

VARIABILITY, OXIDATION RESISTANCE  
AND WEAR OF 'MEDICAL GRADE' ULTRA-  
HIGH MOLECULAR WEIGHT  
POLYETHYLENE

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## **Abstract**

The aim of this project was to examine factors affecting wear mechanisms in total knee replacement (TKR). The hypothesis of this work was that manufacturing, processing and sterilisation techniques for 'medical grade' ultra-high molecular weight polyethylene (UHMWPE) would result in a variability in material properties, oxidation resistance and wear performance.

Examination of stock materials and retrievals showed there were differences in grain structure, extent of consolidation and resistance to oxidation. A novel staining technique was developed which Fourier Transform Infrared spectroscopy showed corresponded to regions of oxidation.

Examination of retrieved TKRs and wear test specimens showed that the development of a sub-surface oxidised band (due to post irradiation damage) was related to delamination wear. It was also found that surface oxidation of UHMWPE was caused by articulation with the femoral component.

The development of an artificial ageing regime allowed the effect of oxidation on the material and wear properties of polyethylene to be investigated. This showed that a critical level of oxidation was required before delamination occurred. Oxidation levels associated with five to ten years of shelf-ageing resulted in a reduction in fatigue life of two orders of magnitude and an increase in crack propagation rates by 10-400 times (depending on manufacturing method). Oxidation also resulted in a reduction in UTS, and brittle fracture of test specimens.

Investigation of a modified polyethylene showed that annealing UHMWPE after irradiation resulted in a three times reduction in the wear rate compared to untreated polyethylene. Annealing also produced a reduction in the level of oxidation induced using artificial ageing and a wear rate which was ten times lower than standard UHMWPE. However this modified material was not totally resistant to oxidation.

Many reports of excellent wear properties and long-term survivorship rates for directly moulded polyethylene components have been published and in my study this material was found to have a greater oxidation resistance than other materials, as well as lower wear rates. In a ten million cycle simulator test, artificial ageing of directly moulded polyethylene resulted in no significant increase in wear rate when compared with un-aged material. Delamination wear did not occur in either shelf-aged or artificially aged directly moulded components, whereas delamination did occur in oxidised non-directly moulded components.

My study demonstrated differences in 'medical grade' polyethylene manufactured by different techniques. This affected the resistance of UHMWPE to oxidation and to wear.

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## CHAPTER ONE

### INTRODUCTION AND LITERATURE REVIEW

## 1.1 Introduction to Orthopaedic Implants

Artificial implants are needed to remedy disease, trauma and congenital defects which can affect any part of the body. The best known implants include heart valves and joint replacements such as hip and knee prostheses. The common requirements for all implants are a reduction of pain and the need for a biologically inert material to replace the part of the anatomy which is no longer able to function adequately for the patients needs. Joint replacement allows restoration of function and improvement in quality of life. Although replacement may originally have seemed a radical course of action, it has been shown in the past three decades to be a successful procedure. Hip and knee prostheses are now generally recognised to have a survivorship of approximately 95% at ten years. This means excellent results for the vast majority of patients. However, in young active patients where the replacements have to last considerably longer than ten years, revision operations may well be expected. In order to increase the longevity of replacements, particularly for young patients, future improvements need to be made. Potential reasons for failure include selection of the wrong prosthesis design, surgical misalignment and inadequate material properties for the required function of the joint. These are problems which researchers are constantly striving to overcome.

The material properties of the prosthesis is one of the greatest challenges. Any artificial material placed in the body is at an immediate disadvantage to a natural joint, because it does not have the ability to adapt to the stresses it experiences and to repair and adjust itself appropriately. This is most clearly shown in hip replacement where the alterations in the stresses within the bone on insertion of a prosthesis, results in stress shielding and bone loss. Within a natural healthy joint lubrication produces exceeding low friction and therefore there is little wear of the articular surfaces. However, in an artificial joint, the coefficients of friction are much higher and this leads to greater wear, which results in the generation of particulate debris which is foreign to the body. It is thought that the amount of debris is important to the response produced by the body, as are the shape and size of particles produced, which can eventually result in osteolysis and bone resorption.

This study was concerned with the wear of the plastic component in total joint replacement (TJR), and more specifically in total knee replacement (TKR). The design of TKR must give suitable stability to the patient, whilst allowing sufficient laxity to allow normal motion to occur. The choice of prosthesis design will depend on the age of the patient, activity level, bone stock available and inevitably, cost. TKRs vary from fixed hinged designs, which only allow flexion-extension motion, through

stabilised designs, aimed at patients with weak ligaments and muscular support to condylar and meniscal designs which allow the greatest range of motion.

Reviewing literature over the last ten to fifteen years indicates that two factors are important in determining wear of an implant. Particularly for knee joint replacement, geometry appears to be a crucial factor determining contact pressures on the polyethylene which can influence the wear of this material. Another more recent factor which plays a significant role in the wear of this material is the quality of the polyethylene.

## 1.2 Hypothesis and Aims

**The hypothesis of this work was that manufacturing, processing and sterilisation techniques for 'medical grade' ultrahigh molecular weight polyethylene result in a variability in material properties, oxidation resistance and wear performance.**

It should be noted that throughout the course of this study the speed of change of the perceived ideas on the affect of manufacturing and sterilisation processes on the properties of UHMWPE has been rapid.

The objectives of this study were

1. to examine various forms of fabricated UHMWPE to discern differences in their microstructure
2. to examine the affect of material consolidation and oxidation resistance on the wear characteristics of various materials, by examination of retrieved tibial components
3. to investigate the oxidation behaviour of UHMWPE by means of an artificial ageing technique and relate this to mechanical and wear properties of UHMWPE
4. examination of modified a UHMWPE to elucidate whether improved wear properties have resulted, and
5. to examine the oxidation resistance and wear of directly compression moulded polyethylene.



### 1.3 Design of Total Joint Replacements

Both total hip and total knee prostheses have similar material pairings for resurfacing the affected joint. Knee prostheses consist of a metallic femoral component to resurface the condyles of the distal femur and a plastic tibial component to resurface the proximal tibial surface, which is usually metal backed to aid fixation. The tibial surface is usually dished to increase stability and reduce stresses on the plastic. A plastic patella button is optional. Similarly, hip prostheses consist of a plastic acetabular cup, seated in the pelvis (usually metal backed) in which articulates a replacement femoral head with an attached stem for insertion and fixation within the femoral canal.

The first hip joint was implanted by McKee in the late 1950s and was metal-on-metal using a cast chromium-molybdenum alloy (28Cr-8Mo). In 1958 Charnley inserted the first PTFE Teflon® cup against a stainless steel femoral head. This was followed by the first UHMWPE cups in 1962, due to the unacceptable wear associated with PTFE. Today in hip and knee replacements, the most widely used materials are cobalt-chrome (Co-Cr) alloy against UHMWPE. In hip joints other metals such as titanium and stainless steel have been used in association with UHMWPE, but other material combinations have also been tried. Ceramic against polyethylene is a preferred combination due to the excellent abrasion resistance of the ceramic, but such components are much more expensive than their metallic counterparts. There are different ceramics available and alumina against UHMWPE is widely used in Europe, though zirconia is reported to have higher impact resistance. Metal on metal articulations have come back into favour recently, but cobalt chrome articulating against itself is associated with high friction. Ceramic on ceramic has also been used, but very strict tolerances of the components are required, but if this can be achieved, very low wear rates can be attained<sup>1</sup>.

The design variables of a prosthesis will affect the wear seen *in vivo*, since the design of the joint and its subsequent conformity will decide the stresses experienced by the polyethylene bearing surfaces. The thickness of the polyethylene will also have a large bearing on the magnitude of the stresses experienced. This is important as contemporary knee designs differ considerably in conformity and also in thickness, two of the factors affecting the stresses associated with surface damage and thus wear debris production<sup>2</sup>.

When choosing a prosthesis for implantation, the conformity of the joint is potentially the most important parameter, not only because of the associated stress distribution, but also because a compromise has to be struck to achieve maximum functionality. Low conformity is needed in a knee joint for freedom of motion and to allow for flexion-extension, adduction, abduction and internal-external rotation. In addition low conformity designs provide less resistance to torsional loads, thus reducing stress at the interface between the prosthesis and underlying bone<sup>3, 4</sup>. The disadvantage with non-conforming designs is that they have small contact areas which produce high contact stresses at the surface of the polyethylene insert. In contrast, if a joint is highly conforming, the tibial surfaces carry a greater portion of the load, so the stresses at its interface with the underlying bone will be larger, since highly constrained prostheses do not allow dissipation of stresses through ligaments and soft tissues. This can lead to a susceptibility of the tibial component to loosening and subsequent failure. Consequently there is a trade off between higher stress at the surface or at the bone/implant interface<sup>5</sup>.

The conformity of a joint depends on the radius of curvature of the tibial component in both the anterior-posterior (A-P) and medial-lateral (M-L) directions. Increasing conformity in the M-L direction increases the constraint to internal-external rotation. The contact stress is also greatly affected by the M-L radius with the lowest contact stresses associated with conformity in the medial-lateral direction<sup>5</sup>. A component that is flat in the A-P direction allows a large range of motion. However, the drawback of this design is that it does not cope well with varus or valgus moments, which can concentrate stresses on the periphery of a component and have been reported to cause delamination and cracking<sup>6</sup>. In addition changing the femoral radius of curvature will also influence the stresses experienced by the polyethylene. Decreasing femoral sagittal radii is designed to allow rollback and an increased range of flexion but this results in tibial components being more conforming in extension than flexion<sup>7</sup>. This is important since the highest loads are imparted when the knee is in flexion, such as stair climbing, when there is a decrease in contact area and thus higher contact stress. The magnitude of changes in contact stresses from one design to another depends mainly on conformity but also on elastic modulus and polyethylene thickness<sup>8</sup>.

