figure 3.55 is:

\[ \int V(t) dt = 1.9818 \times 10^{-5} \text{ Vs} \]

Therefore the calibration factor:

\[ k_L = 190,058 \text{ NV}^{-1} \quad \text{(3.40)} \]

This value is similar to the calibration factor used in the Conventional Dropweight system (190,098 NV^{-1}). Since bar diameter = roller diameter this results is to be expected and gives us confidence in our calibration methods.

3.2.6.4 Data Analysis

The length \( h(t) \) of the sample at time \( t \) is given by:

\[ h(t) = h_0 - u(t) \quad \text{(3.41)} \]

where \( h_0 \) is the initial length of the sample and \( u(t) \)=the displacement of
FIGURE 3.55 Pulse of dynamic calibration from instrumented pressure bar using SHPB system.
the sample is defined as:

\[ u(t) = w(t) - (u_1(t) + u_2(t)) \] .................. (3.42)

where \( w(t) \) the displacement of the whole system i.e. the sample and the bars. \( u_1(t) \) and \( u_2(t) \) are displacement imposed on the incident and instrumented bars, termed as the compliance of the system.

The true stress and true strain is calculated by a program CROSSBOW.BAS (appendix 3.7). In this program both the starting point for displacement and load are determined separately as a rise from the base value. A typical trace obtained from one impact test is shown in figure 3.56. The delay in the load signal is due to the location of the strain gauges far from the point of impact.

The force calibration factor is:

\[ k_L = 190,058 \text{ NV}^{-1} \]

The displacement calibration factor is:

\[ k_D = 0.043 \text{ mm(mV)}^{-1} \]

\( u_1(t) \) and \( u_2(t) \) are determined from a separate impact test on the bar without sample (discussed earlier as the 'Compliance' of the system).

3.2.6.5 Results

Figure 3.57-3.59 shows the stress against strain curve for PEEK, PEK and PES between room temperature to 200°C.
FIGURE 3.56 Load and displacement signals from cross bow impact test
FIGURE 3.57
True Stress Against True Axial Strain For PEEK From Cross-Bow Test (10³ s⁻¹) At 20°C to 200°C
FIGURE 3.58
True Stress Against True Axial Strain For PEK From Cross-Bow Test \((10^3 \text{s}^{-1})\) At 20°C To 200°C
FIGURE 3.59
True Stress Against True Axial Strain For PES
From Cross-Bow Test (10^3 s^{-1}) At 20°C To 200°C
3.3 DISCUSSION

The yield stress of a polymer is expected to rise as the temperature is lowered in all theories of polymer yield [1]. It is well known that in thermally activated deformation processes, the stress necessary to cause a given strain increases with the strain rate.

For a discussion of the effect of the temperature and strain rate upon the form of the stress-strain curve, information on the sensitivity of the stress-strain curve to temperature and strain rate is necessary. The true stress-strain curve of PEEK, PEK and PES from quasi-static test showed a degree of consistency in the stress drop as the temperature is increased. This means that the thermal sensitivity of the polymers used are constant throughout the whole temperature range.

On the other hand, the curve from the dynamic test shows slight inconsistency in the stress drop as the temperature is raised. The changes observed in the strain rate and temperature sensitivity by a combination of Eyring type processes will be explain in a later chapter (Chapter 6). The major fact to emerge from the results is that the yield stress increases with the strain rate. The effect of heat developed during deformation on the stress-strain curve is quite evident, particularly at the transition between isothermal and adiabatic processes where the stress decreases while the strain increases.

It is true to say that the dropweight is a better machine at the medium strain rate because even at 7s\(^{-1}\), the hydraulic testing machine is unable to produce oscillation free pulses. The accompanying stress-strain curve in figure 3.18 to 3.20 shows how there can be an uncertainty in the level
of stress when such pulses are recorded.

In the absence of data at higher strain rates and temperatures it is probably not sensible to speculate on their origin. Nevertheless, the curves from the Improved Dropweight and Cross Bow systems do indicate that both techniques forms a useful method for estimating the flow stress of polymers although unfortunately limited to a narrow range of strain rates. The general agreement between these two systems for determining stress and strain is excellent.

With the Improved Dropweight system there is a noticeable discrepancy with the data at higher strain but this is where the image of the sample extends to the edges of the camera frame where the differing frictional constraints between sample and glass will be of greater importance. If the sample departs from a circular section the data is inadequate to calculate a meaningful strain. In this respect the cross bow method has an advantage over high speed photography which usually records a sample diameter. Essentially the hydraulic ram, Conventional Dropweight and the Cross Bow system provide direct longitudinal strain information whereas the Improved Dropweight system provides direct stress information. Any breakdown in the assumptions used to calculate one from the other will be most evident at high strain.

If accurate absolute measurements are required other experimental method might be employed to achieved synchronization. The department has recently purchased a high speed camera using an ordinary 35 mm film but it is yet to be incorporated into a test system to assess its measuring capability.
3.4 CONCLUSION

Although the yield stress increases with increasing strain rate, the flow stress above a strain of 34\% at 7s\(^{-1}\) and 54\% at 500s\(^{-1}\) tends to be lower than the quasi-static test. For flow stress at 1000 and 2000s\(^{-1}\), it is certain that the observed trend of the stress-strain curve are due to genuine material behaviour since the results have been confirmed by two different testing apparatus.
CHAPTER 4

CRYSTALLINITY AND ORIENTATION OF PEEK AND PEK USING X-RAY DIFFRACTION
4.0 CRYSTALLINITY AND ORIENTATION OF PEEK AND PEK USING X-RAY DIFFRACTION

4.1 INTRODUCTION

It is already established that a crystalline polymer consists of uniformly thick lamellae with the chains normal, or at a specified large angle, to the lamellar interface. The chains are to a large extent folded and thus confined to within a given lamella.

The lamellar thickness of solution grown polymer crystals is typically 100 to 200 Å and the chains are oriented transversely to the lamellar surface. Thus since the chains are much longer than the lamellar thickness, they must fold through 180° at the lamellar surfaces. A simple schematic representation of chainfolding in a polymer lamellae is shown by the edge on view in figure 4.1.

The structure of semicrystalline bulk polymers was visualised as being composed of crystallites, formed by the alignment of neighbouring chains, embedded in a matrix of the amorphous region. This amorphous material being composed of entangled molecules threading their way from one crystallite to another together with chain ends. The viscoelastic and swelling behaviour could be attributed to the amorphous regions, while the crystallites accounted for the X-ray diffraction patterns, low extensibility and mechanical strength.

Since both the distribution and magnitude of crystallite sizes and the degree of lattice distortion affects the mechanical properties of a material, it is useful to be able to determine these parameters. In
FIGURE 4.1 A schematic representation of chainfolding in a polymer lamellar shown by the edge on view.
general, the deformation of a polymer cannot be described in terms of a single structural process. The structural units we shall be concerned with are the crystal lamellae, and in particular their orientation.

As is well known, the lamellar structure gives rise to discrete X-ray reflections at low angles by which both lamellar periodicity (i.e. thickness) and orientation can be assessed, in the simplest approximation, by Bragg's law [50].

The influence of the morphology on the mechanical properties is well recognized. One of the purposes of studying the X-ray diffraction patterns of PEEK and PEK has been to provide a more concrete structural basis for the interpretation of mechanical measurements than would be otherwise available. The problem of how amorphous and crystalline components are mechanically coupled is basic to mechanical studies and is not resolvable in the general case. It is the aim of this work to investigate what crystallographic changes, if any, occur at temperatures above the glass transition but below the melting point.

4.2 X-RAY DIFFRACTION

In general, diffraction occurs only when the wavelength of the wave motion is of the same order of magnitude as the repeat distance between the scattering centres. The Bragg equation which is used to find the distances between the scattering centres (planes) is written as:

\[ d_{hkl} = \frac{\lambda}{2 \sin \theta} \]
\[
\sin \theta = \frac{\lambda}{2d_{hkl}} \tag{4.2}
\]

Experimentally X-rays of known wave length \(\lambda\) are used and the angle \(2\theta\) measured, thus enabling the separation \(d_{hkl}\) of the crystallographic planes giving rise to the Bragg reflection to be determined. For PEEK and PEK, which both have an orthorhombic cell, the spacings of the various planes are given by the following expressions [50]:

\[
d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}} \tag{4.3}
\]

\[
\sin \theta = \frac{\lambda}{2d_{hkl}} = \frac{\lambda}{2} \sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}} \tag{4.4}
\]

\[
\sin^2 \theta = \frac{\lambda^2}{4} \left( \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right) \tag{4.5}
\]

The dimensions of the orthorhombic unit cell of PEEK were taken as \(a=7.75\text{Å}, b=5.86\text{Å}\) and \(c=10.00\text{Å}\) while for PEK \(a=7.63\text{Å}, b=5.96\text{Å}\) and \(c=10.00\text{Å}\) [25].

In polymer physics, X-ray diffraction is most often used for determination of unit cell dimensions and symmetry. X-ray diffraction of bulk polymers reveals the presence of crystalline units. In addition, the presence of disordered or amorphous regions can be inferred from the diffuse scatter. This technique can utilize intensity data from lamellar crystals for a quantitative structural analysis. Here we compare the intensity data from diffractometer and powder photographs and demonstrate their
applicability in determining the crystallinity level and degree of orientation respectively.

The photograph method is not sufficiently accurate to compare crystallinity level in the different samples. But the dependence of orientation on temperature can be qualitatively determined. Since in an oriented sample many crystals are slightly randomized about a common orientation, the reflections no longer appear as spots but as arcs [51]. Ideally the orientation could be defined as the ratio of area of the arc to the area of the background. In this work the degree of orientation is defined quantitatively as the ratio between the minimum and maximum intensities produced on the photograph. Details of the technique is given in section 4.3.1.

Accurate peak positions were determined by using the diffractometer. The crystallinity level was taken as the ratio of the area of the crystalline peaks to the total area. The method of calculation is explained in section 4.3.2.

4.3 EXPERIMENT

4.3.1 The 'Unicam' camera

Tested and untested PEEK samples were both given the same heat treatment i.e. heated at the required temperature for 30 minutes. Photographs of tested and untested PEEK samples were obtained with a 28.65 mm radius 'Unicam' camera and using CuKα radiation. Figure 4.2A shows one typical photograph used for the intensity measurement. The photographs were taken in two mutually perpendicular direction.
FIGURE 4.2A A typical photograph obtained from the film used for the intensity measurement.

FIGURE 4.2B X-ray photograph of an unoriented (random orientation) crystalline polymer
Figure 4.3 shows the definition of the compression and tension directions used in the following discussions. The a, b and c direction were obtained by Dawson [37] and indicate that the b axis of the sample is tends to lie in the plane of the plaque and perpendicular to the direction of impact.

Figure 4.4 shows the Unicam camera used in this work. The X-ray beam was collimated using a 0.5 mm collimator and the beam stopped with a backstop. The X-ray film was wrapped around inside of the 'pot'. The fact that a plane reflects in the equatorial plane of the film implies that it is parallel to the axis of the cylindrical film (figure 4.5) [52]. From figure 4.5:

\[
\frac{s}{2\pi r} = \frac{2\theta}{360} \quad \text{(4.6)}
\]

\[
\theta = \frac{90s}{\pi r} \quad \text{............(4.7)}
\]

If the radius of the film is \(90/\pi=28.65\) mm, 1mm \(s\) measured on the film equals 1 degree \(\theta\). To calculate the lattice spacing \(d\) from the X-ray photograph the following procedure is used:

\[2s \text{ measured on film} = 19.3 \text{ mm}\]
\[s=9.65 \text{ mm}\]

Using (4.7) \(\theta=9.65^\circ\)

\[\text{Sin } \theta = \text{Sin } 9.65^\circ = 0.1676\]

\[n=1 \text{ and } \lambda=1.54\times10^{-10} \text{ m}\]

\[d = \frac{n\lambda}{2\sin\theta} = 4.594 \text{ Å}\]
FIGURE 4.3 Definition of the compression and tension direction from the sample configuration. Direction are a, b and c obtained from Dawson [37].
FIGURE 4.4 The Unicam Camera

FIGURE 4.5 Schematic diagram of the cylindrical film and the reflecting plane.
The camera was mounted on a Philips PW 1130/00 generator with a PW 2233/20 copper X-ray tube. A nickel filter was placed in front of the window. Exposure times of about 2 hours were required with generator settings of 40 kV and 20 mA. The X-ray film used was Kodak X-Omatic AR-5 film (13cmx18cm) with LX-24 X-ray developer and FX-40 X-ray liquid fixer.

The estimation of integrated intensities from the blackening produced on diffraction photographs involves two problem. The first of these is ensuring that the proportionality between the blackening and the amount of incident radiation is known, and the second is devising a method for measuring the total amount of blackening produced.

Fortunately, the first proves to be a comparatively minor difficulty, since it has been shown that the optical density (logIo/I) of film treated with X-rays is linear over a wide range of exposures [53]. This behaviour, which is quite different from the non linear response of the same film to light (figure 4.6) arises because the absorption of a single X-ray quantum is enough to sensitize a silver halide grain to development.

Thus if the processing conditions are held constant and the exposures are kept at a level at which no grain is likely to receive more than one quantum, the total amount of silver produced, and hence the blackening, will be directly proportional to the number of quanta diffracted.

The current methods of estimating blackening depend on light absorption by the deposited silver grains and may be divided into two classes, visual and photometric. To make the intensity measurements, the film is placed on a lightbox. A beam of light passes from the source, through the film,
FIGURE 4.6 The blackening $D$ of the X-ray film against incident radiation.

FIGURE 4.7 A typical trace for intensity measurement obtained from the film shown in the photograph in figure 4.2A.
and arrives at a detector which measures its intensity in an absolute fashion.

