Nano Surface Mechanical Properties
of
Semicrystalline Polymers

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PREFACE

This dissertation is a description of the work carried out in the Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, London, between October 2007 and September 2010, under the supervision of Prof. Brian J. Briscoe and Prof. Paul F. Luckham. Except where acknowledged, the material presented is the original work of the author. No part of this work has been submitted for a degree at this or any other University.

Tanveer Iqbal

Imperial College
London
October 2010
Dedicated to;
My Parents,
Son & Wife.

God made the solids –
but surfaces were the work of devil
Wolfgang Pauli
Quoted by Briscoe 1986

Scratchin’ the surface
Middale English
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All thanks to Almighty ALLAH, the creator and the merciful.

The time I have spent in London during my PhD has been the most important period of my life. This time has been pleasant, though difficult at times. The memories and experience gained will always accompany me in future. I, hereby, do wish to thank those people to whom I have linked during this time.

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ABSTRACT

This Thesis describes a systematic experimental study of the large strain surface mechanical properties of certain semicrystalline polymers, at the nanometre scale. A poly(etheretherketone) (PEEK) was selected as a model semicrystalline polymer for these investigations, as PEEK is currently finding extensive use in high performance composites. The central theme of the Thesis is to elucidate the nano normal indentation response and the scratch deformation mechanisms of semicrystalline polymers. Effective selection and design improvements of materials in surface engineering and tribological applications require knowledge of their near-to-surface mechanical properties. Therefore, this experimental study seeks to elucidate an understanding of the response of semicrystalline polymers in single point contacts.

This Thesis approaches the nano surface mechanical property characterisation using indentation and scratching techniques. Indentation is a relatively simple and virtually non-destructive means of assessing mechanical properties of materials by an indenter, inducing a localized deformation into a solid surface. PEEK and other commercially available common polymers were indented and the data were analysed using a contact compliance method in conjunction with an MTS Nano IIs indenter system. The load-displacement curves, the hardness, the elastic modulus, the plasticity index and the creep response data and associated analysis for the PEEK surfaces are presented as a function of the contact displacement. A comparison of the data for the load-displacement curves, the hardness and the elastic modulus for common commercial polymers is described.

A study of surface deformations of the PEEK surfaces when it undergoes scratching by means of conical indenters drawn along the surfaces under different contact conditions is also described. The scratch deformations produced considerable loss in optical appeal and surface mechanical properties of polymeric materials. The experimental investigation of the scratch response of the PEEK is focused upon the contact conditions. Scratch deformation maps have been constructed showing the effect of the normal load, the strain (the contact geometry), the strain rate (the scratching velocity), the contact temperature, the state of interfacial lubrication and the crystallinity of the polymer upon the scratching behaviour of the polymeric surface. The extent and the geometric characteristics of the surface damage
produced are determined subjectively using scanning electron microscopy (SEM) and optical profilometry techniques.

The nano hardness and the elastic modulus results as a function of contact displacement for PEEK composites are also presented. The fibre oriented PEEK composites were scratched using a pendulum sclerometer to analyze the orientation effects on scratch deformations. Finally, nano indentation results for the modified PEEK surfaces under thermal, solvent and mechanical disruptions are reported.

The major conclusions of this Thesis are that the nanoindentations into the polymers show a surface hardening response and are dependent upon the contact conditions. The semicrystalline polymers have bimodal nanoindentation characteristics due to presence of the hard crystalline lamella and the soft amorphous phase. The semicrystalline polymers exhibit periodic fluctuations in surface mechanical properties with increasing penetration depth. The scratch deformations of semicrystalline polymers depend upon the contact conditions. A peculiar fibrillation of the polymeric surface was observed when scratched under severe contact conditions (high normal load and sharp conical indenters). The scratch deformations of fibre oriented polymers are highly fibre orientation dependent relative to the scratch direction. Surface plasticisation of amorphous PEEK has been observed in organic solvents mainly in chlorinated solvents. Semicrystalline PEEK was seen to exhibit considerable inert behaviour to common organic solvents but chlorinated organic solvents has caused decrease in surface mechanical properties. A surface hardening of amorphous PEEK has been observed after immersion in water. A qualitative methodology, based on nanoindentation data, to analyze subsurface deformations of polymers resulting from scratch deformations are also presented.
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INDEX OF SYMBOLS

Chapter 1

\( \mu \)  
friction coefficient

Chapter 2

\( P \)  
applied normal load during indentation
\( h \)  
indentation displacement
\( P_{\text{max}} \)  
maximum applied normal load
\( h_{\text{max}} \)  
maximum displacement of indenter
\( h_r \)  
residual depth after indentation
\( h_c \)  
residual plastic depth after indentation
\( S \)  
contact stiffness
\( m \)  
power law fitting constant
\( n \)  
power law fitting constant
\( \alpha \)  
correction factor based on indenter geometry
\( A_{\text{max}} \)  
projected contact area at maximum penetration depth
\( E' \)  
reduced elastic modulus
\( \beta \)  
indenter geometry parameter
\( \nu_s \)  
Poisson’s ratio of polymer
\( \nu_i \)  
Poisson’s ratio of indenter
\( E_s \)  
elastic modulus of polymer
\( E_i \)  
elastic modulus of indenter
\( H \)  
normal hardness
\( A \)  
indentation contact area
\( C \)  
indentation area function constant
\( E \)  
elastic modulus
\( \text{ERP} \)  
elastic recovery parameter
\( \dot{\varepsilon} \)  
strain rate
\( k_2 \)  
material constant
\( h \)  
nominal displacement rate
\( P \)\n\( \bar{H} \)\n\( k_3 \)\n\( \psi \)\n\( A_1 \)\n\( A_2 \)\n\( E_{\text{Tot}} \)\n\( E_N \)\n\( E_P \)\n\( E_F \)\n\( E_H \)\n\( H_s \)\n\( W \)\n\( d \)\n\( q \)\n\( H_T \)\n\( F_s \)\n\( A_T \)\n\( H_D \)\n\( E_D \)\n\( V \)\n\( M \)\n\( P_{fr} \)\n\( K_{IC} \)\n\( a \)\n\( \alpha \)\n\( H_N \)

**CHAPTER 3**

\( L \) \( l_0 \) \( l \)

beam length
initial position of the centre of gravity of the system
final position of the centre of gravity
$w_0$ starting angle of the beam
$w$ final angle of the beam
$M$ mass of the system
$g$ gravity acceleration

CHAPTER 4

$\psi$ plasticity index
$\beta$ angle of inclination indenter to sample
$E$ elastic modulus
$H$ hardness
$E'$ reduced elastic modulus
$\nu_s$ Poisson’s ratio of polymer
$\nu_i$ Poisson’s ratio of indenter
$E_s$ elastic modulus of polymer
$E_i$ elastic modulus of indenter

CHAPTER 5

$\varepsilon$ strain
$k$ constant
$\alpha$ indenter attack angle
$q$ material constant
$h$ scratch depth
$d$ scratch width
$\theta$ semi cone included angle
$\mu$ friction coefficient
$x$ material constant
CHAPTER 1
INTRODUCTION

An introduction into the purpose, aims and objectives of the Thesis will be given in this Chapter. A brief introduction into the history, the properties and the uses of poly(etheretherketone), PEEK, the major polymer reported, will be provided in this Chapter to demonstrate the need of surface mechanical characterization of the polymer. A basic introduction and interrelationship between different chapters in the Thesis will also be presented.

1.1 General Introduction

The surfaces of most polymers are highly sensitive to the action of abrasive materials, which can not only reduce their longevity, but can also progressively reduce their aesthetic appeal. Common examples of the usage of polymers are in bearings, composites for furniture and structural applications, electrical and electronics applications, domestic appliances and so on. These applications often involve the contact of the polymeric component with different chemical environments, such as lubricating oils, solvents, detergents and cleaning liquids. A common practical problem with the usage of polymers in such active environmental conditions is that the surface becomes softened, or plasticised, if exposed for a long period of time. Alternatively, the surface may become sensitive to brittle cracking or crazing. The plasticisation of the surface produces a softening effect which changes the surface mechanical and optical properties of the polymer. This effect may cause a drastic decrease in the working life of the polymeric component. Environmental polymer interactions are important also in the study of wetting, adhesion, corrosion, tribology and thin film technology. Similarly, the scratch durability of polymer surfaces is becoming critical for the increasing use of these materials in new industrial applications. Due to a relatively low cost, ease of manufacturing and processing, and low weight, polymers are becoming more and more attractive for an increasing number of industries. But, their operational lifetime is often reduced because of poor surface mechanical resistance, such as wear and mar resistances.
1.2 Problem Statement

The major aim for the work presented in this Thesis was to study and characterize the surface mechanical properties of semicrystalline PEEK systems as a model for liquid crystal polymers (LCP), in general due to their increasing usage. The work focuses on the tribology (surface friction behaviour) of the semicrystalline polymer. The study of the tribology of metals is well developed, and there are a number of experimental and mathematical theories to relate the indentation and scratching behaviour of metals to the surface mechanical properties like hardness. However, polymers differ from metals in that polymers have a viscoelastic-plastic response to strain instead of the mainly plastic response shown by metals. Therefore, theories developed for metals are not usually directly applicable to polymeric materials. Consequently, this work was focused on the development of the interrelationship between the surface mechanical properties to the indentation and scratching behaviour of PEEK. Crystallinity and surface mechanical properties are directly related to each other. There is an increasing trend of hardness of polymeric materials with an increase in crystallinity.

The most challenging aspects of the problems encountered in the compilation of the present Thesis may be summarised as follows;

- To evaluate the convenience of the nano-indentation and scratch hardness methods to determine the surface mechanical properties of semicrystalline polymeric surfaces.

- To study the bimodal indentation response of the semicrystalline polymers such as poly(etheretherketone), PEEK and ultra high molecular weight poly(ethylene), UHMWPE during nanoindentation to establish a link between amorphous and crystalline phases of the polymers.

- To compare the surface mechanical properties of PEEK to the common commercially available polymers like UHMWPE, poly(styrene) PS, poly(methylmethacrylate) PMMA, poly(carbonate) PC and poly(propylene) PP.

- To clarify the surface deformations of PEEK as a model semicrystalline polymer and to compare the deformations with variation in crystallinity.
• To develop scratch deformation maps for PEEK, to illustrate the effects of contact parameters like strain, strain rate, normal load, contact temperature and contact lubrication.

• To study the indentation and the scratching response of fibre oriented polymeric composites.

• To correlate the effects of thermal treatments on the surface mechanical properties of PEEK.

• To investigate the fluctuations in nano surface mechanical properties of semicrystalline PEEK.

• To investigate the plasticisation and/or antiplasticisation of the semicrystalline and amorphous PEEK in different solvents.

• To evaluate the subsurface deformations resulting from scratching of polymers using the nanoindentation method.

1.3 PEEK - An engineering speciality polymer

Poly(etheretherketone), PEEK is a highly aromatic semicrystalline thermoplastic polymer, first synthesized in 1975 (Rose 1975). PEEK belongs to the polyether ketone group of polymeric materials. It has a melting temperature of 343 °C and a glass transition temperature of 143 °C. This means it can be used at elevated temperature but at the same time also needs high temperature melt processing. It can be manufactured in both amorphous and semicrystalline grades with the maximum achievable crystallinity of 48%. PEEK has a specific gravity of 1.265 in the amorphous state and 1.320 with maximum achievable crystallinity. The IUPAC name of PEEK is poly(oxy-1,4-phenylene-oxy-1,4-phenylenecarbonyl-1,4-phenylene) and its structural repeat unit can be represented as

\[
\begin{align*}
\text{O}-\text{C} \quad &\text{O}
\end{align*}
\]

n
Where, n is the degree of polymerization of the polymer and dictates the molecular weight of the polymer. Typical values of molecular weight for the PEEK are 30,000-45,000 (Xing et al. 2004).

PEEK has a unique combination of high performance properties such as toughness, stiffness, thermal stability, chemical resistance, electrical performance, oxidative stability and dynamic fatigue (Nguyen and Ishida 1987; Wood 1987; Rao 1995). In addition PEEK possesses low friction and high wear resistance enabling researchers to use it for tribological applications. PEEK is used in various forms such as fibre, matrix, coating and films for a wide variety of engineering applications in aerospace, automotive, bearings, biomedical and electrical. Its first major use was as an abrasive resistant electrical insulator for wire line applications.

1.3.1 A brief history and production methods

Imperial Chemical Industries (ICI) and E. I. du Pont de Nemours and company (Du Pont) have reported the synthesis of polyether ketones independently in the patent literature in early 1960s (Thornton 1969). The discovery was thought to be under the quest to prepare a fibre containing (crystalline) polymer derivative of polyether sulphones (Bonner Jr. 1962; Goodman 1964). Boner (1962), has reported the synthesis of low molecular weight poly(etherketoneketone) (PEKK) by the polyarylation reaction of either isophthaloyl chloride, or terephthaloyl chloride with diphenyl ether using nitrobenzene as a solvent and aluminium chloride as a catalyst (equation 1.1). Goodman (1964) prepared poly(etherketone) (PEK) by self condensation of p-phenoxy benzoic chloride using aluminium chloride as a catalyst in methylene chloride solvent by the reaction represented in equation 1.2. PEK was also prepared by Iwakura (Iwakura et al. 1967) through self condensation polymerization of p-phenoxy benzoic acid using polyphosphoric acid as a solvent/catalyst as shown in equation 1.3 below.

\[
\text{ArCl}_n + n \text{ArCl}_n \xrightarrow{\text{AlCl}_3} \left[ \begin{array}{c} \text{Ar} \text{O} \text{C} \text{Ar} \\ \text{Ar} \text{O} \text{C} \text{Ar} \end{array} \right]_n + 2n \text{HCl}
\] (1.1)
In all these process routes for PEK synthesis, the major problem remains the selection of a suitable solvent for this process, due to premature crystallization of the polymer that prevents the formation of the desired high molecular weight polyether ketones. The problem of molecular weight was solved at Du Pont (Thornton 1969), who proposed liquid hydrogen fluoride as an effective solvent with BF$_3$ as a catalyst for the self condensation polymerization for either reaction 1.3 and 1.4 to produce poly(aryletherketones). Later it was shown that high molecular weight polymer is required to develop a useful degree of toughness in partially crystalline polymers (Seymour 1986).

In 1972 crystalline copolyetherketonesulphones of high molecular weight were prepared by polycondensations of bis-chlorophenyl ketone, di-potassium derivative of bis-phenol and bis-chlorophenyl sulphone in phenyl sulphone as a solvent at a temperature close to the polymers melting temperature as shown below (Rose 1986).

A major drawback for the product was to compromise on the PES ratio to produce copolymer with adequate crystallinity which failed at process scale up. Although this work
failed, it did provide a route to obtain PEEK using di-halophenyl ketones. A high molecular weight polyether ketone was obtained when the reaction of the corresponding diflouride, instead of chlorophenyl, was conducted at 335 °C using diphenyl sulphone as solvent. The difficulty of producing the dipotassium derivative of the bis-phenol was avoided by reacting potassium carbonate in excess to the mixture of bis-phenol and diflouride in phenyl sulphone to produce PEEK.

\[
\begin{align*}
\text{nF-} & \text{-} \text{C-} \text{F} + \text{nHO-} \text{-} \text{OH} + \text{nK}_2\text{CO}_3 \\
\text{335°C} & \\
\left[ \text{O} \text{-} \text{O} \text{-} \text{C} \text{-} \text{C} \right]_n + 2\text{nKF} + \text{nCO}_2
\end{align*}
\]

PEEK was selected for commercial development by ICI, known as Victrex, as compared to PEK because the hydroquinone bis-phenol required for PEEK production was more readily available commercially as compared to bis-4-hydroxyphenyl ketone for PEK preparation (Rose 1986).

### 1.3.2 Mechanical and tribological properties

PEEK can be processed by conventional extrusion and injection moulding machines, at temperatures above 370 °C (Hay et al. 1984). These high temperatures are necessary to melt the crystals due to the thermal history of the polymer and by ensuring the formation of an amorphous melt (Yu et al. 1990). A desired microstructure and degree of crystallinity can be imparted to the polymer by subsequent melt processing. Fast quenching will give a predominantly amorphous polymer, whereas controlled cooling, isothermal crystallization or annealing of the amorphous polymer melt produces semicrystalline material (Way et al. 1974; Richardson et al. 1985). The mechanical properties such as impact resistance, yield stress and fracture toughness are sensitive to processing history, degree of crystallinity and crystal structure (Yu et al. 1990; Rao 1995; Rae et al. 2007).
Semicrystalline PEEK exhibits yielding, or shear banding, under tensile conditions indicating ductility (Jones et al. 1985). The yield stress was found to follow an inverse relationship with temperature (Nguyen and Ishida 1987). Typical reported tensile properties of PEEK at room temperature are: tensile yield stress $\approx 100$ MPa, tensile modulus $\approx 4$ GPa and tensile elongation $\approx 150\%$. PEEK has a brittle to ductile transition at $-15^\circ$C. Fatigue tests of notched and unnotched samples and three point bend tests have been used to study the fracture toughness of PEEK (Pao et al. 1985; Yau and Chou 1985). Jones et al. (1985) found that flaws in the polymeric material grow resulting in cracks under dynamic stress. It also minimizes plastic deformation due to strain recovery at off-load periods which lowers strength and ductility.

Hamdan and Swallowe (Hamdan and Swallowe 1996; Swallowe et al. 1997) studied the compressive properties of PEEK by varying the crystallinity, temperature and strain-rate. They determined that the crystallinity of the polymers after the tests and postulated that it decreased for strain rates of 60% but increased for higher strain rates. The perfection in crystallites was found to be greater in samples tested at higher temperatures and strain rates due to the adiabatic nature of the high strain-rate tests leading to heating and than annealing of the polymeric material (Rae et al. 2007).

PEEK can be used to construct dimensionally stable components as the creep rate (displacement in the contacting area at interface) is relatively low. The unlubricated sliding friction is quite high (typically $\mu = 0.25$) but the wear rates on rough and smooth surfaces are quite low (Briscoe et al. 1986). Despite these advantages, a typical failure mode of PEEK-ferrous metal contacts is the scuffing behaviour at high sliding speeds (Briscoe et al. 1986; Briscoe, Stuart et al. 1993). The scuffing behaviour is thought to be thermally induced and promoted by the presence of certain carboxylic acid additives in the lubricating medium. These additives are capable of producing subsurface plasticisation at high interface temperatures due to frictional heating in such contacts. This softening of the subsurface leads to an increase in the contact area and hence friction resulting in scuffing failure (Stuart and Briscoe 1996).

### 1.3.3 Uses of PEEK

PEEK was developed primarily as coating and insulation material for high performance electrical wiring under extreme environmental conditions. Currently, it is extensively used in
aerospace, military, nuclear plant, chemical process equipment, oil-well applications and in thermoplastic composites. Good abrasion resistance and solvent resistance make PEEK a useful material to be used in harsh environmental conditions. The composites of PEEK with carbon and other high-strength fibres are used in aircraft structures because of their high stiffness. These are also used in cryogenic tank linings, pressure vessels, solar panel substrates and antenna reflectors.

PEEK is used as a lining material for pumps, containers, pipes and valves owing to its excellent chemical, diffusion and abrasion resistance. It is used as a protective tape for electronics and semiconductor industries where exposure to harsh and critical environments is a major concern. An interesting use of PEEK is as a robot speed reducer and as flexible foil sensors, the speed gears made from the polymer are economical, as well as having a high performance and a higher level of elasticity. Steel has been replaced with PEEK in many hydraulic coupling systems so as to reduce the cost as well as benefits from its thermal and elastic properties. PEEK is also used in compression vanes and in pneumatic tools as a replacement to thermosetting polymers.

PEEK is also used extensively in medical products because of its good mechanical properties, transparency to x-rays, design freedom, sterilizability and biocompatibility. It is used for light weight surgical instrument production and in endoscopes. It has replaced titanium for spinal, orthopaedic, dental and surgical implants where broken bones must be fixed in place or as a bone fragment replacement.

### 1.4 Thesis layout

The layout of the Thesis is as follows. Chapter 2 reviews the current understanding of the indentation and the scratch hardness measurements. A historical perspective of the hardness is briefly presented. Detailed analysis of the contact compliance method, for the measurement of indentation hardness and the elastic modulus, follow. The most common and relevant contact mechanical aspects of the indentation and the scratch hardness have been considered and reported. Finally a detailed description of the scratch hardness models and the scratch deformation modes applicable to polymeric surfaces is described.

A description of the experimental apparatus used in the work, the procedures adopted and the materials investigated are provided in Chapter 3. The experimental equipment can be
divided into three categories; nanoindenter, scratching techniques and surface imaging techniques. A NANO INDENTER® II machine, supplied by Nano Instruments Ltd., Tennessee, USA, was used to determine the normal indentation characteristics of the polymeric surfaces. A linear scratch machine and a pendulum scratching machine were used to scratch polymeric surfaces. Scanning electron microscopy (SEM) and optical profilometry were utilized to analyze the scratch deformation modes and the scratch dimensions.

Chapter 4 presents the experimental data on the normal indentation data for the selection of the polymeric surfaces using the nanoindenter. The load displacement indentation curves, the normal hardness and the elastic modulus data obtained as a function of penetration depth are given for all the polymeric surfaces studied. Frequency distribution analyses on the indentation hardness of the semicrystalline PEEK are performed. Elasticity/plasticity and creep response of the semicrystalline polymeric surface is illustrated based on the indentation experiments.

The scratch hardness, deformations and deformation maps under a range of contact conditions for the semicrystalline PEEK have been obtained and are described in Chapter 5. Scratch deformation maps, illustrating the deformation regimes, were generated for the semicrystalline PEEK obtained through a subjective assessment of the SEM images and optical profilometry. The deformation maps were found to be a convenient and reliable method to report range of parameters influencing the nature of deformation (ductile, brittle, etc) and the dissipation of energy (friction) at the interface.

The surface mechanical properties of selected fibre reinforced PEEK composites are reported in Chapter 6. The load displacement data, the hardness and the modulus of the carbon fibre and the glass fibre reinforced PEEK are analyzed. The effects of scratching direction relative to the fibre orientation of the unidirectional fibre reinforced polymeric composites are presented in detail.

Chapter 7 reports the effects of the thermal treatment, the solvents and the scratch deformations on the nano surface mechanical properties, based on the nanoindentation, of the semicrystalline PEEK. The thermal treatment of the semicrystalline PEEK has produced variations in crystallinity of the polymer. The surface plasticisation and/or antiplasticisation of the semicrystalline and the amorphous PEEK in the presence of solvents is presented based on indentation response. The application of the nanoindentation to unfold the subsurface
morphology and damage induced in the scratched polymeric surfaces, where conventional sub-sectioning and imaging of damaged surfaces seems impractical, are discussed.

Finally, the thesis concludes on the basis of the experiences described. The major conclusions regarding the nano surface mechanical properties of the semicrystalline polymers are presented in Chapter 8.
CHAPTER 2

INDENTATION & SCRATCH HARDNESS OF POLYMERS - A REVIEW

The basic theories, a description of previous experimental work and the characterisation methods which are related to the project are explained in this Chapter. The general history of hardness measurements and basic principles and methods for indentation and scratch hardness studies of polymeric materials are provided in this Chapter. A detailed account of the hardness and the modulus measurements based upon the compliance method is discussed. Finally scratch hardness models and deformation modes applicable to polymeric materials are presented.

2.1 Introduction

Hardness is a widely used and well-established surface mechanical property in material testing and may usefully be used to quantitatively compare the mechanical properties of different surface regions. Hardness is a function of several fundamental properties such as the Young’s modulus and yield stress (Johnson 1970), and the frictional or geometric characteristics of the indenter/material interface. Hardness has no precise physical meaning and is generally regarded as being a measure of the resistance of a material to normal localised deformation (Tabor 1951; Tabor 1996; Hutchings 2009).

The first attempt to rank materials by their hardness, which is reported in literature, was by Bergman (1788-1791). He focused his work on gemstones and ranked for hardness as: diamond (hardest), ruby, sapphire, topaz, hyacinth and emerald. Later on, at the start of nineteenth century, Werner (1805) introduced a scale of hardness on the basis of Huay’s (Huay 1801) work who constructed four groups of materials as ; those which scratch quartz, those which scratch glass, those which scratch calcspar and those which do not scratch calcspar. The common metals were listed as: iron or steel (hardest), platinum, copper, silver, gold, tin and lead.
Mohs (1822) constructed a relative scratch hardness table of commonly available minerals with values ranging from 1 (talc, softest) to 10 (diamond, hardest). The scratch hardness of a material was determined by drawing a mineral from the Mohs Scale on the material and the relative scratch was then decided based on the softest material that produced a scratch on the material. But this method, although a great advancement in the field, did not provide any quantitative material deformation data that can be used for the computation of mechanical properties of a material or for mechanical design. Brinell (1900) developed a hardness methodology by indenting a hard ball on the surface of a material under a normal force and the normal hardness was measured in terms of the mean contact hydrostatic pressure. This test provided an intrinsic plastic property of the material in terms of its resistance to the imposed deformation. This test enabled material scientists to relate the yield and ultimate tensile strengths of metals. Tabor (1951) later showed that the normal hardness, the normal force per unit projected area of indentation, could be linearly related with the plastic yield stress of metals.

Tabor’s (1956) work has provided the basis for the plastic yield determination of metals, which was subsequently extended to polymers, where polymers showed plastic yielding similar to metals. Normal indentation and scratch hardness has been related to the plastic yield properties of metals and ductile polymers. But for elastomers and rubbers hardness is not the plastic yield property due to the large elastic recovery in these materials. One of the most useful techniques to determine the hardness of elastomers during indentation of these materials is the contact compliance method (Oliver and Pharr 1992; Briscoe and Sebastian 1993; Briscoe et al. 1994). This method utilizes the force-displacement curve for the loading and unloading processes during normal indentation, to compute the elastic modulus and hardness of given materials; this method is widely utilized currently in nanoindentation studies. The scratching and abrasive wear failure of rubbers was extensively studied by Schallamch (1952, 1958), who performed experiments on rubber surfaces by sliding sharp needles and blunt indenters. These indenters have produced isolated stress concentration damage. Tearing cracks in the direction of scratching were produced when elastomers were scratched with sharp needles while blunter indenters produced cracks with larger diameter of the elliptical crack perpendicular to the sliding direction. This type of behaviour seen in rubbers is different than that of metals and ductile polymers but has some similarities with ceramics.
The scratch hardness behaviour has been extensively used for modelling a number of dynamic mechanical phenomena such as wear, friction, adhesion and scratch resistance. Scratch hardness shares some advantages over normal hardness as the former technique requires relatively simple machines and can be used for both static and dynamic mechanical property characterization (Challen and Oxley 1979; Briscoe 1981; Stuart and Briscoe 1996).