It can therefore be seen that the geometry of the knee will affect the wear mechanisms experienced by the joint. However, the ideal surface geometry to ensure low wear may not be viable since a consideration in the choice of TKR for a particular patient is the function of their surrounding tissues and ligaments, particularly the cruciate ligaments. Clinically the loss of the anterior cruciate ligament (ACL) does not usually impair low demand activities, but loss of the posterior cruciate ligament (PCL) has a

serious affect on most activities<sup>9</sup>. This is because the PCL is an important biological stabiliser of the knee, capable of absorbing anterior-posterior shearing forces<sup>10</sup>.

In some patients musculature may be weak resulting in the need for prostheses which will substitute for the lacking structures, however some surgeons prefer to resect the cruciate ligaments in the belief that improved performance will be achieved. The ability of the PCL to absorb forces across the joint means that in a knee where the PCL is weak or sacrificed, the forces must be borne by a constrained prosthesis and hence by the bone-cement interface<sup>10</sup>. In patients with normal musculature, cruciate sparing designs are used. These have nearly flat tibial surfaces to allow sufficient laxity of the joint for the PCL to function properly. These components have a large range of motion since they are flat in the A-P direction but they have stability due to the PCL constraint. Thus a PCL retaining design of knee replacement allows maintenance of the normal kinematics of the knee after TKA<sup>10</sup> with fewer problems at the bone-cement interface than in a comparative PCL sacrificing design, but with potentially greater wear at the polyethylene surface. PCL substituting designs give joint stability and provide more conforming surfaces and have demonstrated excellent survivorship and a greater range of motion<sup>11</sup>.

The trade-off between stress at the polyethylene surface or at the bone-implant interface has been illustrated *in vivo*, with certain types of design more prone to certain wear mechanisms. As we have seen low conformity designs are usually associated with high contact stresses. Non-congruent designs have been reported to have greater wear than fully congruent designs<sup>12</sup> with degree of overall wear, cracking and delamination statistically reduced for highly congruent components compared to either curve on curve or flat on flat components<sup>13</sup>. In addition, highly localised severe stresses can occur along the edges of a non-conforming component if there is any varus/valgus misalignment<sup>6</sup> and in conforming components this misalignment results in localised severe stresses along the intercondylar notch region, where these designs resist rotational movements<sup>13, 14</sup>. These localised stresses been reported to lead to localised delamination wear at the tibial spines and insert edges due to the very high contact stresses<sup>13, 14, 15, 16, 17</sup>. Increased wear has been reported in conforming surfaces compared to non-conforming surfaces, due to cement entrapment<sup>18</sup> leading to third body wear.

For partially conforming condylar designs, the contact stresses can be higher than the uniaxial yield strength of the plastic<sup>13</sup> (around 21MPa). Given these conditions, the most important wear mechanism is fatigue, which has been borne out by pin-on-disc and implant retrieval studies<sup>19</sup>. Although the yield stress is often quoted as being exceeded, an FEA study by Bartel et al<sup>2</sup> showed UHMWPE can withstand contact

stresses greater than the yield stress. However, the articulating surfaces of a prosthesis move during flexion-extension resulting in portions of the surfaces being subjected to cyclic stresses. Compression under the contact area and tensile forces near the edges of contact as the polyethylene is stretched, results in shear stresses just below the surface of the material. Continuously exceeding the yield stress with cyclic stress constantly changing from compressive to tensile on some areas of the polyethylene surface will result in a fatigue mechanism of wear.

The contact areas and pressures will also change since UHMWPE components will creep and wear over time. This results in components becoming more conforming, increasing contact areas and thus reducing contact stresses within the polyethylene. The extent of this change has been shown to be small in conforming tibial designs whilst less conforming designs show small decreases in contact stress *in vivo*<sup>20</sup>. The greatest deformation reported on the least conforming designs however was not sufficient to lower the stresses compared with more conforming designs.

The high stresses at the implant/bone interface associated with more conforming designs can be overcome without reducing congruency, with the use of mobile bearing knees. Here the femoral surfaces closely conform with the upper plastic bearing surface but the lower surface is not attached to a tray or to the bone, but is flat and slides on a polished flat metal tray or is guided in tracks. This avoids transmitting high shear to the bone-prosthesis interface, allows rotational misalignment and therefore allow articular surfaces to remain congruent while providing freedom from constraints, to mimic physiological movements of the knee. Low wear rates have been achieved clinically, with reports of very low wear rates for the Oxford unicompartmental meniscal knee, at less than a quarter of a millimetre in ten years<sup>21</sup>. This is in contrast to standard unicompartmental designs which are unconforming and have resulted in failure rates at 10 years which are much higher than those of TKR. The potential disadvantage of meniscal bearing designs however, is the size and morphology of the wear debris produced. This is thought to be of a smaller diameter than that typically seen in TKR, and more akin to that associated with total hip replacement (THR). This is potentially unfavourable as small particle size has been reported to be related to the incidence of osteolysis surrounding hip replacements<sup>22</sup>.

Another design issue related to the wear of total joint replacement (TJR) is of metal backing. Metal backing of polyethylene joints was first introduced for acetabular components in 1971 by W.H. Harris, who developed an interchangeable liner to combat anticipated problems with polyethylene wear<sup>23</sup>. A decade later, FEA studies showed this reduced the stresses in the cement and surrounding bone. These developments were subsequently applied to the knee in both tibial and patella

components to improve durability of fixation. Several experimental studies suggested that metal backing of the tibial component would more evenly distribute load to the bone of the proximal tibia<sup>10, 24</sup>. Stress analysis has demonstrated reduced compressive loads at the bone-implant interface<sup>4</sup> however, the consequent increase in contact stresses was not envisaged. The stresses are elevated with metal backing due to the rigidity of the metal surface<sup>19</sup>. In addition, reduction in polyethylene thickness by 2-3 millimetres to accommodate the metal backing in the same joint space can lead to an unacceptable increase in the contact stresses experienced by the polyethylene and can result in failure. In non-congruent designs, which are normally associated with increased wear, thinner polyethylene has shown greater wear than the same component with a thicker tibial plastic<sup>13</sup>. In hip replacements a 25% increase in wear rate for every 1mm decrease in polyethylene thickness in metal backed components has been found, along with a significantly lower annual volumetric wear rate in all polyethylene components compared to metal backed acetabular components<sup>25</sup>.

Thus the stresses experienced in TJR are a function of the polyethylene thickness of the components. Bartel et al<sup>5</sup> suggested a minimum polyethylene thickness of 8-10mm since reports of components with polyethylene less than 6mm thick had a higher degree of burnishing, pitting, cracking and delamination than thicker bearings (thickness > 6mm)<sup>13</sup>. The stresses in a component will increase as thickness decreases, because the structural stiffness of the polyethylene component increases, even though the elastic modulus stays the same. Therefore to keep the polyethylene to its recommended minimum, increased bone resection is required. This is a disadvantage since the mechanical strength of the tibia decreases with increasing depth of resection, so this may not be desirable, especially in a patient with osteopenic bone<sup>24</sup>.

Metal backing is advantageous in allowing intra-operative flexibility with modular polyethylene inserts. This allows interchangeability during surgery for an alternate thickness of insert or for easy replacement at revision surgery without disturbing the tibial fixation. Metal backing also has the advantage that it allows access for the inclusion of screws to enhance tibial fixation and allows cementless fixation with the use of porous-beaded surfaces for bone ingrowth.

Metal backing of components has introduced another potential wear surface, with wear on the inferior tibial polyethylene surface receiving some attention in recent years. Particular attention has been paid to that occurring around screw holes, but relative motion between the polyethylene and metal tray could lead to abrasion and burnishing on a previously unconsidered surface. Damage scores on the inferior surface of tibial inserts have been significantly correlated to time in use<sup>26</sup>. Polishing the metal backing (cf. machining) has shown only a slight possible benefit in an *in*

*vitro* study simulating of a year of function for various designs<sup>27</sup>. Higher wear scores have also been found for inserts mated against metal trays with holes, compared to trays without holes. This is due to cold flow of polyethylene into screw holes and has been reported by several authors. Collier et al<sup>13</sup> found greater than 1mm creep into screw holes. Wasielewski et al<sup>17</sup> found severity of cold flow into screw holes of the tibial tray increased with implantation time, but was reduced by increasing thickness of polyethylene. Some tibial inserts have been found to have greater cold flow into screw holes due to relative micromotion between the polyethylene and metal tibial tray<sup>17</sup> leading to evidence of osteolysis.

Overall, no improvement in terms of increased survival for TKR has been reported with the advent of metal backing and has been seen has been associated with a number of cases of increased wear.

#### 1.4 Material Properties of UHMWPE

Polyethylene (UHMWPE) has been the material of choice for the past three decades in TJR. Charnley initially manufactured hip replacements from PTFE due to its chemical inertness and its low coefficient of friction. However, within a couple of years the amount of wear seen *in vivo* was unacceptably high so a new material was needed. To keep with low friction couples he tried UHMWPE. Polyethylene also had the desired properties for an implant material of low biological and chemical reactivity. Charnley achieved low friction and low wear rates with UHMWPE and there hasn't been another material used as successfully since. Other materials have been tried over the years, including PTFE, high density polyethylene (HDPE), polyesters, polyacetal and carbon-reinforced UHMWPE with the latter two tried in the 70's and 80's. The use of carbon fibre reinforced polyethylene has been found to increase stresses by up to 88%<sup>28</sup>, which can result in early catastrophic wear<sup>12</sup>. Consequently with only these few exceptions, the only bearing material used since the 1960's is UHMWPE.

Since its introduction polyethylene has generally functioned well. Cases of early failure and reports of long-term need for revision surgery are of great concern and much research has been directed at overcoming the associated problems. These reports of clinical failures bias the picture against what is generally a very successful material, with successful outcomes for many prostheses being around 95% at ten years<sup>29, 30, 31, 32, 33</sup>. However, it is difficult to find a replacement material since this would have to be biocompatible and would need the appropriate mechanical properties to allow it to

function long-term. Consequently research tends to be directed at ways to improve the present material.