The resulting signal is then sent to a read-out device, a computer. The software package used for digitising the signal is called Rheed Vision. The detector is designed to provide a logarithmic response to the changes in the amount of light transmitted, the final output will be directly proportional to the changes in optical density of the film.

Since we are concerned only with the difference between one part of the film and another, i.e., between a spot and its associated background, and as long as we are working in the intensity region in which the density of the film is linearly proportional to the X-ray intensity, it is not necessary to have an absolute measure of the film density, only a relative one.

The film density may be scanned continuously along a preselected line. The output is a trace of the density along the path followed. Figure 4.7 shows one typical trace obtained from the film shown in figure 4.2A. A black pvc cellotape is used as the standard density placed in the centre of the film. The minimum intensities in the middle of the trace (due to the pvc cellotape) is used as a standard intensity for scaling the intensity axis. From a series of line scans across a diameter of the film in different directions various values of intensities are obtained.

The degree of orientation \( f \) is defined as:

\[
f = \frac{I_{\text{min}}}{I_{\text{max}}} \quad \text{(4.8)}
\]
According to this definition, for the extreme case of an isotropic sample (random orientation) $f=1$ and for the other extreme case of ideal orientation $f=0$. The reflections on an X-ray photograph of an unoriented (random orientation) crystalline polymer have a complete angular dispersion, as can be seen in figure 4.2B. Theoretically the degree of orientations of any plane measured from this figure should be 1 (minimum intensity/maximum intensity are equal to 1).

4.3.2 X-ray Diffractometer

All of the diffraction profiles were measured with CuKα radiation at 40kV and 20mA. Intensities were counted at 0.5° intervals ($2\theta$). In the diffractometer, the sample remains in the horizontal plane while the X-ray source and the detector move through corresponding angles in a vertical plane.

An accepted experimental procedure for the determination of degree of crystallinity is applicable to this material in as much as X-ray scattering curves are resolvable into crystalline and amorphous scattering regions. There are regions where the amorphous fraction is appreciable and the crystalline intensity falls to zero (see figure 4.11 and 4.13 for PEEK and PEK tested at room temperature).

In order to make the data more easily comparable, the non crystalline contribution has been subtracted by fitting a scaled curve from the amorphous scattering regions. Ideally an amorphous PEEK diffractogram should be fitted to the present semicrystalline diffractogram. Unfortunately we are unable to obtained a purely amorphous sample and the published amorphous diffractogram of PEEK
[3 & 22] does not necessarily correspond to the amorphous fractions in our semicrystalline PEEK samples.

Estimates of crystallinity were obtained by drawing a straight baseline between 2θ=11° and 34° and then fitting a scaled amorphous curve under the diffraction peaks in the manner indicated by the broken lines (see figure 4.10). The curve of the amorphous region were fitted using the criteria similar to those outlined by Farrow and Preston [54]. The degree of crystallinity was determined from the ratio of the areas under the relevant peaks to the total area [27]. A planimeter is used in all the area measurements.

4.4 RESULTS AND DISCUSSIONS

To understand the reason for the presence of orientation it is necessary to examine the molecular conformation and chain packing of PEEK and PEK. This is shown schematically in figure 4.8 [13] and figure 4.9 [55]. The molecules are located at the corners and centre of the orthorhombic unit cell, in such a manner that the backbone zig-zag planes are parallel to the c axis.

The combined X-ray diffractograms of the annealed and tested PEEK and PEK samples are shown in figure 4.10-4.13 for 2θ ranging from 10°-35°. They are in the described order from room temperature to 200°C. The main hkl reflections are (110) at around 18.5°, (113) near 20.5°, (200) near 22.5° and (213) near 28.5° while the four major calculated peaks by Fratini et al. [31] are at 18.76°, 20.82°, 22.72° and 28.78° respectively. There is a progressive change in the peak intensity with increasing temperature for tested samples. This can be characterized as
FIGURE 4.8 The unit cell of PEEK together with a representation of an isolated repeat unit [12].

FIGURE 4.9 Refined three dimensional structure of PEEK chain together with a planar zig-zag repeat unit of PEEK showing c dimension at 10 Å.
FIGURE 4.10 X-ray diffractogram of annealed PEEK.
FIGURE 4.11 X-ray diffractogram of tested PEEK.
FIGURE 4.12 X-ray diffractogram of annealed PEK.
FIGURE 4.13 X-ray diffractogram of tested PEK.
a change towards higher crystallinities or an increase in crystalline order [26]. Hay et.al [29] found that PEEK crystal size increases and unit cell volume decreases as the temperature increases. But with PEK, they found that there was no trend in crystallographic dimensions with crystallization temperature, and the unit cell volume was essentially constant.

It is the interrelation and interaction between crystals and the amorphous components upon which much of the mechanical properties of polymers depend. It is the amorphous material which is expected to soften more and thus will increase its contribution to the total strain under compression when the temperature is increased. Table 4.1 shows the crystallinity level ($\chi$) for annealed and tested PEEK and PEK with temperature variation.

Tested samples (both PEEK and PEK) shows changes in the crystallinity level as shown in figure 4.14 and 4.15. An increase of crystalline reflections indicate the increase of crystal fraction. Comparing the diffractograms of annealed and tested PEEK and PEK as in figure 4.16 and 4.17, shows a slight changes in the reflection angles and also the disappearance of the (113) and (213) peaks in the tested samples. These changes in reflection angles indicate changes in lattice dimension and the 'loss' of the (113) and (213) peaks indicates that orientation occurs during impact. Another interesting feature to note with the tested PEEK is that the intensity of the (200) peak increases faster than the (110) peak as temperature increase. This shows that the crystallization induced by the heat treatment in combination with the orientation produced during deformation aligns the crystals such that the (200) plane is parallel to the plane of impact i.e. in the tension direction. While
Table 4.1 Crystallinity level ($\%\chi$) for annealed and tested PEEK and PEK with temperature variation

<table>
<thead>
<tr>
<th>Heat Treatment °C</th>
<th>% Crystallinity in PEEK</th>
<th>% Crystallinity in PEK</th>
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<tr>
<td></td>
<td>Annealed</td>
<td>Tested</td>
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<td>80</td>
<td>18.63</td>
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<td>18.60</td>
<td>40.74</td>
</tr>
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<td>160</td>
<td>33.33</td>
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<td>40.00</td>
</tr>
<tr>
<td>200</td>
<td>19.78</td>
<td>53.33</td>
</tr>
</tbody>
</table>
FIGURE 4.14. Crystallinity level (%) against heat treatment (°C) of annealed (——) and tested (-----) PEEK
**FIGURE 4.15** Crystallinity level (%) against heat treatment (°C) of annealed (---) and tested (-----) PEK
FIGURE 4.16 Diffractogram of annealed (---) and tested (-- -) PEEK (depict from figure 4.10 and 4.11).
FIGURE 4.17 Diffractogram of annealed (---) and tested (-----) PEK (depict from figure 4.12 and 4.13).
with annealed PEEK the (110) peak is much higher, an indication of a different preferred orientation of the original samples before impact.

Table 4.2 shows the degree of orientation (%f) of plane (200), (113) and (110) with temperature in the tension and compression direction for annealed and tested PEEK. Figure 4.18 and 4.19 shows the variation of the orientation (in tension and compression direction respectively) for annealed PEEK with temperatures. Figure 4.20 and 4.21 shows the orientation of tested PEEK in tension and compression direction respectively. From these figures it can be concluded that the samples used were initially randomly oriented to a large extent i.e. f<1 as determined from the point at 20°C (i.e. room temperature sample, no heat treatment). In both directions, plane (200) gave rise to the closest towards ideal orientation i.e. f approaching zero (f=0.3 at 60°C and 0.4 at 80°C for tension and compression direction respectively).

Orientation did not appear to vary with annealing temperature in any systematic way except for a general increase in orientation in the region of ~100°C only. The cause of this orientation maximum is not clear but it may be associated with T_g since the maximum occurs just below T_g in each case.

Table 4.3 shows the variation of lattice spacing d with annealing temperature (not measured at that particular temperature) for plane (110), (113) and (200) in the tension and compression direction. Table 4.4 shows the variation of d with testing temperature (at hot stage) for plane (110), (200) and (020) obtained from Blundell et al. [32]. The increase in d corresponds to smaller (and possibly more distorted) crystal and vice versa. In order to measure the effect of annealing and
Table 4.2 Degree of orientation (%f) on plane (200), (113) and (110) with temperature in the tension and compression direction for annealed and tested PEEK

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>(Plane)</th>
<th>Annealed PEEK (%f)</th>
<th>Tested PEEK (%f)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>tension</td>
<td>compress</td>
</tr>
<tr>
<td>20</td>
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<td>76</td>
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<td>113</td>
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<td>113</td>
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<td></td>
<td>113</td>
<td>--</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>80</td>
<td>47</td>
</tr>
<tr>
<td>120</td>
<td>200</td>
<td>69</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>113</td>
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<tr>
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<td>--</td>
<td>--</td>
</tr>
<tr>
<td>160</td>
<td>200</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>113</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
FIGURE 4.18 Degree of orientation (\%f) against heat treatment (°C) for annealed PEEK in tension direction (--- 113, --- 110, —— 200)
FIGURE 4.19: Degree of orientation ($\%f$) against heat treatment ($^\circ$C) for annealed PEEK in compression direction (--- 413, --- 110, --- 200)
FIGURE 4.20 Degree of orientation (gf) against heat treatment (°C) for tested PEEK in tension direction (---113, ---110, ---200)
FIGURE 4.21 Degree of orientation ($\%f$) against heat treatment ($^\circ$C) for tested PEEK in compression direction (——110,——200)
Table 4.3 Lattice Spacing d (Å) for plane (110), (113) and (200) with temperature in the tension and compression direction for annealed and tested PEEK

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>(Plane)</th>
<th>Annealed PEEK d (Å)</th>
<th>Tested PEEK d(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>tension</td>
<td>compress</td>
</tr>
<tr>
<td>20</td>
<td>110</td>
<td>5.0130</td>
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</tr>
<tr>
<td></td>
<td>113</td>
<td>4.5095</td>
<td>4.5970</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>4.1521</td>
<td>4.1521</td>
</tr>
<tr>
<td>60</td>
<td>110</td>
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<td>113</td>
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</tr>
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<td></td>
<td>200</td>
<td>4.1154</td>
<td>4.0806</td>
</tr>
<tr>
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<td>110</td>
<td>4.8272</td>
<td>4.9597</td>
</tr>
<tr>
<td></td>
<td>113</td>
<td>4.4664</td>
<td>4.4664</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>4.0452</td>
<td>4.1521</td>
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<td>113</td>
<td>4.4872</td>
<td>4.4240</td>
</tr>
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<td>200</td>
<td>4.1154</td>
<td>4.1701</td>
</tr>
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<td>140</td>
<td>110</td>
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<td>---</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>160</td>
<td>110</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>113</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>
Table 4.4 Variation of lattice spacing \(d\) with temperature (hot stage) for plane (110), (200) and (020) [32].

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Observed Bragg Spacings (Angstrom)</th>
</tr>
</thead>
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<tr>
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<td>(110)</td>
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</tr>
<tr>
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</tr>
<tr>
<td>145</td>
<td>4.743</td>
</tr>
<tr>
<td>193</td>
<td>4.755</td>
</tr>
<tr>
<td>242</td>
<td>4.778</td>
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<tr>
<td>267</td>
<td>4.786</td>
</tr>
<tr>
<td>291</td>
<td>4.798</td>
</tr>
</tbody>
</table>
testing upon the cell dimension of PEEK, \( d \) in the compression and tension directions (direction as define in figure 4.3) of the sample were calculated from the photograph. Figure 4.22 and 4.23 shows the variation of \( d \) against heat treatment in the tension and compression direction for both annealed and tested PEEK respectively. In general \( d \) only changes slightly in the annealed samples. Tested samples showed a decrease in \( d \) with temperature. This is probably due to increased crystallinity and perfection.

In the annealed PEEK (figure 4.22), it is found that a decrease in \( d \) with temperature in tension direction is associated with an increase in \( d \) in compression direction and vice versa. It can be concluded that annealing alone can cause changes in the dimension of the unit cell with an increase in one direction compensated by a decrease in another direction perpendicular to the former direction. After impact (figure 4.23), drastic change in \( d \) occur in the tension direction for plane (110). These changes are compensated by changes in compression direction for plane (200). It is very clear that testing decreases the lattice spacing for all plane either in the compression or tension direction.

In general figure 4.23 indicates a general shrinkage of \( d \) during test, with greater shrinkage at higher temperature. Figure 4.14 and 4.15 confirmed that an increase in crystallinity in tested samples at higher temperatures occur for both PEEK and PEK.
FIGURE 4.22 Lattice spacing \( d \) (Å) against heat treatment (°C) for annealed PEEK in tension(---) and compression(-----) direction.
FIGURE 4.23 Lattice spacing \( d (\text{Å}) \) against heat treatment (°C) for tested PEEK in tension(—) and compression(—) direction.
CHAPTER 5

THERMAL PROPERTIES OF PEEK AND PEK USING DIFFERENTIAL SCANNING CALORIMETRY (DSC)
5.0 THERMAL PROPERTIES OF PEEK AND PEK USING DIFFERENTIAL SCANNING CALORIMETRY (DSC)

5.1 INTRODUCTION

Semicrystalline polymers are microstructurally and mechanically complex systems and this work demonstrates the problems of trying to establish a direct relationship between crystallinity and the thermal properties. It is not the intention to investigate the decomposition or degradation process of the polymers examined. Obviously the significance to this work of the change in crystallinity and structure can only be assessed if their effects on mechanical properties are understood. Since as received sample have very nearly the same degree of crystallinity, the differences in mechanical properties must be related to the degree of perfection resulting from the different heat treatments.