Normal indentation and scratch hardness are two main forms of the hardness test. A rigid indenter of known geometry is applied to the material surface under normal load in both techniques. The load is applied to the indenter for a specified length of time and the subsequent residual indentation size is measured as in a conventional normal indentation test. The contact compliance method has been recently adopted for hardness computation; this method is based on the imposed displacement/reaction force response. The scratch hardness method involves traversing the indenter over the material surface, under a normal load and at a certain velocity. The resulting frictional forces and scratch width are measured as is the scratch appearance and deformation geometry.

### 2.2 Normal Hardness of Polymers

Indentation is a relatively simple and virtually non-destructive means of assessing the surface mechanical properties of materials by an indenter, inducing a localized deformation into a solid surface. Indentation tests were widely adapted to measure mechanical properties in the 20th century because of the ease and speed with which these can be carried out. Indentation tests were first performed by Brinell (1900), using smooth, spherical ball bearings as indenters to measure the plastic properties of materials (Tabor 1951). The Brinell Test was adopted as an industrial test method soon after its introduction and prompted the development of various macro- and micro-indentation tests (Tabor 1956). Complexity and potential intractability of the associated contact mechanics is one of the central problems with the application of indentation tests. Often experimental variables like strain rate and hydrostatic pressure influence cannot be determined accurately (Briscoe and Sebastian 1996).

There are two distinct methods applied for the determination of indentation hardness: the imaging method and the contact compliance method.
2.2.1 Imaging Method

In this method, the indenter is made to penetrate the material surface under a specified load and withdrawn after a specified residence time. Optical methods are then applied to determine the diameter or diagonal of the residual image. The conventional hardness methods like, Brinell Hardness, Vickers Hardness and Knoop Hardness methods use an imaging method to determine the contact area (Akram 2001). Although this method is well established for hardness determination of simple ductile solids, no information regarding the elastic response of the sample is available from this method. The measurements of load supporting area are also affected by large and unacceptable errors for very shallow indentations as occurs in nano-indentation experiments. Creep in organic polymers after unloading is also one of the major limitations for the application of this method to polymers (Oliver and Pharr 1992; Briscoe and Sebastian 1996; Briscoe 1998; Li and Bhushan 2002; Oliver and Pharr 2004).

2.2.2 Compliance Method

The contact compliance method measures the reaction force on the indenter as a function of an imposed displacement, or vice versa, resulting in a set of loading and unloading curves for each indentation operation (Briscoe and Sebastian 1996). This method has been investigated by Loubet et al. (1984) for ceramic materials and subsequently by various authors (Ion et al. 1990; Briscoe et al. 1994; Briscoe and Sebastian 1996; Briscoe et al. 1998) in the context of organic polymers. The analyses are based upon relationships developed by Sneddon (1965) for the penetration of a flat elastic half space by different probes with particular axisymmetric shapes (e.g; a flat-ended cylindrical punch, a paraboloid of revolution and a cone).

Figure 2.1 represents a typical loading and unloading curve from indentation experiments. This curve is also known as a compliance curve which is a plot of load, P, as a function of depth of penetration (displacement), h. Material properties governing the loading curves are the plastic yield stress and the elastic modulus. The nature of the unloading portion is primarily governed by elastic properties of material. The unloading curve data provides information regarding the elastic, viscoelastic and plastic behaviour.
Figure 2.1: Schematic diagram of indentation load–displacement data for an elastic–plastic material (loading, OB, and unloading, BC, segments). The plastic work done in the viscoelastic–plastic case is represented by the area $A_1$ (OBC). The area $A_2$ (CBC') corresponds to the elastic work recovered during the unloading segment. In case of purely plastic material, the unloading curve is a straight line (BC') and $h_r = h_{\text{max}}$ ($A_2 = 0$).

In figure 2.1, $h_{\text{max}}$ represents the maximum displacement of the indenter corresponding to the maximum load applied, $P_{\text{max}}$, during the indentation and $h_r$ is the residual deformation after removing the indenter. $h_c$ is the intercept of the tangent line drawn from the first part of the unloading curve, which describes the elastic deformation effects (Oliver and Pharr 1992; Briscoe and Sebastian 1996; Briscoe et al. 1998; Beake et al. 2002; Oliver and Pharr 2004; Shen et al. 2004), and the displacement axis. The slope of this line represents the contact stiffness, $S$, evaluated at the maximum displacement and $h_c$ is considered as being the actual value of the material displacement, which occurs mainly (Doerner and Nix 1986), but not exclusively (Oliver and Pharr 1992), in a plastic fashion. From simple geometric considerations (figure 2.1), stiffness can be defined as

$$S = \left( \frac{\partial P}{\partial h} \right)_{h_{\text{max}}}$$

2.1
And
\[ h_i = h_{\text{max}} - \left( \frac{P}{\partial P/\partial h}_{h_{\text{max}}} \right) = h_{\text{max}} - \left( \frac{P}{S} \right)_{h_{\text{max}}} \]  \hspace{1cm} \text{2.2}

The evaluation of stiffness is carried out analytically applying power law to the unloading curve as
\[ P = m(h - h_i)^n \]  \hspace{1cm} \text{2.3}

Here, \( m \) and \( n \) are fitting parameters. The parameter \( m \) is dependent upon indenter geometry, sample elastic modulus, samples Poisson’s ratio, indenter elastic modulus and final unloading depth. The power law exponent \( n \) is related to the geometry of the indenter (VanLandingham 2003).

There may be a zero error uncertainty associated with the location of the point \( O \) (figure 2.1) in the displacement-load coordinates. This uncertainty can be minimized in two ways; either by including a zero offset parameter, \( h_0 \), in the data fitting procedure for the load-displacement data or by monitoring the contact stiffness variation while the indenter tip approaches the sample surface (Briscoe and Sebastian 1996; Briscoe et al. 1998). Using the first method, \( P = m'(h - h_0)^n \) for the loading and \( P = m(h - hr - h_0)^n \) for the unloading segment.

The difference \( (h_{\text{max}} - h_0) \) provides an evaluation of immediate elastic recovery of material if an elastic response is assumed at the incipient unloading (Doerner and Nix 1986; Oliver and Pharr 1992). To avoid errors from the geometry of the indenter as a flat punch, a correction factor, \( \alpha \), should be introduced, so
\[ h_e = h_{\text{max}} - \alpha \frac{P_{\text{max}}}{S} / h_{\text{max}} \]  \hspace{1cm} \text{2.4}

Where \( \alpha = 0.75 \) for Berkovich tip indenter (VanLandingham 2003). The relationship between stiffness and elastic modulus at maximum penetration depth for any indenter geometry is
\[ S_{h_{\text{max}}} = \left( \frac{\partial P}{\partial h} \right)_{h_{\text{max}}} = \frac{2\beta}{\sqrt{\pi}} E^* \sqrt{A_{\text{max}}} \]  

Where \( A_{\text{max}} \) is the projected contact area between the indenter and the material at \( h_{\text{max}} \), \( \beta \) is a parameter which varies with the indenter geometry \((1.026 < \beta < 1.085)\) (Oliver and Pharr 2004) and \( E^* \) is the reduced elastic modulus of the contact. The reduced elastic modulus, \( E^* \), is independent of the penetration depth and accounts for the elastic deformation of both indenter and the sample, is defined as

\[ E^* = \left( \frac{1 - v_s^2}{E_s} + \frac{1 - v_i^2}{E_i} \right)^{-1} \]

Where \( E \) and \( \square \) with subscripts ‘s’ and ‘i’ are the elastic modulus and the Poisson’s ratios of the polymer and the indenter respectively. The normal hardness can be obtained as

\[ H = \frac{P_{\text{max}}}{A_{\text{max}}} \]

Therefore, the Elastic modulus, \( E_s \), and Hardness, \( H \), can be determined if \( A_{\text{max}} \), the projection of the contact area between the indenter and the material, is known. The area is determined by introducing an area function as \( A = A(h_c) \), which correlates the projected area supporting the load during the indentation with the actual contact displacement, \( h_c \). The area function varies for differing indenter geometries. For an ideal Berkovich pyramid, that is perfectly sharp with no defect at the tip, the area function is (Oliver and Pharr 1992; Briscoe et al. 1998; VanLandingham 2003; Oliver and Pharr 2004)

\[ A(h_c) = C h_c^2 \]

Where \( C = 24.5 \). To account for the tip imperfections the area function can be calibrated as

\[ A(h_c) = C h_c^2 + C_1 h_c + C_2 h_c^{1/2} + C_3 h_c^{1/4} + C_4 h_c^{1/8} + \ldots \]

The area function is experimentally calibrated by performing indentations on hard and plastic material surfaces like fused silica in order to reduce the elastic and viscoelastic effects of the response. The smaller the power of terms in equation 2.9, the greater their contribution to the area function value when approaching the surface. Appropriate corrections may be needed for the errors arising due to the Joule effect, thermal drift during indentation,
especially when indentations are being performed for longer periods of time (Briscoe et al. 1998). A recently proposed relationship (Li and Bhushan 2002; Oliver and Pharr 2004) eliminates the requirement of computation of the penetration depth and/or contact area, provided the hardness and elastic modulus do not vary with depth, is

\[ \frac{P}{S^2} = \frac{\pi}{(2\beta)^3} \frac{H}{E^2} \tag{2.10} \]

Beake et al. (2002) have introduced a parameter described as an elastic recovery parameter, ERP. It is linearly related to the ratio of hardness to modulus (H/E). ERP can be defined as

\[ ERP = \frac{h_{\text{max}} - h_r}{h_r} \tag{2.11} \]

ERP defines the overall indentation behaviour and can be used as an index due to its dimensionless nature.

### 2.2.3 The Strain Rate

The imposed rate of deformation during indentation, the strain rate \( \varepsilon \), is correlated with the displacement rate or the loading rate of the indenting body over the softer surface. In normal indentation, the strain rate acts in a direction perpendicular to the surface and may be defined as

\[ \varepsilon = k_2 \left( \frac{h}{h} \right) \tag{2.12} \]

where \( h \) is the displacement, \( h \) is the nominal displacement rate and \( k_2 \) is a material constant, usually taken to be equal to 1 (Briscoe et al. 1998). Therefore, it may be defined as the inverse of the time required for the indenter to traverse a contact displacement unit. If the loading rate, \( P \), is the experimental parameter controlled during the indentation, the strain rate may be expressed as

\[ \varepsilon = k_2 \left( \frac{P}{h(\partial P/\partial h)} \right) \tag{2.13} \]
or, introducing the expression for the hardness from equation 2.7

\[ \varepsilon = k_3 \left( \frac{P}{P_c} - \frac{H}{h} \right) \]  

2.14

Where \( P \) is the imposed load, \( H \) is the hardness of the material at a generic depth, \( h \), and \( H = P/A = \text{const} (P / h^2) \); \( \overline{H} = \partial H / \partial h \), namely the variation of the hardness with the penetration depth, and \( k_3 \) is a material constant, usually equal to 0.5 (Briscoe et al. 1998). Therefore, during the indentations, the strain rate varies continuously and decreases from a theoretically infinite value at the first contact to discrete final values which depend upon the imposed conditions of maximum load or penetration depth.

### 2.2.4 The Plasticity Index

The plasticity index is a parameter which characterizes the relative plastic/elastic behaviour of the material when it undergoes external stresses and strains, and is known as plasticity, \( \psi \). The parameter was introduced by Greenwood and Williamson (1966) to account for the elastic hardness component in the hardness evaluation. In the case of indentation contacts, one of the possible definitions for the plasticity index obtainable from the compliance method of the type described above may be as follows (figure 2.1)

\[ \Psi = \frac{A_1}{A_1 + A_2} \]  

2.15

where \( A_1 \) is the area encompassed between the loading and unloading curves (equal to the plastic work done during the indentation) and \( A_2 \) is the area encompassed by the unloading curve (viscoelastic recovery). It follows that \( \psi = 1 \) (that is, \( A_2 = 0 \)) for a fully plastic deformation, \( \psi = 0 \) (that is, \( A_1 = 0 \)) for a fully elastic case and \( 0 < \psi < 1 \) for viscoelastic–plastic surfaces (Briscoe et al. 1998).

### 2.2.5 The “Nose” Problem

The response of polymeric materials during the unloading segment of the indentation experiment may show a creeping effect; that is, immediately after the unloading segment begins, the penetration depth slightly increases, although the imposed load decreases at a constant rate. This means that the material creeping rate is higher in magnitude than the
imposed unloading rate during the first portion of the unloading; this effect may be encountered even at the highest available unloading rates. The creeping effect may be readily detected by the occurrence of a characteristically round shape of the data, “a nose”, at the correspondence of the loading–unloading peak. This phenomenon, which may be anticipated in view of the highly time-dependent deformation and relaxation nature of polymers, may dramatically affect the evaluation of the hardness of these surfaces (no elastic or viscoelastic recovery seems to occur at the incipient unloading). This problem can be avoided by providing a hold segment at the maximum load for about 10 sec before subsequent unloading as shown in figure 2.2 (Briscoe et al. 1998; Li and Bhushan 2002).

Figure 2.2: Hold segment at maximum load in the compliance curve to avoid the nose problem: The creeping effect.

2.3 Scratch Hardness of Polymers

Polymeric solids have been extensively characterized using the scratch method and various forms of hardness tests (Challen and Oxley 1979; Evans 1989; Baltá Calleja et al. 1992; Stuart and Briscoe 1996a,b; Briscoe 1998; Jardret et al. 1998; Briscoe et al. 1999; Hochstetter et al. 1999; Briscoe and Sinha 2002). This test has been used for coatings, thin films, paints
and bulk property correlations for industrial applications. Polymers are assumed to be elastoplastic or visco-elasto-plastic for hardness modelling. The scratch width and surface micro-features such as cracks, crazes and plastic flows are used to extract the material deformation characteristics. The material bulk response and imposed contact parameters like normal load and speed, and indenter geometry dictate the scratch behaviour of polymers.

Briscoe and co-workers have carried out a number of studies on experiments, modelling and applications of the scratch test. These works include evaluation of cure temperature for glass fiber reinforced polyester (Briscoe and Evans 1989), determination of crystallinity of polymers such as poly(etheretherketone) (PEEK) (Stuart and Briscoe 1996), and the evaluation of scratch deformation maps for polymers (Briscoe and Evans 1989; Briscoe, Evans et al. 1996). The plastically deformed scratch width data were used to calculate the scratch hardness in these works. The surface scratch resistance of different polymers using the scratch tests has been evaluated by Xiang et al. (2001). Their basic observation was that the scratch process is a function of the basic material properties such as the elastic modulus, the yield strength and the tensile strength, as well as material surface characteristics such as the coefficient of friction. A scratch test employing a linear load increase method provides sufficient repeatability of data, was proposed by Wong et al. (Wong et al. 2004), who reviewed scratch testing techniques. The indenter used during a scratch test can be modelled as a sharp asperity to be used for understanding material wear processes. The use of atomic force microscopy (AFM) to study scratching and wear of materials at the micro to the nanometer length scales has been the most recent development in the area (Kaneko and Hamada 1993; Adams et al. 2001). Scratch deformation maps which define a material’s surface damage characteristics under different normal loads, strains, scratching speeds and temperatures can be conveniently developed using scratching techniques (Briscoe et al. 1996).

2.3.1 Scratch Hardness Models

a) Elastic and Plastic Responses

The response of polymers has been modelled as visco-elastic plastic in the case of thermosetting and thermoplastic polymers, while visco-elastic/tearing response for elastomers to a localized induced mechanical strain. When the strain is in the elastic range, part of it will be recovered immediately after removal of the stress while the rest of it will recover over a
period of time. The plastic strain is represented by a permanent change in the dimension of the polymer after visco-elastic recovery. In comparison metals show mainly plastic deformation which can easily be used to determine hardness. The visco-elastic behaviour of polymers creates ambiguities for the determination of the hardness, as the contact area will change over a period of time due to recovery. When polymeric materials are scratched under an indenter, the energy provided by the indenter can be divided into three components; to support the normal load, to overcome the resistance of the material to tangential deformation and the energy loss to overcome the hysteresis loss, mainly in the form of thermal energy, in the material. The deformation component of the energy required can be further divided to two parts as a ploughing component and a traction component. The former is used for elastic and plastic material deformation and the fracture of material, whereas the later involves dissipation of energy in the frictional works associated with indenter’s sliding over the material. Hence we can write an energy equation for the scratching process as (Briscoe and Sinha 2003).

\[ E_{\text{Tot}} = E_N + E_p + E_F + E_H \]  
2.16

Where,  
\( E_{\text{Tot}} \) = Total Energy spent during scratching  
\( E_N \) = Work done against supporting the normal load,  
\( E_p \) = Ploughing component of energy dissipation,  
\( E_F \) = Frictional energy dissipation  
\( E_H \) = Hysteresis loss.

The forces during a scratching process can be modelled as two components, the first component is the normal load, supported by the contact area between material and the indenter, and the second component of the force is the scratch or friction force, this component represents the material’s response against deformation due to indenter dynamics in the tangential direction. These forces are orthogonal to each other and can be used independently for the calculation of scratch hardness and resistance of the material. The two parameters can be inferred on the basis of this concept as the scratch hardness corresponding to the normal force and tangential hardness corresponding to the frictional force.

Therefore, the scratch hardness for an elastic contact, based on the assumption that the material at the rear end of the moving indenter recovers elastically and hence supports the normal load, can be written as (Briscoe et al. 1996)
\[ H_s = \frac{4W}{\pi(d)^2} \]

Where, \( W \) is the normal load and \( d \) is the scratch width after scratching the material. The area of the scratching contact is assumed to be \( \frac{\pi(d)^2}{4} \) for this equation.

The assumption made for this equation is not applicable in case of a plastic, or viscoplastic scratching contact. For these contacts the rear half of the indenter will not be supported by the scratched material, as material will not be recovered due to plastic deformation, and hence the front part of the indenter will only be in contact with the material and supporting the normal load. So, the hardness equation for a perfectly plastic material can be written as

\[ H_s = \frac{2 \times 4W}{\pi(d)^2} \]

Hence, a general equation for scratch hardness can be

\[ H_s = \frac{q(4W)}{\pi(d)^2} \]

Where \( q \) is a parameter depending upon nature of the material’s response and has a value ranging from 1 to 2. It will be equal to 1 for a purely elastic material, any number between 1 and 2 for materials behaving visco-elastic or visco-plastic under scratching and 2 for purely plastic contact (Briscoe and Evans 1989). The hardness values measured in normal indentation and the scratch tests for metals and polymers have been correlated many a times in the past. Williams (Williams 1996) has tabulated the hardness values of metals from literature, he found the ratio of scratch hardness to normal hardness varies from 0.58 to 1.7 for different ductile metals. Briscoe and co-workers (Briscoe et al. 1996) have found that the scratch hardness and normal hardness values for polymers correlate if they are calculated over a similar contact time.

The second type of hardness namely the tangential hardness or scratch resistance can be written as,
\[ H_T = \frac{F_s}{A_T} \]

where \( F_s \) is the scratching force required to move an indenter on the surface of a material and \( A_T \) is the projected contact surface between the material and the indenter in the direction of scratching (tangential direction). Figure 2.3 is a schematic representation of the contact surfaces for the two above mentioned cases. The material’s deformation characteristics, such as the formation of a prow in front of the indenter and the interfacial frictional condition between the scratched material and indenter, and material moving past the indenter dictates the value of \( A_T \). Interfacial lubricant presence may greatly change the scratch response of material. (Pellillo 1997). Stick-slip boundary conditions may be experienced by the material in front of the indenter in the case of an unlubricated scratching experiment due to the adhesive component of scratch force. A first order analysis of the adhesive component of the scratching force with a correlation to experiment for a model visco-plastic material can be found in the literature (Briscoe et al. 1993).

**Figure 2.3**: Schematic representation of the normal and tangential contact surfaces during scratching. For the normal projected surface, the visco-elastic part has also been shown (Briscoe and Sinha 2003).
A relatively new technique to study the scratching properties of polymers is using an indenter or blade attached to the end of a pendulum (Liang et al. 1996; Briscoe et al. 1999). This technique can be used to study dynamic scratching characteristics by producing fine scratches. The pendulum indenter strikes the material surface and makes an arc of scratch along its path. The loss in potential energy during this contact is used to determine the hardness of the materials called the dynamic hardness, and can be represented as

\[
H_D = \frac{E_D}{V}
\]

2.21

Where \( E_D \) is the potential energy loss during scratching contact of a pendulum and \( V \) is the scratch groove volume. Briscoe et al. (1999) have studied the comparison of dynamic hardness and tangential hardness and described them to be similar. The dynamic hardness is also called the specific grooving energy by some authors and also defined as \( E_D/M \) where \( M \) is the mass loss during scratching. The specific grooving energy was found to be equal to approximately 1.21 times the value of the tangential hardness by Liang et.al (1996).

The deformation induced in the scratched material depends on the stresses generated during a scratching contact. These stresses can be modelled as two parts, first is the compressive stress experienced by material in the front of the indenter and secondly the tensile stress on the material at the rear end of the indenter. Hamilton and Goodman (Hamilton and Goodman 1966) have carried out detailed analysis of these stress fields for the case of spherical indenters which is used by Xiang et, al (2001) to calculate the depth of the scratch. The elastic modulus is an important parameter to determine the depth of scratching and the type of damage produced. A high modulus material is more prone to induce stress concentration, leading to failure by cracking and crazing. A high friction coefficient will lead to development of high tensile stresses at rear of the indenter, which may eventually cause cracking of material (Pelillo 1997).

**b) Brittle Response**

The brittle response can be largely suppressed if there is a large hydrostatic pressure (stress) in the stressed region, shear and plastic deformation may be favoured in this case, for brittle material like inorganic glass and ceramics. The same will happen during indentation and scratching as there are high hydrostatic pressure and compressive stress under the indenter tip in normal indentation and at the front of a scratching contact, leading to plastic yielding
instead of brittle failure. But, surface and subsurface, cracks and crazes are found for brittle glassy polymers like PMMA. The cracks nucleate at the edge of the contact, where tensile stresses are the maximum in the case of normal indentation. A residual tensile stress is generated due to strain mismatch in the plastically and elastically deformed regions, this stress can lead to brittle fracture of material (Briscoe and Sinha 2003).

A model, for the normal indentation of brittle solids, based on the concept of linear fracture mechanics has been presented (Lawn and Wilshaw 1975). According to this model the normal load for fracture is

\[ P_{fr} = K_{IC} (\pi a)^{3/2} \tan \alpha \]

Where \( P_{fr} \) is the transition load from ductile to brittle fracture mode, \( K_{IC} \) is the fracture toughness of the material, \( a \) is the radius of the projected contact area and \( \alpha \) is the semi included cone angle. This equation can also be written in terms of normal hardness \( H_N \) as

\[ a = \left( \frac{K_{IC}}{H_N} \right)^2 (\pi)^3 \tan^2 \alpha \]

These equations can be used as a first order model in the case of scratching.

### 2.3.2 Scratch Deformation Modes

The scratching phenomena of polymers are accompanied by a number of surface deformation mechanisms, or modes, under different contact conditions. The appearance of surface damage and the magnitude of the friction coefficient characterise these deformation modes. These deformation modes depend upon the cone angle of the indenter, the normal load, penetration depth, sliding velocity, type of material and interfacial lubrication (Briscoe et al. 1996). The scratch deformation processes identified in the literature, include ductile ploughing, ductile and brittle ploughing, rubber like or elastomeric, ironing and elastic responses as shown in figure 2.4.

A ductile ploughing mechanism occurs when the behaviour of a polymeric surface is similar to ductile metals during scratching where there is an extensive plastic deformation, and the deformation is characterized by ductile flow of the material around the indenter tip. This phenomenon may be accompanied by significant viscoelastic recovery at the rear of the
indenter, and may occur without any evidence of discrete failure. In addition well-defined edges form on the sides of a scratch groove. This type of deformation is normally encountered for lower strains and applied loads and can also be termed as viscoelastic-plastic ploughing. Pelillo (1997) has observed this type of deformation for poly(methyl-methacrylate) at lower contact strains.

In the case of more severe contact conditions such as, higher applied loads, or strains, the sliding indenter will force material into more localised stress fields and the deformation is not fully plastic in this case. There will be crack formation on the edge or within the scratch groove observed specifically for an amorphous polymer which shows brittle mechanical properties, characterized as ductile and brittle deformation. The direction and shape of the crack produced will depend upon the material and the locations of the maximum applied tensile stress. Briscoe et al (1996) have observed this type of deformation for semicrystalline poly(ethylene), where they observed a peculiar regular crack deformation within the track.

The brittle deformation is characterized by a partial plastic flow, this will occur when amorphous polymers are subjected to severe conditions of normal loads and contact strains. There is chip formation along the brittle deformation when the polymers are subjected to the most severe contact conditions, this can also be termed as cutting, or machining, from the analogy to metal processing. The ductile and brittle deformations mainly occur when polymers are scratched by sharp indenters and at higher loads (Briscoe 1998).

On the other hand with blunt indenters and lower loads, there is a “smoothening” effect of the original surface asperities commonly called ironing. This phenomenon is accomplished by a decrease in localized surface roughness. A fully elastic recovery can occur as a result of the scratching process in extremely mild contact conditions. The friction force in this case arises from viscoelastic, or hysteresic loss without permanent damage. A rubber like deformation mode can also be seen for polymers when they are exposed to solvents which make their surfaces soft. Here, the indenter punctures the material and intermittent tears will be formed in the transverse direction of sharp indenter due to an isolated stress concentration in this case (Briscoe and Sebastian 1996).
Figure 2.4: The major deformation mechanisms (a) Ductile Ploughing (b) Ductile and Brittle Deformation (c) Brittle Deformation (d) Rubber like deformation (e) Ironing (f) Elastic (From Briscoe 1998)
2.3.3 Scratch Deformation Maps

Mapping is a common and convenient technique to present a variety of material information. These maps provide information regarding working conditions and material responses under dynamic sliding conditions against a harder counterface for mechanical and tribological applications. There has been a lot of recent work on mapping tribological data of materials recently including wear mechanism diagrams for steel (Lim and Ashby 1987), scratching mode and hardness of metals, wear mode maps of ceramics (Adachi et al. 1997) and wear mode transitions of brittle materials (Hutchings 1992). Lim and Ashby (1987) classified and ordered wear data for steel to construct wear mechanism diagrams. They showed the convenience of mapping to report the wear data and presented the relationship between competing wear mechanisms. Ashby and co-workers (Sharp et al. 1993; Ashby 1998; Ashby and Braechet 2003) have explored the applications of mapping the mechanical properties of the materials and highlighted their convenience for the selection and design of materials. Adachi et al. (1997) constructed wear mode maps reporting scratching or abrasion of ceramics under different contact conditions. Hutchings (1992) described the ductile to brittle transition and wear mechanisms of brittle materials using mapping techniques.