UHMWPE has unique properties making it ideal as an implant material such as abrasion and wear resistance, impact strength, toughness, low frictional characteristics and physiological compatibility. Properties such as high impact strength, excellent wear and abrasion resistance have made it ideal for use in many industries including use as bearings, bushings, drive gears, sliding chutes and hoppers. In fact less than one percent of the worlds production of UHMWPE is used for orthopaedic implants. UHMWPEs unique properties are a result of its high molecular weight which ranges from 2-6 million, compared to high density polyethylene which ranges from 50,000-200,000. Lower molecular weight polyethylenes have a lower wear and abrasion resistance and thus HDPE proved unsuccessful as a bearing material.

Since wear of polyethylene has been directly related to its molecular weight, any process which leads to reductions in the molecular weight of this material should be avoided. Variables identified that can affect molecular weight include quality of resin, irradiation sterilisation and atmosphere during this process<sup>34</sup>. Another factor affecting wear of polyethylene is the material properties of the manufactured material. The manufacturing processes by which UHMWPE can be formed are described later in this section. The properties of the end product depend on the grade of resin used and the method by which it is manufactured. Table 1.1 lists the commonly used resins and manufacturing methods, since the introduction of UHMWPE in the early sixties.

Table 1.1 - Manufacturing methods and resin types for UHMWPE (from Poggie et al.<sup>35</sup>)

Time Frame	Resin Type	Manufacturing Method	Trade Name
1960s - 1990s	GUR 1120	sheet moulding	Chirulen, RCH1000
1972 - early 1980s	1900 resin	sheet moulding	Hercules 1900
Early 1980s - 1995	Himont 1900*	direct moulding	Himont/Hifax 1900
Early 1980s to 1990s	GUR 4150	ram extrusion	GUR4150 extruded bar
Mid 1990s	GUR 1020 & 1050	sheet moulding	compression moulded sheet

\* now Montell 1900H resin.

The classification system for GUR resins is as follows<sup>35</sup>:

first digit:	1 - resin from Hoechst, Germany;	4 - Hoechst, Bayport, TX.
second digit:	0 - no calcium stearate;	1 - contains calcium stearate.
third digit:	2 - Mol. wt. 2-4 million;	5 - Mol. wt. 4-6 million

The 1900 resin is the only resin widely used that is not manufactured by Hoechst. This resin had a molecular weight of 2-4 million during the 1970s but this was increased to 4-6 million during the 1980s<sup>35</sup>. Since the molecular weight is one of the most important parameters determining material and mechanical properties the choice of resin is important. UHMWPE with a molecular weight of 2-4 million is thought to have higher toughness whereas material with a molecular weight of 4-6 million is thought to have a higher abrasion resistance. This was shown in a ring-on disc study by Huber & Plitz<sup>36</sup> who found improved wear rates for 1150 material compared to 1120 material (both pressed material). However, an UHMWPE with a molecular weight between 2-4 million has greater molecular mobility and this may enhance resin consolidation and resistance to degradation via increased crosslinking.

## 1.5 Manufacture and Processing

### 1.5.1 Background

Prior to an examination of the wear of total joint replacements, a full understanding of the raw materials used and the processing requirements to manufacture the final medical device are needed. The raw material used in the production of UHMWPE material is a fine powder which is manufactured by an addition reaction using high purity ethylene gas and Ziegler Natta catalysts. The conditions of manufacture are very important as these affect the range of molecular weight of the powder, which in turn will affect the wear properties of the UHMWPE material.

### 1.5.2 Manufacture of UHMWPE Powder

The manufacture of UHMWPE is a low pressure process. The catalyst used is either titanium chloride or an organo-aluminium compound. Both starting materials and catalysts are sensitive to air and moisture so the process is performed in an inert atmosphere of nitrogen. High purity ethylene gas is fed into the reactor containing the catalyst. Polymerisation takes place at 75-85°C and a pressure of 0.5-2MPa. Ethylene molecules add on to the catalyst particles (5-10µm) until they enclose it (~10,000 ethylene molecules). Molecular weight can be varied by adding small amounts of



hydrogen into the reactor. Alternatively increasing the temperature will lead to an increase in the molecular weight.

From this powder there are three main methods of manufacture used to produce polyethylene, all based on sintering the powder particles. These are ram extrusion, compression moulding and direct compression moulding. Other manufacturing processes such as injection moulding are unsuitable because they degrade the molecular weight of the polymer<sup>39</sup>. The first two processes produce bars and slabs of material which then have to be machined to produce the required final product. The third process can be used to directly manufacture the final component.

### 1.5.3 Ram Extrusion

Ram extrusion is a dynamic, continuous process which is fast and efficient but requires stringent control of 'steady-state' processing conditions. The polymer powder is fed into a screw which compacts and mixes the polymer. The powder flows due to the heat from the barrel walls, and the mechanical action of the screw. The barrel is a parallel section of the same diameter as the final product required. Pressure is a function of the die design as friction is caused at the walls, so the longer the die the higher the pressure. The forces exerted by this process are in the range 30 – 110 MPa . Once the powder melts it is forced through a die and then cooled to form the final product, usually a rod of constant section. During manufacture the molecules are oriented within the die due to shear flow in the direction of extrusion. The rate of cooling of the extrusion may determine the degree of crystallinity and hence affect mechanical and other properties. This process can be performed in an inert gas atmosphere and also the process can be sealed to remove contaminants. This process requires a post-manufacture anneal of the material to reduce stresses imparted in the material by this method of manufacture.

### 1.5.4 Sheet Compression Moulding

Compression moulding produces large sheets of material by pressing the polymer powder to the desired form. The powder is then heated under pressure to form a block of material. Pressure is applied throughout the cycle to remove all gases and voids and to ensure complete consolidation. The platens can be heated, and if so this is usually achieved by oil or steam. During cooling, the part can be held at the recrystallisation temperature to increase the percentage crystallinity of the material. This process has a fairly short cycle time, as a 100mm thick sheet will take approximately 300 minutes to make. The parameters used are very important as rate of applied pressure, heating rate and cooling rate will all affect the final properties and the crystallinity of the material. Sheet compression moulding is a batch process which has advantages of inexpensive

tooling costs due to their simplicity and good material consistency. This process needs to be performed under environment control to reduce airborne contaminants. There is a high material loss to product ratio. This process requires a post-manufacture anneal of the material to reduce residual stresses caused by the forming process.

### 1.5.5 Direct Compression Moulding

This process is more versatile as blanks, semi-finished and finished products can be manufactured using a similar process to that described above. Direct compression moulding to the final component produces a product with a glossy finish which requires no machining to final shape. In this process, much smaller quantities of powder are used and the moulds are shaped to produce the required final shape. Sizing however can be a problem due to shrinkage in the mould. The heating time is a critical parameter as this will affect the UTS and impact strength. The technology for this process is difficult and labour intensive with a requirement for multiple tools. However compression moulding of small components allows for accurate control of processing parameters<sup>38</sup>. Processing can be performed in an inert atmosphere. Other advantages of direct compression moulding include control over bearing surface roughness, optimisation of the applied heat and pressure for each component configuration, avoidance of machined surfaces and direct attachment of the tibial plastic to the base plate.

For all these processing techniques strict processing control is required. The most important processing parameters for moulding techniques are the melt cooling rate and the melt pressure. Ramani & Parasnis<sup>39</sup> and Ramani et al<sup>40</sup> investigated the different processing variables on the quality of the moulded part. They found melt cooling rate affected recrystallisation and consolidation. A slow cooling rate allows the polymer sufficient time to recrystallise imparting good consolidation, a low number of defects, high crystallinity, high modulus and strength. As cooling rate is increased, crystallinity and modulus reduce. A high pressure during melt and recrystallisation causes the individual fold-lamellae time to thicken, increasing the crystallinity of the polymer. Care has to be taken though as too high a pressure (>16MPa) will destroy the crystals. However, if a pressure significantly lower than the compressive strength of the polymer was used, incomplete fusion occurs, resulting in a reduced modulus<sup>39</sup>. The best results are achieved at a pressure close to the compressive strength of UHMWPE. More homogenous products are likely to be produced by pressure driven compression moulding as little flow of the material occurs, compared to ram extruded products where significant shear occurs during the forming process. Ram extrusion is a continuous process, whereas both compression moulding and direct moulding are

batch processes, thus with ram extrusion it is more difficult to control the material properties of the plastic produced due to the larger number of variables.

### 1.5.6 Fusion Defects

When polyethylene powder is converted to a solid form by processes such as ram extrusion and compression moulding, complete consolidation of the powder is extremely difficult due to the high melt viscosity of the powder. The coalescence of the UHMWPE powder particles is driven by the action of surface tension to lower the material free energy by decreasing its total surface area. The mechanical performance of the material will depend on the degree of coalescence and consolidation during manufacture. When the powder particles do not coalesce, fusion defects and voids are left within the material leading to weaknesses in its structure. These weaknesses within the material can compromise the nominal density and the physical properties of UHMWPE<sup>41</sup>. It follows that these unconsolidated regions will affect the wear performance as well. Blunn et al<sup>16</sup> found higher wear rates in polyethylene containing a large number of fusion defects compared to polyethylene with few defects. However, although these defects have been correlated with reduced performance in knee replacements<sup>42, 43, 44</sup> such a correlation has not been shown for acetabular components where the kinematics and thus wear mechanisms are different. However, Oonishi et al<sup>33</sup> found a wide scatter in the number of fusion defects in Charnley hips examined from 1970-1990, which would be expected to lead to variable wear.

Early examination of fusion defects was concerned with how they were produced and what were their constituents. It was initially thought that they may be impurities in the polyethylene introduced during manufacture, which resulted in incomplete fusion. This was rejected in a study by Mayor et al<sup>45</sup> who found no impurities associated with fusion defects and surmised that they were just unconsolidated areas of the same material as the surrounding polyethylene. There were also questions concerning their origin and it was initially thought that they may be a result of *in vivo* wear processes. Again studies<sup>44</sup> showed that fusion defects were as common in unimplanted material as in retrievals and there was no relationship between size of defects and age of component<sup>33</sup>, so they must be a result of the manufacturing process. It has since been understood that the manufacturing process does indeed affect the number of defects found within a piece of UHMWPE. Acceptable levels of fusion defects have been decreed by ASTM and material is periodically examined by manufacturers.