The crystal unit of PEEK has already been discussed in a note by Dawson and Blundell [25] and the synthesis and properties of this class of polymer have been described by Attwood et al. [20]. PEEK exhibits multiple melting and the peaks are related to a melting and recrystallization phenomenon of the initial crystal morphology, which is characteristic of its prior crystallization history. While annealing had no apparent effect on morphology as determined optically, small increases in crystallinity and changes in mechanical properties were observed [51].

In a Differential Scanning Calorimetry (DSC) scan, the temperature is changing continuously. Therefore the increase in perfection of the crystallite occurring during a DSC run is the result of a continuous melting and recrystallization process. At any particular temperature in the
intermediate range during a scan the least perfect crystals will be melting. These will recrystallize to form more perfect crystals at some higher temperature (i.e. later in the scan). Crystals which had previously melted will be recrystallizing. Some crystals will be stable and will not melt until a higher temperature is reached. The net result is a small increase in the average perfection of the crystals.

5.2 BACKGROUND

In semicrystalline polymers at room temperature, the polymer molecules are partially oriented in crystalline domains, known as crystallites, while in between the crystallites, the structure is disordered as in glass-like amorphous polymers. With increasing content of crystallites, expressed as the crystallinity, the polymer becomes harder. The crystallite melting range covers a characteristic range of temperature for each material.

The crystallites are destroyed each time the polymer is melted and reformed on cooling. The amount of crystallite depends on the thermal history and the cooling conditions. Investigation of the crystallinity and of the recrystallization thus gives valuable information for the identification and quality control of semicrystalline polymers.

Amorphous PEEK undergoes crystallization on heating to just above the glass transition temperature, referred to as 'cold crystallization', showing a strong tendency to crystallize from the supercooled glass [12]. Zachmann et al. [56] found only imperfect crystallites formed at low crystallization temperature. Upon heating to higher temperature, the perfection of the crystallites increased. They concluded that this was due to partial melting and recrystallization.
Cebe et al. [9] ascribe the larger upper peak (in the DSC run) to the melting of the main crystal population grown during the isothermal crystallization and the smaller lower peak to the less stable, secondary population formed in intermediate spaces (see figure 5.1). The lower minor DSC peak accordingly marks the point where the original isothermally formed crystals become unstable and where the onset of melting and recrystallization occurs [5].

Blundell [5] suggest that as crystallization proceeds the previously formed crystals isothermally thicken to become more stable entities, so that the onset of melting or recrystallization at the first DSC peak will occur at higher temperature and will become more pronounced. Holdsworth et al. [57] suggested that when Poly-ethylene-terephthalate (PET) is scanned on DSC, crystallites formed at low temperature undergo a continuous perfection process as a result of partial melting and recrystallization during the scan. This leads to an increase in the overall crystallinity. The increase in crystallinity might occur in two ways. Either the total number of crystallites or the average perfection of the existing crystallites may increase.

Depending on factors such as the degree of crystallinity and density, the arrangement of neighbouring chains could range from one of random stacking of adjacent ketone and ether groups to one in which the stacking is more perfect [31]. Disorder can be introduced into the packing of the chains by the misalignment of adjacent molecular chains. If it is accepted that for crystallization at higher temperatures the chains will possess more energy and hence more mobility this provides for a greater possibility of crystallization into more preferential arrangements [30].
FIGURE 5.1 Melting endotherm of amorphous PEEK film [9].
5.3 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The Differential Scanning Calorimeter DSC 20 is used to measure and characterize the thermal properties of materials. DSC revealed the amount of material with high thermal stability. The cell consists of two identical sample holders, one for the sample and the other for the reference pan (figure 5.2). These are both heated at precisely the same rate.

DSC measures the energy required to obtain the same temperature rise in each holder. When a transition such as melting, degradation or crystallization i.e. an endothermic or exothermic reaction occurs, the change in power (mW) needed to keep the sample at the same temperature as the reference pan is recorded as a peak.

The integration of the heat flow during a dynamic or isothermal experiment gives the heat change in the observed reaction directly. A curve is always integrated over a baseline. The DSC curve with the selected baseline can be plotted on the printer or plotter during the course of the evaluation. The recorded data are retained in the memory until a new experiment is run and can therefore be evaluated in different ways.

Inert gas (argon) may be used to purge gas and vapour products formed during analysis from the cell and the DSC cell is thus protected from corrosive gases. Purge gas also remove atmospheric oxygen in order to avoid unwanted oxidation of the sample.
FIGURE 5.2 DSC 20 measuring cell
5.4 EXPERIMENT

The experiment was carried out using a Mettler TA3000 system which incorporates a TC10A TA processor with a DSC20 measuring cell attached. During the experiments, a flow of 80 to 100 cm$^3$ min$^{-1}$ of inert argon was purged into the cell. Samples of approximately 10 mg were cut from the annealed and tested PEEK and PEK, and were crimped inside aluminium sample pans. The heating rate was 20°C min$^{-1}$ and the samples investigated over a range from 20 to 500°C at sensitivities down to 0.01 mJ. The precision in the temperature was ±0.5°C and in energy was ±1 J/g. Both annealed and tested samples had been given the same heat treatment i.e. heated for 30 minutes at the required temperature.

To achieve good confidence in the data, it was necessary to make several runs for each sample material. Qualitatively, the reproducibility of the experiments appeared reasonably good. To assess the quantitative reproducibility, an integration of the area under the peak yields the melting endotherm. The crystallinity is determined by integrating the peak area of a DSC curve, measured dynamically. The heat of fusion obtained from this is directly proportional to the crystallinity. The degree of crystallinity ($\chi$) was calculated from:

$$\chi = \frac{\Delta H}{\Delta H_r} \hspace{1cm} (5.1)$$

where $\Delta H$ is the heat of fusion per gram obtained from non-isothermal DSC scan and $\Delta H_r$ is the heat of fusion of crystallites in the absence of an amorphous fraction, 100% crystalline PEEK is taken as 130J/g [22].
5.5 RESULTS AND DISCUSSIONS

Figure 5.3-5.6 shows DSC thermograms for a series of samples that had been annealed and tested at different temperatures. Three peaks are encountered among the various DSC scans and these are labelled A, B and C. The features of the various melting endotherm have been quantified by integration of heat flow under the peak. The values so obtained gives the heats of fusion $\Delta H$ and the results are given in table 5.1 and table 5.2 for PEEK and PEK respectively.

A polymer is normally expect to crystallize at or above the glass transition temperature ($T_g$), this being the temperature at which the large scale molecular motion necessary to form three dimensional crystals from a random coil conformation is possible [58]. Between the investigated temperatures, 100 to 140°C and 140 to 160°C seems to be the temperature at which the best conditions in terms of mobility and alignment of chains are reached for both tested PEEK and PEK respectively. The most perfect crystals are obtained as indicated by the largest value of the melting endotherm in the tables. This transition temperature is not detected in annealed samples.

The 'cold crystallization' occurred in both tested PEEK and PEK (point A) but it is not recognizable in the annealed samples although both tested and annealed samples were given the same heat treatment. Thus the crystal melting endotherm in the annealed samples is smaller than the tested samples as shown in table 5.1 and 5.2. In the annealed samples, although at $T_g$ the molecules could have some molecular mobility they would not be able to reptate sufficiently to crystallize.
FIGURE 5.3 Thermogram of PEEK samples (a) at room temperature (b) annealed 60°C (c) annealed 80°C.
FIGURE 5.3 Thermogram of PEEK samples (d) annealed 100°C
(e) annealed 120°C.
FIGURE 5.3 Thermogram of PEEK samples (f) annealed 140°C (g) annealed 160°C.
FIGURE 5.4 Thermogram of tested PEEK (a) room temperature (b) 60°C (c) 80°C
FIGURE 5.4 Thermogram of tested PEEK (d) 100°C (e) 120°C (f) 140°C
**FIGURE 5.4** Thermogram of tested PEEK (g) 160°C (h) 180°C
FIGURE 5.5 Thermogram of PEK sample (a) room temperature (b) annealed 60°C (c) annealed 80°C.
FIGURE 5.5 Thermogram of PEK sample (d) annealed 100°C (e) annealed 120°C.
FIGURE 5.5 Thermogram of PEK sample (f) annealed 140°C (g) annealed 160°C.
FIGURE 5.6 Thermogram of tested PEK (a) room temperature (b) 60°C (c) 80°C
FIGURE 5.6 Thermogram of tested PEK (d) 100°C (e) 120°C (f) 140°C
FIGURE 5.6 Thermogram of tested PEK (g) 160°C (h) 180°C
### Table 5.1 The variation of melting temperature, melting endotherm ($\Delta H$) and crystallinity level ($%\chi$) for annealed and tested PEEK with temperature

<table>
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<tr>
<th>Temp $^\circ$C</th>
<th>Annealed PEEK</th>
<th>Tested PEEK</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_m$ $^\circ$C</td>
<td>$\Delta H (J/g)$</td>
</tr>
<tr>
<td>20</td>
<td>342.9</td>
<td>49.723</td>
</tr>
<tr>
<td>60</td>
<td>341.9</td>
<td>42.467</td>
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<td>80</td>
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<td>43.900</td>
</tr>
<tr>
<td>100</td>
<td>346.4</td>
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</tr>
<tr>
<td>180</td>
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</tr>
</tbody>
</table>

### Table 5.2 The variation of melting temperature, melting endotherm ($\Delta H$) and crystallinity level ($%\chi$) for annealed and tested PEK with temperature

<table>
<thead>
<tr>
<th>Temp $^\circ$C</th>
<th>Annealed PEK</th>
<th>Tested PEK</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_m$ $^\circ$C</td>
<td>$\Delta H (J/g)$</td>
</tr>
<tr>
<td>20</td>
<td>375.5</td>
<td>56.648</td>
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<td>51.181</td>
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<tr>
<td>80</td>
<td>374.1</td>
<td>56.362</td>
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<tr>
<td>120</td>
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</tr>
<tr>
<td>180</td>
<td>375.4</td>
<td>57.235</td>
</tr>
</tbody>
</table>
The crystallization of crystals at $T_g$ for the samples tested at room temperature and above (well below $T_g$) seem to suggest that the heat treatment alone has not fully crystallized the sample or only imperfect crystals is formed. At higher testing temperature (above $T_g$) point A in the tested thermograms disappear because complete crystallization occur due to the heat treatment. From the tables it appears that testing produces additional chain alignment which can then undergo cold crystallization after low temperature tests or leads to greater crystallization during higher temperature tests.

Some reorganization and then recrystallization occurs during the DSC scan at a higher temperature (point B). Reorganization during the scan can be expected as a result of low initial cold crystallization temperature, additional crystallization may occur as the temperature is increased. Another possibility is that the perfection of imperfect crystal increases resulting in the exothermic peak. The different degrees of crystal perfection would give different ultimate melting points. The work of Cheng et al. [59] shows that a considerable degree of reorganization occurs as temperature is raised.
CHAPTER 6

ANALYSIS OF RESULTS
AND DISCUSSIONS
6.0 ANALYSIS OF RESULTS AND DISCUSSIONS

6.1 INTRODUCTION

This chapter presents all the stress-strain curves from the low strain rate test using the hydraulic machine combined with the data from the high strain rate test using the Dropweight and Cross Bow systems. The results obtained cover a strain rate range of $10^{-3} - 10^3 \text{s}^{-1}$ and a temperature range 20 to 200°C. These curves form the basis of the analysis in the following sections.

In all the experiments described above, the geometric effects were made consistent by using samples with the same dimensions. Also the same lubricant i.e. petroleum jelly is used throughout. In this way, the intrinsic behaviour could be determined under constant inertial and frictional conditions throughout the whole testing programme. The same heater is used for all heat treatments at elevated temperature testing.

The current investigation was the first to undertake direct strain measurements using a laser-photodiode and high speed photography with the dropweight system in the Physics Department at Loughborough. Consequently, experience had initially to be gained regarding the most suitable technique in obtaining the strain measurement.
6.2 FUNDAMENTAL ANALYSIS

6.2.1 The Stress-Strain Curves

6.2.1.1 General Consideration

One noticeable feature when comparing the stress-strain curves from the five strain rate tests is that there is an apparent sign of transition from the isothermal to adiabatic processes (see figure 6.1 and 6.2). For quasi-static test, PEEK and PEK both showed strain hardening after the yield stress is achieved. At 7 and 500 s\(^{-1}\) both curves showed strain softening after yield. This similarity in the shape of the curve confirms that it is purely due to the behaviour of the polymer because the curves are obtained from two different testing techniques (using hydraulic machine and Conventional Dropweight respectively).

Test conducted at 10\(^3\)s\(^{-1}\) (Improved Dropweight system) shows a significant strain hardening which is neither similar to the shape of the stress-strain curve at quasi-static test nor with the test at 7 and 500 s\(^{-1}\). In view of these uncertainties the Cross Bow system was built. When stress-strain curves obtained from the Improved Dropweight system are compared with corresponding curves from the Cross Bow system, the features of the stress-strain curves were apparently similar.

Although the Cross Bow system was not successful in achieving a strain rate in the order of 10\(^4\)s\(^{-1}\) (initially built for this purpose), it proved to be of great importance in confirming the shape of the curve from the Improved Dropweight system.
FIGURE 6.1
Stress versus strain for PEEK at 20°C tested at five different strain rates.
FIGURE 6.2
Stress versus strain for PEK at 20°C tested at five different strain rate
This provided evidence that although the shape of the curve from the Improved Dropweight system deviates from the curve obtained from the hydraulic and Conventional Dropweight machine, generally the agreement of the Improved Dropweight curve with the Cross Bow curve is reasonably good. This agreement implies that the mechanical properties observed here are independent of the type of the testing machines used. From the foregoing considerations it was concluded that the stress-strain curves at very high rates of strain are valid. Table 6.1 and 6.2 shows the variation of flow stress with temperature at various strain obtained from the stress-strain curves of PEEK and PEK tested at five different strain rate.