Briscoe et al (Briscoe et al. 1987; Briscoe and Evans 1989; Briscoe et al. 1996; Briscoe and Sinha 2003) have adopted the scratch deformation mapping of polymers to describe the scratching or wear mechanisms modes and their ductile to brittle transitions for γ-irradiated PTFE, scratch deformation transitions of polymers and glass fibre reinforced polyesters. These maps were usually generated from a visual assessment of the damage through SEM imaging and relating these assessments with number of experimental parameters of scratching undertaken. Briscoe et al. (1987, 1996) related the friction coefficient with the scratching contact parameters and the deformation mechanisms to generate friction maps of polymers.

2.3.4 Polymer plasticisation

The mechanical properties and scratch resistance of polymeric surfaces may also be affected by the adsorption of external agents (solvents) which might induce plasticisation or crazing. A substance which can partially dissolve a solid polymer is a potential plasticiser. The plasticiser, once absorbed in the polymeric molecular structure, may attenuate the
intermolecular forces of attraction, and hence produce greater freedom of movement between macromolecules of the polymer. This results in reduced tensile strength and chemical resistance as well as enhanced flexibility and plasticity of the polymeric material. Solubility behaviour of the two materials is a basic factor in describing the plasticisation. The chemical compatibility of two materials, ability of the material molecules to coexist in single phase, dictates the solubility behaviour of the materials. Therefore, if the materials have stronger intermolecular forces between their molecules than the molecules of individual material, they will be considered compatible for plasticisation. Solubility parameter, based on the heat of vaporization or sublimation per mole, is a typical measure of the molecular interactions. The solubility parameter of the polymers can not be calculated directly, since they do not vaporize without decomposition. Therefore, solubility of the polymer is estimated based on the solubility parameter of the solvent which can dissolve the polymer without reaction or association. Poly(etheretherketone) is reported to have solubility parameter closer to that of acetone (Parvatareddy et al. 1996). The fracture mechanics and the stress behaviour of polymers in chemical environments, plasticisers, is reported in literature (Arzak et al. 1993; Arzak et al. 1994; Kawagoe et al. 1994).

2.4 Summary

This Chapter has presented a brief historical perspective and established models for evaluating the indentation and scratch hardness of polymers. The contact compliance method, to determine the hardness and the elastic modulus using indentation, has been described in detail. The most common and relevant contact mechanical parameters of indentation and scratch hardness are detailed. The scratch hardness models and the scratch deformation modes, commonly experienced by polymers, are reported. A brief introduction to the scratch deformation maps and plasticisation of the polymers in solvents has also been made.
CHAPTER 3

EXPERIMENTAL TECHNIQUES

In this Chapter the experimental equipment and materials to be used for the current work will be described. The experimental apparatus utilized for this project can be divided into three sections: Nano-Indenter, surface scratching techniques and surface imaging techniques. The nanoindentor was used to obtain the compliance curve, the indentation hardness and the elastic modulus of the polymeric surfaces. The sample surfaces were scratched using a linear scratching machine and a pendulum scratching machine to access the surface deformations and the scratch hardness. Scanning electron microscopy (SEM) and optical profilometry were utilized to obtain the qualitative and quantitative data of the scratched surface topography and deformations. Finally the range of polymers adopted for this work is presented.

3.1 Introduction

The apparatus and materials used in the work presented in this Thesis are described in this Chapter. An MTS Nano-Indenter II, (NANO INDENTER® II machine, supplied by Nano Instruments Ltd., Tennessee, USA), was used to obtain nano-hardness and elastic modulus of the polymers. A linear scratching machine and a pendulum sclerometer were used for scratching polymeric surfaces. The subsequent scratched surfaces were analyzed for qualitative surface deformations using a scanning electron microscope, SEM JSM-5610 LV, JEOL, Japan, and geometry of the deformation using an optical profilometer, Wyko 9100NT Optical Profiling System, Veeco Instruments Inc. US. The principal material used for this work was poly(etheretherketone) (PEEK) sheets, (catalogue # EK303031) Goodfellows, Cambridge, UK, supplied in the form of 1mm thick sheets were taken as a model of semicrystalline polymers. Amorphous (quenched) and crystalline (annealed) grades of PEEK, produced by thermal treatment of the semicrystalline PEEK, and commercially available fibre oriented PEEK supplied by Victrex polymers, UK, were also analyzed. A range of polymers including amorphous polymers (a polypropylene, Goodfellow catalogue # PP303100, a polycarbonate, Goodfellow catalogue # CT303050 and a
poly(methylmethacrylate), Goodfellow catalogue # ME303013), semicrystalline polymers (a ultra high molecular weight polyethylene, Goodfellow catalogue # ET303060) and brittle polymers (a polystyrene, Goodfellow catalogue # ST313120) were selected for, nanoindentation based surface mechanical properties, comparison to the semicrystalline PEEK properties. A table of relevant physical and mechanical properties of the polymeric materials are also presented in this Chapter.

3.2 Nano Indenter IIs

The normal indentation hardness tests were conducted using a nano-indenteter system, NANO INDENTER® IIs machine, supplied by Nano Instruments Ltd., Tennessee, USA. A schematic representation of the nanoindenter is shown in figure 3.1. A contact compliance indentation mode has been adopted with this machine. Therefore, the machine has the ability to calculate the hardness and the elastic modulus of the material being tested without actually measuring the area of indentation. A conventional hardness tester requires the optical assessment of area of deformation, for example by an optical microscopy or an AFM method, normal to the loading plane. By comparison, in compliance mode indentation the area is determined by using depth of an indent and the geometry of the indenter tip. The depth of indent could be determined by constantly monitoring the indenter position relative to the specimen surface. The geometry of the indenter tip was determined by indenting against fused silica and performing the indent area calibrations. The machine has the option to adopt continuous stiffness method which allows the determination of the hardness and the modulus as a continuous function of indenter displacement.

The nano-indenter consists of three main structural components: an indenter column, an optical microscope and a precision table to transport the sample between microscope and indenter as shown in figure 3.1. The thermal stability of the specimen sample and apparatus was ensured by enclosing the apparatus in a wooden cabinet. The temperature in the wooden cabinet remained within 25±3 °C. The indenter could be accessed through a hinged leaf door located on the front of the cabinet. The indenter assembly was suspended on a pneumatic vibration table inside the cabinet to isolate it from building vibrations. This table was designed to attenuate at least 90% of the floor vibrations at 7 Hz or higher and functioned with compressed air (NANO INDENTER® IIs, Operating Instructions). The equipment was mounted in a basement laboratory as a further step to reduce the ambient vibration.
continuous stiffness method and the load frame stiffness calibrations of the nanoindenter are presented in appendix A and B.

![Figure 3.1: Schematic representation of MTS NANO INDENTER® II s and its various system components (From Mohammed, H., 2004)](image)

### 3.2.1 The Indenter Column

The Indenter Column consisted of a dual-tube assembly as shown in figure 3.2. The inner stainless steel tube was the load bearing element. The outer tube, made of a low thermal expansion iron-nickel alloy (INVAR), was connected to the middle plate of the three plate displacement capacitor. This capacitive displacement sensor measures the displacement of indenter tip using a data acquisition system. The height of examined specimen topography was limited by the distance between the outer plates of the capacitor. These plates were separated by 200 µm, so that the maximum indentation depth must be less than this (NANO INDENTER® II s, Operating Instructions). Four leaf springs with low stiffness (40-80 N/m) in vertical and high stiffness (10^4 N/m) in lateral direction were attached to the outer tube. These springs were used to detect increase in load during surface detection and to stabilise motion of indenter shaft.
A trigonal diamond pyramid tip was housed at the bottom of the indenter column. The indenter tip was a Berkovich Indenter which made $65.3^\circ$ with the normal to the base (Briscoe et al. 1998; Maung 2000). An electromagnetic aluminium coil surrounded by a solenoid magnetic field was connected at the top of inner indenter tube. The application of current to the coil generated the force to operate the indenter. The MTS NANO IIs was capable of operating at constant loading rate, step loading, constant displacement rate and constant strain rate loadings. The constant loading rate and step loadings were achieved by multiplication of an appropriate factor to the current change in the load coil. In a constant displacement rate loading indent, a feedback system on continuously measured indenter displacements was used to adjust the loading rate to required displacement rate. The constant strain experiments were conducted by stepwise application of either constant loading rate or constant displacement rate loadings.

Figure 3.2: Schematic representation of an Indenter Column (From Akram, A., 2001)
3.2.2 The Optical Microscope

An optical microscope was built over the precision table. This microscope had a magnification of X80 and was remotely connected to a TV screen via a CCD video camera. The sample was focused using height (z-direction) adjustment on the precision table. The position of indents was selected using images on TV screen from the microscope.

3.2.3 The Precision Table

An XYZ table with specimen holder was used to hold the samples during indentation. A joystick arrangement was used to control the location of the specimen relative to the microscope and the indenter. The position of indents was selected by movement in the XY plane with a spatial resolution of ca. ±400 nm. Z direction motion focused the microscope. The specimen holder was a rectangular metal plate with recessed holes. The samples were glued on circular metal disks being held in recessed holes of the specimen holder. Bolts were used to tighten the specimen holder on the moving plateform.

3.3 The Surface Scratching Techniques

The surface scratching techniques involved drawing a rigid indenter of known geometry along a flat surface of the material. Two types of surface scratching machines were utilized during this work, a linear scratching machine and a pendulum sclerometer.

3.3.1 Linear Scratching Machine

A linear scratching machine consisted of a balanced beam originally designed by Eldrige and Tabor (1955) as shown in figure 3.3. The indenter was mounted on one side of a beam above the polymer specimen. Normal loads were placed on a holder directly above the indenters. The beam was mounted on a lathe bed which was driven by a step controlled motor to draw the cone across the polymer surface. A pair of strain gauges were mounted on spring steel sections of the beam to monitor the frictional force by a carrier wave frequency bridge. The signal from these strain gauges was stored on a computer via a PAXS, strain gauge meter from Red Lion Controls, York, USA.
The nominal imposed strain of the contact can be defined by the geometry of the conical indenters. Hence the variation of the cone angles of indenters provided strain variation. Steel conical indenters with different internal cone angles (30° to 130°) were used. The scratching velocity was varied to investigate the effects of the contact strain rate on scratching. The imposed scratching velocity was varied between 0.3 mm/sec to 3 mm/sec. Normal loads were varied from 0.5 N to 5 N for fixed geometry of an indenter to observe the effects of contact pressure on scratch deformations. A metallic sample holder with heating electrical cartridges was used to study scratching at different material bulk temperatures. The heating elements were controlled by a proportional–integral–derivative (PID) controller and maintained the temperatures to ±1 °C. The scratches were produced in the presence of a petroleum jelly, commercially available ointment Vaseline Jelly which is a mixture of semi solids (Viscosity ≈ 1500 Poise) between the indenters and the polymeric samples to account for the effects of interface lubrication on the scratch deformations and the friction.

Figure 3.3: Schematic diagram of a Linear Scratch Testing Machine (From Stuart and Briscoe 1996)
3.3.2 Pendulum Sclerometer

The pendulum sclerometer was a type of dynamic scratching machine. The scratch produced with a pendulum machine had a variable scratch depth across the scratch length. The pendulum machine consisted of a rigid loaded beam, pivoted at one extremity, with an indenter or blade, attached at the other extremity. The beam was free to oscillate around the pivot and contacted a polymer sample surface at its lowest position with maximum grooving force and velocity at the lowest contact point. A load was applied by attaching number of dead weights to the beam. The length and the depth of the scratch were controlled by varying the relative distance between the pivot and the sample surface and were readily achieved using a vertically moveable pivot head.

![Pendulum Sclerometer Diagram](Briscoe et al. 1999)

**Figure 3.4:** A schematic Representation of Pendulum Sclerometer (Briscoe et al. 1999). With experimental parameters as: $L$: beam length; $l_0$: initial position of the centre of gravity of the system; $l$: final position of the centre of gravity; $\omega_0$: starting angle of the beam; $\omega$: final angle of the beam; $M$: mass of the system including the mass of the beam and the weights; $g$: gravity acceleration.
The indenter attached to the pendulum was brought to a chosen height to gain the inertia through potential energy and then released. The pendulum arm made a free swing upon release whereby the indenter scratched the surface of the material as it approached the lowest height. The pendulum swung to the other side of the vertical axis reaching a certain height. The difference between the height of release and the height attained on the other side represented energy lost during scratching of the material. The friction losses at the pivot had also been taken into account by the calibration. The calibration curve for the friction losses was constructed by measuring the percentage of potential energy lost during single oscillations in the absence of scratching contact at different applied loads. It was assumed that these losses accurately represent the losses during the scratch deformation due to pivot friction.

3.4 Surface Imaging Techniques

The subsequent surface deformations and scratch topography were determined using a scanning electron microscope (SEM JSM-5610LV JEOL, Japan) and an optical profilometer (Wyko 9100NT Optical Profiling System, Veeco Instruments Inc. US).

3.4.1 Scanning Electron Microscope

The scratched polymeric surfaces were analyzed using a Scanning Electron Microscope, SEM JSM-5610 LV, JEOL, Japan, for assessment of the surface deformation. The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. An excitation voltage of 15 KV was applied to produce electron beam. The sample chamber of the SEM was evacuated (≈0.1 atm) to minimize the ionization of air in the chamber. The electrons interacted with the atoms that make up the sample producing signals that contain information about the sample. Electronic devices were used to detect and amplify the signals and display them as an image on a cathode ray tube in which the raster scanning was synchronised with that of the microscope. The image, from high resolution cathode ray tube, was digitally captured and displayed on a computer monitor. The polymeric samples were coated with thin layer (15-20 nm) of gold coating to impart the conductive characteristics to the polymeric surfaces. An Emitech K550 sputter coater, Emetich, England, was used to apply the gold coating on the polymeric surface. The coating was performed under 20 mA deposition current.
for 2 min in Argon gas environment. The samples were mounted on steel stubs using an adhesive tape. A conductive bridge, between the polymeric surface and the stub, was established using silver coating paint.

The deformation characteristics of the scratches, for example ductile or brittle deformations, presence of cracks etc, were identified from the subjective qualitative assessment of SEM images. Therefore, SEM only provided qualitative data that could not be used for the measurement of scratch width or depth data. Therefore an optical profilometer was used to measure scratch geometry. The optical profilometer used principle of laser light reflection from the surface of the specimen to estimate the surface roughness, scratch width and scratch depth.

### 3.4.2 Optical Profilometer

A noncontactive optical profilometer, Wyko 9100NT Optical Profiling System, Veeco Instruments Inc. US, was used to study the topography of the scratched polymeric samples. A schematic of the optical profilometer is presented in figure 3.5. The Wyko profilometer works on two modes; phase shift interferometry (PSI) and vertical scanning interferometry (VSI) mode. The PSI mode, based on the phase shift measurement of the light reflected from the reference and the sample, is used to measure smooth surfaces and small steps. The VSI mode, based on interference fringe of the light reflected from a reference mirror and the light reflected from the sample surface, is used to measure rough surface profiles and steps. The VSI mode was utilised in the present work to obtain the surface topography of the scratched polymeric samples. The white light in VSI is filtered through a neutral density filter to produce the short coherence of the light. The resulting degree of fringe modulation or coherence is measured to obtain the surface profile of the sample. The Wyko profilometer, in the VSI mode, is capable of measuring the surface profile within a range of 2 mm with vertical resolution of 3 nm. The scratched surfaces were scanned in orthogonal direction to scratches at different locations selected randomly to obtain a representative description. The width and depth of the scratches were determined by the optical profilometer. These data were utilized to calculate the scratch hardness of polymer surfaces.
3.5 Materials

Commercially available semicrystalline PEEK 1.2 mm thick sheets were purchased from Goodfellow, UK. The polymer samples were annealed at a temperature of 380-400°C to produce crystalline and amorphous samples. The crystalline samples were produced by allowing the sample to cool gradually to ambient temperature. The crystallinity of the semicrystalline sample was estimated to be 40% by the differential scanning calorimetry (DSC). Whereas quenching the heated samples in cold water produced amorphous samples, which had negligible crystallinity. The 30% (w/w) carbon fibre reinforced PEEK (Victrex PEEK-90CA) and 30% (w/w) glass fibre reinforced PEEK (Victrex PEEK-90GL) samples were supplied by Victrex polymers, UK.

Poly(methylmethacrylate), PMMA (Catalogue # ME303013), ultra high molecular weight polyethylene, UHMWPE (Catalogue # ET303060), polycarbonate, (Catalogue # CT303050), polypropylene, PP (Catalogue # PP303100) and polystyrene, PS (Catalogue # ST313120), sheets were selected for a comparative study using nanoindentation. These samples were purchased from Goodfellow, UK and used as received without any prior surface treatment. The sample characteristics of the materials reported in the Thesis are listed.
The most relevant physical and mechanical properties found in literature (material data sheet provided by suppliers) are listed in the table 3.1.

Table 3.1: Sample Characteristics of the materials reported in the Thesis

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Supplier Material Code</th>
<th>Treatment</th>
<th>Fibre Volume</th>
<th>Crystallinity %</th>
<th>Physical State</th>
<th>Dimensions</th>
<th>Mol. Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PEEK</strong></td>
<td>Goodfellow EK303031</td>
<td>As received</td>
<td>-</td>
<td>40±2</td>
<td>Semicrystalline</td>
<td>10cmX10cm x1.2mm</td>
<td>30,000-45,000</td>
</tr>
<tr>
<td></td>
<td>Goodfellow EK303031</td>
<td>Quenched</td>
<td>-</td>
<td>&lt; 3</td>
<td>Amorphous</td>
<td>10cmX10cm x1.2mm</td>
<td>30,000-45,000</td>
</tr>
<tr>
<td></td>
<td>Goodfellow EK303031</td>
<td>Annealed</td>
<td>-</td>
<td>31±3</td>
<td>Semicrystalline</td>
<td>10cmX10cm x1.2mm</td>
<td>30,000-45,000</td>
</tr>
<tr>
<td><strong>Carbon fibre reinforced</strong></td>
<td><strong>PEEK</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Victrex 90CA</td>
<td>As received</td>
<td>30 (w/w)</td>
<td>43±2</td>
<td>Semicrystalline</td>
<td>10cmX10cm x1.2mm</td>
<td>30,000-45,000</td>
</tr>
<tr>
<td><strong>Glass fibre reinforced</strong></td>
<td><strong>PEEK</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Victrex 90GL</td>
<td>As received</td>
<td>30 (w/w)</td>
<td>43±2</td>
<td>Semicrystalline</td>
<td>10cmX10cm x1.2mm</td>
<td>30,000-45,000</td>
</tr>
<tr>
<td><strong>PMMA</strong></td>
<td>ME303013</td>
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<td>-</td>
<td>&lt; 3</td>
<td>Amorphous</td>
<td>10cmX10cm x1.2mm</td>
<td>50,000-500,000</td>
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<tr>
<td><strong>UHMWPE</strong></td>
<td>ET303060</td>
<td>As received</td>
<td>-</td>
<td>60</td>
<td>Semicrystalline</td>
<td>10cmX10cm x1.2mm</td>
<td>3.10x10^6-5.6x10^6</td>
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<tr>
<td><strong>PP</strong></td>
<td>PP303100</td>
<td>As received</td>
<td>-</td>
<td>10</td>
<td>Amorphous</td>
<td>10cmX10cm x1.2mm</td>
<td>3.10x10^6-5.6x10^6</td>
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<tr>
<td><strong>PC</strong></td>
<td>CT303050</td>
<td>As received</td>
<td>-</td>
<td>&lt; 3</td>
<td>Amorphous</td>
<td>10cmX10cm x1.2mm</td>
<td>10,000-30,000</td>
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<tr>
<td><strong>PS</strong></td>
<td>ST313120</td>
<td>As received</td>
<td>-</td>
<td>&lt; 3</td>
<td>Amorphous/Brittle</td>
<td>10cmX10cm x1.2mm</td>
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<td>Material Properties</td>
<td>Material</td>
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<td>PEEK-30% (w/w) CF</td>
<td>PEEK-30% (w/w) GF</td>
<td>PMMA</td>
<td>UHMWPE</td>
<td>PS</td>
</tr>
<tr>
<td>---------------------</td>
<td>----------</td>
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<td>------------------</td>
<td>------------------</td>
<td>------</td>
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<td>----</td>
</tr>
<tr>
<td>Tensile Strength (at break)/ MPA</td>
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<td>200±20</td>
<td>150±20</td>
<td>65±10</td>
<td>20±5</td>
<td>60±20</td>
<td>30±5</td>
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<td>Elongation at Break (%)</td>
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<td>1.7</td>
<td>2.7</td>
<td>5±1</td>
<td>400±50</td>
<td>1.6±0.3</td>
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<td>200±20</td>
<td>150±20</td>
<td>65±5</td>
<td>30</td>
<td>60±20</td>
<td>30±5</td>
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<tr>
<td>Tensile Modulus/ GPa</td>
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<td>25</td>
<td>11.8</td>
<td>2.8±0.5</td>
<td>0.7</td>
<td>2.35</td>
<td>1.2±0.3</td>
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<td>Rockwell Hardness</td>
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<td>M99</td>
<td>M99</td>
<td>M100±5</td>
<td>R50</td>
<td>M75</td>
<td>R80-100</td>
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<tr>
<td>Izod Impact Strength/ Jm⁻¹ notch</td>
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<td>95</td>
<td>100</td>
<td>24±6</td>
<td>1000</td>
<td>700</td>
<td>60±40</td>
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<td>Poisson Ratio</td>
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<td>0.4</td>
<td>0.4</td>
<td>0.33</td>
<td>0.4</td>
<td>0.35</td>
<td>0.4</td>
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<tr>
<td>Density/ gcm⁻³</td>
<td>1.30</td>
<td>1.40</td>
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<td>1.17</td>
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<td>Compressive Strength/ MPa</td>
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<td>300</td>
<td>250</td>
<td>105</td>
<td>160</td>
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<td>80</td>
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<td>Compressive Modulus/ GPa</td>
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<td>23</td>
<td>11.3</td>
<td>4</td>
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<td>3.4</td>
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<td>Thermal Conductivity/ Wm⁻¹K⁻¹</td>
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<td>0.95</td>
<td>0.30</td>
<td>0.2</td>
<td>0.49</td>
<td>0.19</td>
<td>0.15</td>
</tr>
</tbody>
</table>
3.6 Summary

In this Chapter, the experimental techniques and the material used in this experimental study were described. The nanoindentation technique was used to obtain the load-displacement behaviour of the polymers studied. The loading curves obtained from nano-indentation were used to access the hardness and the elastic modulus. The linear and the pendulum scratching machines were utilized to impose scratch deformations on polymeric samples. The strain gauge assembly with the data acquisition unit was used to record the frictional force during scratching on the linear scratching machine. A scanning electron microscope was utilized to qualitatively determine the scratch deformations and subsequently construct the scratch deformation maps. The scratch width and topography data for scratch hardness determination was determined using a Wyko optical profilometer. Finally, the materials used for the study were described with their most relevant physical and mechanical properties.
CHAPTER 4

NORMAL INDENTATION HARDNESS

The experimental results obtained from nanoindentation into semicrystalline poly(etheretherketone) (PEEK) surfaces are presented in this Chapter. Selected data and the associated analysis for the load-displacement curves, the hardness, the elastic modulus and the creep response of the PEEK are given. A comparison of the nanoindentation results of semicrystalline PEEK with other commercially available polymers has also been made. A bimodal indentation response of the semicrystalline PEEK and UHMWPE has been found depending on whether a crystalline or amorphous region has been indented. PMMA is found to be the hardest polymer of the selection whereas UHMWPE and PP are observed to be softer polymeric surfaces using nanoindentation.

4.1 Introduction

The evaluation of material properties at the very first surface molecular layers has always been a challenge. It is believed that these govern some aspects of the contact performance of these materials especially in most surface engineering and tribological applications. Therefore, material selection and design for such applications needs knowledge of near surface properties. Indentation at the nano scale has been established as a means to investigate the mechanical properties of materials at reduced penetration depth for past two decades (Pethica et al. 1983; Loubet et al. 1984; Oliver and Pharr 1992; Briscoe and Sebastian 1996; Briscoe et al. 1998; Li and Bhushan 2002; Jiang et al. 2008; Babu and Kang 2010).

The near surface mechanical properties investigation is challenging. The imaging technique, which requires the optical evaluation of the contact area after indentation is not suitable due to large and unacceptable errors for shallow indentations. This problem has been largely overcome by the use of the compliance method as discussed in Chapter 2. The hardness and elastic modulus are computed directly from the analysis of load displacement...
curves obtained from loading-unloading cycles performed on material surfaces. Therefore, the measurement of residual contact area is not needed in this method (Page et al. 1998; Oliver and Pharr 2004; Tze et al. 2007). The inevitable physical presence of imperfections in indenter tip geometry is another problem encountered during hardness evaluation by indentation (Ion et al. 1990; Oliver and Pharr 1992; Briscoe et al. 1996). These tip defects could be comparable to the full indent size and might cause a significant error in property values. Briscoe and Sebastian (1996) have looked into this problem for polymeric materials and proposed an analytical method based on tip defect estimation.

The indentation of polymeric surfaces poses further difficulties due to the complex viscoelastic-plastic response of such materials. Polymers show different behaviour under different contact conditions due to strain and strain-rate dependence of their properties. Therefore, the surface mechanical properties of polymers are a function of the imposed contact conditions, such as the indenter geometry, the penetration depth (the strain), the loading rate (i.e. strain rate) and the ambient temperature. This chapter presents the experimental data and subsequent analysis obtained from nanoindentation to PEEK and other commercially available polymers.