The method of manufacture has been shown to play a crucial role in the number of defects within a piece of material. Wrona et al<sup>44</sup> found that GUR4120 had variable numbers of fusion defects depending on the manufacturing method. In the past, most

polyethylene components for joint replacements were made from ram extruded material as it was believed to result better consolidation. Ram extruded material is however known to contain voids<sup>46</sup> or dead zones due to material shrinkage, possible changes in pressurisation or changes in polymer consistency. These irregularities can alter the molecular weight of the material and thus leads to decreased wear resistance. However, recent trends have reversed this viewpoint with tighter processing controls improving consolidation in compression moulded material as shown by Johnson et al<sup>38</sup> who found no fusion defects in compression moulded material.

### 1.5.7 The Role of Calcium Stearate

Initial concerns over the formation of defects and the influence of impurities has been raised again recently, with particular attention to the role of calcium stearate. Calcium stearate is used as an anti-oxidant and corrosion inhibitor to prevent damage to the manufacturing moulds, as an anti-sticking agent and to enhance the flow of the material within the mould. Reports such as those by Muratoglu et al<sup>41</sup> using Fourier Transform Infrared Spectroscopy (FTIR) have shown calcium stearate in the boundaries of fusion defects and speculated that the defects are formed due to the poor mixing of stearate with polyethylene particles before consolidation. Bhambri et al<sup>46</sup> found calcium peaks using energy dispersive x-ray analysis (EDXA) at the void boundaries of a ram extruded 4150 acetabular component. These findings are backed by other authors who have found no or a limited number of defects in stearate-free polyethylene. Muratoglu et al<sup>41</sup> examined Himont 1900 and GUR4050 and found they contained virtually no fusion defects. Schmidt & Hamilton<sup>47</sup> found no fusion defects or grain boundaries in GUR1020. Swarts et al<sup>48</sup> also found better consolidation in calcium stearate free material.

The detrimental affect of defects on the material properties of polyethylene is well documented, with defects recognised as an indicator of non-fully consolidated material. This will result in a material less resistant to fatigue<sup>45</sup> and in addition, diminished tensile strength, yield strength and percent elongation have been associated with large diameter defects<sup>33</sup>. Hamilton et al<sup>49</sup> found a lack of fusion defects in GUR1020 resulted in higher ultimate mechanical properties. The detrimental affect of defects on wear properties has also been reported both *in vitro* and *in vivo*. Schmidt & Hamilton<sup>47</sup> found a lower wear rate for GUR 1020 (no defects) compared to GUR1120 in hip simulator studies. Retrieval studies such as that by Landy and Walker<sup>43</sup> suggested delamination appeared to be initiated by intergranular material defects and propagated by excessive sub-surface stresses beneath the contact zone. Mayor et al<sup>45</sup> found a statistically significant correlation between the extent of fusion defects and cracking and delamination in retrieved tibial plastics. However Blunn et al<sup>6</sup> found delamination in both the presence and absence of defects.

Some grades of polyethylene have always been manufactured without the addition of calcium stearate and recent trends have seen some manufacturers change their manufacturing procedures to incorporate this non-stearate containing material. European manufacturers in the past have mainly used GUR 1120 material, although some manufacturers are now switching to GUR 1020. In America, GUR 4150 has been the material of choice but this is now being replaced with GUR 1020 and 1050 materials<sup>35</sup>.

## 1.6 Sterilisation Methods and their Effect on UHMWPE

### 1.6.1 Sterilisation Methods

Prior to implantation, all components need to be sterilised to kill potentially harmful bacteria which could otherwise cause an infection. Early hip replacements which had PTFE as a bearing surface were sterilised using steam. However, the introduction of UHMWPE precluded the use of this method and chemical solutions were needed instead, since polyethylene has a lower temperature stability. Sterility was then obtained by soaking components in chemical solutions such as Hycolin (iodine alcohol solution), prior to implantation. From 1970/1971 onwards polyethylene components have been gamma irradiated. Other sterilisation processes are now used such as electron beam sterilisation or gas sterilisation techniques such as gas plasma or ethylene oxide. However gamma irradiation has continued to be the preferred sterilisation method, due to ease of mass sterilisation, with components then stored until required.

In recent years concern has spread about the potentially detrimental effects of gamma irradiation, especially in air. Reports of early failures of components with fatigue type wear mechanisms have been linked to a deterioration in material properties brought about by irradiation. Reports from the 1970s such as that by Chapiro<sup>50</sup> reported on the potentially detrimental affects of ionising radiation on polymers, but it hasn't been until the last decade that the affect on the long term wear performance on UHMWPE has been realised and investigated. Consequently, in recent years many manufacturing companies have switched to alternate methods of sterilisation including irradiation in an inert atmosphere or under vacuum, or the gas sterilisation techniques. The following presents a brief overview of the alternate methods of sterilisation currently employed for UHMWPE and then goes on to discuss the affects of each method (but

specifically gamma irradiation, as this has been the preferred method of sterilisation) on material, mechanical and wear properties, both *in vitro* and *in vivo*.

#### 1.6.1.1 Irradiation Processes

Gamma irradiation and electron beam sterilisation utilise high energy electrons which penetrate the thickness of the component destroying any bacteria, viruses or other microbial species which may be present. Radiation doses are measured in either Mrads or kGrays (1 Mrad = 10 kGys). A minimum dose of 25kGy is used to ensure complete sterilisation and destruction of micro-organisms.

Gamma radiation sterilisation uses a cobalt 60 source with irradiation times taking between one and a half and eighteen hours. The main advantages of gamma irradiation are its high effectivity and lack of need for a post-sterilisation treatment. The effectivity of gamma irradiation was clearly shown in a study by Masri et al<sup>51</sup> who investigated the levels of irradiation required to kill typical levels of bacteria associated with medical implants. They found the current guidelines (FDA) to be 6-10 times higher than necessary, with an acceptable level of 0.4Mrads.

Whereas gamma irradiation can take relatively long periods of time, electron beam sterilisation has a short process time<sup>52</sup> as it uses much higher energy than that used for gamma irradiation<sup>53</sup>. Other process characteristics are similar with the use of a minimum dose of 25kGray. This can be achieved in a single pass in minutes, as opposed to hours needed for gamma irradiation.

#### 1.6.1.2 Gas Sterilisation Processes

Two gas sterilisation techniques are currently used. Ethylene oxide sterilisation utilises a gas to sterilise the component by reacting with bacteria rendering them inactive. The advantage of this processes is a low cost investment for a sterilisation unit<sup>54</sup>. However, disadvantages include the time taken, elaborate process controls and post-sterilisation treatments. This process works under specific conditions and therefore stringent controls are required to ensure effective sterilisation. The concentration of gas, exposure time, humidity and temperature all have to be closely controlled. There has been some concern<sup>55</sup> over the use of this sterilisation method for medical devices since ethylene oxide is a toxic, carcinogenic substance. However, so long as guidelines are followed, there should be no risk to the patient since the gas dissolves out of the polyethylene after an aeration period. It could be argued however that no concentration is safe and complete removal of the gas is impossible. Studies such as that by Ries et a<sup>56</sup> found EtO can safely and effectively sterilise UHMWPE, in an *in vitro* study of an inoculated metal backed patella component.

Gas plasma sterilisation utilises an ionised body of gas that sterilises the surface of the component by oxidising bacterial cellular components. This is a dry, low pressure, low temperature technique that is performed under a partial vacuum.

There are some concerns with gas sterilisation techniques that complete sterilisation may not be achieved in samples with voids or defects within the polymer and also in components with irregular surfaces, screws holes or directly moulded components.

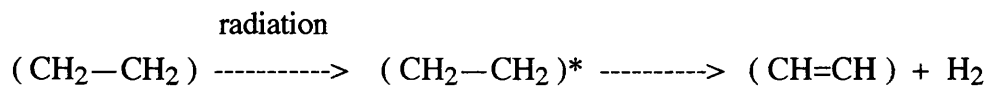
## 1.6.2 Effect of Irradiation on the Chemical Structure of Polyethylene

Irradiation sterilisation results in chemical reactions within the polymer. Chemical chains are broken, free radicals are created and these lead to further reactions, including crosslinking and chain scission. The changes in macroscopic and mechanical properties are dependent on the extent to which the molecular structure changes and this in turn depends upon the time and ambient conditions employed during irradiation<sup>58</sup>. Consequently the total absorbed dose and irradiation atmosphere are crucially important since long irradiation times of several hours are needed for gamma radiation.

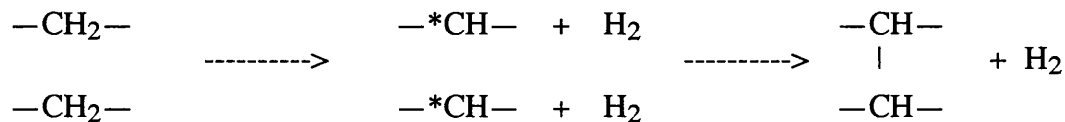
### 1.6.2.1 Free Radicals

In general, the concentration of free radicals produced upon irradiation is proportional to the radiation dose. A free radical is characterised by the presence of one or more unpaired electrons. The type of free radicals produced, their reactivity and their relative proportions has been of great interest to researchers trying to eliminate this reactive species and thus prevent long-term oxidative degradation. Free radicals are basically either primary radicals such as allyl and alkyl radicals or peroxy radicals which form when the primary radicals react with oxygen. Peroxy radicals are predominately of the scission type<sup>59</sup> leading to a reduction in molecular weight of the polymer. Free radicals are classed according to the number of carbon atoms directly attached to the carbon atom that has the unpaired electrons. Primary radicals are the least stable and tertiary radicals are the most stable.

Once a free radical is formed there may be a large number of further reactions before termination occurs. Radiation induced scission of a primary chemical bond is called radiolysis. This reaction results in hydrogen abstraction and unsaturates the polymer chain<sup>60</sup>.