6.2.1.2 High Strain Rate Testing

Obviously there is considerably more fluctuation on the stress-strain curve from the Improved Dropweight system. Although the presence of high frequency noise in the stress measurement is so dominant, this noise is predominantly at one frequency and so it is filtered out smoothly by the FFT algorithm (see section 3.2.5.7). The strain measurement i.e. measurement of the diameter of the expanding sample during deformation from the film projection relies on the accuracy of the judgement by eye of the position of the edge of the polymer disc.

A bigger enlargement of the sample diameter (from film) by a slide projector created a smaller error in the increment reading. But too large a projection means the boundary of the projected diameter is less well defined. The computer plotted points (in bold) in figure 6.3 and 6.4 were based on the average of the original two tests while the mean curve has been fitted by eye. It was felt that this method of determining the mean
Table 6.1A Variation of stress with temperature at various strain measured from the stress-strain curve of PEEK tested at $3 \times 10^{-3}$ s^{-1}

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Table 6.1B Variation of stress with temperature at various strain measured from the stress-strain curve of PEEK tested at 7 s^{-1}

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Table 6.1C Variation of stress with temperature at various strain
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Table 6.1D Variation of stress with temperature at various strain
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Table 6.1E  Variation of stress with temperature at various strain measured from the stress-strain curve of PEEK tested at 2000 s\(^{-1}\)

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Table 6.2A Variation of stress with temperature at various strain measured from the stress-strain curve of PEK tested at $3 \times 10^{-3}$ s$^{-1}$

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Table 6.2B Variation of stress with temperature at various strain measured from the stress-strain curve of PEK tested at 7 s$^{-1}$

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Table 6.2C  Variation of stress with temperature at various strain measured from the stress-strain curve of PEK tested at 500 s\(^{-1}\)

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Table 6.2D  Variation of stress with temperature at various strain measured from the stress-strain curve of PEK tested at 1000 s\(^{-1}\)

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<td>145</td>
<td>155</td>
<td>165</td>
<td>178</td>
<td>228</td>
</tr>
</tbody>
</table>
FIGURE 6.3
Stress versus strain for two PEEK samples tested at 20°C using Improved Dropweight. Bold points are the average result.
FIGURE 6.4
Stress versus strain for two PEK samples tested at 20°C using Improved Dropweight. Bold points are the average result.
curve was more accurate than any numerical averaging procedure which may produced distorted final stress-strain curves since eye fitting includes 'automatic' realistic weighting factors from the points.

The deviation from the average value is less than ±5% which is considered satisfactory in view of the effect of lubricant on the image of the edge of the deforming sample captured on the film. The accuracy of the projection from the slide projector had been checked by projecting images of a regular grid (i.e. photocopy of a graph paper on a transparency). It is found that the projection produces effectively 100% uniformity on the whole image.

It can be seen that although there is a significant amount of inaccuracy in the Improved Dropweight curves and the yield points are not well defined, the level of flow stress recorded is consistent with that of the Cross Bow curves (which is at similar order of strain rates $10^3 \text{s}^{-1}$) for strain up to 15%.

There is one interesting difference to note in these two systems. Although the poisson's ratio $v$ is assumed 0.5 for the stress and strain calculation in both systems, the Improved Dropweight system measures radial increment while the Cross Bow system measures axial decrement. Since both systems yield almost similar results, it can be concluded that the assumption used ($v=0.5$) is valid at high strain rate testing. The poisson's ratio at quasi-static test has been shown to be 0.5 (see section 3.1.4).

In figure 6.5 a set of four stress-strain curves for PEEK from the Cross Bow compression test at room temperature is presented. They showed
FIGURE 6.5
Stress–Strain Curve For Four PEEK Samples Tested At Room Temperature Using The Cross Bow System
FIGURE 6.6
Stress versus strain for three PEEK samples tested at 200°C using Cross Bow system.
the degree of consistency possible with this type of test. The Cross Bow test proved to be equally consistent at higher temperature as illustrated in figure 6.6 obtained directly from three tests at 200°C.

The typical variation in flow stress for PEEK at room temperature was ±10 MPa for strains below 20%. The greater variation observed at higher temperatures suggest that small variation in heat treatment at a particular temperature alters the results obtained (±15 MPa for strain below 20% when PEEK was tested at 200°C). On the other hand, in the Improved Dropweight result, the scatter in the results was considerably larger at ±20 MPa for strains below 10% (figure 6.3). This is due to the fact that eye judgement of the diameter measurement could not be repeated exactly.

6.2.2 Stress Versus Strain Rate (Strain Rate Sensitivity)

Before proceeding further in the discussion of the strain rate behaviour of the polymers, it will be useful to interpret the constant strain rate behaviour on the basis of a simple mechanical model.

In order to present the results from mechanical tests over a range of strain rates, it is necessary to construct a curve of stress at a given strain against strain rate from a family of stress-strain curves. The strain rate used represents the mean plastic strain rate for each test. Figure 6.7 to 6.11 shows the mean plastic strain rate for each test. The consistency of the curves for a given plastic strain rate is good.
FIGURE 6.7
Strain versus time for quasi static test
Best Fitting (Strain Rate): $3.5 \times 10^{-3} \text{s}^{-1}$
FIGURE 6.8
Strain versus time for dynamic test
Best Fitting (Strain Rate): 6.66 s⁻¹
FIGURE 6.9
Strain versus time for Conventional Dropweight Best Fitting (Strain Rate): $5.47 \times 10^2 \text{s}^{-1}$
Strain versus time for Improved Dropweight Best Fitting (Strain Rate): $1.30 \times 10^3 \text{s}^{-1}$
FIGURE 6.11
Strain versus time for Cross Bow System
Best Fitting (Strain Rate): $2.04 \times 10^3 \text{s}^{-1}$
As frequently explained in the literature [38-40], strain rate sensitivity can be determined from the stress against log strain rates plots. At a given strain level, \( \varepsilon \), the strain rate sensitivity, \( S \) may be defined by:

\[
S = \frac{d\sigma}{d\log\varepsilon}
\]

Figure 6.12 and 6.13 give the relationships between the flow stress and log strain rate at 10\%, 15\%, and 20\% strain for PEEK and PEK at 20 and 100\(^\circ\)C. The data points are obtained directly from the stress-strain curves at various strain rates shown in figure 6.1 and 6.2. It can be seen that the experimental points are aligned on straight lines within a narrow error band. A curve is fitted through the points with an error band of \( \pm3\% \). Table 6.3 show the values of the strain rate sensitivity for PEEK and PEK at 10\%, 15\% and 20\% strain at 20 and 100\(^\circ\)C.

Walley et al. [60] suggests that the maximum stress (yield stress) should be used in the strain rate sensitivity. He argued that although yield does not necessarily take place at the same strain for all strain rates, it is likely to occur when the polymer is in the same microstructural state. In the present work neither PEEK nor PEK show a load drop to indicate a maximum stress and this approach is not applicable.

Both PEEK and PEK exhibited a bilinear relationship between the stress and log strain rate where the strain rate sensitivity increases sharply at a strain rate of about 500 \( \text{s}^{-1} \). For strain rate up to 500 \( \text{s}^{-1} \), the strain rate sensitivity for PEEK at 20\(^\circ\)C is 3-5 MPa per decade of strain rate while at 100\(^\circ\)C the value drop to 2-4 MPa per decade of strain rate. This fall in
FIGURE 6.12a
True stress against Log strain rate for PEEK at 20°C at 10%, 15%, 20% strain
FIGURE 6.12b
True stress against Log strain rate
for PEEK at 100°C at 10%, 15%, 20% strain
FIGURE 6.13a
True stress against Log strain rate for PEK at 20°C at 10%, 15%, 20% strain
FIGURE 6.13b
True stress against Log strain rate for PEK at 100°C at 10%, 15%, 20% strain
Table 6.3 Strain Rate Sensitivity $S$ (MPa per decade of strain rate) for PEEK and PEK at 10%, 15% and 20% strain at 20 and 100 °C

<table>
<thead>
<tr>
<th>%E</th>
<th>$S_{20^\circ C}$</th>
<th>$S_{100^\circ C}$</th>
<th>$S_{20^\circ C}$</th>
<th>$S_{100^\circ C}$</th>
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<tr>
<td>20</td>
<td>3</td>
<td>2</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>
the strain rate sensitivity shows that PEEK softens at elevated temperature.

The strain rate sensitivity for PEK at 20 and 100°C are 3-5 and 3-6 MPa per decade of strain rate respectively. It can be concluded that up to 100 °C the strain rate sensitivity of PEK is not sensitive to the increase in temperature. Strain hardening occurred as the strain rate was raised from 500 to $10^3\text{s}^{-1}$.

Since the strain rate sensitivity depends only weakly on strain, and showed a high degree of consistency over the strain rate studied (up to $500\text{s}^{-1}$), an average strain rate sensitivity is calculated. For the range of strain rates from $10^{-3}$ to $500\text{s}^{-1}$, the average strain rate sensitivity for both PEEK and PEK were 4 MPa/decade of strain rate.

At around $500\text{s}^{-1}$, both polymers showed a sharp increase in the strain rate sensitivity although from the work of Walley [60], the strain rate sensitivity of the polymers studied showed a sudden change at $10^3\text{s}^{-1}$. The strain rate sensitivity obtained at strain rate greater than $500 \text{s}^{-1}$ for both PEEK and PEK are 60 MPa/decade of strain rate, ten times higher than the strain rate sensitivity obtained at strain rate below $500 \text{s}^{-1}$.

6.2.3 Stress Versus Temperature

6.2.3.1 Self Induced Heating

The heating effect is obviously particularly important for polymers since their mechanical properties show a much greater temperature dependence than metals. Stress at a given strain increases with
increasing strain rate but decreases as temperature is increased. At high strain rate, the time scale for the flow of heat from the sample is greater than the duration of the experiment itself. Therefore rapid increase in temperature occur. The temperature rise will produce strain softening instead of strain hardening as in the quasi-static test.

From thermodynamical considerations it can be shown that the deformation of polymers will take place isothermally at strain rates below $0.04 \text{s}^{-1}$ and adiabatically at rates above $4 \text{s}^{-1}$ [21]. The onset of adiabatic shear occurs when the loss of strength owing to heating exceeds the gain in strength owing to the combined effects of strain hardening and of strain rate hardening [61]. Although an increase in strain rate raises the yield stress, the deformation after yield generates heat, causing a fall in the flow stress. This is indicated by the curve obtained at 7 and $500 \text{s}^{-1}$.

The plastic work done on the tested sample is equivalent to the increases in thermal energy. The plastic work is calculated by measuring the area under the stress-strain curve with a planimeter. The temperature rise is then calculated using the following equation:

\[ \text{Specific Heat } C_p = \text{Joules/Kg K} \] \hspace{1cm} (6.2)

\[ \text{Temperature Rise } \Delta T = \frac{\text{JouleKg}^{-1}}{C_p} \] \hspace{1cm} (6.3)

\[ \text{Area under stress strain curve} = \int \sigma d\varepsilon \text{ Joules/Volume} \] \hspace{1cm} (6.4)

\[ \text{Density } \rho = \text{Kg/Volume} \]
\[ \text{Temperature Rise } \Delta T = \frac{\int \sigma d\varepsilon}{\rho C_p} \quad \text{.................................................. (6.5)} \]

The first step is to work out the dependence of bulk temperature rise in the sample on the compressive strain for each test condition. This relationship is determined from the equation above, in which the integral (energy per unit volume) was evaluated by measuring the area under the stress-strain curve at various strain levels. The bulk temperature rise for the tested sample have been determined by Dawson in her PhD thesis using a similar Conventional Dropweight at a strain rate of 700 s\(^{-1}\) [37].

The effect of heat developed during deformation on mechanical properties of materials investigated is quite evident, particularly at the medium strain rate 500 s\(^{-1}\) where the stress in the materials decreases while the strain is increasing. Table 6.4 shows the temperature rise with strain rate at 10%, 15% and 20% strain. Figure 6.14 shows the plot of temperature rise against log strain rate for PEEK. The rise in temperature decreases at 2000 s\(^{-1}\) possibly because plastic work is converted to internal energy for thermal softening processes to occur.