4.2 Nano Indentation results of PEEK

Continuous stiffness nanoindentation experiments were conducted on semicrystalline PEEK samples obtained from Goodfellow, UK at constant loading rates, constant strain rates and constant displacement rates to analyze the hardness, the elastic modulus, the stiffness and the plasticity index of the sample. The constant loading rate indentation experiments were performed at a rate of 300 µN/sec to a maximum depth of 5000 nm. A constant strain rate of 0.025 sec\(^{-1}\) was selected to analyze the surface mechanical properties of the semicrystalline PEEK under constant strain rate indentation. The constant displacement rate indents were made at 5 nm/sec to a maximum depth of 1000 nm. The PEEK samples were loaded to a depth of 1500 nm at 300 µN/sec and then holding the load for times from 100 sec to 600 sec (10 min) in different experiments to analyze the creep behaviour. A final hold segment after 80% unloading was applied to account for the thermal drift during all indentation experiment.
4.2.1 Load-displacement curves

Figure 4.1 shows typical loading unloading data obtained from nanoindentation of the semicrystalline PEEK. Complete data set of all the indents on the polymeric surface is presented in figure D1 of appendix D. These indents were performed by applying indentation at loading and unloading rates of 300 µN/sec to a maximum depth of 5000 nm depth. The indenter was held for 50 sec at the maximum load to account for the creep behaviour of the polymer surface. The indents were spaced 100 µm from each other.

As can be seen from the figure 4.1, the indentation response of semicrystalline PEEK can be characterized as a multi phase response, similar to metal alloys (Chen et al. 2009; Gerday et al. 2009; Chen et al. 2010; Xia and Wang 2010). A harder phase as shown by curve SCPK-1 (black line) on figure 4.1, required 150-170 mN to impose a penetration depth of 5000 nm. In comparison the softer phase required about one third load 50 mN to impose the same penetration depth, curve SCPK-2 (blue line) on the figure represent the typical indentation response from the softer phase of the polymer. Intermediate curves (curve SCPK-3 and SCPK-4) can also be seen requiring approximately indentation loads of 100 mN. These multi phase responses were believed to be from the crystalline and amorphous regions of the polymer. The crystalline region was believed to be the one showing harder response whereas the amorphous regions were softer. The indents represented by intermediate regions, were at places where the indentation depth was more than the thickness of crystalline lamellae. The indentation load remained approximately zero at the onset of the loading segment for all indents. This was due to the uncertainty of the experimental zero point originated by imprecise surface detection during the approach segment. This uncertainty in surface determination is termed as the induction phase, and is higher for rougher surfaces (Mohammad 2004).

Figure 4.2 represented the compliance curves of semicrystalline PEEK at a constant effective strain rate of 0.025 sec\(^{-1}\). The effective constant strain rates were achieved by applying constant displacement rate segments in terms of increasing displacement rate. These were selected as displacement rate of 1nm/sec till 40nm depth, than 2 nm/sec till 80 nm, 4 nm/sec till 160 nm and so on to a displacement rate of 64 nm/sec to maximum depth of 2560 nm. A similar multiphase behaviour as observed in constant loading rate segments was also observed in this type of experimentation. The ratio of peak loads for harder and softer phases
of PEEK was found to be the major difference for constant loading rate segment and the constant strain rate indentation. The load displacement data at constant loading rate has shown 3:1 harder to softer phase peak loads. Whereas for constant strain rate experiments the ratio was observed to be 3:2. The constant displacement rate indentation load-displacement data is shown in figure 4.3. Again multiphase behaviour is evident from the curves and a ratio similar to the one observed in the constant strain rate experiments was seen.

**Figure 4.1:** Indentation load-displacement data for the as received PEEK sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. The compliance curves were obtained from the nanoindentation of the semicrystalline PEEK nominally 100 µm apart. (See figure D1 for complete experimental data set of all indents in appendix D)
**Figure 4.2:** Indentation load-displacement data for the as received PEEK sample at constant strain rate. The strain rate was maintained at 0.025 sec$^{-1}$ during loading segment. The compliance curves were obtained from the nanoindentation of the semicrystalline PEEK nominally 100 µm apart. (See figure D2 for complete experimental data set of all indents in appendix D)

**Figure 4.3:** Indentation load-displacement data for the as received PEEK sample at constant displacement rate. The displacement rate was maintained at 10 nm/sec during loading segment. The compliance curves were obtained from the nanoindentation of the semicrystalline PEEK nominally 100 µm apart. (See figure D3 for complete experimental data set of all indents in appendix D)
4.2.2 **Indentation Hardness and Elastic Modulus**

Hardness and elastic modulus were calculated as a continuous function of penetration depth using the continuous stiffness indentation mode (NANO INDENTER® IIIs, operating instructions; Pethica and Oliver 1989; Lucas et al. 1998) (See appendix A for the continuous stiffness method). The continuous stiffness method utilizes superimposition of a very small AC current onto the DC current loading ramp system. As a result the probe tip oscillates at 1nm amplitude at a frequency of 45 Hz during the indentation loading segment. Therefore, small compliance curves consisting of the loading and unloading from superposition were generated across actual indentation loading process. Hence the material parameters like hardness and modulus were deduced as a continuous function of indentation displacement. The continuous stiffness mode is particularly useful for polymeric materials due to the large variation in mechanical properties and the presence of the negative slope in the initial unloading segment due to creep (Briscoe et al. 1998). The hardness and the elastic modulus were computed using the corrected tip area function produced using indentations on fused silica.

The normal indentation hardness as a function of indentation depth is presented in figures 4.4 to 4.6. The graphical data shown below correspond to indentation experiments performed at constant loading rate, constant strain rate and constant displacement rate loadings respectively. The exceptional large uncertainties were seen for hardness values at lower scales specifically at low penetration depths (<50 nm). These values were thought to be due to errors present in surface determination, the tip geometry defects and indentation size effects (Briscoe et. al. 1998; Bonne et. al. 2005). These values were not regarded as physically significant. A peculiar harder and more diverse response can be seen at near-to-surface layers particularly at penetration depth (100 nm- 500 nm) from all the figures. This can be attributed to localized modifications of the physical properties due to environmental exposure some time before experiments or during the fabrication processing of polymeric materials. These near-to-surfaces modifications may have resulted from aging or localized oxidation of polymeric surfaces. It is interesting to note that the trends are similar in almost all cases. The observed near to surface hardness response is similar to the one reported by Briscoe and co-workers (1998). They have reported large uncertainties in the hardness of polymers for different polymeric systems with nanoindentation without continuous stiffness mode.
Therefore the hardness values corresponding to indentation depths of more than 500 nm will be considered mainly for the property evaluations. The multiphase behaviour, as depicted earlier from the load-displacement compliance curves of PEEK, can be confirmed from these hardness-depth graphs. The diverse multiphase response of PEEK can be interpreted from the figure 4.5. The curve SCPK-2 (blue line) in the figure correspond to the softer phase with hardness of approximately 0.2 GPa and curve SCPK-1 (black line) representing the harder phase present in the polymeric material with 0.55 GPa indentation hardness. The curve 3 (green) and the curve 4 (red) represent the indentation through multiphase regions that is harder and softer regions of the polymers. An interesting fact can be noted from the two curves that they were either harder or softer initially and than switch the properties at approximately 2000 nm. It is hard to find the data comparable to this from literature. Only a comparison in terms of harder and softer phase’s bimodal indentation response could be made to the metal alloys (Chen et al. 2009; Chen et al. 2010; Xia and Wang 2010).

Figure 4.4: Indentation hardness as a function of indentation displacement data for the as received PEEK sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. The hardness data were obtained from the nanoindentation of the semicrystalline PEEK nominally 100 µm apart. (Data less than 300 nm may not be accurate due to surface approach and tip calibration factors.)
Figure 4.5: Indentation hardness as a function of indentation displacement data for the as received PEEK sample at constant strain rate. The strain rate was maintained at 0.025 sec\(^{-1}\) during loading segment. The hardness data were obtained from the nanoindentation of the semicrystalline PEEK nominally 100 µm apart. (Data less than 200 nm may not be accurate due to surface approach and tip calibration factors.)

Figure 4.6: Indentation hardness as a function of indentation displacement data for the as received PEEK sample at constant displacement rate. The strain rate was maintained at 10 nm-sec\(^{-1}\) during loading segment. The hardness data were obtained from the nanoindentation of the semicrystalline PEEK nominally 100 µm apart. (Data less than 100 nm may not be accurate due to surface approach and tip calibration factors.)
Figure 4.5 and 4.6 provided further evidence of the bimodal response of PEEK during indentation. The indentation hardness as a function of displacement is shown in these figures under constant strain rate and displacement loadings respectively. As can be seen from the figures a strain softening response for the harder phase and a strain hardening response for the softer phase is evident.

It is difficult to find data comparable with the experimental results presented here from the literature. Deslandes and Alva (Deslandes and Rosa 1990) investigated the microhardness of PEEK systems with different crystallinity. They obtained the hardness of 0.26 GPa for 34% crystalline samples and 0.135 GPa for amorphous PEEK. The indentations were performed using a diamond square pyramid with a tip angle of 136°. The hardness was measured by measuring the physical dimensions of indent impression from 100 g load for 5 minutes. The fact that those experimental hardness values are lower than the present work can be partially explained by the difference in experimental procedure followed. Also, the hardness of their crystalline samples is actually the overall macrohardness of the sample considering both amorphous and crystalline portions. The present work quotes the hardness for crystalline and amorphous regions separately.

![Figure 4.7: Frequency density distribution based on Indentation hardness of semicrystalline PEEK sample. The frequency is calculated on sample width of 0.05 GPa. The continuous stiffness indentation experiments at constant loading rate of 300 mN/sec were used to obtain hardness data. (Raw data shown in figure D1, appendix D.)](image-url)
Figure 4.8: Frequency density distribution based on Indentation hardness of semicrystalline PEEK sample. The frequency is calculated on sample width of 0.1 GPa. The continuous stiffness indentation experiments at constant loading rate of 300 mN/sec were used to obtain hardness data. (Raw data shown in figure D1, appendix D.)

Figure 4.9: Frequency density distribution based on Indentation hardness of semicrystalline PEEK sample. The frequency is calculated on sample width of 0.2 GPa. The continuous stiffness indentation experiments at constant loading rate of 300 mN/sec were used to obtain hardness data. (Raw data shown in figure D1, appendix D.)
The indentation hardness frequency density distribution, based on a sample length of 0.05 GPa, is represented in figure 4.7. The data were based on a step length of 0.05 GPa hardness and 40 total numbers of indents. The presences of two peaks in the distribution clearly indicate the bimodal nature of the semicrystalline PEEK. The first peak at approximately 0.2 GPa represented the softer amorphous phase of the polymer. The harder crystalline phase had given rise to second peak at about 0.55 GPa. The crystalline portion was estimated to be 36% on the basis of area count, which is similar to the crystallinity of the polymer as estimated by the DSC analysis. Figures 4.8 and 4.9 are the frequency density distributions based on 0.1 GPa and 0.2 GPa sample lengths. The bimodal character is also evident from figure 4.8 frequency distribution. Although the frequency data presented in figure 4.9 with a step length of 0.2 GPa is comparatively linear, the choice of step length greater than 0.1 GPa seems inappropriate for the polymeric surfaces.

**Figure 4.10:** Elastic Modulus as a function of indentation displacement data for the as received semicrystalline PEEK sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. The modulus data were obtained from the nanoindentation of the semicrystalline PEEK nominally 100 µm apart. (Data less than 300 nm may not be accurate due to surface approach and tip calibration factors.)
Figure 4.11: Elastic Modulus as a function of indentation displacement data for the as received semicrystalline PEEK sample at constant strain rate. The strain rate was maintained at 0.025 sec\(^{-1}\) during loading segment. The modulus data were obtained from the nanoindentation of the semicrystalline PEEK nominally 100 µm apart. (Data less than 200 nm may not be accurate due to surface approach and tip calibration factors.)

Figure 4.12: Elastic Modulus as a function of indentation displacement data for the as received semicrystalline PEEK sample at constant displacement rate loading. The displacement rate during loading was maintained at 10 nmsec\(^{-1}\) during loading segment. The modulus data were obtained from the nanoindentation of the semicrystalline PEEK nominally 100 µm apart. (Data less than 100 nm may not be accurate due to surface approach and tip calibration factors.)
The elastic modulus of semicrystalline PEEK as a function of indentation displacement is represented in figures 4.10, 4.11 and 4.12 for different loading conditions. These curves do conform to the presence of multi phases in the semicrystalline polymer as discussed above with indentation hardness. The hard crystalline phase is estimated to have 8 GPa (curve SCPK-1) elastic modulus and the amorphous soft phase approximately 4 GPa (curve SCPK-2). Similar results were seen for elastic modulus values from indentation performed under constant strain rate and constant displacement rate. As can be seen from the figures 4.11 and 4.12, the two curves are smoother in the softer phase, whereas there were higher fluctuations present in the harder crystalline phases. These fluctuations might be due to higher plastic deformations taking place in the hard phase, another reason might be the indentation depth has exceeded the crystal size of this phase exposing amorphous and crystalline phase boundaries.

4.2.3 Elasticity/Plasticity analysis

The plasticity index was evaluated on the basis of relationship based on the hardness and the elastic modulus proposed by Mikic (1974) for perfect cones.

\[ \psi = \tan \beta \frac{E}{H} \]  

Where, \( \beta \) is the angle of inclination of the indenter to the sample surface. The index is based on the relationship developed by Greenwood and Williamson (1966). The original plasticity index values, in its most usually adopted form, contain the yield stress rather than the hardness term and the \( \tan \beta \) term is raised to the half power. Since \( \beta \), the angle of inclination of indenter, is constant for a Berkovich Tip indenter used in the present study therefore the elastic modulus to the hardness as a function of indentation depth is presented for plasticity index. The hardness and the elastic modulus were evaluated from the continuous stiffness indentations mode as reported above for PEEK. This relationship has been discussed by Johnson (1985) and used by Briscoe and Sebastian (1996) for PMMA. Johnson (1992) tabulated the plasticity index values of different materials. The modulus to the hardness ratio was reported to be less than 10 for elastic materials. For perfectly plastic material the ratio was seen to be more than 100. The intermediate values of the ratio represent the elastic-plastic response of the materials. Therefore, a material with higher values of the modulus to hardness ratio is more plastic.
Figure 4.13 presents the plasticity index in terms of $E/H$ as a function of indentation displacement of semicrystalline PEEK. The black curve represents the harder phase (as proposed earlier) and the blue curve is for the softer phase. As can be seen from the figure 4.13, the harder phase is more elastic than the softer phase. This is explained by the ductile nature of the soft amorphous phase. There is an increasing trend of the $E/H$ ratio for the softer phase indicating increased plasticity in the lower surfaces. In comparison the harder phase was observed to show comparatively constant $E/H$ ratio. The uncertainty in the ratio values at lower penetration depths is likely to be, due to the actual physical properties of the surface layers. The physical properties are thought to show a gradient at the surface resulting from the polymer manufacturing processes. These trends may have arisen from inappropriate procedures for tip calibration and/or the sample roughness.

![Figure 4.13: Plasticity Index as a function of indentation displacement data for the PEEK sample at constant loading rate. The loading and unloading rates were maintained at 300 $\mu$N/sec. (Data less than 300 nm may not be accurate due to surface approach and tip calibration factors.)](image)

### 4.2.4 Indentation creep analysis

The nanoindentation experiments were performed on PEEK samples to determine the creep which is a time dependent deformation under constant load. The indenter was loaded on to the sample at a constant rate of 300 $\mu$N/sec to 1500 nm displacement and then the load was
held constant for 600 seconds during which the creep depth was monitored. The applied load was then relieved at 300 µN/sec to 80% unloading and then held constant for 100 seconds to record the thermal drift rate corrections as shown in figure 4.14.

The creep deformation of PEEK during the hold segment is represented in figure 4.15. The creep curve in figure 4.15 can be divided into two sections, an initial transitional behaviour (~50 second) termed as primary creep and a constant gradient creep curve known as secondary creep. Primary creep is due to viscoelastic and viscoplastic effects termed as lagging deformations, while the viscosity or flow deformations are termed as secondary creep. The primary creep for PEEK was observed to occur for 50 seconds of the hold segment. During this segment an abrupt change in indentation depth of 100 nm was observed. Similar indentation creep behaviour was observed by Li and Ngan (2010) for polyethylene, Wei et al. (2008) for PMMA and by Li and Bhushan (2002) for PTFE film.

Figure 4.16 and 4.17 shows the representative mean contact stress and contact stiffness data of the continuous stiffness mode indentation creep test on the semicrystalline PEEK. The indenter was oscillated at 1nm peak-to-peak displacement at 45 Hz frequency during the hold segment. The contact hardness measured in continuous stiffness has been taken as mean stress. The mean stress was observed to decrease with increasing time while the contact stiffness remains almost constant with time. This decrease in mean stress is representative of time dependent deformations of PEEK as observed by Li and Bhushan (2002) for PTFE films. Another possibility for the decrease in hardness during hold time might be strain rate hardening of the polymers in the loading period of indentation.
Figure 4.14: Load as a function of time for nano-indentation of semicrystalline PEEK sample for creep analysis. The indenter was loaded at a rate of 300 µN/sec to indentation displacement of 1500 nm and then held constant for 600 seconds before unloading at the same rate. Final hold segment (100 seconds) was provided after 80% unloading to account for thermal drift.

Figure 4.15: Indentation creep as a function of time for semicrystalline PEEK. The indentation creep was measured at the conditions as described in figure 4.14.
Figure 4.16: Mean contact stress as a function of time calculated during indentation hold segment of semicrystalline PEEK sample.

Figure 4.17: The contact stiffness as a function of time calculated during indentation hold segment of semicrystalline PEEK sample.
4.3 Nanoindentation results of semicrystalline UHMWPE

The continuous stiffness nanoindentation experiments were performed on an ultra high molecular weight polyethylene (UHMWPE). The indentations were performed at a constant loading rate 300 µN/sec under displacement controlled continuous stiffness mode. Multi modal response was observed for the semicrystalline UHMWPE as shown in figure 4.18. The load displacement curves of four representative indents were taken at different locations of the UHMWPE surface nominally 100 µm apart. Indent number PE-4 represent the harder phase as it required maximum normal load to induce the similar penetration depth. While indentation at softer phase of the polymer can be represented by indent number PE-3. An indentation load of 12 mN was needed for the softer phase as compared to 27 mN in harder phase to impose comparable indentation displacements. Indent numbers PE-2 and PE-3 are thought to be present in the multiphase region. A possible explanation for this argument could be the sudden changes in gradients of the loading curves.

The normal hardness and the elastic modulus as a function of indentation contact displacement for the UHMWPE are presented in figures 4.19 and 4.20 respectively. The uncertain computed values at lower penetration depths result from the calibration effects (discussed later in § 4.4). The multiphase behaviour as discussed for load- displacement data can be seen. The harder phase represented by indent number 4 has indentation hardness of \( \approx 0.05 \) GPa and an elastic modulus of \( \approx 2 \) GPa. The softer phase has 0.025 GPa and 1 GPa, the hardness and the elastic modulus respectively as shown in figures 4.19 and 4.20. Briscoe and co-workers (1998) have reported the hardness 0.04 GPa and the elastic modulus of 1.3 GPa for the nanoindentation of UHMWPE without the continuous stiffness mode. Therefore, the values calculated by them represent the average property values for the system. Hence, the current data is thought to be comparable to that in terms of the mean hardness and the elastic modulus values.
Figure 4.18: Load-displacement data for the UHMWPE sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. The compliance curves were obtained from the nanoindentation of the semicrystalline UHMWPE nominally 100 µm apart. (See figure D4 for complete experimental data set of all indents in appendix D.)

Figure 4.19: Indentation hardness as a function of indentation displacement data for the UHMWPE sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. The hardness data were obtained from the nanoindentation of the semicrystalline UHMWPE nominally 100 µm apart. (Data less than 800 nm may not be accurate due to surface approach and tip calibration factors.)
Figure 4.20: Elastic modulus as a function of indentation displacement data for the UHMWPE sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. The modulus data were obtained from the nanoindentation of the semicrystalline UHMWPE nominally 100 µm apart. (Data less than 800 nm may not be accurate due to surface approach and tip calibration factors.)

4.4 Nano-Indentation results of PMMA, PC, PEEK, PS, UHMWPE and PP

The nanoindentation experiments were carried out for six commercially available polymers: a poly(methylmethacrylate) (PMMA), a high molecular weight poly(ethylene) (UHMWPE), a poly(propylene) (PP), a poly(carbonate) (PC) and a poly(styrene) (PS). The sample characteristics and the common mechanical and physical properties of polymeric samples are given in table 3.1 and 3.2.
Figure 4.21: Load-displacement data for the PMMA, the PC, the PEEK and the PS samples at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. (Experimental data set of all indents are shown in appendix D.)

Figure 4.22: Load-displacement data for the UHMWPE and the PP samples at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. (Experimental data set of all indents are shown in appendix D.)
Figure 4.21 and 4.22 shows experimental load-displacement data for the six polymeric surfaces: the PMMA, the PC, the PEEK and the PS. The data has been presented in two separate graphs for the sake of clarity. The constant loading and unloading rates of 300 µN/sec were imposed to obtain this data. The maximum displacements were in the range 4500-5500 nm. The representative curves were selected on the basis of the median of the curves especially for the semicrystalline polymers where large deviations (for PEEK 80±50 mN and for UHMWPE 15±10 mN at maximum displacement) were observed in the consecutive indents due to presence of multiphases as explained in section 4.2. The plot illustrates the harder nature of the PMMA and the PEEK surfaces. To impose a penetration of 5000 nm on PMMA surface an approximately 100 mN force was needed while for PEEK imposing 80 mN has the same penetration displacement. The PC and the PS were indented to 5000 nm at approximately 50 to 60 mN loads. A rapid change in gradient of the curves for loading and unloading curve of PEEK was observed at indentation displacements of 3000 nm and 4000 nm. A harder response was seen at 3000 nm during the loading segment and an increased recovery rate after unloading to 4000 nm. These features were not observed in other polymeric materials. This might be due to the presence of the multiphase in the semicrystalline PEEK. The UHMWPE and the PP were seen to be the softer polymers as shown in figure 4.19. These polymeric surfaces required a load of 14 -16 mN in comparison to other polymers (>60 mN) normal loads to induce similar penetration depths (≈5000 nm). The softer polymers were also seen to exhibit large creep depths than the harder polymeric surfaces during the hold segments.

Figures 4.23 and 4.24 provide experimental indentation hardness results retrieved from continuous stiffness experiments on polymeric surfaces. The displacement controlled continuous stiffness experiments were performed at a frequency of 45 Hz with an amplitude of 1 nm during loading and unloading cycles. The hardness was calculated using the corrected indenter area function with indentations performed on silica and includes zero error corrections (The data and experimental procedure is presented in appendix B.) The typical uncertainty in values at lower penetration depth (<500 nm) are not physically significant. These uncertain data points result from well recognised errors introduced by the deficiency in the procedures and applications to determine the tip geometry and the indentation size effects (Briscoe et al. 1998; Bonne et al. 2005). The figures show decreasing trends of indentation hardness for the amorphous polymers with increasing penetration depths. Briscoe and co-workers (1998) have also seen a similar response for amorphous polymers with normal
indentation without continuous stiffness mode. The differences in decreasing trends can be attributed to the different scales of surface hardening resulting from the material preparation, treatments and environmental interactions for these polymers. The semicrystalline polymers, the PEEK and the UHMWPE, have shown complete deviations from such trends in the hardness data. For the UHMWPE there was a decreasing trend in indentation hardness initially and then it remained constant. The hardness has decreased suddenly and then increases for the PEEK. These deviations could find a possible explanation in the multiphases present in semicrystalline polymers as discussed above for the PEEK. The computed hardness values have small deviations, as is shown in table 4.1, from the ones reported by Briscoe and co workers (1998) for the same polymers with indentation without the continuous stiffness mode. These deviations are thought to be the differences in experimental conditions. They have performed the experiment at a constant strain rate of 0.1 sec\(^{-1}\) and only computed the hardness at maximum penetration depths.

The elastic modulus of the polymeric surfaces as a function of indentation displacement is represented in figures 4.25 and 4.26. The elastic modulus was calculated using equation 4.2.

\[
E^* = \left( \frac{1 - v_s^2}{E_s} + \frac{1 - v_i^2}{E_i} \right)^{-1}
\]

4.2

Where the \(E^*\) is the reduced elastic modulus computed from the gradient of unloading curve and the area function of the indenter (discussed in chapter 2). The reference elastic modulus (\(E_i\)) was taken as 1141 GPA and the Poisson’s ratio (\(v_i\)) of 0.07 for the diamond tip used. The figure shows uncertainties at lower penetration depths and this variation could be due to the same factors as discussed for the indentation hardness earlier. An increasing elastic modulus trend can be seen with decreasing penetration depth for all polymers could find a possible explanation in localized modification of properties at polymeric surfaces. These modifications might be the result of exposure to light and air and/or fabrication processes. The semicrystalline polymers have shown changes from the general trend at higher penetration depth, as noted earlier for their hardness behaviour, with penetration depth.
Figure 4.23: Indentation hardness as a function of indentation displacement data for the PMMA, the PC, the PEEK and the PS sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. (Data less than 500 nm may not be accurate due to surface approach and tip calibration factors.)

Figure 4.24: Indentation hardness as a function of indentation displacement data for the PP and the UHMWPE sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. (Data less than 500 nm may not be accurate due to surface approach and tip calibration factors.)
Figure 4.25: Elastic Modulus as a function of indentation displacement data for the PMMA, the PC, the PEEK and the PS sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. (Data less than 500 nm may not be accurate due to surface approach and tip calibration factors.)

Figure 4.26: Elastic Modulus as a function of indentation displacement data for the UHMWPE and the PP sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. (Data less than 500 nm may not be accurate due to surface approach and tip calibration factors.)
Table 4.1: Comparison of the reported surface mechanical properties of polymeric surfaces with literature at indentation displacement of 3000 nm.