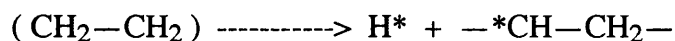


Cleavage of adjacent CH chains can result in crosslinking<sup>60</sup>:

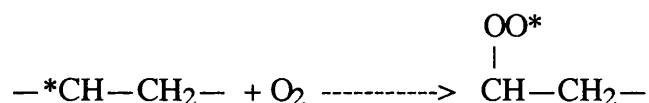


For irradiation in air, oxidative degradation of the polymer chain occurs. The following represents a possible reaction scheme<sup>50</sup>.

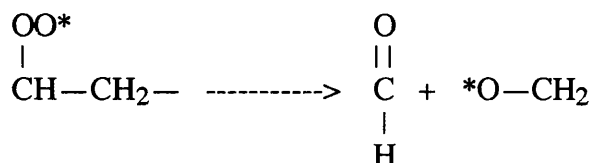
1. radiolysis of polyethylene:



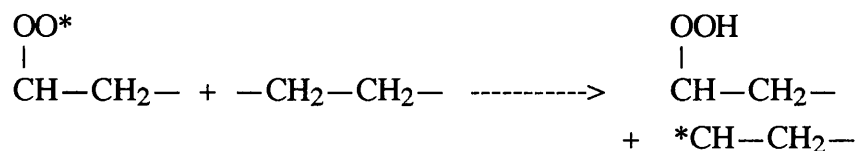
2. addition of oxygen to the polymeric radical:



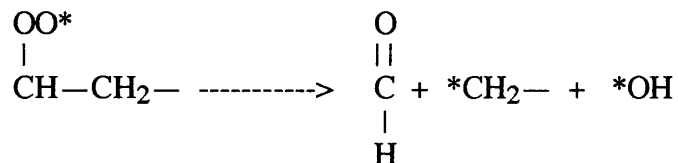
3. rearrangement of the peroxy radical:



4. hydrogen abstraction from a neighbouring molecule converts the peroxy radical to a hydroperoxide molecule and a new radical, which can continue to react:



5. a hydroperoxide group is inherently unstable and eventually decomposes on further irradiation or on subsequent storage into two new radicals:



Thus it can be seen that this reaction will continue until enough radicals are formed for termination processes to become appreciable and then a steady state is reached. These processes can clearly be seen to result in chain scission and a significant change in molecular weight.



The most common method for examining free radicals and their production is electron spin resonance (ESR). This method was used by Lee et al<sup>61</sup> who found the temperature at which irradiation is carried out is more important than atmosphere for the type of free radicals produced. At room temperature allyl radicals were formed whereas at 77K (Kelvin), alkyl radicals were formed. They found no peroxide radicals indicating the allyl radicals would not easily react with oxygen to form peroxy radicals. Other authors<sup>62, 63</sup> however have reported that primary radicals have a high affinity for reacting with oxygen. In contrast to Lee et al<sup>61</sup> and Gsell et al<sup>64, 65</sup> found that vacuum was more significant than temperature in the reduction of oxidation occurring upon gamma irradiation. The reason given for low oxygen indices for samples irradiated under vacuum at 77K was that most alkyl radicals produced at such low temperatures would recombine without the production of peroxy radicals due to the absence of oxygen.

The type of radical produced and its affect on chemical structure depends on the atmosphere around the material. Peroxy radicals are produced when oxygen is present, so these type of radicals are often found in high concentrations in surface areas. Primary radicals are usually found deeper within the material where there is a lack of oxygen. The surface layer of the material has been reported to act as an oxygen barrier, so primary sub-surface radicals are exposed to minimal oxygen and exist for several years after sterilisation<sup>62</sup>. However some peroxy radicals will be found sub-surface due to oxygen dissolved within the polymer.

The reaction of free radicals with oxygen leads to the formation of certain oxidation products. These oxidation products are easily identified using spectroscopic analysis. Fourier Transform Infrared Spectroscopy (FTIR) is used most frequently as it is useful in the identification of certain functional groups within a molecule. When molecules of a chemical compound are exposed to electromagnetic radiation they absorb energy. The particular energies absorbed provide an indicator of the structure and a spectrum is produced which gives a graphical representation of the absorbance pattern. The type of oxidation product is important since some reactions will result in chain scission with a consequent reduction in molecular weight. Gamma irradiation of UHMWPE is thought to lead mostly to ketone formation, which does not necessarily break the UHMWPE molecule, but it is a potential location for degradation *in vivo*<sup>66</sup>. Further chemical reactions occur post sterilisation both when stored prior to implantation and once implanted. These are discussed in detail in section 1.6.6.1.

### 1.6.3 Effect of Sterilisation Atmosphere on Material Properties of Polyethylene

Gamma irradiation results in chain scission which can then lead to crosslinking or oxidation and the predominance of one reaction will depend on the atmosphere present. If oxygen is present, free radicals will react preferentially with it, thus causing oxidation of the material. In the absence of oxygen, free radicals can react with each other or the polymer chain resulting in crosslinking. An understanding that elimination of oxygen during the irradiation process will promote crosslinking over oxidation has resulted in the use of inert gases and low vacuum, during sterilisation. Hawkins & Gsell<sup>67</sup> found irradiation in an inert (nitrogen) atmosphere reduces oxidation to essentially zero, whereas in ambient air, significant oxidation occurred. They<sup>67</sup> also found that the extent of oxidation diminished with depth into the sample. Although crosslinking may preferentially occur during gamma sterilisation in inert atmospheres, it has been found to have little effect on the long term oxidation of implants<sup>68</sup>. This has been attributed to the inert gas being unable to prevent the formation of free radicals or ensure their complete reaction. Thomas et al<sup>69</sup> and Trieu et al<sup>63, 70</sup> used ESR to study free radicals in shelf-aged UHMWPE after irradiation. They both found significant concentrations of free radicals after several years and suggested that even samples irradiated in an inert atmosphere could be a potential cause of long term oxidation, due to long lived radicals. This was also reported by Sanford & Saum<sup>71</sup> who found that nitrogen packaging will only retard oxidation during storage, as once this environment is removed the radicals within the polymer can then react with oxygen. Argon packaging has also been reported to be ineffective in eliminating or significantly reducing irradiation induced oxidation<sup>72</sup>.

A further potential consequence of switching to irradiation in the absence of oxygen is that it may have a significant influence on the sensitivity of the irradiation process for inactivation of bacterial spores. Many current practices have changed to the use of inert atmospheres, with no apparent regard to the effect of this to the efficacy of sterilisation<sup>73</sup>.

Due to the existence of free radicals post irradiation, non-irradiation sterilisation methods are preferred by some manufacturers, as studies have reported the absence of free radicals in these materials. Jahan et al<sup>62</sup> found minimal to no free radicals in the surface and core regions of EtO sterilised samples and this has been reported to lead to prevention of oxidation on the shelf or *in-vivo*<sup>74</sup>.

### 1.6.3.1 Effect of Irradiation and Oxidation

UHMWPE as the name implies has a very high molecular weight which imparts its major advantages as a bearing material, namely excellent abrasion resistance and toughness. Due to the chemical changes which occur upon irradiation, molecular weight is decreased<sup>52</sup>. This can lead to an increase in crystallinity, density and brittleness<sup>75, 76, 77</sup>. These properties will be seen to significantly affect the mechanical properties of this material and its wear resistance. The latter was shown in a study by Brossa et al<sup>78</sup> who found an increase in wear rate as the molecular weight of compression moulded 4150 resin decreased.

### 1.6.3.2 Effect of Crosslinking

Upon irradiation, it has been seen that alterations in chemical structure occur. The result of this change depends on the atmosphere present. Crosslinking of UHMWPE can occur by different chemical reactions. In the absence of oxygen, crosslinking is formed between carbon atoms, but if oxygen is present crosslinking may also form peroxide linkages<sup>79</sup>. The degree of crosslinking thus depends on the diffusion speed and oxygen concentration in UHMWPE.

Crosslinking is measured by determining the gel content and it has been reported that gel fraction decreases after gamma irradiation in the presence of air, but in an inert atmosphere such as nitrogen, the gel fraction increases with higher radiation doses<sup>52</sup>. This is because crosslinking is inhibited in a reactive (oxidising) environment, which terminates free radicals before cross-linking can occur. This highlights the importance of packaging environment during irradiation.

The degree of crosslinking which occurs upon irradiation can be increased by reducing the radiation time<sup>52</sup>. Gamma irradiated samples absorb much more oxygen during and after irradiation than samples that have undergone electron beam radiation, due to the much longer radiation time needed for gamma radiation at the same dose level. Thus, unlike gamma radiation where a rapid decrease in gel fraction occurs, electron beam radiation which has a much shorter radiation time, can cause an increase in gel fraction<sup>52</sup>. Electron beam radiation can therefore be used to control the relationship between degree of crosslinking and oxidative chain scission<sup>52</sup>.

Crosslinked polyethylene has a higher deformation resistance with irradiation in air leading to a higher creep resistance than irradiation in nitrogen<sup>52</sup>. Streicher<sup>53</sup> found irradiation resulted in increased oxidation and crystallinity, leading to a less ductile and more creep resistant material. Wear resistance also increases with increasing gel content<sup>80, 81</sup> and the cross-linking benefits of irradiation are thought to provide long-term usage in the hip, due to the conforming nature of this joint. Oonishi et al<sup>82</sup> studied the effect of crosslinking by gamma irradiation on the wear of polyethylene in total hip prostheses. Using doses of 100, 500 and 1000 Mrad and investigating such

properties as wear, frictional torque and creep deformity they advocated the use of a dose slightly over 100 Mrads. In a separate study of retrieved acetabular components Oonishi et al<sup>33</sup> found that 100Mrads irradiation produced less than one sixth the linear wear and one third the volumetric wear compared to a Charnley prosthesis.

Although the standard view is that crosslinking is increased in an inert atmosphere, several reports have found contrary results. Brossa et al<sup>78</sup> found greater cross-linking occurring in air than in vacuum and nitrogen respectively and Sun et al<sup>83</sup> found that irradiation in air increased gel content significantly. Deng et al<sup>79</sup> found that at dose levels of 1.25 and 2.5 Mrads (12.5 and 25k Grays) crosslinking dominated in air and acetylene, while chain scission dominated in nitrogen irradiated samples. Crosslinking in acetylene crosslinked samples was dominated by reactions between carbon atoms.