Although temperature rise is evidently high at high strain rate, at elevated temperature testing heating reduces adiabatic process. Table 6.5 shows the variation of temperature rise with testing temperature at various strains for PEEK tested at 1000 and 2000 s\(^{-1}\). Figure 6.15 shows the plot of temperature rise against testing temperature at 10%, 15% and 20% strain for PEEK tested at 1000 and 2000 s\(^{-1}\). The effect of heat treatment on the flow stress is described by the thermal sensitivity factor in the following section.
Table 6.4 Temperature rise (ΔT) increment with strain rate (\(\dot{\varepsilon}\)) at various strain (10%, 15% and 20% \(\varepsilon\))

<table>
<thead>
<tr>
<th>(\dot{\varepsilon}) (s(^{-1}))</th>
<th>(\Delta T_{10%\varepsilon}) (°C)</th>
<th>(\Delta T_{15%\varepsilon}) (°C)</th>
<th>(\Delta T_{20%\varepsilon}) (°C)</th>
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</thead>
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<tr>
<td>7</td>
<td>6.52</td>
<td>14.99</td>
<td>23.60</td>
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<tr>
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<tr>
<td>2000</td>
<td>8.77</td>
<td>18.50</td>
<td>25.99</td>
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</tbody>
</table>
FIGURE 6.14
Temperature Rise Against Log Strain Rate
For PEEK at 10%, 15% and 20% True Strain
Table 6.5A Variation of temperature rise ($\Delta T$) and specific heat $C_p$ with heat treatment (T) at various strain for PEEK tested at 1000 s$^{-1}$

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$C_p$</th>
<th>$\Delta T_{10%e}$ (°C)</th>
<th>$\Delta T_{15%e}$ (°C)</th>
<th>$\Delta T_{20%e}$ (°C)</th>
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<td>20</td>
<td>0.95</td>
<td>11.16</td>
<td>18.82</td>
<td>27.80</td>
</tr>
<tr>
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<td>1.08</td>
<td>8.77</td>
<td>14.24</td>
<td>21.75</td>
</tr>
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<td>80</td>
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<td>10.54</td>
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<tr>
<td>160</td>
<td>1.46</td>
<td>4.26</td>
<td>7.63</td>
<td>11.31</td>
</tr>
</tbody>
</table>

Table 6.5B Variation of temperature rise ($\Delta T$) and specific heat $C_p$ with heat treatment (T) at various strain for PEEK tested at 2000 s$^{-1}$

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$C_p$</th>
<th>$\Delta T_{10%e}$ (°C)</th>
<th>$\Delta T_{15%e}$ (°C)</th>
<th>$\Delta T_{20%e}$ (°C)</th>
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<td>18.50</td>
<td>25.99</td>
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<td>16.89</td>
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<td>6.89</td>
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<td>11.88</td>
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<td>1.60</td>
<td>4.52</td>
<td>7.55</td>
<td>10.39</td>
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</table>
FIGURE 6.15A
Temperature Rise Against Heat Treatment From High Strain Rate Test ($10^3\text{s}^{-1}$) At 10\%, 15\% and 20\% True Strain
FIGURE 6.15B
Temperature Rise Against Heat Treatment From High Strain Rate Test ($2 \times 10^3$ s$^{-1}$)
At 10\%, 15\% and 20\% True Strain
6.2.3.2 Thermal Sensitivity (dσ/dT)

The stress-strain curves obtained at a high strain rate is affected by the temperature rise and this temperature rise could account to the observed reduction in flow stress with increasing strain. It is necessary to determine the adiabatic correction due to thermal softening and use the corrected curve for the production of constitutive models of the polymer behaviour.

The thermal sensitivity $d\sigma/dT$ over a wide temperature range can be established by carrying out mechanical tests at various temperatures. $d\sigma/dT$ for all ranges of strain rate over a wide temperature range is shown in figure 6.16-6.20 and 6.21-6.25 for PEEK and PEK respectively. From these figures it is obvious that the thermal sensitivity can be divided into two regions by the transition temperature.

Table 6.6 and 6.7 shows the variation of $d\sigma/dT$ below and above transition temperature with strain rate for PEEK and PEK respectively. It can be concluded that $d\sigma/dT$ is very significant below these transition temperatures. Below the transition temperature, $d\sigma/dT$ for both PEEK and PEK increases with strain rate. Above the transition temperature $d\sigma/dT$ for the quasi-static test (isothermal process) is relatively small (less than 0.1 MPa/°C) while at 7 and 500s⁻¹, $d\sigma/dT$ falls to 0.1 - 0.2 MPa/°C for both PEEK and PEK. $d\sigma/dT$ is almost constant above the transition temperature except for the quasi-static test where the isothermal process does not contribute to the temperature rise in the bulk material. The high values of $d\sigma/dT$ with strain rate is in line with the bulk temperature rise increase with strain rate increase (figure 6.14).
FIGURE 6.16
Flow Stress Against Heat Treatment For PEEK From Quasi Static Test \((3 \times 10^{-3} \text{s}^{-1})\)
At 10%, 20% and 40% True Strain
FIGURE 6.17
Flow Stress Against Heat Treatment For PEEK From Dartec Hydraulic Machine (7s⁻¹)
At 10%, 20% and 40% True Strain
FIGURE 6.18
Flow Stress Against Heat Treatment For PEEK From Conventional Dropweight (500s⁻¹)
At 10%, 20% and 30% True Strain
FIGURE 6.19
Flow Stress Against Heat Treatment For PEEK From Improved Dropweight (1000s$^{-1}$) At 10%, 15% and 20% True Strain
FIGURE 6.20
Flow Stress Against Heat Treatment For PEEK From Cross Bow System (2000s⁻¹) At 10%, 15% and 20% True Strain
FIGURE 6.21
Flow Stress Against Heat Treatment For PEK From Quasi Static Test ($3 \times 10^{-3} \text{s}^{-1}$)
At 10%, 20% and 40% True Strain
FIGURE 6.22
Flow Stress Against Heat Treatment For PEK From Dartec Hydraulic Machine (7s\(^{-1}\))
At 10%, 20% and 40% True Strain
FIGURE 6.23
Flow Stress Against Heat Treatment For PEK From Conventional Dropweight (500s$^{-1}$)
At 10%, 20% and 30% True Strain
FIGURE 6.24
Flow Stress Against Heat Treatment For PEK From Improved Dropweight (1000s⁻¹) At 10%, 15% and 20% True Strain
Flow Stress Against Heat Treatment For PEK From Cross Bow System (2000s⁻¹) At 10%, 15% and 20% True Strain
Table 6.6 Variation of thermal sensitivity $d\sigma/dT$ and transition temperature $\tau$ with strain rate $\dot{\varepsilon}$ for PEEK

<table>
<thead>
<tr>
<th>$\dot{\varepsilon}$ (s$^{-1}$)</th>
<th>$\tau$ (°C)</th>
<th>$d\sigma/dT_{T&lt;\tau}$ (MPa °C$^{-1}$)</th>
<th>$d\sigma/dT_{T&gt;\tau}$ (MPa °C$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3x10$^{-3}$</td>
<td>100</td>
<td>-0.35</td>
<td>-0.09</td>
</tr>
<tr>
<td>7</td>
<td>140</td>
<td>-0.46</td>
<td>+0.13</td>
</tr>
<tr>
<td>500</td>
<td>120</td>
<td>-0.35</td>
<td>-0.24</td>
</tr>
<tr>
<td>1000</td>
<td>120</td>
<td>-0.60</td>
<td>-0.30</td>
</tr>
<tr>
<td>2000</td>
<td>60</td>
<td>-0.63</td>
<td>-0.30</td>
</tr>
</tbody>
</table>

Table 6.7 Variation of thermal sensitivity $d\sigma/dT$ and transition temperature $\tau$ with strain rate $\dot{\varepsilon}$ for PEK

<table>
<thead>
<tr>
<th>$\dot{\varepsilon}$ (s$^{-1}$)</th>
<th>$\tau$ (°C)</th>
<th>$d\sigma/dT_{T&lt;\tau}$ (MPa °C$^{-1}$)</th>
<th>$d\sigma/dT_{T&gt;\tau}$ (MPa °C$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3x10$^{-3}$</td>
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<td>-0.20</td>
<td>-0.08</td>
</tr>
<tr>
<td>7</td>
<td>140</td>
<td>-0.43</td>
<td>+0.13</td>
</tr>
<tr>
<td>500</td>
<td>140</td>
<td>-0.38</td>
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<tr>
<td>1000</td>
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<td>-0.25</td>
</tr>
<tr>
<td>2000</td>
<td>60</td>
<td>-0.90</td>
<td>-0.18</td>
</tr>
</tbody>
</table>
A simple explanation for the different thermal sensitivity (below the transition temperatures) at different strain rate comes from the temperature rise consideration. At quasi-static rates the difference in temperature rise at different experimental temperatures is smaller (small difference in area under the stress-strain curve) compared to the high strain rate tests. Follansbee [62] suggested that this degree of thermal softening could explain an overlap of quasi-static stress-strain curves with dynamic curves at certain strains. The reduction in stress $\Delta \sigma$ in the stress-strain curve can be written as following:

$$\Delta \sigma = (d\sigma/dT)\Delta T \ldots \ldots \ldots (6.6)$$

where $\Delta T$ is the bulk temperature rise calculated from equation (6.5).

Table 6.8 and 6.9 shows the reduction in stress $\Delta \sigma$ due to both temperature rise $\Delta T$ and the variation of thermal sensitivity $(d\sigma/dT)$ with testing temperature in PEEK and PEK tested at 1000 and 2000s$^{-1}$.

### 6.3 APPLICATION OF EYRING VISCOSITY THEORY TO THE RESULT AT DIFFERENT STRAIN RATE

In the formulation of a constitutive equation to explain the strain rate and temperature sensitivity, a combination of the Eyring type processes are used. A standard constitutive equation relating to the stress $\sigma$ with the strain $\varepsilon$ and the strain rate $\dot{\varepsilon}$ has been selected and is compared with the experimental data to test its applicability to PEEK and PEK.

As noted in the previous section, the flow stress is an increasing function of both strain and strain rate. The influence of strain rate on flow stress is
Table 6.8 Reduction in stress ($\Delta \sigma$) at 20%$\varepsilon$ due to temperature rise ($\Delta T$) in PEEK tested at 1000 and 2000s$^{-1}$ at various testing temperature

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>Strain Rate($\dot{\varepsilon}$)=1000s$^{-1}$</th>
<th>Strain Rate($\dot{\varepsilon}$)=2000s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta T$ (°C)</td>
<td>$\Delta \sigma$ (MPa)</td>
</tr>
<tr>
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<td>27.80</td>
<td>16.68</td>
</tr>
<tr>
<td>60</td>
<td>21.75</td>
<td>13.05</td>
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<tr>
<td>200</td>
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</tr>
</tbody>
</table>

Table 6.9 Reduction in stress ($\Delta \sigma$) at 20%$\varepsilon$ due to temperature rise ($\Delta T$) in PEK tested at 1000 and 2000s$^{-1}$ at various testing temperature

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>Strain Rate($\dot{\varepsilon}$)=1000s$^{-1}$</th>
<th>Strain Rate($\dot{\varepsilon}$)=2000s$^{-1}$</th>
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<tbody>
<tr>
<td></td>
<td>$\Delta T$ (°C)</td>
<td>$\Delta \sigma$ (MPa)</td>
</tr>
<tr>
<td>20</td>
<td>26.44</td>
<td>19.30</td>
</tr>
<tr>
<td>60</td>
<td>21.56</td>
<td>15.74</td>
</tr>
<tr>
<td>80</td>
<td>17.49</td>
<td>12.77</td>
</tr>
<tr>
<td>100</td>
<td>15.24</td>
<td>3.81</td>
</tr>
<tr>
<td>120</td>
<td>12.42</td>
<td>3.11</td>
</tr>
<tr>
<td>140</td>
<td>11.46</td>
<td>2.87</td>
</tr>
<tr>
<td>160</td>
<td>11.26</td>
<td>2.82</td>
</tr>
<tr>
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<td>---</td>
</tr>
<tr>
<td>200</td>
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</tr>
</tbody>
</table>
not very large. Table 6.10 and 6.11 shows the variation of $\sigma_{\gamma}/T$, $\sigma_{20\%}/T$ and $(\sigma_{20\%} + \Delta\sigma)/T$ (flow stress correction $\Delta\sigma$ for isothermal process, see equation 6.6) with testing temperature for PEEK and PEK respectively. The straight line obtain by plotting $\sigma_{\gamma}/T$ against log strain rate for both PEEK and PEK are in accordance with the prediction by Eyring theory (see figure 6.26 and 6.27). In the present work the Eyring theory was obeyed well for five decades ($10^{-3}$ to $10^5$ s$^{-1}$) of strain rate at all strains but breaks down at higher rates. Above 500 s$^{-1}$, $\sigma_{\gamma}/T$ increased drastically with strain rate. Figure 6.28 and 6.29 shows the plot of $\sigma_{20\%}/T$ against log strain rate for PEEK and PEK respectively. Also included in the figure is the correction for isothermal processes i.e. $(\sigma_{20\%} + \Delta\sigma)/T$.

This observation is opposite to the results obtained by Dawson [37] where $\sigma_{\gamma}/T$ decreased with log strain rate at the highest strain rate (700s$^{-1}$). This opposite observation is explained as due to the inaccuracy of the dropweight system at low strain (using the integration method in the strain calculation) in determining the yield point or yield stress.