<table>
<thead>
<tr>
<th>Material</th>
<th>Literature (Briscoe et. al. 1998)</th>
<th>Present work</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hardness (GPa)</td>
<td>Modulus (GPa)</td>
</tr>
<tr>
<td>PMMA</td>
<td>0.26±0.05</td>
<td>4.25±0.10</td>
</tr>
<tr>
<td>PC</td>
<td>0.18±0.03</td>
<td>3.00±0.10</td>
</tr>
<tr>
<td>PEEK</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PS</td>
<td>0.29±0.03</td>
<td>4.3±0.10</td>
</tr>
<tr>
<td>PP</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>0.04±0.02</td>
<td>1.30±0.20</td>
</tr>
</tbody>
</table>

4.5 Conclusion

This Chapter presents the experimental results from normal indentations performed upon a selection of polymers (PEEK, UHMWPE, PMMA, PS, PC and PP) at depths of 0 to 5 µm. A bimodal response to indentation is observed for semicrystalline polymers (PEEK and UHMWPE). A method to calculate the crystallinity of the semicrystalline polymers by non destructive indentation has been developed. The plasticity index and creep data of PEEK is presented. The PEEK has shown considerable surface softening during load hold segment of creep evaluation. Data for the elastic modulus and the hardness are presented for all polymeric materials and are found to be dependent on contact conditions. These properties appear to be unreliable at penetration displacements close to the surface. This can be due to change in the mechanical and physical properties of polymers due to their manufacture or aging. However, the most probable reason might be the precise unestablished imperfections in the indenter tip calibration. The PMMA surface appears to be the hardest and the UHMWPE is the softest at all penetration depths for the current selection of polymers. The amorphous polymers are found to follow the similar trends in the properties at all indentation displacement and reach a constant value after certain depths, whereas the semicrystalline
polymers (PEEK and UHMWPE) do not show any specific trends for different indents due to presence of amorphous and crystalline regions. Finally, the continuous stiffness method appears to be a convenient means to evaluate the mechanical properties of polymers, which show viscoelastic-plastic behaviour during indentation. The results show that this method is particularly applicable to study the properties of different phases present in heterogeneous materials.
CHAPTER 5

SCRATCH HARDNESS AND DEFORMATIONS

This Chapter presents the experimental results obtained from the scratching of semicrystalline poly(etheretherketone) (PEEK). Various surface mechanical properties of the PEEK such as the hardness, the friction coefficient, the scratch depth and the prevailing deformation mechanisms are presented in the form of scratching maps, generated as a function of the contact conditions. These scratch maps provide a first order evaluation of the relative scratch resistance of materials for comparison purposes. Scratches were produced on the PEEK surfaces using rigid cones of different cone included angles and under different normal loads. The prevailing deformation mechanism and geometry of damage on the scratched polymeric surfaces were assessed using scanning electron microscope (SEM) and an optical profilometer.

5.1 Introduction

A better understanding and control of the surface mechanical properties of polymers is required for their optimal use as engineering materials. This is particularly important when these materials are used to improve the contact mechanical properties, where polymers are adopted in optical, coatings and plastic engineering applications for consumer products, or tribological performance of bearings. Scratching of an asperity contact on the material surface is one of the most significant stresses from the widest range of chemical and mechanical stresses that a solid polymeric product might experience in its life. The scratching process is a well known concept and is generally defined as a kind of surface abrasion, provoked by the relative friction of two material objects where one is significantly sharper and harder than the other. Perceiving, or assessment, of a scratch is usually correlated to the visual detection by the observer as these may be of any size and length. Scratches may reduce the appeal and shorten the life of the polymeric objects especially in optical products; a scratched product loses both its original mechanical and chemical properties. A scratch may create a localised overstressed field and initiation of a premature fracture and collapse of
material or it may allow a deeper corrosion or plasticisation by external reactive agents (Briscoe and Stolarski 1991). Local light reflection and refraction of the surface may also change dramatically in the presence of scratches. Conversely, in scientific applications, scratch testing of materials provides a convenient means of evaluating several surface mechanical properties, for example the scratch hardness, the adhesion to substrates, the presence of density gradients, the friction coefficients, etc (Briscoe 1999).

The present work reports on the scratch deformation modes, the friction, the hardness and the penetration depth of semicrystalline PEEK in un-lubricated and lubricated contact conditions. The scratches were produced on the semicrystalline and the amorphous PEEK surface using rigid cones of various included angles and under different normal loads. These scratched surfaces were assessed with scanning electron microscope (SEM) and an optical profilometer for the prevailing deformation mechanism and the geometry of damage. The scratched polymeric surfaces were coated with a thin layer of gold, 10-15 nm thickness, before imaging in the SEM in order to impart electrical conductive properties. The conductive coating is required to stop charge build up on the sample surface which may results in a poor image. A further precaution was the application of a silver conductive paint as a conductive bridge between the coated polymeric surface and sample holding stud.

5.2 Scratch Deformations of PEEK

The scratching phenomena of polymers are accompanied by a number of surface deformation mechanisms or modes under different contact conditions. The appearance of surface damage and the magnitude of the friction coefficient characterises these deformation modes. These deformation modes depend upon the cone angle of the indenter, the normal load, the penetration depth, the sliding velocity, the type of material and the interfacial lubrication. The scratch deformation processes identified in the literature include ductile ploughing, ductile and brittle ploughing, rubber like or elastomeric deformation, ironing and elastic responses of the polymeric surfaces. Figure 5.1 shows such scratch deformation processes and the transitions between them under different normal loads and various conical indenters when as received semicrystalline poly(etheretherketone) (PEEK) was scratched at room temperature (20 °C) at a scratching speed of 3 mm/sec in an un-lubricated contact.
Figure 5.1: Scratch deformation map for the as received semicrystalline PEEK showing results from scratch tests performed for a range of cone included angles and normal loads at room temperature (20 °C) and a scratching velocity of 3 mm/sec. The PEEK surfaces were not subjected to any treatment prior to scratching. Filled circles in the figure represent experimental data points.

The semicrystalline PEEK did not deform permanently in extremely mild conditions in terms of applied normal load and blunter indenter. The frictional force in such an instance was the only indication that there was elastic recovery as a result of the scratching process. The frictional force then arises from viscoelastic hysteresis loss, apparently without any permanent damage, or deformation.

The elastic response of material changed to a smoothening effect of the original surface asperities, mainly under the heavier loads and blunter indenters, commonly called ironing. This phenomenon was accomplished by a decrease in localized surface roughness along with elastic recovery from the bulk of the material. A 90° cone was the sharpest indenter to show ironing deformation, during the scratching of the PEEK surfaces, at the nominal load (<0.5 N), whereas the blunter indenters (cone angle >135°) needed higher normal loads to produce the same material deformation. Figure 5.2 shows a SEM image of one such deformation (the arrow head shows the direction of scratching).
A ductile ploughing mechanism occurs when the behaviour of polymers was similar to the ductile metals during the scratching process. The extensive plastic deformation caused by the ductile flow of the material around the indenter tip as can be seen in figure 5.4. The ductile ploughing of the PEEK surface was accompanied by significant viscoelastic recovery at the rear of the indenter (Figure 5.3), and may occur without any evidence of discrete failure. This recovery was mainly the result of the lower contact strains. In addition well defined edges were seen on sides of the scratch groove in these material deformations. These well defined scratch edges were the only differentiation between the simple ductile ploughing and viscoelastic response accompanying ductile ploughing, in the later case there was apparently no or very little material accumulation on scratch edge due to recovery processes whereas in the former a much heavier material pile up was observed. The ductile ploughing was seen to be the dominant deformation process during scratching of the PEEK at the lower normal loads for the sharp indenters and at higher normal loads with blunt indenters. An elasto-plastic recovery of the PEEK surfaces were observed with ductile ploughing if it was scratched with sharp indenters (cone included angle <75°) at the normal loads less than 1 N and for the blunt indenters (>75°) under the higher normal loads (>3 N).

Figure 5.2: Ironing. SEM (x500) of a scratch on PEEK under the contact conditions of cone included angle: 105°; normal load: 1 N; scratching velocity: 3 mm/s; T = 20 °C; no lubricant. Arrow head shows direction of scratching.
Figure 5.3: Elasto-plastic ductile ploughing. SEM (x500) of a scratch on PEEK under the contact conditions of cone included angle: $105^0$; normal load: 2 N; scratching velocity: 3 mm/s; $T = 20^0$C; no lubricant. Arrow head shows direction of scratching.

Figure 5.4: Ductile ploughing. SEM (x250) of a scratch on PEEK under the contact conditions of cone included angle: $75^0$; normal load: 2 N; scratching velocity: 3 mm/s; $T = 20^0$C; no lubricant.
Figure 5.5: Ductile ploughing and crack initiation. SEM (x250) of a scratch on PEEK under the contact conditions of cone included angle: 75\(^\circ\); normal load: 3 N; scratching velocity: 3 mm/s; T = 20 \(^\circ\)C; no lubricant.

Figure 5.6: Ductile ploughing and crack formation. SEM (x250) of a scratch on PEEK under the contact conditions of cone included angle: 90\(^\circ\); normal load: 5 N; scratching velocity: 3 mm/s; T = 20 \(^\circ\)C; no lubricant.
When the load was further increased, the PEEK surfaces deforms with the formation of load cracks within the scratch. There was no sharp boundary formed between the ductile ploughing and crack formation during the scratching of the polymer. A peculiar regular crack formation was seen, which can be due to partial reorganisation of the microstructure in the semicrystalline polymers when subjected to surface stresses. The material deformation into cracks could start appearing at the lower normal loads of even 1N for the sharpest indenter and might extend to the heavier normal loads for the blunter indenters. Figures 5.5 and 5.6 shows the scanning electron images of scratched PEEK, the deformation mode was seen to be ductile ploughing while cracks initiate for cone angle of 75° and 3N (Figure 5.5) whereas crack formation was dominant when PEEK was scratched with a 90° indenter and under a 5 N load (Figure 5.6). Along with these cracks, some lateral damage in the form of small crevices was found, as is shown in figure 5.7. These crevices might be due to the presence of crazing during the scratching of the semicrystalline PEEK surface.

The brittle deformation was characterized by a partial plastic flow. This would occur when polymeric surfaces were subjected to severe contact conditions in terms of the normal loads and the contact strains. There was chip formation along the brittle deformation zone when the polymers were subjected to the most severe contact conditions. This can also be termed as cutting or machining as from the analogy with metal processing. In the most severe contact conditions (higher normal loads and sharp cone included angles) of the scratching
process on the semicrystalline polymer, fibrillation of the material surface was observed (figure 5.8). These fibrills were believed to be formed from the crystalline lamella since such deformations were not observed at all in the amorphous PEEK surfaces (discussed later). Figures 5.8 to figure 5.12 represent the subsequent brittle deformation regimes.

Figure 5.8: Fibrillation. SEM (x1000) of a scratch on PEEK under the contact conditions of cone included angle: 30°; normal load: 5 N; scratching velocity: 3 mm/s; T = 20 °C; no lubricant.

Figure 5.9: Cutting and deep grooving. SEM (x500) of a scratch on PEEK under the contact conditions of cone included angle: 45°; normal load: 4 N; scratching velocity: 3 mm/s; T = 20 °C; no lubricant.
Figure 5.10: Brittle cutting and chip formation. SEM (x100) of a scratch on PEEK under the contact conditions of cone included angle: $30^\circ$; normal load: 3 N; scratching velocity: 3 mm/s; $T = 20^\circ$C; no lubricant.

Figure 5.11: Brittle machining and chip formation. SEM (x100) of a scratch on PEEK under the contact conditions of cone included angle: $45^\circ$; normal load: 3 N; scratching velocity: 3 mm/s; $T = 20^\circ$C; no lubricant.
In addition to the above mentioned scratch deformations of the PEEK surfaces, a lip formation and subsurface damage of the polymeric material were observed when the surfaces were scratched at elevated contact temperatures. As can be seen in figures 5.14 and 5.15, a rubber like lip formation of the polymeric surface was observed when the PEEK was scratched at temperatures above 200 °C. These tearing type deformations were mainly
observed previously for low density elastomeric polymers by Schallamach (1952) and Ratner (1967). The chip formations of the PEEK surface with evident subsurface damages has been shown in figures 5.16 and 5.17. These deformations were observed when the polymeric surface was scratched at the lowest possible temperatures of 0 °C. These deformations conform to the rupture like damage of poly(vinylacetate) at low temperatures observed by Porzzucek and Lefebvere (1993). They proposed that the perforation mechanism induces such deformations in polymeric surfaces at lower temperatures. The SEM images of the observed deformations are summarized in table 5.1.

Figure 5.14: Lip formation, SEM (x200) of a scratch on PEEK under the contact conditions of cone included angle: 60°; normal load: 2 N; scratching velocity: 3 mm/s; T = 200 °C; no lubricant.

Figure 5.15: Lip formation, SEM (x50) of Scratch performed on PEEK at 250 °C with a conical indenter of 30° included cone angle at scratching speed of 3 mm/sec without lubrication.
Figure 5.16: Subsurface damage, SEM (x2000) of a scratch performed on virgin PEEK at 25° C with a conical indenter of 45° included cone angle at scratching speed of 2.7 mm/sec without lubrication.

Figure 5.17: Subsurface damage, SEM (x1800) of a scratch performed on virgin PEEK at 50° C with a conical indenter of 30° included cone angle at scratching speed of 2.7 mm/sec without lubrication.
Table 5.1: SEM images of the observed surface deformations of the semicrystalline PEEK

<table>
<thead>
<tr>
<th>Deformation Mode</th>
<th>SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Undeformed</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Elastic</strong></td>
<td></td>
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<tr>
<td><strong>Ironing</strong></td>
<td></td>
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<tr>
<td><strong>Ductile ploughing</strong></td>
<td></td>
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<tr>
<td><strong>Crack associated ductile ploughing</strong></td>
<td></td>
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<tr>
<td><strong>Brittle</strong></td>
<td></td>
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<tr>
<td><strong>Brittle machining</strong></td>
<td></td>
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<tr>
<td>Brittle machining and chip formation</td>
<td><img src="image1.png" alt="Image" /></td>
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<tr>
<td>-------------------------------------</td>
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</tr>
<tr>
<td>Cutting and deep grooving</td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>Fibrillation</td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>Crazes</td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>Subsurface damage</td>
<td><img src="image5.png" alt="Image" /></td>
</tr>
<tr>
<td>Lip formation</td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
</tbody>
</table>
5.3 Scratch hardness and deformation Maps of PEEK

A selection of scratch hardness and deformation maps generated through subjective evaluation of the scratched surface images obtained using an SEM under different experimental conditions are presented in this section. The maps were constructed to elaborate the dependence of the scratch deformation mechanisms upon the contact conditions for example the contact angle, the scratching velocity, the temperature of the surface and the contact lubrication etc. The scratch maps were constructed using nominal contact strain, one of the basic parameters used to evaluate the extent of deformation in indentation and scratching contact, as ordinate. The nominal effective contact strain dictates the severity of the contact and was found to be a function of the gradient of the attack angle, which is the angle formed between the material surface and the indenter approaching surface. The effective strain, for conical indenters, has been defined by Tabor and co-workers (Tabor 1948; Tabor 1951; Tabor 1956; Atkins and Tabor 1965; Bowden and Tabor 1986) as

\[ \varepsilon = k \tan \alpha \]  

Where, \( k \approx 0.2 \) for work hardening metal surfaces. Briscoe and co-workers have argued that although the constant is slightly lower in magnitude for polymers, however the same value may be applicable for most practical purposes (Briscoe and Sebastian 1996; Briscoe and Sinha 2003). Therefore, the effective nominal contact strain increases when sharper conical indenters, that is the indenter with higher attack angle or lower cone included angle, are used and vice versa.

5.3.1 Scratch Hardness Map

Figure 5.18 presents a map of the scratch hardness and deformations produced plotted against the effective contact strain, for the semicrystalline PEEK scratched with conical indenters at a scratching velocity of 3 mm/sec at ambient temperature (20 °C) for an un-lubricated contact. The scratches were produced on the polymeric surfaces utilising the conical indenters for cone included angles varying from 30° to 135°, under the normal loads of 0.5 N to 5 N. Assumption of viscoelastic material behaviour (\( q = 1.5 \)) was used for the computation of scratch hardness in equation 2.19. An optical profilometer, Wyko 9100NT Optical Profiling System, Veeco Instruments Inc. US, was used to determine the scratch width to be used in the
calculation of the scratch hardness and the scratch depth. The SEM images of the scratched polymeric surfaces were subjectively evaluated to access the deformation modes.

The full elastic recovery was seen to be the deformation produced at lowest contact strains (i.e; \(\varepsilon <0.05\)), scratch hardness values for the elastic deformations cannot be computed using equation due to the material recovery. Ironing mode deformation was also seen at lower strains (\(\varepsilon <0.1\)). An imposed contact strain in the range of 0.05 and 0.25 has produced viscoelastic deformations. A ductile ploughing deformation was noted for the scratches performed under strains of 0.05 to 0.40. Viscoelastic recovery of the material was the dominant process under ductile ploughing, on the lower side of the strain, whereas at higher strains the ductile deformation accompanied by brittle crack formation was observed. The deformation was observed to be brittle upon increasing the level of strain. Machining, cutting and fibrillation of crystalline lamella were the deformations produced at the highest possible applied strains.
The scratch hardness data as shown in figure 5.18 exhibits a maximum at intermediate levels of the nominal contact strains. The computed scratch hardness decreases at higher contact strains and at higher normal loads due to thermal softening of the polymeric surfaces. The data are partially consistent with the expected behaviour on the basis of the bulk yield stress, which is an indication of ductile-brittle transition, is a function of the strain rate, the strain and the temperature. The adiabatic frictional heating of the polymeric surfaces appears to be a significant cause for softening behaviour as observed by Lancaster (1973) with an increasing scratching velocity.

5.3.2 Scratch Mode maps

Figure 5.19 represents a scratch mode map of PEEK showing the dependence of surface deformation on contact strain and applied normal load. Purely elastic or ironing deformation was observed at lower contact strains and lower loads. The deformations were ductile ploughing for lower strains and higher normal loads, and vice versa. These ductile ploughing deformations were accompanied by a viscoelastic response at milder contact conditions, lower strains and normal loads, while crack formation on comparatively severe side, higher strains and normal loads, of the deformation regime. It can be observed that viscoelastic recovery is present at the ironing to ductile ploughing transition and crack formation can constitute a border between ductile ploughing and brittle deformations. Brittle fracture is observed at more severe contact conditions (ε >0.35). Chip formation, cutting and fibrillations are the severest forms of the brittle fracture observed at the highest strains and increased normal loads.

The scratching map in figure 5.20 describes the effect of scratch depth on deformation regimes with variable strains and normal loads. The deformation modes and their transitions were observed solely depend on scratch depth. The applied normal load and contact strain variations were thought to be the source for scratch depth variations. The map was constructed after subjectively analyzing the SEM images of scratches, the scratches were produced using variable cone angles and applied normal loads. The scratch depth was computed using scratch depth (h) and width relationship (d) as represented in equation 5.2 (Briscoe et al. 1996).

\[
h = \frac{d}{2 \tan \theta}
\]
Where, $2\theta$ is the cone included angle of the indenter surface to the material surface. The equation 5.2 is based on the assumption that the viscoelastic recovery of the polymeric material is much less than the recovery in the width of the scratch. Therefore, the scratch depth data calculations based on the scratch width data is a more realistic and economic approach (Sinha and Lim 2006). In the mildest contact conditions (lower strains and/or loads), the indenter has not pushed the polymeric material beyond its elastic limit, so the material recovers after deformation. Therefore, the scratch depth may not be observable in this case. The ironing mode deformation was observed for scratch depth values less than 20 microns and can be seen when lower strains and normal loads were applied. The ductile ploughing response is observed when the scratch depth for PEEK scratching is between 20 to 100 microns. Ductile ploughing indicates the plastic response of the polymers, so stresses on the material at the contact have reached the yield point of the polymer. When the scratch depth was between 100 to 160 microns brittle deformations were observed indicating the material failure. Deformations were severe like chip formation, cutting and fibrillation of the crystalline lamella, when the scratch depth is more than 160 microns. One possible reason for the increase of the severity with the scratch depth could be increase in strain density on the polymeric surface.

A map to illustrate the dependence of the scratch deformation of PEEK on the scratch velocity and the contact velocity is shown in figure 5.21. The scratches were produced with range of conical indenters ($30^\circ$ to $135^\circ$) and the scratching velocities (0.5 to 5 mm/sec) under a constant load of 1 N. At lower imposed velocities, the brittle deformation was seen to be the major deformation mechanism. While increasing scratch velocity reduces the extent of brittle fracture. One possible explanation is that at higher scratching velocities the rate of energy dissipation is higher at the point of contact which leads to a local adiabatic heating which can be observed by measuring an increase in the temperature of the material surface (This has not been observed directly in this work). Pelillo (1997) observed the similar decrease in extent of brittle deformation with increasing scratching speeds for PMMA.
Figure 5.19: Scratch mode map of semicrystalline PEEK. Filled triangles in the figure represent experimental data points. The plot shows the dependence of deformation modes of the PEEK on nominal contact strain and normal load. The contact strain was approximated using equation 5.1 based on the attack angle of the indenters to the material surface. The scratches were produced at 3 mm/sec scratching velocity and room temperature, 20 °C. The PEEK samples were not subjected to any treatment prior to scratching.

Figure 5.20: Scratch mode map of the semicrystalline PEEK. Figure legends in the figure represent experimental data points. The plot shows the dependence of deformation modes of the PEEK on nominal contact strain, scratch depth and normal load. The contact strain was approximated using equation 5.1 based on the attack angle of the indenters to the material surface. Equation 5.2 was used to compute the scratch depth data from the scratch width and the cone angle of the indenter. The scratches were produced at 3 mm/sec scratching velocity and room temperature, 20 °C. The PEEK samples were not subjected to any treatment prior to scratching.
Figure 5.21: Scratch mode map of semicrystalline PEEK. Filled triangles in the figure represent experimental data points. The plot shows the dependence of deformation modes of the PEEK on scratching velocity and contact strain. The nominal contact strain was approximated using equation 5.1 based on the attack angle of the indenters to the material surface. The scratches were produced at 1 N normal load and room temperature, 20 °C. The PEEK samples were not subjected to any treatment prior to scratching.

Figure 5.22: Scratch mode map of semicrystalline PEEK. Filled triangles in the figure represent experimental data points. The plot shows the dependence of deformation modes of the PEEK on contact strain and temperature. The nominal contact strain was approximated using equation 5.1 based on the attack angle of the indenters to the material surface. The scratches were produced at 3 mm/sec scratching velocity and under 2 N load in unlubricated contact conditions. The PEEK samples were not subjected to any treatment prior to scratching.
Figure 5.22 presents a scratching map generated through subjective SEM imaging in order to assess the deformation regimes of semicrystalline PEEK when it is subjected to scratching under a constant load of 2 N at bulk temperature from -25 °C to 250 °C. The scratching velocity was maintained constant at 3 mm/sec and the contact strain was varied using conical indenters of included cone angle 30° to 130°. At lower contact strain and temperature ironing is found to be the main deformation mode but it is suppressed by elastic deformation at higher temperatures for lower strains and by crack formation in ductile ploughing and brittle deformations at higher contact strains and lower temperature. The subsurface cracks along with brittle deformation were found when PEEK is scratched at strains above 0.5 and temperature less than 0 °C. When the contact strains were between 0.2 to 0.45 ductile ploughing, favouring viscoelastic recoveries at lower contact strains and tending to crack formation at higher strains, was observed for temperature ranges 25 °C to 175 °C. Brittle deformations were seen for PEEK scratching under contact strains more than 0.5 and temperatures -25 °C to 175 °C. Fibrillation and brittle machining was seen for contact strains above 0.6 but these were suppressed by brittle deformations at 150 °C that is at temperature above the glass transition temperature (Tg) of PEEK (143 °C). Subsurface deformation with microcracks was observed with 30° and 45° indenters that is at highest possible contact strains for scratches performed at 0 °C. Lip formation, a rubber like deformation, was observed at temperatures above 200 °C as can be seen in figure 5.19 and 5.20. Finally deep grooves with material fracture, a deformation mode seen in amorphous polymers like PMMA (Briscoe et. al. 1996), was observed above 150 °C for higher contact strains scratching of PEEK.
Figure 5.23: Scratch mode map of semicrystalline PEEK. Filled triangles in the figure represent experimental data points. The plot shows the dependence of deformation modes of the PEEK on contact strain and normal load in lubricated contact conditions. The nominal contact strain was approximated using equation 5.1 based on the attack angle of the indenters to the material surface. The scratches were produced at 3 mm/sec scratching velocity and room temperature, 20 °C. The virgin PEEK samples were lubricated by application of petroleum gel layer.

Figure 5.24: Scratch mode map of amorphous PEEK. Filled triangles in the figure represent experimental data points. The plot shows the dependence of deformation modes of the PEEK on nominal contact strain and normal load. The nominal contact strain was approximated using equation 5.1 based on the attack angle of the indenters to the material surface. The scratches were produced at 3 mm/sec scratching velocity and room temperature, 20 °C. The amorphous PEEK samples were not subjected to any surface treatment prior to scratching.
Figure 5.23 shows a scratch deformation map for semicrystalline PEEK under lubricated contact conditions. The polymeric surfaces were scratched using a range of conical indenters (cone included angle 30° to 135°) under constant normal loads varying from 0.5 N to 5 N at a constant scratching velocity of 2 mm/sec. The lubricant in use was a commercial Petroleum Gel (see Chapter 3). The map shows that the polymeric material tends to deform in a more ductile manner with the presence of this lubricant. Figure 5.24 illustrates a scratching mode map of the amorphous PEEK system. The map defines the surface scratch deformation of the amorphous PEEK scratched with a range of conical indenters (cone included angles 30° to 135°) at a constant speed 3 mm/sec⁻¹ under different applied loads ranging from 0.5 to 5 N. The amorphous PEEK samples were prepared by melting the virgin PEEK samples in hot press to 400 °C and then quenching in liquid nitrogen. The crystallinity of the amorphous sample was estimated to be negligible by differential scanning calorimetric method. At low contact strains (<0.25) and lower normal loads (<2.5 N) the elastic and ironing mode deformations were observed. The ductile ploughing of the material was observed to be the major deformation mechanism for the amorphous polymeric surface. The ductile to brittle transition of the surface deformation was followed by the crack formation in the material surface. The severity of the brittle mode deformation was found to increase with increasing contact strains. Under the most severe contact conditions the material damage was observed to be the chip formation and machining. In comparison to the scratch mode map of semicrystalline PEEK (Figure 5.19), the fibrillation of the surface was not observed for the amorphous PEEK at any contact conditions. The fibre formation is thought to be formed from the harder crystalline lamella present in the semicrystalline polymer.

5.3.2 Friction Mode Map

Figure 5.25 illustrates the correlation of the experimental friction coefficient (the ratio of the scratch force to the normal load) and the surface deformations observed after scratching semicrystalline PEEK at a velocity of 3 mm/sec for variable normal loads and conical indenters. The experimental friction coefficients were in a fairly good agreement with of the evaluated friction coefficient with the straight line using equation 5.3 developed by Tabor (1956) for perfectly plastic ploughing deformation by conical indenters at the intermediate contact strains. Bowden and Tabor (1954) proposed, a well known two term model of the friction, that when a harder material is slid across a relatively softer material, the shear between the surfaces give rise to friction forces (interfacial component) and the grooving
component arising from the ploughing of the softer material by the harder surfaces. Scratching of the material surfaces can be represented by the ploughing component of the friction model. Czichos (1978) showed that for the conical indenters, the ploughing component of the friction coefficient is directly proportional to the gradient of the indenter surface to the material surface as presented in equation 5.3.

\[ \mu = \left( \frac{x}{\pi} \right) \tan \alpha = \left( \frac{x}{\pi} \right) \cot 2\theta \]  

5.3

Where, \( \mu \) is the friction coefficient, \( \alpha \) is the attack angle (the angle between the indenter approaching surface and the material surface), \( 2\theta \) is the cone included angle and \( x \) is a material constant based on the material response. For visco-elastic-plastic grooving the value of \( x \) ranges from \( 1 \leq x \leq 2 \). Brittle machining and cracking of the material surfaces provide additional energy loss models (Evans 1987).