### 1.6.3.3 Crystallinity

Chain scission results in the disruption of tie chains and thus allows for recrystallisation. This is a result of chain cleavage in the amorphous zones of the polymer, which leads to recrystallisation because of the increased molecular mobility of the shortened CH chains. Oxidation in amorphous domains releases constraints on inter-lamellar tie molecules due to chain scission thus allowing the chains to form new crystallites<sup>84</sup>. Choudhury and Hutchings<sup>85</sup> suggested that a high radiation dose (100kGys) promotes molecular chain scission resulting in shorter chains with greater mobility, and that these can crystallise more readily. The subsequent increase in crystallinity brought about by irradiation and the introduction of oxygen containing groups into the polymer matrix, results in an increase in density<sup>86</sup>. Recombination reactions have been reported to be more likely to occur in the amorphous regions where there is more space for movement of the free radicals, producing the increase in crystallinity<sup>87</sup>. However, increase in crystallinity has also been reported to be most likely to occur in the boundary layer between the crystalline and disordered areas, due to the high strain energy levels in these areas, which are particularly prone to scission degradation rather than cross-linking<sup>88</sup>.

### 1.6.3.4 Effect of Dose Level

The dose level and time for irradiation play a significant role in the chemical changes introduced in the polymer network. The main changes which are easily measured are in oxidation and crystallinity, which have been shown to increase with increasing dose and exposure<sup>53, 67</sup>. However at a high dose, degradation of the polymer will result and this will result in a decrease in crystallinity. Typical sterilisation doses of 25-37.5 kGrays will result in increased crystallinity.

#### 1.6.4 Effect of Sterilisation on Mechanical Properties

The changes in chemical structure brought about by irradiation sterilisation have been reported to result in changes in mechanical properties compared to the unsterilised material, with the extent dependent on the radiation dose and the environment used. Mechanical properties pertinent to fatigue and wear such as yield stress and elastic modulus are linearly proportional to density<sup>89</sup>. Thus the density increase as a result of oxidation leads to increases in yield strength, hardness and therefore creep resistance<sup>88</sup>. The yield stress has also been reported to increase with increasing radiation dose<sup>90, 91</sup>. Since the elastic modulus is extremely sensitive to density changes and increasing the elastic modulus has been shown to increase the stress associated with surface damage<sup>92</sup>.

Collier et al<sup>93</sup> reported that oxidation resulting from gamma sterilisation in air reduces static strength and elongation properties and significantly decreases the resistance of polyethylene bearings to fatigue. Other authors have found that as oxidation increases or density increases, fatigue strength decreases and modulus increases<sup>68, 91, 92</sup>. An increase in stiffness leads to a consequent increase in contact stresses *in vivo*, a decrease in fatigue strength and a decrease in wear resistance. Ries et al<sup>68</sup> found a significant decrease in fatigue strength in cantilever rotating beam tests for polyethylene which had been sterilised by gamma irradiation in air compared to ethylene oxide sterilisation. Sanford et al<sup>94</sup> found fatigue life immediately after gamma irradiation was 4-5 times lower than inert packaged gamma or gas plasma levels ( $p < 0.05$ ). These results are comparable to those of Ries et al<sup>68</sup> and Fisher et al<sup>95</sup>. Although there are many reports on decreased fatigue life due to the chemical and structural changes initiated by irradiation, Megremis and Hulbert<sup>96</sup> found packaging in either air or inert gas for irradiation had no observable difference on the crack growth rate. A lower molecular weight has also been associated with lower fatigue resistance, while more crystalline material has been associated with higher fatigue resistance, due to the relative ease with which the polymer chains disentangle during cyclic loading<sup>97</sup>.

Others have reported changes in tensile properties, with reduced tensile strength, reduced elongation, higher friction coefficient and lower toughness<sup>98</sup> resulting with an increase in oxidation. Elongation to failure has been reported to decrease with increasing radiation dose and also ageing time<sup>90, 91, 99</sup>. In contrast Megremis & Hulbert<sup>100</sup> found no significant changes in tensile properties for EtO sterilised or argon environment gamma irradiated specimens, but Deng et al<sup>79</sup> found both the dose (1-5Mrad) and the atmosphere affected tensile properties of nitrogen and acetylene irradiated UHMWPE.

### 1.6.5 Effect of Sterilisation on Wear Properties

In addition to alterations in mechanical properties upon sterilisation, changes in molecular weight and their consequent affect on abrasion resistance, will lead to alterations in wear behaviour. However, whereas many of the chemical changes associated with irradiation seem to adversely affect material and mechanical properties, crosslinking has a beneficial effect on wear performance. This has been shown in many studies. Schroeder & Pozorski<sup>101</sup> found compression moulded material had a 42% reduction in wear when gamma irradiated in an inert atmosphere as compared with EtO sterilised material. Sommerich et al<sup>102</sup> also found a significant decrease in wear for vacuum packed and gamma sterilised polyethylene compared to EtO sterilised polyethylene. Wang et al<sup>103</sup> found much lower wear in air irradiated material than non-sterile or EtO sterilised material and Polineni et al<sup>104</sup> found a 60% reduction in wear rate for gamma in air over EtO. McKellop et al<sup>105</sup> tested gas plasma and irradiation under four regimes and found that materials not irradiated had a constant wear rate. The irradiated acetabular cups had a two phase wear rate, depending on the post irradiation treatment and the depth that oxidation was maximal and cross-linking occurred. The wear of samples gamma irradiated then stored in air was initially higher due to a more oxidised surface layer. There was then a lower wear rate as this surface layer was worn through and more crosslinked material was exposed. The potential advantage of crosslinking brought about during irradiation was suggested to account for sustained wear resistance against three body abrasion in a study by Wang et al<sup>103</sup>.

However, Hamilton et al<sup>106</sup> found no change in the wear rate for polyethylene gamma sterilised in air up to 40kGy. In addition no significant difference was seen in the wear rate between gamma in vacuum and non-sterilised polyethylene, up to 28.5kGy. There have also been isolated reports of irradiation leading to increased wear. Trieu et al<sup>107</sup> found a significant reduction in the fatigue wear resistance of gamma sterilised polyethylene compared to ethylene oxide gas. Fisher et al<sup>108</sup> found slightly higher wear for irradiated compared to unsterilised material in a pin-on-disc test with pins machined from acetabular cups. Mosleh et al<sup>109</sup> found the wear of gamma irradiated (25kGray) polyethylene to be substantially higher than that of non-irradiated, EtO and gas plasma sterilised samples in pin-on-disc testing, and suggested that this could be due to accelerated crack nucleation and propagation. In another pin-on-disc study, Mosleh et al<sup>98</sup> found gamma irradiation (25 and 50 kGray) caused delamination even under relatively low contact stress and advise an alternative sterilisation technique was required which did not result in oxidation of the polyethylene.

Hip simulator studies have been particularly favoured in the investigation of the affects of sterilisation method and atmosphere on the wear of UHMWPE. This is because hip

simulators reproduce the wear mechanisms and wear rates seen *in vivo* more accurately than pin on disc tests. This increase in wear performance is brought about by cross-linking especially in hip simulator tests has to be cautioned though, because in most of these tests there had been no time for long-term oxidation effects to occur. UHMWPE is known to undergo significant oxidation during implantation, which may degrade abrasion resistance, accelerating debris production and consequent prosthesis failure<sup>110</sup>.

### 1.6.6 Effect of Shelf Ageing and *In Vivo* Ageing on UHMWPE Properties

The chemical changes brought about by irradiation alters the molecular structure of polyethylene with time. The crystallinity of irradiated specimens increases with shelf-ageing time, due to chain scission followed by recrystallisation<sup>84, 91</sup>, a reaction not found in un-irradiated specimens. Small-angle x-ray diffraction (SAXS) has shown that this increase occurs due to the growth of new crystallites in the amorphous domains<sup>84</sup>.

The increase in crystallinity and associated increase in density and modulus can result in an undesired increase in contact stress and decrease in wear properties. Fisher et al<sup>108</sup> compared unsterilised, recently irradiated (air) and shelf-aged (5-7 years) irradiated (air), pin-on-disc specimens machined from acetabular cups. They found higher wear factors for the aged irradiated material compared to the other two conditions. Cristante et al<sup>111</sup> have found gamma sterilised UHMWPE to have a lower fatigue wear resistance than EtO sterilised UHMWPE which has been shelf-aged (~54 months), but Greer and Flynn<sup>112</sup> could find no correlation between shelf age, oxidation level and pitting wear in pin-on-disc tests of shelf-aged components. They suggested that other variables such as lot to lot variations in raw materials, fabrication and irradiation conditions must have existed.

Artificial ageing regimes (see chapter five for details) have been used to investigate the affect of oxidation on the properties of UHMWPE, in the absence of shelf-aged components. There has been particular interest in the affect of irradiation versus non-irradiation sterilisation methods. Fisher et al<sup>113</sup> studied the affect of artificial ageing on gamma irradiated and gas plasma sterilised samples. They found a 50% increase in wear factor for the gamma irradiated material and in artificially aged material the increase in wear factor was three fold. In contrast the gas plasma sterilised material showed no increase in wear factor once aged, and no oxidative degradation was detected, implying considerable potential benefits in the application of gas plasma sterilisation. Sanford et al<sup>114</sup> performed a similar study and found that ageing had no

effect on the wear rate of gas plasma sterilised components but the gamma irradiated components had a five fold increase in wear after ageing. It can be concluded that oxidative degradation outweighs the short term benefits of the cross-linking which occurs upon gamma irradiation in air.