Although polymers tend to be strong as strain rate is raised, at certain temperatures above 120°C, both semicrystalline PEEK and PEK showed a decrease in $\sigma_{\gamma}/T$ when plotted against log strain rate. This phenomenon is against the prediction of the Eyring theory. However Fleck and coworkers [15] have shown that the activation flow model is quite satisfactory for engineering applications over a wide range of temperature and strain rate up into the high strain rate regime ($10^3$ s$^{-1}$) for Poly-Carbonate (PC) and Poly-methyl-metha-acrylate (PMMA). Hence that temperature and strain rate are reciprocal variables.
Table 6.10A Variation of $\sigma_y/T$ (MPa/°K) with $T$ for PEEK tested at various strain rate

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$\sigma_y$/$T$</th>
<th>$\sigma_y$/$T_{3x10^{-3}s^{-1}}$</th>
<th>$\sigma_y$/$T_{50s^{-1}}$</th>
<th>$\sigma_y$/$T_{1000s^{-1}}$</th>
<th>$\sigma_y$/$T_{2000s^{-1}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.452</td>
<td>0.512</td>
<td>0.546</td>
<td>0.648</td>
<td>0.683</td>
</tr>
<tr>
<td>40</td>
<td>0.415</td>
<td>0.460</td>
<td>0.479</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>60</td>
<td>0.368</td>
<td>0.414</td>
<td>0.426</td>
<td>0.511</td>
<td>0.505</td>
</tr>
<tr>
<td>80</td>
<td>0.331</td>
<td>0.334</td>
<td>0.380</td>
<td>0.460</td>
<td>0.467</td>
</tr>
<tr>
<td>100</td>
<td>0.284</td>
<td>0.306</td>
<td>0.343</td>
<td>0.416</td>
<td>0.429</td>
</tr>
<tr>
<td>120</td>
<td>0.277</td>
<td>0.249</td>
<td>0.285</td>
<td>0.382</td>
<td>0.387</td>
</tr>
<tr>
<td>140</td>
<td>0.257</td>
<td>0.225</td>
<td>0.264</td>
<td>0.351</td>
<td>0.351</td>
</tr>
<tr>
<td>160</td>
<td>0.236</td>
<td>0.224</td>
<td>0.240</td>
<td>0.312</td>
<td>0.289</td>
</tr>
<tr>
<td>180</td>
<td>0.219</td>
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<td>0.225</td>
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<td>0.252</td>
</tr>
<tr>
<td>200</td>
<td>0.211</td>
<td>0.216</td>
<td>0.190</td>
<td>---</td>
<td>0.258</td>
</tr>
</tbody>
</table>

Table 6.10B Variation of ($\sigma_{20\%}$)/$T$ and ($\sigma_{20\%} + \Delta\sigma$)/$T$ with $T$ for PEEK tested at various strain rate

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$\sigma_{20%}$/$T$</th>
<th>$\sigma_{20%}$/$T_{3x10^{-3}s^{-1}}$</th>
<th>$\sigma_{20%}$/$T_{50s^{-1}}$</th>
<th>$\sigma_{20%}$/$T_{1000s^{-1}}$</th>
<th>$\sigma_{20%}$/$T_{2000s^{-1}}$</th>
<th>$\sigma_{20%} + \Delta\sigma$/$T_{3x10^{-3}s^{-1}}$</th>
<th>$\sigma_{20%} + \Delta\sigma$/$T_{50s^{-1}}$</th>
<th>$\sigma_{20%} + \Delta\sigma$/$T_{1000s^{-1}}$</th>
<th>$\sigma_{20%} + \Delta\sigma$/$T_{2000s^{-1}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.468</td>
<td>0.495</td>
<td>0.512</td>
<td>0.870</td>
<td>0.927</td>
<td>0.720</td>
<td>0.776</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.431</td>
<td>0.454</td>
<td>0.455</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>0.383</td>
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<td>0.408</td>
<td>0.676</td>
<td>0.715</td>
<td>0.562</td>
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</tr>
<tr>
<td>80</td>
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<td>0.357</td>
<td>0.363</td>
<td>0.538</td>
<td>0.571</td>
<td>0.521</td>
<td>0.538</td>
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<td></td>
</tr>
<tr>
<td>100</td>
<td>0.303</td>
<td>0.322</td>
<td>0.332</td>
<td>0.496</td>
<td>0.524</td>
<td>0.483</td>
<td>0.496</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>0.290</td>
<td>0.254</td>
<td>0.280</td>
<td>0.407</td>
<td>0.430</td>
<td>0.471</td>
<td>0.483</td>
<td></td>
<td></td>
</tr>
<tr>
<td>140</td>
<td>0.266</td>
<td>0.235</td>
<td>0.264</td>
<td>0.400</td>
<td>0.410</td>
<td>0.416</td>
<td>0.427</td>
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<td>0.238</td>
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<td>0.331</td>
<td>0.339</td>
<td>0.366</td>
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</tr>
<tr>
<td>180</td>
<td>0.225</td>
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<td>0.219</td>
<td>---</td>
<td>---</td>
<td>0.283</td>
<td>0.304</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>0.224</td>
<td>0.224</td>
<td>0.186</td>
<td>---</td>
<td>---</td>
<td>0.285</td>
<td>0.306</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 6.11A Variation of $\frac{\sigma_y}{T}$ (MPa/K) with $T$ for PEK tested at various strain rate/Temp

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$\frac{\sigma_y}{T}$ $3 \times 10^{-3}\text{s}^{-1}$</th>
<th>$\frac{\sigma_y}{T}$ $7\text{s}^{-1}$</th>
<th>$\frac{\sigma_y}{T}$ $500\text{s}^{-1}$</th>
<th>$\frac{\sigma_y}{T}$ $1000\text{s}^{-1}$</th>
<th>$\frac{\sigma_y}{T}$ $2000\text{s}^{-1}$</th>
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</thead>
<tbody>
<tr>
<td>20</td>
<td>0.512</td>
<td>0.580</td>
<td>0.601</td>
<td>0.717</td>
<td>0.730</td>
</tr>
<tr>
<td>40</td>
<td>0.444</td>
<td>0.519</td>
<td>0.543</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>60</td>
<td>0.398</td>
<td>0.450</td>
<td>0.471</td>
<td>0.541</td>
<td>0.534</td>
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<tr>
<td>80</td>
<td>0.361</td>
<td>0.416</td>
<td>0.433</td>
<td>0.482</td>
<td>0.510</td>
</tr>
<tr>
<td>100</td>
<td>0.302</td>
<td>0.367</td>
<td>0.386</td>
<td>0.456</td>
<td>0.450</td>
</tr>
<tr>
<td>120</td>
<td>0.305</td>
<td>0.272</td>
<td>0.346</td>
<td>0.407</td>
<td>0.433</td>
</tr>
<tr>
<td>140</td>
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<td>0.266</td>
<td>0.300</td>
<td>0.375</td>
<td>0.412</td>
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<tr>
<td>160</td>
<td>0.261</td>
<td>0.268</td>
<td>0.277</td>
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<td>0.358</td>
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<tr>
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<td>0.256</td>
<td>0.265</td>
<td>0.247</td>
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<td>0.310</td>
</tr>
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<td>0.237</td>
<td>0.242</td>
<td>0.211</td>
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<td>0.307</td>
</tr>
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</table>

Table 6.11B Variation of $\frac{\sigma_{20\%e}}{T}$ and $\frac{(\sigma_{20\%e} + \Delta\sigma)}{T}$ with $T$ for PEK tested at various strain rate/Temp

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$\frac{\sigma_{20%e}}{T}$ $3 \times 10^{-3}\text{s}^{-1}$</th>
<th>$\frac{\sigma_{20%e}}{T}$ $7\text{s}^{-1}$</th>
<th>$\frac{\sigma_{20%e}}{T}$ $500\text{s}^{-1}$</th>
<th>$\frac{\sigma_{20%e}}{T}$ $1000\text{s}^{-1}$</th>
<th>$\frac{\sigma_{20%e} + \Delta\sigma}{T}$ $400\text{s}^{-1}$</th>
<th>$\frac{\sigma_{20%e} + \Delta\sigma}{T}$ $2000\text{s}^{-1}$</th>
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</thead>
<tbody>
<tr>
<td>20</td>
<td>0.519</td>
<td>0.556</td>
<td>0.572</td>
<td>0.819</td>
<td>0.885</td>
<td>0.939</td>
</tr>
<tr>
<td>40</td>
<td>0.454</td>
<td>0.492</td>
<td>0.505</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>60</td>
<td>0.405</td>
<td>0.443</td>
<td>0.443</td>
<td>0.661</td>
<td>0.708</td>
<td>0.586</td>
</tr>
<tr>
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<td>0.377</td>
<td>0.411</td>
<td>0.418</td>
<td>0.538</td>
<td>0.574</td>
<td>0.567</td>
</tr>
<tr>
<td>100</td>
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<td>0.359</td>
<td>0.365</td>
<td>0.563</td>
<td>0.573</td>
<td>0.488</td>
</tr>
<tr>
<td>120</td>
<td>0.321</td>
<td>0.277</td>
<td>0.336</td>
<td>0.478</td>
<td>0.486</td>
<td>0.483</td>
</tr>
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<td>0.276</td>
<td>0.291</td>
<td>0.424</td>
<td>0.431</td>
<td>0.436</td>
</tr>
<tr>
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<td>0.270</td>
<td>0.273</td>
<td>0.496</td>
<td>0.503</td>
<td>0.416</td>
</tr>
<tr>
<td>180</td>
<td>0.265</td>
<td>0.274</td>
<td>0.249</td>
<td>---</td>
<td>---</td>
<td>0.393</td>
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<tr>
<td>200</td>
<td>0.249</td>
<td>0.254</td>
<td>0.211</td>
<td>---</td>
<td>---</td>
<td>0.376</td>
</tr>
</tbody>
</table>
Figure 6.26
Yield Stress (MPa)/Temperature (K) versus log strain rate (1/second) for PEEK at various temperatures.
Figure 6.27

Yield Stress (MPa)/Temperature (K) versus log strain rate (1/second) for PEK at various temperatures
Figure 6.28
Flow stress at 20% strain/Temperature versus log strain rate for PEEK at various testing temperature. (-- --)corrected isothermal curves
Figure 6.29
Flow stress at 20% strain/Temperature versus log strain rate for PEK at various testing temperature. (---) corrected isothermal curves
6.4 ACTIVATION VOLUME $V_A$ AND ACTIVATION ENERGY $\Delta H$

In the development of theories of yield based on molecular considerations, yield and flow are usually regarded as thermodynamically activated processes with associated activation volumes and energies [40]. The activation volume deduced from figure 6.12a (i.e. using the strain rate sensitivity parameter $S$) and using equation 2.13 is calculated as following. From equation (2.13):

$$\sigma = \frac{kT}{V_A} \ln \frac{\varepsilon}{\varepsilon_0}$$

$$\sigma = \frac{kT}{V_A} (\ln \varepsilon - \ln \varepsilon_0) \ldots \ldots \ldots (6.6)$$

$$\sigma = \frac{kT}{V_A} \ln \varepsilon - \frac{kT}{V_A} \ln \varepsilon_0 \ldots \ldots \ldots (6.7)$$

The strain rate sensitivity $S$ (4 MPa/decade of strain rate) which is equivalent to the gradient of the curve in figure 6.12a is equated to $kT/V_A$.

$$\frac{kT}{V_A} = 4 \times 10^6$$

$$V_A = \frac{1.381 \times 10^{-23} \times 293}{4 \times 10^6}$$

$V_A = 1.01 \text{ nm}^3$

$\varepsilon_0$ is obtained by equating $kT/V_A (\ln \dot{\varepsilon} - \ln \dot{\varepsilon}_0)$ (from equation 6.7) to $Q$ (the point where the curve crosses the $y$ axis of figure 6.12a i.e. 132 MPa), taking $\ln \dot{\varepsilon} = 0.001$ and $kT/V_A = 4 \text{ MPa}$ i.e. the gradient of the curve.
\[ 132 \text{ MPa} = (4 \text{ MPa})(0.001 - \ln \dot{\varepsilon}_0) \] .............. (6.8)

\[ 132 \text{ MPa} / 4 \text{ MPa} = 0.001 - \ln \dot{\varepsilon}_0 \]

\[ \ln \dot{\varepsilon}_0 = 0.001 - 33 = -32.999 \]

\[ \dot{\varepsilon}_0 = \exp(-32.999) = 4.66 \times 10^{-15} \text{ s}^{-1} \]

Using the same procedure to figure 6.13a \( V_A \) and \( \dot{\varepsilon}_0 \) for PEK at 20°C were found to be 1.01 nm\(^3\) and 5.88x10\(^{-18}\) s\(^{-1}\) respectively.

Alternatively the activation volume for PEEK can be calculated from figure 6.26 (i.e. using the plot of \( \sigma_y/T \) against log strain rate) and using equation (2.10). From equation (2.10):

\[ \frac{\sigma}{T} = \frac{\Delta H}{V_A T} + \frac{R \ln 2}{V_A} \frac{\dot{\varepsilon}}{\dot{\varepsilon}_0} \]

\[ \frac{\sigma}{T} = \frac{\Delta H}{V_A T} + \frac{R \ln 2}{V_A} - \frac{R}{V_A} \ln \dot{\varepsilon}_0 + \frac{R}{V_A} \ln \dot{\varepsilon} \] .... (6.9)

Equating the gradient of the slope in figure 6.26 (i.e. 0.018 MPa/Kelvin/decade of strain rate for temperatures and strain rates up to 100°C and 500s\(^{-1}\) respectively) to \( R/V_A \) (from equation 6.9) the following is obtained:

\[ \frac{R}{V_A} = 0.018 \text{ MPaK}^{-1} \]

\[ V_A = \frac{R}{0.018 \text{ MPaK}^{-1}} \]
\[ V_A = \frac{8.314 \text{ NmK}^{-1}\text{mol}^{-1}}{0.018 \times 10^6 \text{ Nm}^{-2}\text{K}^{-1}} \]

\[ V_A = 461.9 \times 10^{-8} \text{ m}^3\text{mol}^{-1} \]

\[ N_A = \text{avogadro number} = 6.022 \times 10^{23} \text{mol}^{-1} \]

\[ V_A = \frac{461.9 \times 10^{-8} \text{ m}^3\text{mol}^{-1}}{6.022 \times 10^{23} \text{mol}^{-1}} = 0.8 \text{ nm}^3 \]

The similarity of the value of \( V_A \) from the two calculations gives us confidence that the results are real. Dawson [37] found that \( V_A \) is 4 nm\(^3\) and \( V_A \) calculated by Walley [60] from the strain rate sensitivity are unrealistically large (0.64 – \( 5.1 \times 10^6 \text{nm}^3 \)). The activation volume for other polymers is shown in table 6.12 for comparison [1].

The effect of temperature should be studied so as to obtain the activation energy \( \Delta H \). From equation 6.9 and the intersection of \( \sigma_v/T \) at 20°C with the y axis (see figure 6.26), the following is obtained:

\[ \frac{\Delta H}{V_A T} + \frac{R}{V_A} \ln 2 - \frac{R}{V_A} \ln \varepsilon_0 = 0.44 \text{ MPaK}^{-1} \]

\[ \Delta H = V_A T \left( 0.44 + \frac{R}{V_A} \ln \frac{\varepsilon_0}{2} \right) \]

\[ \Delta H = 9.4 \times 10^4 \text{ Jmol}^{-1} \]

where \( V_A = 461.9 \times 10^{-8} \text{ m}^3\text{mol}^{-1} \), \( \varepsilon_0 = 4.66 \times 10^{-15} \text{s}^{-1} \) and \( T = 293 \text{K} \)
Table 6.12  A comparison of the statistical segment volume for a polymer measured in solution with the flow volumes derived from the Eyring Theory [1].