![Friction mode map of semicrystalline PEEK. The plot shows the deformation modes and the dependence of the friction during scratching of the PEEK on contact strain and normal load. The contact strain was approximated using equation 5.1 based on the attack angle of the indenters to the material surface. The scratches were produced at 3mm/sec scratching velocity and room temperature, 20°C. The PEEK samples were not subjected to any treatment prior to scratching. (The map was constructed using 35 data points)](image)

**Figure 5.25:** Friction mode map of semicrystalline PEEK. The plot shows the deformation modes and the dependence of the friction during scratching of the PEEK on contact strain and normal load. The contact strain was approximated using equation 5.1 based on the attack angle of the indenters to the material surface. The scratches were produced at 3mm/sec scratching velocity and room temperature, 20°C. The PEEK samples were not subjected to any treatment prior to scratching. (The map was constructed using 35 data points)

The friction coefficient was higher than the theoretical one in the elastic and deformation regions, an effect that can be attributed to the viscoelastic recovery of material in
such deformations. In the brittle deformation regime, lower experimental friction coefficients were seen due to machining processes at high strains. In the machining deformation regime, the internal shear angle of deformation defines the contact geometry, hence the cone angle definition of strain is less apparent for friction coefficient in these conditions (Pelillo 1997). Brittle deformation and chip formation results from shearing of the material surface across an internal shear plane. The shear plane angle in this case, is less than the attack angle of the conical indenter, hence independent of the cone attack angle of the indenter. Therefore, plastic flow during chip forming deformations takes place at an angle less than the attack angle of the indenter (Evans 1987).

5.4 Conclusion

Deformation maps of the PEEK surfaces have been constructed under various contact conditions using the scratching technique. These maps provide a convenient means to report the deformation behaviour of the polymeric surfaces when the imposed scratch conditions are changed. The penetration depth of the imposed scratch in the material has a significant bearing on the resultant deformation, in addition to the previously reported effects of the indenter velocity, normal loads and attack angle. This effect further might be associated with tip defects, invariably present on the indenters, and uncertainty in the measurement of scratch depth due to viscoelastic recovery of the polymeric materials (Sinha 2006; Sinha and Lim 2006). The crystalline regions present in the semicrystalline PEEK tend to respond in the form of fibres during scratching in the severe contact conditions as opposed to the amorphous polymers like PMMA (Briscoe 1996). The differences in scratch hardness under different contact conditions indicate the variation of the energy dissipation related to particular deformation processes that is elastic, ironing, ductile or brittle. The hardness values show maxima at the intermediate values of contact strain and for ductile deformations like PMMA (Briscoe 1996) and PC (Briscoe et. al. 1996).
CHAPTER 6

SURFACE MECHANICAL PROPERTIES OF

PEEK COMPOSITES

The experimental results obtained from the nanoindentation and the scratching of PEEK composites are presented in this Chapter. The load displacement, the hardness and the elastic modulus of the carbon fibre PEEK composites and the glass fibre PEEK composites are evaluated as a function of indentation displacement. The semicrystalline PEEK and the carbon fibre oriented PEEK were scratched using conical indenters on a pendulum sclerometer. The subsequent deformations of the surfaces were assessed through subjective evaluation of the images obtained from the SEM.

6.1 Introduction

Organic polymers are now widely used as tribological materials but there are some inherent shortcomings, like the high coefficient of thermal expansion, lower load carrying capacity, higher friction and wear rates as compared to liquid lubricated metals, poor thermal conductivity and limited dimensional stability particularly at elevated temperatures. Polymer composites have been fabricated, in the past, to overcome these problems by the addition of various components to the virgin polymers. Polymer composites are increasingly used in applications where friction and wear are important parameters. Examples range from gears, seals and rollers; to bearings, brakes and artificial joints. Polymers are often preferred over other materials due to their ease of processing into the finished product, their high strength-to-weight ratio and their chemical resistance. Furthermore, polymer composites generally have a low coefficient of friction (µ) even under dry-sliding conditions. This property can be utilized in applications especially where the addition of lubricants such as oil or grease cannot be tolerated such as in artificial joints. Sliding wear behaviour of polymers against a steel counterface indicates an increase in wear loss with increasing load or sliding speed, while wear rate decreases with sliding distance. In the case of polymer composites, wear behaviour
is dictated by the matrix wear, fibre sliding wear, fibre fracture and interfacial debonding (Cirino et al. 1988; Lu and Friedrich 1995; Elliott et al. 1998).

In this Chapter the load displacement curves, the hardness and the elastic modulus from the indentation response of carbon fibre PEEK and glass fibre PEEK composite are presented as a function of contact depth. A comparative study of the scratch deformations of the semicrystalline PEEK and the carbon fibre oriented PEEK is presented. The orientation effects on the scratch deformations of the unidirectional carbon fibre oriented PEEK are also discussed.

6.2 Nano-Indentation of PEEK composites

The continuous stiffness mode indentation experiments were conducted on the carbon fibre and the glass fibre composite samples supplied by Victrex Polymers, Lancashire, UK. The fibre loading for both samples was 30% (w/w) as reported by the supplier. The nano-indentation experiments were performed with a constant loading rate (300 µN/sec) to a maximum indentation displacement (5 µm). A 50 second hold segment was included at the maximum load to account for any creep effects followed by an unloading segment to 80% unloading; at this point a final hold segment of 100 seconds was applied to account for any thermal drifts during indentation experiments.

6.2.1 Load displacement Curves

Representative load-displacement data curves obtained from the indentation experiments performed on the carbon fibre PEEK composite are illustrated in figure 6.1. Indent number SCPK-1 represent the indentation in the material matrix region which is a softer phase and hence required ≈ 70-85 mN load to impose a penetration depth of 5000 nm. The indentation into harder fibrous material is represented by the load displacement curve SCPK-2. A higher indentation force ≈ 140 mN was needed to apply the same penetration depth for the harder regions. The load displacement data represented by curve SCPK-3 (the indentation force ≈ 100-110 mN) in figure 6.1 is from the indent in the interphase region of the polymeric composites. Large deviations were observed in the compliance curves of the matrix material and the interphase region. These deviations might be due to the variations in the crystallinity of the polymers in these samples. A similar pattern of the nanoindentation response with
comparatively lower peak loads was observed for the glass fibre PEEK composite as is shown in figure 6.2.

**Figure 6.1:** Load-displacement data for the 30% (w/w) carbon fibre PEEK composite sample at constant loading rate. The loading and unloading rates were maintained at 300 μN/sec. The curves represent experimental data nominally 100 μm apart on the polymeric composite. (Experimental data set of all indents are shown in appendix D.)

**Figure 6.2:** Load-displacement data for the 30% (w/w) glass fibre PEEK composite sample at constant loading rate. The loading and unloading rates were maintained at 300 μN/sec. The curves represent experimental data nominally 100 μm apart on the polymeric composite. (Experimental data set of all indents are shown in appendix D.)
6.2.2 Hardness and Elastic Modulus Evaluations

Figure 6.3 and 6.4 represent the computed hardness and the elastic modulus respectively, as a function of the indentation contact displacement of the carbon fibre PEEK composite calculated using the continuous stiffness indentation method. The indentation results belong to the indents represented by their load-displacement curves in figure 6.1. There was uncertainty in the calculated hardness and the elastic modulus values at low penetration depths which can be attributed to the indentation size effects (as is discussed in the Chapter 4). The indentation into the matrix material showed a peculiar surface hardening response of the polymeric material. Higher hardness values were observed near the surface for the harder phase (fibre and interphase regions) indentations. Quantitatively the measured hardness values for the material matrix were similar to the ones observed for the virgin PEEK under similar indentation contact conditions. Similarly the multiphase trends in the measured elastic modulus values were observed as shown in figure 6.4. The hardness and the elastic modulus as a function of indentation displacement data are presented in figures 6.5 and 6.6 for the 30% (w/w) glass fibre PEEK composites. Comparatively higher values of the hardness and the elastic modulus were observed for the carbon fibre PEEK composites as compared to the glass fibre PEEK composites.

Figure 6.3: Indentation hardness as a function of indentation displacement data for the 30% (w/w) carbon fibre PEEK sample at constant loading rate. The loading and unloading rates were maintained at 300 μN/sec. The curves represent experimental data nominally 100 μm apart on the polymeric composite. (Data less than 300 nm may not be accurate due to surface approach and tip calibration factors.)
Figure 6.4: Elastic Modulus as a function of indentation displacement data for the 30% (w/w) carbon fibre PEEK sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. The curves represent experimental data nominally 100 µm apart on the polymeric composite. (Data less than 300 nm may not be accurate due to surface approach and tip calibration factors.)

Figure 6.5: Indentation hardness as a function of indentation displacement data for the 30% (w/w) glass fibre PEEK sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. The curves represent experimental data nominally 100 µm apart on the polymeric composite. (Data less than 300 nm may not be accurate due to surface approach and tip calibration factors.)
Figure 6.6: Elastic Modulus as a function of indentation displacement data for the 30% (w/w) glass fibre PEEK sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. The curves represent experimental data nominally 100 µm apart on the polymeric composite. (Data less than 300 nm may not be accurate due to surface approach and tip calibration factors.)

6.3 Scratching of PEEK composites

Fibre reinforcement (short, long and continuous) in polymers generally increases wear resistance and reduces the coefficient of friction but may have an opposite effect on the sliding wear behaviour. At lower sliding distances, matrix wear is reported while at higher abrading distances, both polymer matrix and fibre damage is observed for short glass fibres (Suresha et al. 2007). The wear resistance of polymer composites depends upon various factors including the type of matrix material (thermoset or thermoplastic), type of fibres material (carbon, aramid and glass), sliding direction (normal, parallel, anti-parallel) along with the normal scratching factors. PEEK, a thermoplastic tougher material, has a higher wear resistance than brittle epoxy resin in composites. Fibrous materials effects are reported as more pronounced on wear resistance in case of high wearing materials as compared to high wear resistance materials. A carbon fibre can give the highest wear resistance in the matrix as compared to aramid fibres and glass fibres which have the lowest wear resistant matrix. The
wear rate will be higher in the normal direction of sliding whereas parallel and anti-parallel gives almost the same level as reported by Friedrich and Reinicke (1998).

Carbon and glass fibres are mainly used in applications requiring internal lubrication and reinforcements in polymer matrixes. Glass fibres due to their relatively high hardness show little improvement to the friction coefficient. In comparison, carbon fibres act as a solid lubricant which decreases the interfacial shear force due to the partial graphitic structure of these fibres. Glass fibres normally fail to prevent micro-cracking of the resin which leads to cracking of exposed fibre ends. Carbon fibres due to their lower hardness and friction reducing ability do not show micro-cracking (Cirino et al. 1988; Larsen et al. 2007). Mechanical properties of advanced composite materials depend upon the matrix and fibre material, fibre loading and interfacial adhesion between matrix and reinforcing fibre and fibre architecture.

The unidirectional carbon fibre oriented PEEK samples were scratched under similar contact conditions of normal weight and scratch length using a pendulum sclerometer to analyze the deformation modes in these polymers. The fibre oriented samples were scratched in the parallel, orthogonal and transverse directions relevant to the fibre orientation. These scratched samples were analyzed using Scanning Electron Microscopy (SEM) to determine the damage modes.

6.3.1 Scratch Deformations of PEEK and Unidirectional Fibre Oriented Polymers

The Poly(etheretherketone) (PEEK) and the unidirectional carbon fibre oriented PEEK samples were scratched using a 45° conical indenter on the pendulum scratching machine. The fibre oriented samples were scratched parallel and transverse to the fibre orientation.

SEM images of the scratched PEEK showed that there is a formation of ridges on the sides of the scratch, as can be in figure 6.7 and 6.8. These ridges are thought to be formed due to stick slip motion of the indenter on the material. The indenter pulls the material in the scratching direction; the extension of the material takes place until the material reaches the yield strength and induces the fracture of material along the scratching direction. Therefore cracks are formed across the scratch edges. This response can also be termed as ductile ploughing. Briscoe et al (1996) have reported a similar kind of deformation in the
semicrystalline poly(ethylene) scratching under similar contact conditions. The inner side of scratch shows ductile machining and cutting response of PEEK, showing the severity of the scratching conditions in this case. The fibrillation of the crystalline lamella as indicated in figure 6.8 (b-c) were also observed.

![Figure 6.7: Ductile ploughing and cutting (×70) of the virgin PEEK scratched with a 45° conical indenter at room temperature in an unlubricated contact.](image)

Scratching of the carbon fibre oriented PEEK transverse to the fibre orientation has produced sharp fibre cutting along the scratch direction (figure 6.9). Debris of the material was also seen on the edge of the scratch indicating that there is brittle deformation of the matrix material. Some of the fibres have been bent across the sliding direction due to compressive forces on the fibres. Friderich et al (1998) have proposed a similar type of damage of fibres using finite element analysis and experimentation on the carbon fibre oriented PEEK. Compressive and frictional loads of the indenter have caused bending of the fibres into the surface and in the sliding direction. In the enlarged portion of the fibre matrix there were crushed fibres present along with peeled-off PEEK.
Figure 6.8: Internal view of the scratch. SEM image (a×700, bx750, c x850) of the virgin PEEK scratched with a 45° conical indenter at room temperature in unlubricated contact.
Crushed Fibre Matrix Material

Peeled off PEEK from Fibres

Sharp Cutting of Fibres across a straight line

(Figure continued on page 124)
Figures 6.9 (a-e): SEM images taken as (a) × 700 (b) × 750 (c) × 100 (d) ×120 (e) × 700 of the carbon fibre oriented PEEK scratched transverse to fibre direction with a 45° conical indenter. Arrow head shows the direction of scratching.

When carbon fibre oriented PEEK was scratched along the fibre orientation, the fibre debonding of the fibres from the surface of matrix was observed (figure 6.10). This debonding of fibres is mainly the result of normal and tangential forces acting on the composite due to the sliding of the indenter (Ovaert 1995). There was cutting of fibres present while some of the images also highlighted micro-cracks formed inside the scratched section. In the bottom of the scratch there were some crushed fibres also present along with some matrix debris, but there was no evidence of peeled PEEK in normal scratching, unlike the transverse sliding case.
(Figure continued on page 126)
6.3.2 Scratch orientation effects on the surface deformations of PEEK composites

There have been a number of studies on the wear behaviour of continuous fibre reinforced polymer composites in the literature. The wear behaviour of these polymer composites are influenced by the type of polymer composite, fibre orientation and sliding conditions (Ovaert 1995; Ovaert 1997). The unidirectional oriented fibre matrix composites show significant tribological anisotropy due to heterogeneities. The higher resistance has been predicted in the case of sliding normal to the fibre orientation, while the lowest was observed in the case of scratching normal to the fibre direction and lowest in transverse sliding configuration. The coefficient of friction in such polymer composites is a function of material combination, fibre orientation and surface roughness. There are opposing observations for the dependence of the friction coefficient on fibre orientation. Sung and Suh (1979) showed the friction coefficient was a minimum for scratching normal to fibre areas in the case of epoxy/graphite composites, whereas the friction is higher when an epoxy/Kevlar composite is scratched in the orthogonal direction. Tribological simulations for the unidirectional fibre composites have also been reported in the literature assuming the fibres to be a beam lying on a foundation (Friedrich et al. 2001).

Wear tests on carbon/kevlar hybrid composites show a higher friction coefficient at the start of the experiment that drops to a constant value after a certain time. It was proposed...
that initially the surfaces of the steel counterpart and composite were rough, causing interlocking resulting in the higher friction. With the wear process there is smoothening of these rough surfaces due to the formation of a transfer film, hence the friction decreased. The corresponding wear rate also showed similar patterns to the friction coefficient. The friction coefficient and wear rate are much lower under lubricated conditions as compared to unlubricated conditions. Abrasive wear is the dominant mechanism at lower loads while adhesive failure, in terms of fibrillation, is observed at higher loads. The level of load for a specific type of wear mechanism is increased substantially with lubrication. There is lower wear in the case of carbon fibres as compared to the Kevlar fibres (Wan et al. 2007). Liang et al (1996) have carried out single pendulum scratching on graphite oriented polyamide composites with a fibre loading of 60%. The effect of fibre orientation angle in comparison to scratching on specific energy and coefficient of friction is described. Scratching in the transverse direction produced higher friction due to a delamination mechanism as compared to longitudinal direction.

The unidirectional carbon fibre oriented PEEK samples were scratched along the fibre orientation direction with conical indenters (45 to 130° cone included angle) using the pendulum sclerometer. Figure 6.11 shows the SEM image of unidirectional carbon fibre PEEK composite when scratched with a 130° included angle conical indenter. The debonding of the material matrix and the fibres was seen along the scratch direction. Material debris was also seen in the scratch track. The breakage of the fibres was seen along with matrix fibre debonding when the PEEK composite was scratched with a sharper indenter (90° conical indenter as is shown in figure 6.12). Sharp indenters induce the cutting of the material as is shown in figure 6.13 and 6.14. The presence of tensile stresses induced in the surface fibres during parallel scratching produces fibre breakage and may lead to fibre matrix debonding. The matrix material was peeled off and parallel fibres appeared on the groove walls in the case of the scratching with 45° and 60° conical indenters. In addition, breakage of some fibres suggests higher frictional interaction between scratch wall and the indenter in such cases.
**Figure 6.11:** Fibre matrix debonding. SEM (x450) of a scratch on carbon fibre oriented PEEK along the fibre orientation under the contact conditions of cone included angle: $130^\circ$; $T = 20^\circ$C; no lubricant. Arrow head shows direction of scratching.

**Figure 6.12:** Fibre matrix debonding and fibre breakage. SEM (x350) of a scratch on carbon fibre oriented PEEK along the fibre orientation under the contact conditions of cone included angle: $90^\circ$; $T = 20^\circ$C; no lubricant. Arrow head shows direction of scratching.
Scratching carbon fibre oriented PEEK transverse to the fibre direction with blunt indenters produced bending and micro cracks in the material, as can be seen in figure 6.15. This bending of the fibres was thought to be the result of torsion yielding from the transverse compression of the surface fibre layers in such polymeric systems (Goda et al. 2004). But
material cutting and the fibre debonding deformations were observed when the scratch was performed with a 90° conical indenter. Scratching the PEEK composite in the transverse direction with sharp indenters produced the deep grooving of the surface along with the fibres bending in the scratch direction (figures 6.17 and 6.18).

![Image](image1.png)

**Figure 6.15:** Material bending and crack formations. SEM (x500) of a scratch on carbon fibre oriented PEEK transverse to the fibre orientation under the contact conditions of cone included angle: 130°; T = 20°C; no lubricant. Arrow head shows direction of scratching.

![Image](image2.png)

**Figure 6.16:** Material cutting. SEM (x430) of a scratch on carbon fibre oriented PEEK transverse to the fibre orientation under the contact conditions of cone included angle: 90°; T = 20°C; no lubricant. Arrow head shows direction of scratching.
Figure 6.17: Fibre bending and cutting. SEM (x430) of a scratch on carbon fibre oriented PEEK transverse to the fibre orientation under the contact conditions of cone included angle: 60°; T = 20 °C; no lubricant. Arrow head shows direction of scratching.

Figure 6.18: Material cutting. SEM (x430) of a scratch on carbon fibre oriented PEEK transverse to the fibre orientation under the contact conditions of cone included angle: 45°; T = 20 °C; no lubricant. Arrow head shows direction of scratching.

The most pronounced deformation of the fibre oriented PEEK composites were seen when the scratches were performed orthogonal to the fibre orientation. A combination of the transverse and longitudinal stresses in the orthogonal scratching has induced greater deformations as compared to parallel and transverse scratching. The bending of the surface
fibre layers with the formation of cracks in the surface was observed when the composite surface was scratched with a $130^0$ indenter as is shown in figure 6.19. The debris of material as can be seen in figure 6.20 was formed when the composite was scratched with a $90^0$ cone in an orthogonal scratch direction. Scratching the polymeric composite in the orthogonal direction to the fibre orientation with sharper indenters has produced cutting of the fibres as represented in figures 6.21 and 6.22. Lower fibre layers were also seen to be exposed in sharp asperity contacts. The deformation on the two sides of the orthogonal scratch was found to be different. This can be attributed to the different angles formed between the indenter and fibre orientation. On the side with an obtuse angle bending and breakage of the fibres was observed, whilst the tensile forces on the acute angle side have aligned the fibres parallel to the scratching direction and peeling of the matrix material is also observed.

Figure 6.19: Material cutting. SEM (x430) of a scratch on carbon fibre oriented PEEK orthogonal to the fibre orientation under the contact conditions of cone included angle: $130^0$; $T = 20^0$C; no lubricant. Arrow head shows direction of scratching
Figure 6.20: Fibre bending and material debris formation. SEM (x370) of a scratch on carbon fibre oriented PEEK orthogonal to the fibre orientation under the contact conditions of cone included angle: 90°; T = 20 °C; no lubricant. Arrow head shows direction of scratching.

Figure 6.21: Material cutting. SEM (x350) of a scratch on carbon fibre oriented PEEK orthogonal to the fibre orientation under the contact conditions of cone included angle: 60°; T = 20 °C; no lubricant. Arrow head shows direction of scratching.
Figure 6.22: Material cutting and fibre bending. SEM (x330) of a scratch on carbon fibre oriented PEEK orthogonal to the fibre orientation under the contact conditions of cone included angle: $45^0$; $T = 20^0$C; no lubricant. Arrow head shows direction of scratching.

6.4 Conclusion

The results from the nanoindentation and scratching experiments performed on the PEEK composites are presented in this Chapter. The nanoindentation experiments were performed on the 30% (w/w) carbon fibre PEEK and the 30% (w/w) glass fibre PEEK composites. The bimodal response, as expected from the fibres and material matrix, was observed during indentation. The presence of carbon fibres was found to increase the surface mechanical properties much more than the glass fibres in the PEEK composites. The carbon fibre oriented PEEK composites were scratched using a pendulum sclerometer in different orientations. The deformations induced in the fibre oriented PEEK composites were found to be a strong function of the angle formed between the indenter and the fibre orientation. Scratching the PEEK composites with blunter indenters mainly produced bending of the surface fibres and microcrack formation. The sharper conical indenters were found to induce material and fibre cutting with consequent debris formation and the exposure of the lower fibre layers.
CHAPTER 7

SURFACE MODIFICATION EFFECTS ON THE
MECHANICAL PROPERTIES OF
POLY(ETHERETHEREKETONE)

The mechanical properties of the modified PEEK surfaces obtained from nanoindentation experiments are presented in this Chapter. The Chapter is divided to three different individual topics on the basis of the selected surface treatments: thermal treatment, plasticisation in solvents and scratch deformation effects. All three relate to the local surface mechanical properties of the polymers in thermal, solvent and mechanical disruptions. Amorphous and crystalline PEEK samples were obtained using the thermal treatment of PEEK followed by quenching and annealing respectively. A typical harder indentation response was seen for the polymer with higher crystallinity. Seven different solvents were selected from the wide range of Hildebrand (1963) solubility parameters to study the plasticisation of the amorphous and the semicrystalline PEEK. The properties of amorphous PEEK were found to be affected by almost every solvent whereas the semicrystalline polymer has shown greater resistance to solvent attack. Finally, nano indentation responses of the scratched poly(styrene), the scratched poly(methylmethacrylate) and the scratched poly(etheretherketone) are presented with emphasis on the detection of subsurface crazing damage.

7.1 Introduction

This Chapter presents the results of an experimental study of thermal treatments, chemical environmental (solvent immersion) and scratch deformations inducing subsurface damage of polymeric surfaces. The mechanical properties of semicrystalline polymers are strongly influenced by the degree of crystallinity of the polymer (Chu et al. 2008). The degree of crystallinity can be varied by following different thermal treatments of the semicrystalline
polymers. The semicrystalline PEEK samples were melted and then quenched (rapid cooling) in water, to produce the amorphous PEEK and annealed (slower or controlled cooling) to produce the crystalline polymer. The load-displacement curves, the hardness and the elastic modulus data obtained from the nanoindentation of the amorphous and the crystalline PEEK surfaces are reported in section 7.2.

Most often application of polymers involves the contact of the polymeric surface with aggressive environments, such as solvents, lubricating oils, detergents and cleaning solutions. The polymeric surface becomes plasticised, or softened, if exposed to such chemical environments for a long period of time (Briscoe et al. 1997). The plasticisation of the polymer produces softening of the surface which deteriorates the surface mechanical and optical characteristics of the polymer. Therefore, the hardness and the elastic modulus behaviour of the amorphous PEEK and the semicrystalline PEEK following immersion in octane, chloroform, tetrachloroethane, dichlorobenzene, PEG, methanol and water are reported in this Chapter.

Abrasion of the polymeric surfaces in the scratching contacts can reduce, not only their longevity, but also the aesthetic appeal. The surface deformation and scratch hardness evaluations are well established. A detailed study on the scratch deformations, scratch hardness and the friction of the semicrystalline PEEK is presented in the Chapter 5. But, the effect of scratching on the material deformation and character beneath the visible surface layer has always been problematic in polymers, as the effective sectioning following imaging of damaged polymeric surface is not possible as for the metals and ceramics (Blackman et al. 2000). The scratched polymeric surfaces were indented using nanoindenter and the load-displacement data is presented to show the occurrence of subsurface deformations.

### 7.2 Nanoindentation response of thermally treated PEEK

The nanoindentation studies were conducted on the quenched (negligible degree of crystallinity), the annealed (crystallinity 31±3% see appendix C) and the virgin polymeric samples (crystallinity 40±2%). The quenched and the annealed samples of the semicrystalline PEEK were prepared by the thermal treatment of the PEEK sheets provided by Goodfellow Chemicals, Cambridge, UK. The quenched samples were produced by heating the samples on hot plates, 3 mm thick aluminium plates, to 380-400 °C and then quenching immediately in
cold water. The crystallinity of the quenched samples was estimated to be negligible by differential scanning calorimetric analysis (DSC). The annealed samples were prepared by melting the polymer at a temperature of 380-400 °C and then annealing by allowing the sample to cool gradually overnight to ambient temperature.