Although the physical properties of UHMWPE deteriorate during sterilisation, storage and implantation, the effect on clinical wear rate in hips has been found to be negligible, with the lowest wear rates in acetabular cups with the most distinct oxidation (sub-surface)<sup>115</sup>. Wang et al<sup>116</sup> came to a similar conclusion when they found no detrimental affect of shelf-ageing on the wear rate in a hip simulator study up to 10 million cycles, for components gamma irradiated in air and shelf-aged for one to seven years. However, Muratoglu et al<sup>81</sup> did find a strong correlation between wear and embrittlement. They also found that retrieved acetabular components showed regions of embrittlement, with 74% of cups with embrittled UHMWPE manufactured between 1982-1989, but only 17% between 1970-1982.

#### 1.6.6.1 Oxidation Products

Gamma irradiation of UHMWPE is thought to lead mostly to ketone formation, which does not necessarily break the polyethylene molecule but has been attributed to be a potential location for degradation *in vivo*<sup>66</sup>. However, the presence of carbonyl acid absorption does indicate chain scission, as does aldehyde absorption, however the latter is usually masked by the strong ketone absorption<sup>66</sup>. Thus only acid and aldehyde types of oxidation products result in chain scission which can lead to decreased molecular weight, recrystallisation and subsequent embrittlement<sup>117</sup>. The presence of a carbonyl group within an FTIR spectra implies oxidative degradation of polyethylene indicating an increase in chain terminals<sup>118</sup>, and a decrease in molecular weight<sup>119</sup>. Streicher<sup>99</sup> found an increase in carbonyl content with irradiation and Jahan et al<sup>62</sup> found a strong carbonyl peak at the surface of shelf-aged components.

#### 1.6.6.2 Rate of Oxidation on the Shelf and *In Vivo*

There has been some debate as to the extent of oxidation occurring during and after irradiation sterilisation. During irradiation, internal heat is generated, increasing the reaction rate, so that during the sterilisation process oxidation is limited by oxygen diffusion. For shelf ageing the free radical concentration is the rate controlling step. Several investigators have used FTIR on retrieved polyethylene components and concluded the polyethylene oxidises *in vivo*<sup>77, 119, 120, 121, 122</sup>. The extent of oxidation varies with depth from the articulating surface. Bostrom et al<sup>123</sup> performed a study of UHMWPE which was characterised as stock material, again after fabrication into components (including gamma irradiation) and finally after retrieval from patients.



They found degradation initiates upon irradiation and that it continues at a significant rate during shelf storage and subsequent implantation. Muratoglu et al<sup>124</sup> concluded that both *in vitro* and *in vivo* oxidation of gamma sterilised UHMWPE components takes place sub-surface through the reaction of oxygen that diffuses along the grain boundaries. Diffusion occurs through the amorphous regions, therefore this is where recrystallisation in the post-irradiation period takes place.

The sub-surface 'white band' has been attributed to oxidation of UHMWPE. This is a result of scission producing shorter chains which have higher mobility and can recrystallise post-irradiation. The associated increase in crystallinity can result in embrittlement and upon cutting sections through this region a 'white band' is often observed due to micro-cracking within this embrittled region. This microcracking can occur at the surface of a specimen, but it is usually associated with the band which is generally seen between one and two millimetres below the surface of a component. This sub-surface band is a function of radiation dose distribution, diffusion of oxidants and temperature<sup>125</sup>. A generalised reaction mechanism to explain the location of the oxidation maximum has been proposed<sup>125</sup> and this is explained in greater detail in chapter four.

#### 1.6.6.3 Oxidation Products of Shelf Ageing and *In Vivo* Ageing

Particular interest has evolved in the levels of different oxidation products found in shelf-aged and retrieved materials. Different oxidation products would indicate contrasting reactions occurring on the shelf and *in vivo*. Ester-carbonyl absorption ( $1740\text{cm}^{-1}$ ) has been detected in wear test specimens and retrieved material and has been found to be location dependent and predominant near the surface<sup>117, 118, 126</sup>. Ester-carbonyl absorption has been reported not to be substantially present in shelf-aged components<sup>121, 123, 127</sup>. Keto-carbonyl absorption ( $1720\text{cm}^{-1}$ ) and acid-carbonyl absorption ( $1698\text{cm}^{-1}$ ) have been found in both shelf-aged and retrieval material and Imlach et al<sup>117</sup> found acid concentrations to increase with depth. Ambrosio et al<sup>119</sup> found the level of surface oxidation changed significantly around retrieved hip cups, however the ester-carbonyl intensity remained unchanged. Imlach et al<sup>117</sup> found a constant relationship between type of oxidation products at the mid-point in the 'white band' in retrieved acetabular components, which was independent of the *in vivo* duration of the implant. Some studies show no link between oxidation and white banding. Possibly due to strong contribution of non-chain scission products (ketones and esters) to overall oxidation.

The extent of oxidation seen in retrieved UHMWPE components was first questioned by James et al<sup>128, 129</sup> in a study of retrieved acetabular components. They claimed most oxidation products were the result of esterified fatty acids which could be removed by extraction with hexane. However they did find some evidence of oxidation, which was variable on new cups and they attributed this oxidation to the processing of polyethylene. Currier et al<sup>132</sup> also used hexane extraction and found that certain carbonyl species (esters) were adsorbed to the tibial bearings and much was removed by extraction. However, they did find that other carbonyl species (ketones, aldehydes, acids) were products of polyethylene oxidation, with essentially no difference observed by FTIR, before and after extraction.

In contrast, McKellop et al<sup>130</sup> found hexane extraction of lipids reduced carbonyl ratios at the free surface of retrieved implants, but had no effect at a depth greater than 0.1-0.2mm, indicating the absorbance ratios were not solely an artefact of absorbed lipids. Sun et al<sup>118</sup> found water soluble and heptane soluble contaminants. In their FTIR study, the affect of solvent extraction was investigated on the common peaks found in shelf-aged and retrieved components. They found two major carbonyl peaks in clinical retrievals. The first was the ketone group ( $1717\text{ cm}^{-1}$ ), commonly observed in irradiated UHMWPE and this was found to be little affected by heptane washing (i.e. not an artefact). The second peak was associated with ester-carbonyl absorption at  $1740\text{ cm}^{-1}$  and was eliminated after water/heptane washing, but not by water alone. After washing they still found evidence of oxidation, unlike James et al<sup>128, 129</sup>, but the latter studied different absorption peaks. Sun et al<sup>118</sup> also found a change in oxidation index of 30-58% after heptane washing, and attributed this to contamination of chemical species from synovial fluid or calf serum. Yu et al<sup>131</sup> found that hexane extraction substantially reduced the apparent surface oxidation at both the worn and non-worn regions, in hip simulator specimens. This was attributed to the removal of absorbed proteins (i.e. amino acids @  $1740\text{ cm}^{-1}$ ).

In a variation to these studies, Muratoglu et al<sup>124</sup> used xylene extraction and found selective extraction along grain boundaries, indicating grain boundary diffusion of oxygen into the material. Hot xylene has also been reported<sup>133</sup> to be more sensitive to oxidation than 'white banding', indicating areas of increased oxidation compared to the bulk material that are not necessarily evidenced on sectioning a material.

## 1.7 Wear Testing and Wear Mechanisms

The lifetime of UHMWPE components in joint replacement are limited by their wear characteristics. Catastrophic wear of the component will obviously result in the need for revision surgery, but less catastrophic wear can be problematic too, due to the wear debris produced and subsequent biological reaction.

### 1.7.1 Types of Wear

There are two types of wear which occur in both hip and knee replacements. These are abrasive and adhesive wear. Abrasive wear is caused by third bodies such as cement particles or by scratches on the alloy surface. Adhesive wear occurs by shearing of the microscopic asperities on the surface when the interfacial shear strength exceeds that of UHMWPE<sup>134</sup>. This results when there is a local breakdown in the boundary lubrication and transfer films are formed. Adhesive and abrasive wear are predominant in the hip and result in the release of small particles<sup>9</sup>. In the knee, fatigue and abrasive wear are more common<sup>135</sup>. Surface fatigue wear is a result of microscopic fatigue of asperities and microcracking on the polymer surface. Sub-surface fatigue results from cyclic compression-tension and results in pitting and delamination wear. These types of wear generally occur simultaneously, but the amount of each will depend on the joint, its design and kinematics.

Although the work in this thesis is more concerned with UHMWPE as a bearing material in TKR, its use in THR gives us useful insights into how it behaves under different kinematic conditions. Stresses in knee prostheses are more complex due to more complex kinematics i.e. rolling and sliding versus sliding only in the hip. The former produces cyclic tension and compression at surfaces and shear below. The intensity of these stresses is influenced by the contact stresses which are a function of design and conformity. Calculations have led to the conclusion that stresses at the knee are higher than those at the hip<sup>136</sup>. In TKA applied loads are similar to those in the hip, however in the knee these must be resisted over smaller contact areas, resulting in increased contact stresses<sup>8</sup>. For example, for a 3000N load, the maximum surface stress in a 22mm diameter femoral head is 18MPa. For a Total Condylar knee, the stress in flexion for the same load is 40MPa<sup>136</sup>. The stresses in the knee are also influenced by the weight and activity level of the patient and in addition, the force distribution which is a function of alignment of the prosthesis and the gait cycle<sup>9</sup>. Not only are the magnitudes of stress different in these two joints but their kinematics mean that the shear stresses are exhibited at different points. The maximum shear stresses in a hip joint are at the articulating surface. The maximum shear stresses in a

knee joint are 1-2mm below the articulating surface. The increased stresses in the knee have been related to increased wear. Retrieval studies by Wright & Bartel<sup>8</sup> and Landy & Walker<sup>43</sup> found significantly greater damage in TKR than THR (when adjusted to mean weight and implantation time). This has also been seen in *in vitro* tests such as those by Rose et al<sup>137</sup>.