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Volume of statistical link in solution (nm$^3$)</th>
<th>Eyring flow volume $v$ (nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinylchloride</td>
<td>0.38</td>
<td>8.6</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>0.48</td>
<td>6.4</td>
</tr>
<tr>
<td>Polymethylmethacrylate</td>
<td>0.91</td>
<td>4.6</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>1.22</td>
<td>9.6</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>2.06</td>
<td>8.8</td>
</tr>
<tr>
<td>Cellulose trinitrate</td>
<td>2.62</td>
<td>6.1</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>2.05</td>
<td>17.4</td>
</tr>
</tbody>
</table>
6.5 DISCUSSION OF RESULTS

The results clearly indicate that the mechanical behaviour of both PEEK and PEK can be described by 4 main regions:

(I) Strain rates below $\sim 10^3 \text{s}^{-1}$ and temperatures below $\sim 120^\circ\text{C}$;
(II) Strain rates above $\sim 10^3 \text{s}^{-1}$ and temperatures below $\sim 120^\circ\text{C}$;
(III) Strain rates below $\sim 10^3 \text{s}^{-1}$ and temperatures above $\sim 120^\circ\text{C}$;
(IV) Strain rates above $\sim 10^3 \text{s}^{-1}$ and temperatures above $\sim 120^\circ\text{C}$.

These regions can clearly be distinguished with reference to figures 6.26 - 6.29. The rapid change in flow stress as a function of temperature (confirmed by tests on different types of equipment) above $\sim 10^3 \text{s}^{-1}$ is clearly evident as is the distinct change in slope of the curves at temperatures above $\sim 120^\circ\text{C}$.

The standard Eyring type model fits the data well for region (I) with realistic values of both activation energies $\Delta H$ and activation volume $V_A$. It is expected that use of a model with two values of $\Delta H$ and $V_A$ representing the simultaneous operation of two distinct molecular processes could be used to model the complete strain rate range at temperatures below $\sim 120^\circ\text{C}$. Following Ree and Eyring [1] it has been proposed that equation 2.10 (see chapter 2) should be extended by assuming that there is more than one activated rate process with all species of flow units moving at the same rate, the stresses being additive. The equivalent equation to equation 2.10 is then:

$$\frac{\sigma}{T} = \frac{\Delta H_1}{V_A 1} + \frac{R}{V_A 1} \ln 2 \left( \frac{\dot{\varepsilon}}{\varepsilon_0 1} \right) + \frac{R}{V_A 2} \sinh^{-1} \left( \frac{\dot{\varepsilon}}{\varepsilon_0 2} \exp \frac{\Delta H_2}{RT} \right)$$

...(6.10)
where the two activated processes are denoted by the subscript symbols 1 and 2 respectively. At high temperatures and low strain rates (region (III)) process 1 predominates and this has a comparatively low strain rate dependence ($V_{A1}$ is large). Process 2 also becomes important at low temperatures and high strain rates (region (II)) and shows a much higher strain rate dependence ($V_{A2}$ is small compared to $V_{A1}$). However there is not sufficient very high strain rate data to confirm this as a constitutive model of the materials below $-120^\circ C$.

Above a test temperature of $-120^\circ C$ the material undergo a transition in which the flow stress decreases much less rapidly as a function of strain rate. This is probably due to the increase in strain induced crystallinity at these temperatures (chapters 4 and 5). The behaviour at a strain rate of $-7s^{-1}$ is anomalous in that the flow stress increases with temperature. The explanation for this is not clear and will require further investigation.

It has been demonstrated that the temperature rises associated with adiabatic heating at high strain rates are relatively modest at low strains (see figure 6.15) but become increasingly important as the strain increases. The data also shows that the temperature rise is far less dramatic for tests carried out at high temperature. A combination of these results with the data on temperature sensitivity of flow stress (see figure 6.16-6.25) provides a clear explanation of the observed cross-over in the stress-strain curves at the highest strain rates.

From the results and analysis above it can be concluded that the Dropweight and Cross-Bow systems are successful in obtaining high strain rate data at a strain rate that is virtually constant throughout the test.
6.6 SOURCES OF ERROR

A feature of all impact tests is the scatter present in the results. Scatter always occur in experiment but impact generally shows higher levels of scatter than other tests. The source of scatter in the high strain rate axial tests comes from a number of sources, including:

(i) Variations in material response due to different amount of machining damage,
(ii) Slight variations in the test temperature in the sample,
(iii) Slight variation in the area of contact.

The force and displacement measurement from the experimental apparatus in the Improved Dropweight system are both parametric in time and so it is a trivial matter to reduce them to the stress against strain curve. The deconvolution procedure using FFT which was carried out to reduce the effects of high frequency noise was applied selectively only at a particular frequency and above. The changing area of the sample is taken into account through the constant volume assumption of full plasticity. In practice the deformation may not be completely homogeneous.

6.6.1 Barrelling

The stresses are calculated on the instantaneous cross section, assuming the material to be incompressible, and the cross section to be uniform along the sample length throughout the test. Both of these assumptions are likely to introduce small errors, but this representation is considered to give a more direct picture of the stress-strain behaviour of
the material than the use of stresses calculated on the unstrained cross section.

In this investigation, even though all sample ends were lubricated with petroleum jelly, a small barelling was observed at large strains beyond 10 percent of strain (this is in accordance with the observation of Dawson [37]). This effect of the end constraint on the results due to friction is estimated at less than 3% at the maximum strain of 20%.

6.6.2 Temperature variation

At elevated temperature testing, fluctuation of the sample temperature occurs, therefore a correction should be derived for the temperature lag between the sample and the hot stage heater. The maximum inaccuracy in the temperature was estimated to be 2°C.
CHAPTER 7

CONCLUSIONS AND SUGGESTIONS
7.0 CONCLUSIONS AND SUGGESTIONS

7.1 CONCLUSIONS

A Dartec Hydraulic machine, a Conventional Dropweight, an Improved Dropweight and a Cross-Bow system were used to measure the stress-strain curves. In the range of strain rates studied, methods based on direct measurements were used without wave propagation effects becoming important. The optical methods used for strain measurements were employed since they afford a direct measurement of stress (from photograph) and strain (from laser-photodiode).

The mechanical response of PEEK and PEK has been investigated in compression at strain rates of $10^{-3} - 10^3 \text{s}^{-1}$ at various temperatures ranging from 20-200°C. It appears that the shape of the stress-strain curves of PEEK and PEK are similar. The differences between the flow stress are not very pronounced. This is because the structure of PEEK and PEK are similar.

Changes in both the rate of loading and temperature produce a series of stress-strain curves. These comprehensive sets of curves can be used to gain a thorough understanding of the time and temperature dependences of material mechanical properties. The results obtained are of great importance to evaluate the ability of existing yield theory to account for the influence of temperature and strain rate upon the yield stress and flow stress of polymers.

Although the yield stress of the polymers investigated was temperature and strain rate dependent, the essential theoretical idea which appears
to be correct from the experimental evidence is that polymer plasticity is controlled by thermally activated processes. Increasing strain rate increases the yield stress, but the process becomes adiabatic and hence reduces the flow stress at higher strains.

In the range of strain rates studied, there is an obvious transition from isothermal to adiabatic processes observed in the stress-strain curves although not easily observed in the stress-log strain rate plot due to lack of data at a range of low strain rates. Results obtained at various strain rates showed that the cross-over of stress-strain curves at certain strain rates (i.e. at 7 & 500s^{-1}) is due to thermal softening caused by adiabatic processes. These correspond to an increase in the temperature of the sample. At higher strain rates (i.e. at 1000 and 2000s^{-1}) strain hardening reappears. Although the process is adiabatic the fast rate causes the polymer to become brittle.

In the range of temperature studied, it is clear that a major change occurs on passing through the glass transition temperature (T_g) despite the presence of the crystalline fraction. This transition is obviously related to T_g of the semicrystalline polymers and cold crystallization which occurs with the greater molecular mobility around T_g. Since there is very little published information on the effects of temperature on the mechanical properties of semicrystalline polymers, particularly at other than quasi-static strain rates, the present results cannot be compared with published data.

At high strain rate testing (i.e at 1000 and 2000s^{-1}), cross-over of stress-strain curves occur above a certain temperature which is related to T_g. Increasing the temperature up to T_g obviously reduces the polymer
strength, but above $T_g$ the effect of crystallinity can strengthen the polymer significantly. Since below $T_g$, the amorphous component is in a glassy state, the flow stress decreases with increase in temperature. Above $T_g$, this behaviour strongly depends on the degree of crystallinity. For testing above $T_g$, we see that an increased degree in crystallinity results in increased flow stress.

The data seems to suggest that at around $T_g$ the best conditions in terms of mobility for alignment of chains (orientation) and crystal growth are reached. The actual temperature at which orientation occurs depends on the previous degree of orientation and the amount of crystallinity present. For testing near $T_g$ we see that an increased degree of orientation causes an increased in flow stress. Above $T_g$, although the mobility is higher, the system is predominantly in the rubbery state and therefore relaxation phenomena behave as competitive mechanisms to the chain orientation.

The ability of the Eyring viscosity theory to fit the data obtained is limited to strain rates up to $500 \text{s}^{-1}$. There is some argument as to whether the large increase in flow stress observed at very high rates is a genuine effect but the results obtained at $1000$ and $2000 \text{s}^{-1}$ are thought of as genuinely true since they are shown by two different samples namely PEEK and PEK, and two different measuring methods. Although compression at high strain rates is theoretically adiabatic, the temperature rise effect in the corrected stress is not significant enough to show any changes in the Eyring theory fitting.

Investigation into the behaviour around $T_g$ was done using X-ray diffraction and DSC. The DSC thermograms confirmed the X-ray
diffraction results. Both techniques showed that increasing the heat
treatment in the absence of strain produced only slight increases in the
degree of crystallinity. The results are wholly satisfactory for comparative
purposes. It is clear that changing the test temperature produces
different degrees of crystallinity in both polymers studied as determined
by X-ray diffraction. These changes again occur in the way in which we
would expect from the DSC results, viz that the crystallinity is associated
with the cross-over of the stress-strain curves in the high strain rate
testing. The introduction of crystals due to recrystallization at elevated
temperatures causes an increase in the flow stress for testing above the
$T_g$.

The WAXD study demonstrate that variations in crystalline packing
shown by changes in the lattice spacing $d$ for PEEK occur in both
annealed and tested samples. Apparently, the flow stress is a direct
function of its crystalline morphology, i.e. the thicker the lamellae and the
larger the spherulite size, the higher the flow stress. The results based
on thermal analysis indicate that the presence of secondary crystallites,
with a low degree of stability, may also have a direct effect on the flow
stress.

The primary value of the X-ray data is to facilitate the interpretation of
the DSC thermograms. The increase of melting endotherm on increasing
the annealing temperature means that at higher temperature, the
number of chains able to crystallize increases and more perfect crystals
are formed. The increase in crystallinity might involve an increase in the
total number of crystallites or the average perfection of existing
crystallites.
7.2 SUGGESTIONS

In all the calculations, Poisson's ratio was assumed to be 0.5 as derived from the quasi-static measurement. At higher strain rate, it is thought that both the axial and radial strain could be measured through the combination of the displacement measuring techniques involve in the Conventional and Improved Dropweight systems. At the same time both direct stress and strain measurements can be incorporated in one system by combination of the laser-photodiode and camera systems to produce true stress-strain curves without the assumption of volume conservation. This would constitute a further improvement in the experimental technique.

Since the sample diameter measurements from the film projections (using slide projector) are not exactly repeatable, the measurements would be more accurately taken using the CCD (close circuit display) camera incorporating the Rheed Vision computer software package (mention earlier in chapter 4).

In this work, the Conventional Dropweight was used to obtained a strain rate at \(-500\text{s}^{-1}\). It should be beneficial to have data at a strain rate of order \(10^3\text{s}^{-1}\) with this system. These data hopefully would confirm the result obtained from the Improved Dropweight system. To predict the exact strain rate where transition from isothermal and adiabatic processes occur it is suggested that more tests be conducted from as low as \(10^{-4}\text{s}^{-1}\) and the rate increased by steps of \(10\text{s}^{-1}\). Since heat treatment affect the stress-strain curves significantly at high strain rate, testing other types of semicrystalline polymer could confirm the effects of
temperature on the mechanical properties of semicrystalline polymers in general.