Figure 7.1: Load-displacement data for the quenched PEEK, the annealed PEEK and the virgin PEEK sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. (Experimental data set of all indents are shown in appendix D.)

Figure 7.1 shows the representative load displacement compliance curves obtained from the indentation experiments on the quenched, the annealed and the virgin PEEK samples. The polymeric samples were indented with a Berkovich Tip at constant loading and unloading rates of 300 mN/sec. The maximum indentation displacement was limited to 5000 nm. The load was held constant at the maximum displacement to account for the creep effects and then after 80% unloading of the indenter to account for the thermal drift. The respective compliance curves presented in figure 7.1 for the polymeric surfaces are the median of the curves from the indentation responses. As shown in the figure 7.1 the quenched PEEK sample was found to be the softer as it was indented to 5000 nm requiring a minimal of the indentation force of 30-35 mN. The virgin PEEK was observed to be the harder polymeric surface. The harder polymeric surfaces required higher normal loads to induce a comparable indentation penetration. Multiple peak behaviour of the load displacement data for the
annealed and the virgin PEEK samples were found (see appendix D). The compliance curves for the quenched samples were seen to be coinciding the same curve as the one is shown in figure 7.1. The multiple peak behaviour of the virgin and the annealed PEEK conform to the bimodal indentation response of semicrystalline polymers as discussed in Chapter 4.

The indentation hardness as a function of penetration depth for the polymeric surfaces is presented in figure 7.2. A peculiar surface hardening of the polymeric surfaces was observed for all the polymers. Comparatively higher gradients in the surface hardening response were seen for the thermally treated polymers as compared to the virgin semicrystalline polymers. These higher surface hardening gradients can be attributed to the thermal treatment history of the polymers. The induction phase, lower indentation displacement, hardness values originated from the tip calibration defects at lower penetration depths can be neglected. An increasing trend of the measured hardness was observed with the increase of the crystallinity of the PEEK surfaces. The calculated hardness values for the amorphous PEEK were similar to the ones reported by Deslandes and Rosa (1990). They have established an interrelationship between the crystallinity of PEEK and the micro hardness, by adopting the micro indentation. Although the trends in increasing crystallinity were similar, comparatively lower hardness values were observed in the present study (as computed) by Deslands and Rosa (1990) for crystalline PEEK surfaces (255±20 MPa). These differences in the computed hardness values can be attributed to the indentation scale effects and the differing experimental procedures. They have performed the experiment using Buehler Micromet II microhardness tester equipped with a diamond square pyramid tip of included angle 136° under a load of 100 g for 5 seconds. The hardness was then evaluated by determining the indentation area by an imaging technique.
Figure 7.2: Hardness as a function of indentation displacement data for the quenched PEEK, the annealed PEEK and the virgin PEEK sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. (Data less than 300 nm may not be accurate due to surface approach and tip calibration factors.)

Figure 7.3: Elastic Modulus as a function of indentation displacement data for the quenched PEEK, the annealed PEEK and the virgin PEEK sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. (Data less than 300 nm may not be accurate due to surface approach and tip calibration factors.)
Figure 7.3 shows the elastic modulus data of the PEEK surfaces as a function of indentation contact displacement, computed using the continuous stiffness method. The modulus was evaluated using a modulus of 1141 GPa and a poisson’s ratio of 0.07 for the diamond indenter. The figure shows a strong increasing trend for the modulus values with the decreasing of the indentation depth for all the systems. These trends are similar to those observed for the normal hardness (figure 7.2). The possible localized minor modification or surface crystallinity of the material properties of the near-to-surface layers of the PEEK during fabrication could give an acceptable explanation for the higher modulus near to the surface compared to the bulk values. The elastic modulus was found to be increasing with the increasing crystallinity of the polymer. The fact that the modulus curves for the semicrystalline polymers were noisier than the amorphous polymers especially at lower penetration depths could be possibly due to complex discontinuous deformation processes during indentation into the semicrystalline polymers.

The physical origin of the fluctuations observed in the nanoindentation data for the presence of any regularity or periodicity was analyzed by correlation analysis. The experimental data were used to obtain a polynomial function in the range with minimum experimental errors i.e, 2000 nm to 3000 nm indentation displacement. The overall trend of the data were then removed to observe the periodicity or regularity. Figures 7.4 to 7.6 present some selected data showing the fluctuations, after removal of the established trend from the experimental data for the elastic modulus of the quenched, the annealed and the virgin PEEK (the data points are linked for the sake of clarity). As can be seen from the figure 7.4 the data is reasonably smooth for the quenched PEEK. Periodic fluctuations in properties of the semicrystalline polymers were observed as can be seen in figures 7.5 and 7.6. These fluctuations do appear to be governed by discontinuities in the polymeric materials and can be related to the spherulites present in the semicrystalline PEEK. The period (≈200 nm) of these fluctuations corresponds to the size of spherulites. Since the spherulite size of PEEK in case of crystallization across carbon fibre composites were reported to be 10-20 µm (Wang and Jeronimidis 1991). Therefore it might be the thickness of mesophase of the crystals in the polymer (Singh 2002). A clear morphological description of the semicrystalline PEEK is not available without extensive and costly investigation. This might include X-ray, transmission electron microscope (TEM) and neutron scattering although precedents have not been clearly established.
Figure 7.4: Data trend based on removal of the main trend for the elastic modulus of quenched PEEK as a function of indentation displacement data in the range 2000 nm to 3000 nm.

Figure 7.5: Data trend based on removal of the main trend for the elastic modulus of annealed PEEK as a function of indentation displacement data in the range 2000 nm to 3000 nm.
7.3 Effect of solvents on Surface Mechanical Properties of PEEK

Dissolution of a solid polymeric surface in a solvent is a slow process. The dissolution process can be divided into two stages. A swollen gel is produced in the first step, where the solvent molecules diffuse into the polymer structure. This process takes place in the case when the polymer-polymer molecular interactions are large compared to the affinity of the solvent to polymer molecule. If the solvent-polymer interactions are stronger, a gel like solution of the polymer will be formed in the solvent. The solvent penetration through the polymeric surface reduces the intermolecular forces causing a partial relaxation of the polymer chains with a strain relaxation. The rate of the diffusion of the solvent determines the depth to which surface plasticisation will take place (Briscoe et al. 1997).

The effect of solvents on the surface mechanical properties of the amorphous and the semicrystalline PEEK were analyzed by the nanoindentation experiments. The amorphous PEEK and the semicrystalline PEEK samples were immersed in selected solvents in sealed containers at room temperature for 14 days prior to the experiments. The solvents were
selected on the basis of their Hildebrand solubility parameters (Hildebrand and Scott 1962). The solubility parameter was defined as the square root of the cohesive energy density, which is the heat of vaporization divided by the molar volume. The solubility parameter is an indication of the relevant solvency behaviour of a solvent. The solvents following next to each other with similar values will dissolve a solid that falls in the same category; therefore a band of the solvents that can dissolve a particular solid can be defined on the basis of solubility parameter. The dissolution of a solid will only take place if the solvent and the solid have similar solubility parameters. The heat of vaporization of the polymers cannot be determined directly due to thermal degradation. Therefore, the solubility parameter of the polymers cannot be computed directly. A dissolution/swelling approach is adopted to determine the solubility parameters of polymers as explained in figure 7.7 for a dried linseed oil film. As can be seen from figure 7.7, chloroform has produced the highest degree of swelling in the linseed oil film therefore the Hildebrand solubility parameter of linseed oil film is between 19 and 20. Parvatareddy et al. (1996) have shown that the solubility parameter of the PEEK is closer to acetone. The Hildebrand's solubility parameter of the selected solvents is provided in table 7.1.

![Figure 7.7 Swelling of Linseed Oil Film in Solvents Arranged According to Solubility Parameter](taken from Feller et al. 1985)
Table 7.1: Hildebrand Solubility parameter of selected solvents (Burke 1984)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solubility Parameter / (J cm$^{-3}$)$^{1/2}$</th>
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<tbody>
<tr>
<td>Octane</td>
<td>15.5</td>
</tr>
<tr>
<td>Chloroform</td>
<td>18.7</td>
</tr>
<tr>
<td>Tetrachloroethane</td>
<td>19.6</td>
</tr>
<tr>
<td>Acetone</td>
<td>19.7</td>
</tr>
<tr>
<td>Dichlorobenzene</td>
<td>20.5</td>
</tr>
<tr>
<td>Poly(ethyleneglycol) (PEG)</td>
<td>22.0</td>
</tr>
<tr>
<td>Methanol</td>
<td>29.7</td>
</tr>
<tr>
<td>Water</td>
<td>47.8</td>
</tr>
</tbody>
</table>

The continuous stiffness mode indentation experiments were conducted on the untreated and the immersed PEEK samples. The immersed polymeric samples were dried in the ambient conditions for 1 hour before indentation. The drying was performed to remove liquid molecules from the polymeric surface to avoid the lubrication effects of liquid during indentation. The indentation experiments were performed with a Berkovich tip indenter at a constant displacement loading rate (10 nm/sec) to a maximum depth of 1000 nm. The load was then held constant for 20 seconds to allow for material creep before unloading at the same displacement rate. Another hold segment after 80% unloading was allowed to account for the thermal drift rates during indentation. The hardness and the modulus as a function of the indentation displacement were calculated using the continuous stiffness method.

The hardness and the elastic modulus of the untreated amorphous PEEK and the amorphous PEEK immersed in octane and chloroform are presented in figures 7.8 and 7.9 respectively. Figures 7.10 and 7.11 shows the respective surface mechanical properties of the semicrystalline PEEK immersed in octane and chloroform solvents. The surface mechanical properties of the amorphous PEEK samples were observed to decrease after immersion in octane. The decrease in the surface mechanical properties was seen to be not influenced by the crystallinity of the sample. The surface plasticisation due to sorption of the octane by the amorphous and the semicrystalline polymer is the possible reason for the decrease in the properties. The properties diverge at larger penetration depths for the amorphous samples whereas a converging behaviour was seen for the semicrystalline PEEK samples. This implies that the penetration has occurred to a larger depth for the amorphous samples than the semicrystalline polymer. The converging behaviour of the hardness curve for the octane treated semicrystalline PEEK indicates that the plasticisation has taken place to lower depths.
compared to that of the amorphous PEEK in the same solvent. Mensitieri et al (Mensitieri et al. 1989) have also observed the sorption of n-heptane by amorphous PEEK. A linear fit to the properties indicates that the values calculated for the chloroform treated PEEK samples are lower than those of the untreated samples. This reduction may be explained by the strong plasticising nature of the chloroform. The plasticisation of the polymeric samples by chloroform has caused significant softening. There is no convergence of the treated and untreated PEEK samples. This observation indicates that the plasticisation of the PEEK samples has occurred at depths greater than 1000nm. Briscoe and Stuart (1996) have observed similar reductions in the scratch hardness of the semicrystalline PEEK in the chloroform. Stuart and Williams (1994) have reported the sorption of chlorinated organic solvents (chloroform and dichlorobenzene) by PEEK and reported the effects on properties.

**Figure 7.8:** Hardness as a function of indentation displacement data for the untreated amorphous PEEK and the amorphous PEEK immersed in the chloroform and the octane solvents at constant displacement loading rate. The loading and unloading displacement rates were maintained at 10 nm/sec. (Data less than 100 nm may not be accurate due to surface approach and tip calibration factors.)
Figure 7.9: Modulus as a function of indentation displacement data for the untreated amorphous PEEK and the amorphous PEEK immersed in the chloroform and the octane solvents at constant displacement loading rate. The loading and unloading displacement rates were maintained at 10 nm/sec. (Data less than 100 nm may not be accurate due to surface approach and tip calibration factors.)

Figure 7.10: Hardness as a function of indentation displacement data for the untreated semicrystalline PEEK and the semicrystalline PEEK immersed in the chloroform and the octane solvents at constant displacement loading rate. The loading and unloading displacement rates were maintained at 10 nm/sec. (Data less than 100 nm may not be accurate due to surface approach and tip calibration factors.)
Figure 7.11: Modulus as a function of indentation displacement data for the untreated semicrystalline PEEK and the semicrystalline PEEK immersed in the chloroform and the octane solvents at constant displacement loading rate. The loading and unloading displacement rates were maintained at 10 nm/sec. (Data less than 100 nm may not be accurate due to surface approach and tip calibration factors.)

Figure 7.12: Hardness as a function of indentation displacement data for the untreated amorphous PEEK and the amorphous PEEK immersed in the tetrachloroethane and the dichlorobenzene solvents at constant displacement loading rate. The loading and unloading displacement rates were maintained at 10 nm/sec. (Data less than 100 nm may not be accurate due to surface approach and tip calibration factors.)
The amorphous PEEK samples were seen to be severely degraded in tetrachloroethane as represented by the computed hardness and the elastic modulus values in figures 7.12 and 7.13. The surface mechanical properties of the amorphous polymer drop to negligible values after immersion in tetrachloroethane. The degradation in the properties is the result of plasticisation of the amorphous PEEK by chlorinated organic solvents (Hay et al. 1984; Hay and Kemmish 1988). Figures 7.14 and 7.15 represent the hardness and the elastic modulus values comparison of the untreated semicrystalline PEEK and the one immersed in tetrachloroethane. Similar values of the surface mechanical properties of the semicrystalline polymer were seen near the surface before and after the treatment. This observation is consistent to the one reported in the literature as the semicrystalline PEEK is not affected by tetrachloroethane (Arzak et al. 1992; Arzak et al. 1993). A peculiar decreasing trend of the surface mechanical properties of the semicrystalline PEEK was found after a penetration depth of 400 nm. This dual effect can be explained by the plasticisation and the solvent induced crystallization taking place in the polymer; antiplasticisation. The first effect of the penetration of the solvent into the polymer was to induce plasticisation. When the sample was dried the loss of solvent from the top layers of the polymer activated the crystallization of the top layers and hence a dual effect on the nano surface mechanical properties was observed. The immersion of the polymeric samples in dichlorobenzene have produced similar process to the one observed when the PEEK surfaces were immersed in tetrachloroethane but to a less pronounced effect, see also figures 7.12 to 7.15. In comparison to the semicrystalline material a greater surface crystallization as well as higher subsurface plasticisation were observed as can be seen from the steep gradients in figures 7.12 and 7.13. These results are in accordance with the swelling of the amorphous PEEK in tetrachloroethane observed by Stuart and Williams (1994), who presented the spectral properties of the polymer.
Figure 7.13: Elastic modulus as a function of indentation displacement data for the untreated amorphous PEEK and the amorphous PEEK immersed in the tetrachloroethane and the dichlorobenzene solvents at constant displacement loading rate. The loading and unloading displacement rates were maintained at 10 nm/sec. (Data less than 100 nm may not be accurate due to surface approach and tip calibration factors.)

Figure 7.14: Hardness as a function of indentation displacement data for the untreated semicrystalline PEEK and the semicrystalline PEEK immersed in the tetrachloroethane and the dichlorobenzene solvents at constant displacement loading rate. The loading and unloading displacement rates were maintained at 10 nm/sec. (Data less than 100 nm may not be accurate due to surface approach and tip calibration factors.)
Figure 7.15: Elastic modulus as a function of indentation displacement data for the untreated semicrystalline PEEK and the semicrystalline PEEK immersed in the tetrachloroethane and the dichlorobenzene solvents at constant displacement loading rate. The loading and unloading displacement rates were maintained at 10 nm/sec. (Data less than 100 nm may not be accurate due to surface approach and tip calibration factors.)

Figure 7.16 and 7.17 shows the hardness and the elastic modulus data respectively for the amorphous PEEK and the amorphous PEEK immersed in poly(ethyleneglycol) (PEG), methanol and water. Slight plasticisation of the amorphous PEEK surface was observed in the presence of PEG as can be seen by the decreasing trend of the surface mechanical properties with increasing indentation displacement in figures 7.16 and 7.17. The immersion of the semicrystalline PEEK in PEG has not affected the mechanical properties of the polymers as shown in figures 7.18 and 7.19. Similarly methanol does not affect the properties of the semicrystalline PEEK. Slight near surface plasticisation of the methanol treated amorphous PEEK was observed from the hardness data in figure 7.16 and 7.17. The surface damage of the surface is limited to less than 800 nm penetration depth. The variations in the curves for the untreated PEEK surfaces and the methanol immersed surfaces can be due to the experimental observations and errors.
Figure 7.16: Hardness as a function of indentation displacement data for the untreated amorphous PEEK and the amorphous PEEK immersed in the poly(ethyleneglycol) (PEG), methanol and water solvents at constant displacement loading rate. The loading and unloading displacement rates were maintained at 10 nm/sec. (Data less than 100 nm may not be accurate due to surface approach and tip calibration factors.)

Figure 7.17: Elastic modulus as a function of indentation displacement data for the untreated amorphous PEEK and the amorphous PEEK immersed in the poly(ethyleneglycol) (PEG), methanol and water solvents at constant displacement loading rate. The loading and unloading displacement rates were maintained at 10 nm/sec. (Data less than 100 nm may not be accurate due to surface approach and tip calibration factors.)
Figure 7.18: Hardness as a function of indentation displacement data for the untreated semicrystalline PEEK and the semicrystalline PEEK immersed in the poly(ethylene glycol) (PEG), methanol and water solvents at constant displacement loading rate. The loading and unloading displacement rates were maintained at 10 nm/sec. (Data less than 100 nm may not be accurate due to surface approach and tip calibration factors.)

Figure 7.19: Hardness as a function of indentation displacement data for the untreated semicrystalline PEEK and the semicrystalline PEEK immersed in the poly(ethylene glycol) (PEG), methanol and water solvents at constant displacement loading rate. The loading and unloading displacement rates were maintained at 10 nm/sec. (Data less than 100 nm may not be accurate due to surface approach and tip calibration factors.)
Significant surface hardening was observed for the amorphous PEEK immersed in water as can be observed in figure 7.16 and 7.17. It would seem that water has caused a rigidification of the polymer, due to cleaning of the surfaces and hence removing the impurities present in the polymeric surface. In comparison the semicrystalline polymer was plasticised and hence decreases in the normal hardness and the elastic modulus was observed after immersion in water (see figures 7.18 and 7.19). These results are consistent with those observed by Arzak et al. (1993). They had observed an increase in tensile properties of amorphous PEEK after 48 hrs immersion in water and a slight decrease in the properties of the semicrystalline PEEK. They concluded the property changes of the polymer were due to experimental errors although the results shown here exhibit a significant modification of the mechanical properties of the PEEK surfaces. The plasticisation of the PEEK surfaces may also be associated with the removal of impurities present in the polymer. The PEEK contains smaller amounts (<1%) of fluorine containing impurities from the manufacturing processes as described in the Chapter 1. A comparative table to illustrate the effects of solvents on surface mechanical properties of amorphous and semicrystalline PEEK are presented in table 7.2.

Table 7.1: Effect of solvents on surface mechanical properties of amorphous PEEK

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Hardness (GPa)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.20±0.02</td>
<td>3.0±0.10</td>
</tr>
<tr>
<td>Octane</td>
<td>0.15±0.02</td>
<td>2.7±0.10</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.10±0.01</td>
<td>2.6±0.15</td>
</tr>
<tr>
<td>Tetrachloroethane</td>
<td>0.08±0.005</td>
<td>2.0±0.10</td>
</tr>
<tr>
<td>Dichlorobenzene</td>
<td>0.01±0.001</td>
<td>0.40±0.05</td>
</tr>
<tr>
<td>PEG</td>
<td>0.18±0.01</td>
<td>2.8±0.10</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.18±0.01</td>
<td>3.0±0.10</td>
</tr>
<tr>
<td>Water</td>
<td>0.30±0.01</td>
<td>4.5±0.5</td>
</tr>
</tbody>
</table>

Table 7.2: Effect of solvents on surface mechanical properties of semicrystalline PEEK

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Hardness (GPa)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.30±0.10</td>
<td>4.1±1.00</td>
</tr>
<tr>
<td>Octane</td>
<td>0.25±0.10</td>
<td>3.8±0.08</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.19±0.06</td>
<td>3.6±0.07</td>
</tr>
<tr>
<td>Tetrachloroethane</td>
<td>0.25±0.05</td>
<td>3.4±0.10</td>
</tr>
<tr>
<td>Dichlorobenzene</td>
<td>0.25±0.05</td>
<td>3.6±0.30</td>
</tr>
<tr>
<td>PEG</td>
<td>0.30±0.10</td>
<td>3.9±1.0</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.30±0.10</td>
<td>3.8±1.0</td>
</tr>
<tr>
<td>Water</td>
<td>0.18±0.10</td>
<td>3.0±0.7</td>
</tr>
</tbody>
</table>
7.4 Indentation response of Scratched Polymers

The effects of imposed strains on the polymeric surfaces during scratching on the material deformation beneath the visible surface have not been reported in the literature. The major concern for the polymeric surfaces is the problems related to the effective sectioning for imaging unlike metal and ceramics. The positive wear volumes have also been used to comment on the presence of subsurface crazing (Blackman et al. 1999). Bonne et. al. (2005) have proposed a method to determine the subsurface damage of polymers using the nano indentation technique. The pop-in events in the loading section of the indentation were used to predict the presence of voids in scratched PMMA surface. The presence of a sufficient tensile stress during the sliding action would be anticipated to generate the subsurface voids or crazes. Craze formation and its morphology is well documented for glassy polymers (Haward et al. 1978; Bucknall 2007). Melick et al. (2003) have utilized the micro-indentation method to determine the craze initiation stress in glassy polymers. Development of voids in tensile and scratched elastomeric surfaces is also reported (Schallamach 1952; Cho et al. 1987; Gent and Wang 1991; Gent and Wang 1992).

The present work reports on the presence of such subsurface crazes in the scratched poly(styrene) (PS), the poly(methylmethacrylate) (PMMA) and the poly(etheretherketone) (PEEK) surfaces. The polymeric surfaces were scratched using a 90° conical indenter on a pendulum sclerometer. The SEM images of the scratched polymeric surfaces are presented in figures 7.20 to 7.22. Ductile ploughing of the polymeric surfaces was seen to be the major deformation process for all polymeric surfaces. The nano indentation experiments were performed inside and outside of the scratched polymeric surfaces at a constant displacement loading rate of 5 nm. The polymeric surfaces were indented to a maximum depth of 1 micron. A major concern was to address the difficulty for the determination of the mechanical zero point for the indentation in the scratches. A rapid two times increase in the sample stiffness from the nano indenter was used to detect the surface. It was recognised that the the presence of rough and possibly friable materials debris in the scratched surfaces makes the identification of a sensible mechanical zero point problematic but not impractical.
Figure 7.20: Ductile ploughing (×150) of the polystyrene scratched with a 90° conical indenter at room temperature in an unlubricated contact. Arrow head shows the direction of scratching.

Figure 7.21: Ductile ploughing (×150) of the PMMA scratched with a 90° conical indenter at room temperature in an unlubricated contact. Arrow head shows the direction of scratching.
Figure 7.22: Ductile ploughing (×150) of the PEEK scratched with a 90° conical indenter at room temperature in an unlubricated contact. Arrow head shows the direction of scratching.

A part of the loading segment from the typical indentation response of the PEEK surface outside the scratch is presented in figure 7.23 (Similar curves were observed for the PS and the PMMA surfaces outside the scratch region). A smooth loading curve following the power law of the indentation represents the homogeneous response of the material. The indentations inside the scratched surfaces produced two types of responses. One conforming to the one observed outside the scratch and typically statistically more pronounced in the scratched PEEK (about 75% of the indents performed) and less common in PS (about 40% of the indents performed). The part of the loading curve from the nano indentation response relative to second type of indentation response inside the scratched PS is shown in figure 7.24. The data set for the scratched PS appear to follow periodic fluctuations in the given loading range. Similar fluctuations in the load displacement data were observed for the scratched PMMA (Figure 7.25) and the scratched PEEK surfaces (Figure 7.26. These data sets for the scratched surfaces represent a pronounced and recognisable discontinuous but almost linear load displacement response.

The deviations of the compliance data for the scratched polymers were similar to those observed by Bonne et al. (2005) for scratched PMMA. Similar deviations of the load displacement data were seen in porous foams and agglomerates (Ashby and Gibson 1983; Adams et al. 2001). In foams, the indentation response follows linear elasticity at lower stresses followed by a collapsed plateau, which is truncated by a dense regime with
increasing stress. Mohammad et al. (2004) have seen the similar force displacement behaviour with semi brittle pharmaceutical tablets such as of Paracetamol. While they observed a smooth and hardening force displacement response for the ductile compacts formed from microcrystalline cellulose. The deviations observed in the indentation response can be correlated to inhomogeneities in the surface and the subsurface structures. At the damaged surfaces, the indenter progressively encounters comparatively lesser resistance than found for an undeformed polymeric surface. The load displacement responses in the hold and unloading segment were indistinguishable for the undeformed and the scratched polymeric surfaces and hence not presented in the data shown here.

**Figure 7.23:** Part of the representative Load-displacement data for the PEEK sample outside the scratch. The data was obtained using constant loading rate, maintained at 5 nm/sec. Similar curves were observed for the PS and PMMA surfaces outside the scratch region.
Figure 7.24: Part of the Load-displacement data for the scratched PS sample at constant loading rate. The loading rate was maintained at 5 nm/sec.

Figure 7.25: Part of the Load-displacement data for the scratched PMMA sample at constant loading rate. The loading rate was maintained at 5 nm/sec.
Figure 7.26: Part of the Load-displacement data for the scratched PEEK sample at constant loading rate. The loading rate was maintained at 5 nm/sec.

The physical origin, of any regularity or periodicity, of the fluctuations observed in the load displacement indentation data, were quantitatively assessed by using a polynomial function to represent the general trend of the data. The overall general trend of the data was then removed from the experimental data so as to leave behind fluctuations in the data as presented in figure 7.27. The result indicates that a repetitive phenomenon produces fluctuations at regular intervals in the scratched polymeric surfaces. The fluctuations in the load displacement data can be correlated to the sudden collapse of the subsurface voids. The possibility that the intrinsic machine noise had produced these fluctuations can be eliminated because these periodic oscillations were only seen in certain scratched polymeric surfaces.
Figure 7.27: A typical load displacement curve following removal of the main trend for the indentation of scratched polystyrene sample. Similar fluctuations in the data trend were found for the scratched PMMA and the scratched PEEK samples. Part of the Load-displacement data for the scratched PMMA sample at constant loading rate. The loading rate was maintained at 5 nm/sec.

7.5 Conclusion

The effects of thermal treatment, immersion in solvents and the scratching on surface mechanical properties of the semicrystalline PEEK are presented in this Chapter. The quenching of the melted polymer has produced the amorphous samples while the crystalline samples were obtained by annealing the polymer melt. The load displacement curves, the hardness and the elastic modulus determined from the nanoindentation of the PEEK surfaces were found to be a strong function of the crystallinity of the polymer. The calculated properties were found to be lower in amorphous samples and show an increasing trend with increasing crystallinity of the polymer. The effect of the solvent on the properties of the amorphous and semicrystalline PEEK were also studied. Significant changes were observed in the properties of amorphous PEEK in the presence of solvents. The chlorine containing organic solvents were seen to plasticise the amorphous PEEK to a greater extent. Especially
the tetrachloroethane has degraded the polymer surface to the negligible hardness and modulus values. A decrease in the surface mechanical properties was also seen for the amorphous PEEK immersed in octane, PEG and methanol. Although these effects were less significant than that observed for the chlorine containing organic solvents. A near surface crystallization behaviour was also seen in the plasticised amorphous PEEK surface. A rigidification of the amorphous PEEK surface resulting in sharp increase in the properties was found after its immersion in water. The effects of solvent on the surface mechanical properties of the semicrystalline PEEK were less pronounced. The semicrystalline polymer appeared to be fairly resistant to PEG, methanol and octane. The chlorine containing organic solvents induced plasticisation but to a lesser extent than in amorphous PEEK. Water has been seen to induce a considerable decrease in the properties of the semicrystalline PEEK. The load displacement compliance data from the nano indentation of the scratched PS, the PMMA and the PEEK are presented. The undeformed polymers followed the classical power law indentation response of homogeneous materials. In comparison a discontinuous and a near linear behaviour was observed for the indentation performed inside the scratch. These variations can be the result of subsurface deformations in the scratched polymeric surfaces. This Chapter has demonstrated that the nano indentation technique is capable of sensing the small variations in properties resulting from the thermal treatments, the solvent effects and the subsurface morphological features resulting from scratch deformations.
CHAPTER 8

SUMMARY AND CONCLUSIONS

This Thesis has sought to describe the surface mechanical properties of selected semicrystalline polymers probed at nanometric scales. Poly(etheretherketone) PEEK, a highly aromatic semicrystalline thermoplastic polymer was chosen as a model for these experimental investigations. PEEK, due to its excellent mechanical and thermal characteristics, is widely used in aerospace, military and nuclear plants, oil well applications and thermoplastic composites. PEEK and its composites are thought to be the future replacement material for metals in many applications. An introduction to the brief history, methods of preparation, mechanical properties and uses of PEEK was provided in the chapter 1. A better understanding and control of surface mechanical properties of polymers are required for their use as engineering materials. The near to surface mechanical properties are an important factor for the effective selection and design of materials for surface engineering and tribological applications. These are particularly important when these materials are used to improve contact mechanical performance that is where polymers are adopted in optical, coating and bearing applications. Single point contacts consisting of indentation and scratching response of the semicrystalline polymers were evaluated in this Thesis to elucidate the surface mechanical properties of the polymeric surfaces. A major aim of the work was to evaluate the possibility of multimodal surface mechanical response from the semicrystalline polymers due to presence of crystalline and amorphous phases. The investigation was designed to evaluate the load-displacement indentation response (the compliance curves), the normal hardness, the elastic modulus, the scratch hardness and the most common scratch deformation mechanisms of the semicrystalline polymers.

Chapter 2 introduces the historical perspective of the indentation and scratch hardness techniques. Ever since the introduction of hardness in the early eighteenth century, it has been used as an early empirical method to rank minerals and metals, and is still being used to effectively evaluate surface mechanical properties of materials. The basic concept of the contact mechanics of indentation and scratching phenomena, however, remains unchanged; a hard and sharp object used to deform a softer surface, the deformation resistance of the softer surface being characterized as its hardness. Indentation is virtually a non-destructive means...
of assessing mechanical properties of a material. The introduction of the contact compliance method, based on measures of reaction force on the indenter as a function of imposed displacement, has largely overcome the problems associated with the conventional imaging methodology to measure the contact area of indentation. A scratch is a kind of surface abrasion provoked by the relative friction of a hard material against a softer one. Scratching is one of the most significant stresses that a solid polymeric product experiences in its life. Although the mechanical responses in indentation and scratching are similar, provided the modes of the deformation are the same, scratching does not provide good estimates of the material properties requiring contact area calculations and time dependent analysis; for example the Young’s modulus. The scratching method corresponds to the sliding deformations at asperity contacts. The most relevant contact mechanical concepts of the indentation and the scratching were reviewed in the chapter 2. This theoretical introduction provided a broad overview of experimental situations which might be encountered during the indentation and the scratching of the semicrystalline polymers.

A NANO INDENTER® II machine, supplied by Nano Instruments Ltd., Tennessee, USA was used to obtain the indentation compliance data, the nano normal hardness and the elastic modulus of the polymeric surfaces. The nano indenter, consisted of an indenter column, an optical microscope and a precision table, is capable of probing the material surfaces at the nanometric scale. Two different techniques were used for scratching the polymeric surfaces; a linear scratching technique, where a loaded conical indenter is drawn along a flat polymeric surface, and a pendulum scratching technique, where variable scratch depth is produced along the scratch length, also called dynamic scratching technique. A scanning electron microscopy (SEM) and an optical profilometry technique were used to evaluate the scratch deformation modes and the scratch dimensions induced on the polymeric surfaces.

The experimental results from the indentation experiments performed on the selection of polymeric surfaces; a poly(etheretherketone) (PEEK), an ultra high molecular weight poly(ethylene) (UHMWPE), a poly(methylmethacrylate) (PMMA), a poly(styrene) (PS), a poly(carbonate) (PC), and a poly(propylene) (PP) are presented in the Chapter 4. A constant loading rate, a constant strain rate and a constant displacement rate continuous stiffness indentation experiments were conducted on the semicrystalline PEEK surfaces. The subsequent analysis of the compliance, the hardness and the elastic modulus data obtained
from the indentation experiments have demonstrated the presence of two distinctive material property phases in the semicrystalline PEEK. A statistical frequency density distribution on indentation hardness of the semicrystalline polymer was performed and a strong bimodal indentation response, normally a characteristic of multiphase metal alloys, was found. The two modes in the frequency analysis were thought to be corresponding to the softer amorphous phase and the harder crystalline phase. The crystallinity of the semicrystalline PEEK was calculated on the area count basis of frequency data from the indentation hardness and found to be similar to the one observed by differential scanning calorimetric analysis (DSC) of the polymer. A bimodal indentation response was also observed for the semicrystalline UHMWPE surfaces. The properties of the harder and the softer phase were found to be related by a factor of 2 in the semicrystalline polymeric surfaces.

A comparison into the indentation response based on the compliance data, the hardness and the elastic modulus of the common commercially available polymers (PEEK, UHMWPE, PMMA, PC, PS and PP) was made. The PMMA and the PEEK surfaces were found to be the hardest while the UHMWPE and the PP surfaces were seen to be softest among all the polymers. The hardest polymeric surfaces required higher normal loads to impose similar penetration depths. A peculiar surface hardening response, higher hardness and modulus at lower penetration depths, was observed for all of the polymeric surfaces. This surface hardening response of the polymers can be attributed to a change in the physical and mechanical properties of these systems due to the methods of production or the aging of the polymeric surfaces. The calculated hardness and the modulus values were found to be unreliable near to the surface. These deviations can be attributed to the indenter tip imperfections and the calibration procedures. The tip area function and the contact stiffness of the indenter were calibrated against fused silica, which has a much higher modulus than the polymeric surfaces, prior to indentation experiments on the polymers. The requirement of a standard material having comparable modulus to the polymeric surfaces, for the tip area calibrations and the stiffness, is much anticipated for the future. An unsuccessful effort was made to calibrate the tip area function against the PS surfaces; the surface hardening of the PS was thought to be the major reason for this failure. Finally, the indentation compliance method, based on the continuous stiffness mode, appears to be a convenient method for investigating the surface mechanical properties of viscoelastic-plastic polymeric surfaces. The surface mechanical properties were found to be influenced by the testing procedures and the penetration displacements utilized.
The visualization of the most commonly encountered scratch deformation mechanisms of the semicrystalline polymers are shown in chapter 5. Subjective assessments of the SEM images facilitate the identification of the different deformation regimes resulting from the scratching of the polymeric surfaces by conical indenters. The deformation modes were seen to be influenced by the imposed experimental parameters; such as the contact geometry, the load, the nominal sliding velocity, the contact temperature and the contact lubrication. In addition to the common deformations mechanisms observed in amorphous polymers; ranging from elastic, ironing, viscoelastic plastic ploughing and brittle deformations, a fibrillation of the semicrystalline PEEK was seen when the polymeric surface was scratched under the severe contact conditions (the higher contact strains and the normal loads). The fibrillations of the semicrystalline polymers were thought to be from the scratch deformations in the crystalline lamella. This fibrillation in the scratched surfaces was not found in the amorphous PEEK surfaces. Scratching maps, illustrating the observed surface deformations of the semicrystalline PEEK as functions of the contact parameters, are a convenient tool for visualising and predicting the scratch deformation regimes. The scratch hardness, by analogy with other surface mechanical properties of the semicrystalline polymers, is influenced by the viscoelastic plastic characteristics of the polymeric material, which govern the extent of the scratching contact parameters and the deformation mechanism. The frictional mode map illustrated that the energy dissipation mechanisms plays a vital role in the deformation mechanisms. The required energy level does not increase with increasing contact severity (load or strain), as can be inferred from the friction data. This is due to the fact that internal shear angles regulate the cutting deformation, but not from the external strain conditions, as in ductile ploughing. Finally, it can be concluded that the combination of the frictional data, the SEM imaging and the optical profilometry provide the best means of investigating the scratch hardness and the scratch deformation mechanisms for the semicrystalline polymers.

The surface mechanical properties of the selected PEEK composites (glass and carbon fibre) are presented in chapter 6. The load displacement curves, the calculated hardness and the modulus obtained through the continuous stiffness mode indentation of the glass fibre and the carbon fibre reinforced PEEK composites were analyzed. A typical multiphase response of the composite surface was depicted from the analysis of the indentation data for the composites. The observed experimental results show that the presence of the carbon fibres in PEEK matrix increases the surface mechanical properties of the PEEK composites higher.
than the glass fibres in the matrix. The carbon fibre oriented PEEK composites were scratched in the parallel, the orthogonal and the transverse direction to the fibre orientation using the pendulum scratching machine. Fibre matrix debonding, matrix material debris formation, and fibre breakage were observed to be the dominant deformation mechanisms of the carbon fibre oriented composites scratched along the fibre direction. Scratching the PEEK composites using blunter indenters, in the transverse and in the orthogonal directions, has produced fibre buckling and the formation of microcracks. The material and fibre cutting, debris formation and the exposed surface layers were observed when the scratches were performed using sharp conical indenters in the transverse and the orthogonal directions. The scratch deformations of the fibre oriented composites were found to be strongly dependent on the fibre orientation relative to scratching direction in addition to the normal scratching contact parameters (strain, strain rate, load etc).

Chapter 7 can be divided into three distinctive topics; thermal treatment, solvent plasticisation effects on the surface mechanical properties of the semicrystalline PEEK and the evaluation of the subsurface deformations in the scratched polymeric surfaces using nano indentation. The thermal treatment, melting the polymer and quenching or annealing the PEEK samples, produced amorphous and crystalline PEEK. The surface mechanical properties of the polymer were shown to be dependent on the crystallinity of the polymer. The amorphous PEEK was found to be the softest of the selection and an increasing trend of the hardness and the modulus of the semicrystalline PEEK was observed with increasing degree of crystallinity of the polymer. The effects of solvents on the surface mechanical properties of the semicrystalline and the amorphous PEEK were observed using a selection of solvents based on the Hildebrand’s solubility criterion. The amorphous PEEK was observed to be plasticised by all organic solvents. The chlorine containing organic solvents have caused drastic reduction in the hardness and the modulus of the amorphous PEEK. A significant surface hardening due to rigidification of the amorphous PEEK was observed when it was immersed in water. The semicrystalline PEEK was unaffected by the normal organic solvents such as octane, methanol and poly(ethylene glycol). The chlorine containing organic solvents, although have induced the plasticisation of the semicrystalline PEEK but less than that observed in amorphous PEEK. A decrease in the hardness and the modulus values were observed for the semicrystalline polymers immersed in water. The nano indentation results from the scratched polymeric surfaces have demonstrated that significant subsurface morphological changes of the damaged surfaces can be detected using nano indentation. The
undeformed polymeric surfaces, PEEK, PS and PMMA, were seen to follow the classical power law indentation compliance response of the homogeneous surfaces. A linear but discontinuous load displacement, similar to the indentation response of porous foams, were observed for the scratched polymeric surfaces. The experimental indentation data of the scratched polymeric surfaces was found to be more illustrative than the quantitative, however, the method does provide a useful tool for monitoring the subsurface damage in polymeric surfaces where conventional sub-sectioning and imaging methods can not be applied practically.

The main conclusions that can be drawn from this work are outlined as follows.

- The continuous stiffness mode nanoindentation method is found to be a convenient method for investigating surface mechanical properties of semicrystalline polymers which show viscoelastic-plastic behaviour. The surface mechanical properties were seen to be influenced by the indenter loading conditions and the penetration displacements utilized.

- The frequency distributions of the hardness show a bimodal nature for the semicrystalline polymers. The bimodal response was thought to depend upon whether the polymer is indented in the softer, amorphous phase or the harder, crystalline phase. The proportion of the two regions was found to be similar to the ratio of crystallinity of the polymer.

- Semicrystalline polymers undergoing scratching exhibit a wide range of scratch deformation modes. The deformation mechanisms depend upon the imposed contact conditions during scratching and may range from a fully elastic, to an ironing, to a ductile ploughing, to a crack formation, to a brittle machining, to a cutting or to a fibrillation damage of the polymeric surfaces.

- Mapping the scratching data, of the semicrystalline polymers, is a convenient tool for visualising and predicting the scratch deformation modes as a function of imposed scratching contact parameters. The scratch deformations are influenced by the contact geometry (the strain), the nominal sliding velocity (the strain rate), the normal load, the contact temperature and the chemical environment (lubrication).
• Fibre reinforcements in the semicrystalline polymers increase the surface mechanical properties. The high modulus carbon fibre reinforcement was seen to increase the surface mechanical properties of the composites higher than the glass fibre reinforcement.

• Scratch deformations of unidirectional fibre oriented polymeric composites are strongly influenced by the fibre orientation relevant to the scratching direction in addition to the normal scratch contact parameters. The fibre oriented composites show fibre buckling, fibre matrix debonding, debris formation, cutting and exposed fibre layers damages during the scratching.

• The surface mechanical properties of the semicrystalline polymers are a function of degree of crystallinity. Higher the crystalline content of the polymer, more ordering of the molecular chains, higher the surface mechanical properties of the polymeric surface.

• Periodic fluctuations in the surface mechanical properties of the semicrystalline polymers were found with increasing penetration depths. These fluctuations were likely to arise from the material heterogeneties, namely crystalline spherulites in the semicrystalline polymers. Morphological investigations of the smicrystalline polymers would further elucidate these fluctuations.

• Organic solvents induce surface plasticisation of the amorphous PEEK. The chlorinated organic solvents, such as chloroform, tetrachloroethane and dichlorobenzene have induced greater surface plasticisation of the polymeric surfaces.

• Immersion of the amorphous PEEK in water has produced a significant increase in the hardness of the polymeric surface. The water hardening of the polymeric surface needs discussion and further evaluations. The hardening of the surface could have resulted from the washing out of contaminants/additives.

• The semicrystalline PEEK is found to be substantially inert to the common organic solvents like octane, methanol and poly(ethyleneglycol). Plasticisation of the semicrystalline PEEK was observed when immersed in chlorinated organic solvents and water. A near surface antiplasticisation behaviour was seen in the amorphous and
the semicrystalline PEEK due to loss of solvents in the top layers of the polymeric surface.

- Nanoindentation data of damaged polymeric surface provides a qualitative methodology to estimate the subsurface damages and craze formations. This methodology is important in the context of polymers where conventional effective sectioning of the damaged surface to analyze the subsurface deformations might not be possible.

This Thesis has focused upon the nano surface mechanical properties of the semicrystalline polymers based on the nano indentation and the scratching techniques. A die has been thrown into the knowledge through the findings of the Thesis regarding the bimodal character and presence of fluctuations in the surface mechanical properties of the semicrystalline polymers at nanometric scales. A further exploration of semicrystalline polymers scratching at the nano metric scales would be interesting as the response is expected to be like bumps on smooth profiles. The nanoindentation technique would provide a convenient means to understand morphological description of the polymeric surfaces. Finally, the subsurface damages in the deformed polymeric surfaces may be a practically significant aspect yet to be seen.
APPENDIX A

CONTINUOUS STIFFNESS (DYNAMIC) NANOINDENTATION

The continuous stiffness (dynamic) mode indentation measures the contact stiffness during the loading portion of an indentation test. The sample stiffness is measured continuously without the discrete unloading cycles, as in conventional indentation method, and in a relatively smaller time constants. The method provides a convenient way for determining the stiffness and, hence, the hardness and the elastic modulus of surfaces at a few nanometers and as a continuous function of the penetration displacement. The method is specifically useful in measuring indentation properties of polymeric materials where creep is an important factor during unloading segment (Oliver and Pethica 1989; Lucas et al. 1998; Akram 2001).

![Figure A1: Schematic of a typical load-displacement curve of the continuous stiffness loading cycle](image)

A very small alternating current (AC) of known frequency is superimposed on the direct current (DC), which determines the force on the indenter, during loading ramp in this method. The AC current cause the indenter to oscillate with amplitude and a phase shift based on the stiffness of the material. A two phase lock-in amplifier compares the phase and amplitude of the indenter oscillations with that of the imposed AC signal to compute the
contact stiffness. The imposed driving force \((F_0)\) and the displacement \((a_0)\) for the AC signal and the respective responses of the indenter is represented in equations A1 and A2.

\[
F = F_0 e^{i\omega t} \quad \text{A1}
\]

\[
a = a_0 e^{i(\omega t - \varphi)} \quad \text{A2}
\]

As is presented in equations A1 and A2, the displacement oscillates at the same frequency, \(\omega\), as that of the imposed force but lags by \(\varphi\). The imposed amplitudes of the force and the displacement response ratio can be written in the form of equation A3.

\[
\frac{F_0}{a_0} = \sqrt{\omega^2 c^2 + (K - m\omega^2)^2} \quad \text{A3}
\]

And the phase angle \((\varphi)\) can be written as

\[
\tan(\varphi) = \frac{\omega D}{(K - m\omega^2)} \quad \text{A4}
\]

Where, \(c\) is the damping factor for the central plate of the capacitor, \(m\) is the indenter mass and \(K\) is the combined spring constant of the system (presented in figure A2) in equation A5.

\[
K = K_S + \frac{1}{\frac{1}{s^2} + \frac{1}{K_f}} \quad \text{A5}
\]

Figure 1B: Schematic representation of the dynamic model (Pethica and Oliver 1989)
Above equations can be solved to give the contact stiffness, $S$, and the due to the air gaps
between the capacitor plates, $\omega C$, as in equations A6 and A7 (Li and Bhushan 2002).

\[
S = \left[ \frac{F_0}{h(\omega)} \cos \varphi - (K_S - m\omega^2) - K_f^{-1} \right]^{-1} \tag{A6}
\]

\[
\omega C = \frac{F_0}{a_o} \sin \varphi \tag{A7}
\]
APPENDIX B

TIP AREA FUNCTION AND LOAD FRAME STIFFNESS CALIBRATIONS OF NANOINDENTER

The nanoindenter was calibrated for tip area function of the diamond tip and load frame stiffness calibrations using indentation experiments performed on fused silica. The tip area function is important to account for the imperfections in the tip caused by the wearing process during its life. These imperfections in the tip cause changes in the experimental indentation area and hence inaccuracy in the hardness and the elastic modulus calculations. The measured indentation displacement, and hence the contact area, is a function of the load frame compliance of the indenter. The load frame compliance is much more important in continuous stiffness mode, where the stiffness is calculated in smaller time constants. Therefore, the tip area function and the load frame stiffness calibrations of the indenter need to be performed regularly to obtain most precise results.

Figure B1: A schematic representation of the real indenter tip and the perfect indenter tip (From Manual Nano Indenter)
Standard continuous stiffness mode (NANO INDENTER® II, Operating Instructions) experiments were conducted on the fused silica sample in load range 0 and load range 3 under effective constant strain rate of 0.025 sec\(^{-1}\). The data obtained from 20 indentation experiments was averaged and then were run through an iterative process for determination of the load frame stiffness. The iterative algorithm involves plotting total compliance as a function of inverse of the square root of the indenter area based on perfect Berkovich Tip. The calculation of load frame stiffness is derived from intercept values as the total compliance of the sample needs to be zero at infinite depth as is shown in figure B2. The load frame stiffness of the nanoindenter was calculated to be \(7.046987266 \times 10^7\) N/m.

![Figure B2](image_url)  

**Figure B2:** A schematic representation of curve of the contact compliance plotted as inverse of square root of the contact area to determine load frame compliance b (From Manual Nano Indenter)

The calculated load frame stiffness was used to obtain the hardness and the elastic modulus of the fused silica sample based on another iterative process for diamond area calibrations. The data obtained was used to plot the experimental contact area as a function of the contact depth. The curve obtained was run through a curve fit based on the polynomial function as presented in equation B1.

\[
A = 24.5h_c^2 + m_1 h_c + m_2 h_c^{1/2} + m_3 h_c^{1/4} + m_4 h_c^{1/8} + m_5 h_c^{1/16} + m_6 h_c^{1/32} + m_7 h_c^{1/64} + m_8 h_c^{1/128}
\]

B1
Where, $A$ is the area based on indentation displacement, $h_c$. Initial factor of 24.5 is used to account for the perfect Berkovich tip indenter. The coefficients in the equations $B_1$, $m_1$ to $m_2$ accounts for the imperfections in the tip and were calculated from the curve fit analysis of the area and the contact displacement data. Figure B3 presents the experimental data obtained during calibration of the nanoindenter.

**Figure B3:** Experimental area as a function of contact displacement for diamond tip area function calibration using indentation experiments performed on the fused silica.
APPENDIX C

CRYSTALLINITY DETERMINATION OF THE SEMICRYSTALLINE POLYMERS

The degree of crystallinity determination of the semicrystalline polymers was determined by differential scanning calorimetry (DSC), using a DSC from Thermal Analysis (TA) Instruments, UK. The polymeric samples, approximately 5-10 mg, were weighed in aluminium pans and heated at a constant rate of $10^0\text{C/min}$ in the DSC. The samples were heated from room temperature to $400^0\text{C}$, a temperature well above melting point of PEEK ($T_m \approx 343^0\text{C}$). An inert atmosphere during calorimetric analysis was provided using nitrogen gas circulation in the DSC chamber. A typical of the DSC curve obtained for crystalline (annealed) PEEK is shown in figure C1. An exothermic peak can be observed at approximately $150^0\text{C}$, this corresponds to the glass transition of the semicrystalline polymeric sample. A final endothermic peak was observed at melting temperature ($\approx 340^0\text{C}$) of the polymeric sample. The heat absorbed by the polymeric sample in the endothermic peak corresponds to the heat of fusion of the polymer. The degree of the crystallinity can then be calculated using equation C1.

$$\chi = \frac{\Delta H_f}{\Delta H_m}$$

(1)

Where, $X$ is the crystallinity of the semicrystalline polymer, $\Delta H_f$ is the heat of the fusion of the semicrystalline polymer and $\Delta H_m$ is the heat of fusion/melting corresponding to a 100% crystalline sample. Since the semicrystalline polymers cannot be manufactured with 100% crystallinity, therefore it is the extrapolated value. The melting enthalpy of 100% crystalline PEEK sample is reported as 130 J/g in literature (Tregub A. et. al. 1994, Naffakh M. et al. 2006)
Figure C1: A typical DSC curve for the annealed PEEK sample with a heating rate of 10 °C/min to a maximum temperature of 400 °C.
APPENDIX D

NANOINDENTATION EXPERIMENTAL DATA SETS

Figure D1: Indentation load-displacement data for the as received PEEK sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. The compliance curves were obtained from the nanoindentation of the semicrystalline PEEK nominally 100 µm apart.
Figure D2: Indentation load-displacement data for the as received PEEK sample at constant strain rate. The strain rate was maintained at 0.025 sec$^{-1}$ during loading segment. The compliance curves were obtained from the nanoindentation of the semicrystalline PEEK nominally 100 µm apart.

Figure D3: Indentation load-displacement data for the as received PEEK sample at constant strain rate. The displacement rate was maintained at 10 nmsec$^{-1}$ during loading segment. The compliance curves were obtained from the nanoindentation of the semicrystalline PEEK nominally 100 µm apart.
**Figure D4:** Indentation load-displacement data for the as received UHMWPE sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. The compliance curves were obtained from the nanoindentation of the semicrystalline UHMWPE nominally 100 µm apart.

**Figure D5:** Indentation load-displacement data for the as received PMMA sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. The compliance curves were obtained from the nanoindentation of the PMMA nominally 100 µm apart.
**Figure D6:** Indentation load-displacement data for the as received PC sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. The compliance curves were obtained from the nanoindentation of the PC nominally 100 µm apart.

**Figure D7:** Indentation load-displacement data for the as received PS sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. The compliance curves were obtained from the nanoindentation of the PS nominally 100 µm apart.
**Figure D8:** Indentation load-displacement data for the as received PP sample at constant loading rate. The loading and unloading rates were maintained at 300 μN/sec. The compliance curves were obtained from the nanoindentation of the PP nominally 100 μm apart.

**Figure D9:** Indentation load-displacement data for the 30%(w/w) carbon fibre PEEK composite sample at constant loading rate. The loading and unloading rates were maintained at 300 μN/sec. The compliance curves were obtained from the nanoindentation of the composite nominally 100 μm apart.
Figure D10: Indentation load-displacement data for the 30% (w/w) glass fibre PEEK composite sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. The compliance curves were obtained from the nanoindentation of the composite nominally 100 µm apart.

Figure D11: Indentation load-displacement data for the quenched PEEK sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. The compliance curves were obtained from the nanoindentation of the polymeric sample nominally 100 µm apart.
Figure D11: Indentation load-displacement data for the annealed PEEK sample at constant loading rate. The loading and unloading rates were maintained at 300 µN/sec. The compliance curves were obtained from the nanoindentation of the polymeric sample nominally 100 µm apart.
REFERENCES


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