It will be interesting to investigate the density of the tested and annealed sample. Since testing can cause destruction of the crystal structure and/or void formation it is expected that the density of the tested sample will decreased. At the same time effect of temperature treatment upon density (the density is expected to increase as a result of increase chain packing) can be used to confirm the results obtained from the X-ray diffractions and DSC thermograms. The measurements of the X-ray diffraction at elevated temperatures ought to be made in an electrically heated, thermocoupled-controlled oven.
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APPENDIX 3.1 POISSON.BAS
APPENDIX 3.2 DSA.BAS
APPENDIX 3.3 LOADDISP.BAS
APPENDIX 3.4 IPTME.BAS
APPENDIX 3.5 DROP.BAS
APPENDIX 3.6 STRESS.BAS
APPENDIX 3.7 CROSSBOW.BAS
APPENDIX 3.1 POISSON.BAS

REM POISSON BAS
REM Poisson Ratio Measurement
DIM disp(100),finhig(100),vd(100),mv(100)
DIM axistr(100),radstr(100),poison(100)
PRINT "please input the datafile"
INPUT filename$
ext3$="p.rat"
ext4$="v.rat"
filevolt$=filename$+ext4$
fileratio$=filename$+ext3$
OPEN #3 INPUT fileratio$
INPUT #3 d0,h0,vd0,n
enlarge=vd0/d0
FOR i=1 TO n
INPUT #3 vd(i)
v(i)=vd(i)/enlarge
radstr(i)=LOG(vd(i)/d0)
NEXT i
CLOSE #3
OPEN #4 INPUT filevolt$
FOR i=1 TO n
INPUT #4 mv(i)
disp(i)=mv(i)/5.324
finhig(i)=h0-disp(i)
axistr(i)=LOG(finhig(i)/h0)
poison(i)=radstr(i)/axistr(i)
NEXT i
CLOSE #3
CLOSE #4
fileout$=filename$+".prt"
OPEN #5 OUTPUT fileout$
PRINT #5 "diameter| height | radstr | axistr | poison"
FOR i=1 TO n
PRINT #5 vd(i);"|";finhig(i);"|";radstr(i);"|";axistr(i);"|";poison(i)
NEXT i
CLOSE #5
APPENDIX 3.2 DSA.BAS

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 111
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 111
CLS

REM *** read the original record from *.DSC ***

PRINT "please input the name of data file"
INPUT filename$
ext$=".dsc"
datafile$=filename$+ext$
fileinno=5
reclength=1
RECORD n; dsa$ FIXED 1
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$(i)=" " THEN 310
IF it=0 THEN itb=i
t$=t$+header$(i)
it=it+1
IF header$(i)="S" THEN 320
310 NEXT i
320 FOR i=49 TO 100
namee$=namee$+header$(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
BOX 300;200,4000,3210
FOR i=1 TO 9
x=x+400
LINE x;200,x;3400
NEXT i
FOR i=1 TO 7
y=y+400
LINE 300;y,4300;y
NEXT i
FOR i=1 TO 496 STEP 4
x=i+300
y=1940+((result(i)-128)*400)/30
PLOT x;y COLOUR (2); NEXT i

REM *** cut the needed range from the curve ***

REM input the cut range

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 " i ";
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

4344 PRINT " please input the file name for storing the results"
INPUT re$
filename=6
filename$=re$".zxw"

REM *** calculate the value of v/div and t/div ***

FOR i=26 TO 25+iv
ii=i-25
vt(ii)=ASC(header$(i))-=48
NEXT i
GOSUB translation
vdiv=tran
FOR i=l TO 5
vt(i)=0; NEXT i
FOR i=itb TO itb+it-l
ii=i+1-itb
vt(ii)=ASC(header$(i))-48
NEXT i
GOSUB translation
tdiv=tran

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

OPEN #fileoutno OUTPUT filename$
PRINT #fileoutno namee$
PRINT #fileoutno datee$
PRINT #fileoutno timee$
PRINT #fileoutno number
FOR i=nub TO nue
 t=tdiv*i/lOO
 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 ***

PRINT COLOUR(2);" please check following number,"
PRINT COLOUR(2);" they should be exact the same"
PRINT COLOUR(2);" v/div=";v$
PRINT COLOUR(2);" v/div=";USING "##,##,##,##";vdiv
PRINT COLOUR(5);" t/div=";t$
PRINT COLOUR(5);" t/div=";USING "##,##,##,##";tdiv
PRINT COLOUR(7);" The data have been stored in the file"
PRINT "of":filename$
PRINT COLOUR(7);" When you want read data from ";filename$
PRINT COLOUR(7);" please use following format"
PRINT COLOUR(7);" open #fileno input"
PRINT CHR$(34);filename$;CHR$(34)
PRINT COLOUR(7);" input #fileno name$, date$, time$
PRINT COLOUR(7);" input #fileno number"
PRINT COLOUR(7);" for i=1 to number"
PRINT COLOUR(7);" input #fileno t(i),v(i)"
PRINT COLOUR(7);" next i"
PRINT COLOUR(7);" close #fileno"
PRINT
PRINT COLOUR (4);" that's OK!"
CLOSE #fileinno;END

REM ****************************
REM * END OF THE MASTER PROGRAM *
REM ****************************
LABEL translation

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

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

REM *** END OF SUBROUTINE TRANSLATION ***

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
APPENDIX 3.3 LOADDISP.BAS

REM LOAD DISPLACEMENT BAS
REM A PROGRAM FOR LOAD AND DISPLACEMENT CALCULATION
DIM l(2010),d(2010),a(209),b(209)
PRINT "please input the datafile"
INPUT filename$
ext2$="1.zxw"
ext3$="d.zxw"
filestress$=filename$+ext2$
filestrain$=filename$+ext3$
OPEN #6 INPUT filestress$
OPEN #3 INPUT filestrain$
FOR i=1 TO 1000
INPUT #6 l(i)
INPUT #3 d(i)
l(i)=-l(i)
d(i)=-d(i)
NEXT i

REM determine the starting point for load l(j),
REM assign d(j) as starting point for displacement
FOR i=1 TO 1000
IF l(i)>0.04 THEN GOTO 10
NEXT i
10 j=i
dispo=d(j-1)
loado=l(j-1)
PRINT j,loado
a(l)=0
b(l)=0
k=l
FOR p=j TO 1000 STEP 10
suml=0
sumd=0
k=k+1
FOR m=0 TO 9
suml=suml+l(m+p)
sumd=sumd+d(m+p)
NEXT m
a(k)=suml/10
b(k)=sumd/10
REM 1 volt load equal 5 kN
REM 1 volt dispalcement equal 10 mm
b(k)=dispo-b(k)
b(k)=-b(k)*10
a(k)=a(k)*5000
NEXT p
CLOSE #6
CLOSE #3
REM open file for output
fileout$=filename$+.dat"
OPEN #9 OUTPUT fileout$
PRINT " disp (mm) | load (kN) "
FOR k=1 TO 1000/10
PRINT #9, b(k);" | ";a(k)*1.0e-3
NEXT k
CLOSE #9
APPENDIX 3.4 IPTME.BAS

REM  A PROGRAM FOR STRESS AND STRAIN CALCULATION
REM 1 volt load equal 5000 Newton, 1 volt displacement equal 10 mm
REM  \( Y = 64.275 \times 10^2 + 40.131x - 0.15398 \) is the machine compliance equation
DIM l(20),d(20),area(20),b(20),a(20),x(20)
PRINT "please input the datafile"
INPUT filename$
ext1$="n.dhn"
ext2$="l.zxw"
ext3$="d.zxw"
filedhn$=filename$+ext1$
filestress$=filename$+ext2$
filestrain$=filename$+ext3$
OPEN #5 INPUT filedhn$
OPEN #6 INPUT filestress$
OPEN #3 INPUT filestrain$
INPUT #5 d0,h0,n
FOR i=1 TO n
INPUT #6 l(i)
INPUT #3 d(i)
l(1)=1.5-l(i)
NEXT i

d0=d0*1E-3
h0=h0*1E-3
a0=0.7855*d0*d0
IF l(i)>0.02 THEN GOTO 10
NEXT i

j=1
disp=d(j-1)
load=l(j-1)
PRINT j,load

a(1)=0
b(1)=0
k=1
FOR p=j TO n STEP 10
suml=0
sumd=0
FOR m=0 TO 9
suml=suml+l(m+p)
sumd=sumd+d(m+p)
NEXT m

a(k)=suml/10
b(k)=sumd/10
a(k)=a(k)*5000
b(k)=disp-b(k)
b(k)=b(k)*1E-2
x(k)=(-40131+SQR(40131^2+4*64275*a(k)))/(2*64275)
b(k)=b(k)-(x(k)*1E-3)

area(k)=a0*h0/(h0-b(k))
a(k)=a(k)/area(k)
b(k)=-LOG((h0-b(k))/h0)

NEXT p
CLOSE #5
CLOSE #6
CLOSE #3
REM open file for output
fileout$=filename$+.dat"
OPEN #4 OUTPUT fileout$
PRINT #4 " strain(%) | stress(MPa) "
FOR k=1 TO n/10
PRINT #4 b(k)*100 "|";a(k)*1E-6
NEXT k
CLOSE #4
APPENDIX 3.5 DROP.BAS

REM A PROGRAM FOR STRESS AND STRAIN CALCULATION
DIM x(400), l(400), d(400), area(400), b(400), a(400)
DIM strain(400), stress(400)
PRINT "please input the datafile"
INPUT filename$
ext1$="n.dhn"
ext2$="lz.dat"
ext3$="dz.dat"
filedhn$=filename$+ext1$
filestress$=filename$+ext2$
filestrain$=filename$+ext3$
OPEN #5 INPUT filedhn$
OPEN #6 INPUT filestress$
OPEN #3 INPUT filestrain$
INPUT #5 d0, h0, n
FOR i=1 TO n
INPUT #6 l(i)
INPUT #3 d(i)
d(i)=d(i)-0.733333349
l(i)=l(i)-0.026667001
NEXT i

IT0=d0*1.0e-3
h0=h0*1.0e-3
a0=0.7855*d0*d0

FOR i=1 TO n
IF l(i)>0.0 THEN GOTO 10
NEXT i

10 j=i
dispo=d(j-1)
loado=l(j-1)
PRINT j, loado, dispo
a(1)=0
b(1)=0
k=1
FOR p=j TO n STEP 10
suml=0
sumd=0
k=k+1
FOR m=0 TO 9
suml=suml+l(m+p)
sumd=sumd+d(m+p)
NEXT m
a(k)=suml/10
b(k)=sumd/10
b(k)=b(k)-dispo
b(k)=b(k)*0.043*1.0e-3
a(k)=a(k)*190098
area(k)=(h0/(h0-b(k)))^0.8
stress(k)=a(k)/area(k)
strain(k)=-LOG((h0-b(k))/h0)
NEXT p
CLOSE #5
CLOSE #6
CLOSE #3
fileout$=filename$+".dat"
OPEN #4 OUTPUT fileout$
PRINT #4 " strain(%) ; stress(MPa) ; k "
FOR k=1 TO n/10
PRINT #4 strain(k)*100 " ;";stress(k)*1E-6 " ;"; k
NEXT k
CLOSE #4
APPENDIX 3.6 STRESS.BAS

REM STRESS BAS
REM A PROGRAM FOR STRESS AND STRAIN CALCULATION
REM This is a program to calculate stress from the force & area,
REM calculate radial strain from initial area & area from photo.
REM The force is calculate from the voltage translation(dsa.bas)
REM The area is calculate from the diameter of the photo
REM k is the calibration of the accelerometer in meter per second
REM square per volt and m is the mass of the drop weight in kg
REM n is the number of voltage translation & number of diameter
REM from photo, bv & bd is the voltage translation & diameter of
REM photo before impact,diameter0 & high0 is the initial
REM diameter & height of the sample
REM input data from *v.trn for voltage & *p.inp for diameter
REM input data from datafile
DIM volt(140),force(140),diameter(140),area(140),stress(140),
DIM radstr(140) tastr(140)
PRINT
"please input the datafile"
INPUT filename$
ext1$="v.trn"
filetran$=filename$+ext1$
OPEN #3 INPUT filetran$
INPUT #3 n,bv
FOR i=1 TO n
INPUT #3 volt (i)
volt(i)=volt(i)+bv
NEXT i
CLOSE #3
ext2$="p.inp"
filediam$=filename$+ext2$
OPEN #4 INPUT filediam$
INPUT #4 n,bd,diameter0,height0
enlarge=bd/diameter0
FOR i=1 TO n
INPUT #4 diameter(i)
diameter(i)=diameter(i)/enlarge
NEXT i
CLOSE #4
REM calculate force, area, stress, radstrain
k=9250
m=5.98
FOR i=1 TO n
force(i)=k*m*volt(i)
area(i)=diameter(i)*diameter(i)*3.142/4
stress(i)=force(i)/area(i)
area0=diameter0*diameter0*3.142/4
radstr(i)=0.5*LOG(area(i)/area0)
tastr(i)=2*radstr(i)
NEXT i
fileplot$=filename$+".dat"
OPEN #6 OUTPUT fileplot$
PRINT #6 "frame {stress(Mpa)\tastr"
z=1E6
FOR i=1 TO n
PRINT #6 i; "|";stress(i)"|";tastr(i)*100
NEXT i
CLOSE #6
DIM l(1000), d(1000), c(1000), area(1000), stress(1000), strain(1000)

PRINT "please input the datafile"
INPUT filename$

ext1$="n.dat"
ext2$="lz.dat"
ext3$="dz.dat"

filecom$=filename$+ext4$
filedhn$=filename$+ext1$
filestress$=filename$+ext2$
filestrain$=filename$+ext3$

OPEN #3 INPUT filedhn$
OPEN #6 INPUT filestress$
OPEN #7 INPUT filestrain$
OPEN #8 INPUT filecom$

INPUT #3 d0, h0, n, loado, dispo

a0=0.7855*dO*dO

FOR i=1 TO n

INPUT #6 l(i)
INPUT #7 d(i)
INPUT #8 c(i)
c(i)=0.004-c(i)

REM 1 volt load equal 190,058 kilonewton,
REM 1 volt displacement equal 42.738 mm

l(i)=l(i)-loado
d(i)=dispo-d(i)
d(i)=d(i)-c(i)
l(i)=l(i)*190058
d(i)=d(i)*42.738*1.0E-3
area(i)=a0*h0/(h0-d(i))
stress(i)=l(i)/area(i)
strain(i)=-LOG((h0-d(i))/h0)

NEXT i

REM open file for output
fileout$=filename$+.dat"

OPEN #4 OUTPUT fileout$

PRINT #4 " strain(%) ; stress(MN) ; i "
FOR i=1 TO n
PRINT #4 strain(i)*100 " ;";stress(i)*1E-6 " ;";i
NEXT i

CLOSE #4