### 1.7.2 Types of Wear Testing

*In vitro* wear test studies are used to investigate the wear of existing and new materials to ensure their long-term functionality. Pin-on-disc and pin-on-plate are standard tests used for the screening of new material combinations for the use in TJR. As the name suggests, a pin articulates against a disc of material. The choice of which material is used for each, depends on the contact stresses and design you wish to simulate. Typically a polymer pin on a metal disc is used to simulate a hip configuration and a metal pin on a polymer disc to represent a knee. This type of testing is relatively easy and inexpensive, tests parts are relatively easily fabricated and results can be generated in a short period of time. However, uniaxial testing regimes of this type are coming under increased criticism<sup>134, 138, 139</sup> for not being realistic and producing low wear rates (which are sometimes exceeded by fluid absorption during testing). The criticism of testing with unidirectional reciprocating motion such as in pin-on-disc testing, is that the polyethylene surface appears to become oriented and strain hardened<sup>80, 134, 139, 140, 141</sup>. This is due to a reorientation of molecules which takes place within a thin surface layer during articulation. This leads to strengthening along the direction of orientation, but weakening in the perpendicular direction. The preferential orientation of polymer chains due to plastic deformation has been termed orientation softening. Bond rupture will occur more easily when a force is imposed perpendicular to the orientation.

It is this orientation induced softening process that determines the failure strength under multi-axial motion conditions since the constant re-orientation leads to shearing and wear particle formation. Therefore the molecular orientation induced by plastic deformation during joint articulation is undesirable for the wear resistance of UHMWPE acetabular and tibial components. However, radiation induced crosslinking retards molecular movement, limiting orientation effects and thus improving wear resistance, particularly in acetabular components<sup>80, 101, 103</sup>. Wang et al<sup>134</sup> proposed that in unidirectional testing the wear resistance of unirradiated UHMWPE should be greater than that of irradiated UHMWPE since crosslinked irradiated polyethylene will resist molecular alignment (leading to increased wear). This has been seen in some pin on disc testing<sup>98, 108, 109</sup>.

## 1.8 New Materials

Recently a number of modified UHMWPEs have been produced. So far only short term *in vivo* wear data and *in vitro* test results are available. However, use of one modified UHMWPE (Hylamer) does not appear to confer better wear rates.

Hylamer was developed from the concept that increased crystallinity, without a detrimental alteration in molecular weight would produce advantageous physical properties in UHMWPE used for TJR<sup>142</sup>. The application of a carefully controlled high temperature, high pressure and cooling sequence meant conventional UHMWPE (crystallinity 45-55%) could be turned into a higher crystalline material (57-68%). This increase in crystallinity brings about an increase in density, melting point, yield strength, tensile modulus and resistance to deformation and also a slower fatigue crack growth rate<sup>142</sup>. Differential Scanning Calorimetry (DSC) analysis<sup>143</sup> has indicated a crystallinity as high as 73% with a corresponding density of 0.9585 for Hylamer. Other changed properties reported included a 70% increase in modulus, increased tensile yield strength and reduced ductility and toughness.

This 'enhanced' UHMWPE exhibits extended chain morphology, where the increase in crystallinity is obtained by lamellae thickening<sup>144</sup>, by reheating and cooling under high pressure. Conventional UHMWPE forms a folded chain morphology. Chain extended morphology has high crystallinity due to the elimination of amorphous regions, with a consequent reduction in the number of tie molecules compared to chain folded morphology. Lamellae thickness in chain folded morphology 200-500nm, whereas for conventional UHMWPE the thickness is 20-30nm. In HDPE and other polymers, chain extension causes embrittlement of the polymer and a loss of useful properties<sup>144</sup>.

Hylamer was first available in 1990 and in the relatively short intervening time most published data for *in vitro* testing and occasionally for *in vivo* wear rates, has found little difference between this 'enhanced' polyethylene and conventional polyethylene. Rimnac et al<sup>145</sup> in an *in vitro* cyclic loading experiment performed in distilled water and hydrogen peroxide environments, found no difference in any changes in mechanical and physical properties between Hylamer and conventional UHMWPE. Huber et al<sup>146</sup> concluded that Hylamer presents comparable wear behaviour to Chirulen in ring-on-disc wear testing. Sanford et al<sup>94</sup> in a study on the effect of sterilisation and oxidation on fatigue life, found qualitatively similar results for Hylamer and GUR4150HP. McKellop et al<sup>105</sup> found Hylamer to have a similar wear rate to non-sterilised and gamma irradiated (air) polyethylene. However this last study

did note that specimens were tested within six months of sterilisation, so the effect of late oxidation could not be discussed. The only report indicating any difference was by Agrawal et al<sup>147</sup> in a study of creep characteristics of Hylamer and conventional UHMWPE. They found significant differences between them with Hylamer having a 46% higher aggregate modulus and a significantly lower equilibrium creep.

Because standard mechanical and wear testing has not shown any advantage for Hylamer, several investigators have examined its resistance to oxidative degradation, since this is now known to be an important determinant in a materials wear resistance. King et al<sup>148</sup> examined Hylamer and indicated that its oxidation resistance during gamma irradiation was attributed to its high degree of crystallinity. However they actually found that there was equivalent oxidation after artificially ageing (7 days), which they attributed to oxidation of the amorphous phase tie molecules. Sanford et al<sup>114</sup> found the wear rates of gas plasma sterilised GUR4150 and Hylamer were indistinguishable before and after artificial ageing in a hip simulator wear test. Sanford & Saum<sup>71</sup> in a study to investigate an artificial ageing regime also studied Hylamer which had been gamma irradiated in a nitrogen environment. It was found to be significantly oxidised, although not quite to the extent of the GUR 4150 UHMWPE which had been gamma irradiated in air.

These reports have not shown a significant advantage for Hylamer over conventional UHMWPE and anecdotal reports of early *in vivo* failure have not given Hylamer a good reputation. Schmalzried et al<sup>149</sup> reported wear rates for Hylamer to be 2-4 times higher than those typically reported for polyethylene in acetabular components, but high patient activity level and third body wear due to entrapped metal particles were cited as mitigating circumstances. Livingston et al<sup>150</sup> also found increased wear for Hylamer cups and reported that after two years follow-up, the wear rate was twice that of conventional polyethylene. Prior to these reports, Ries et al<sup>151</sup> reported delamination and gross pitting in a Hylamer-M tibial insert after 2.5 years of clinical use. Factors attributed to this failure included increased stiffness<sup>152</sup> which results in increased contact stress and an apparent greater susceptibility to oxidation following gamma irradiation<sup>72</sup>, compared to conventional UHMWPE. In this latter study by Weaver et al<sup>72</sup>, oxidation of Hylamer was three to four times that of unmodified GUR4150 which had been radiation sterilised. Chmell et al<sup>153</sup> have published the most comprehensive review of Hylamer in a study of a series of 193 THA between 1990 and 1992. They found that survivorship (with failure defined as revision due to eccentric wear) was 86% at four years, although no explanation was given for the high wear rates. Polyethylene with a high percent crystallinity may be more prone to long-term oxidative ageing as free radicals are trapped in crystalline regions. This ties in with the fact that 'enhanced' polyethylene has been reported to have higher oxidation than standard UHMWPE<sup>154</sup>.

However not all *in vivo* data has been negative. Thomas et al<sup>155</sup> found no statistical difference in wear rates between standard and enhanced polyethylene (Hylamer) from in-vivo data after approximately three and a half years in patient matched groups. However using equations to correlate patient age and activity, Hylamer had a lower wear rate and therefore was seen to be preferentially for younger and potentially more active patients. Sychtez et al<sup>156</sup> in a radiographic study of femoral head penetration also found that on average Hylamer liners had a lower penetration rate compared with cups made from Enduron (GUR4150).

Another 'new' material called 'Stabilised Polyethylene' was developed in the mid 1990s by Howmedica, and aimed to combine the advantages of eliminating free radicals to improve the long and short term oxidation resistance and increased crosslinking, which results in improved wear and creep resistance, as well as other mechanical properties<sup>95</sup>. This was achieved by irradiating in an inert atmosphere, followed by a post-irradiation annealing step, where the component is stored at a slightly elevated temperature for a sufficient time to crosslink the reactive free radicals. Greater details of this material, its processing and *in vitro* testing can be found in Chapter 5.

The latest and possibly most exciting development is that of 'melt irradiated polyethylene'. This material is again a modified form of conventional UHMWPE. The manufacturing process involves appropriately dimensioned machined specimens which are then irradiated in an air tight chamber which is continuously flushed with nitrogen. The samples are then heated above their melting points, where the temperature is kept constant for at least thirty minutes before irradiation commences using electron beam. The resulting material is highly crosslinked with low crystallinity and low oxidation. A reduction in Young's modulus over conventional UHMWPE also occurs. The hypothesis behind the development of this modified UHMWPE was to manufacture a material which will resist the 'wear polishing' types of wear mechanisms seen on most retrievals. This 'wear polishing' occurs due to plastic deformation of the surface, resulting in the creation of anisotropic structures which are weakly bonded and easily disrupted under transverse motion. Therefore the melt irradiated polyethylene is designed to resist the creation of these weak anisotropic structures making a more wear resistant material. This material was first reported in 1997 so little work has been published to date, but early simulator testing is encouraging. Premnath et al<sup>157</sup> reported on this 'melt irradiated polyethylene' as a highly crosslinked, low crystallinity material, which produced no ESR signals for allyl or alkyl radicals. It also has a reduced crystallite size compared to conventional UHMWPE. Jasty et al<sup>158</sup> reported results for a hip simulator study to approximately

three million cycles, and showed it had virtually no wear as confirmed by gravimetric, volumetric and microscopy measurements.

A similar material to the 'melt irradiated polyethylene' was reported on in 1996, but nothing has been published since. This work was performed by Oka et al<sup>159</sup> and they produced a 'newly improved' UHMWPE by firstly gamma irradiating a block of UHMWPE at 10-30kGrays to introduce light crosslinking. This material is then compressed between metal plates at 180-200°C. The theory behind the process is that the lightly crosslinked blocks are crystallised from melt under uniaxial compression, a unique molecular alignment in the crystalline phase occurs. In pin-on-disc tests, with roughened zirconia discs, the wear factor of this 'new' material was statistically significantly lower than that of the non treated polyethylene.

It should be noted however with all 'new' materials that the *in vitro* testing and preliminary *in vivo* results are potentially quite different and only long term *in vivo* results can show whether a 'new' material is an improvement.



## CHAPTER TWO

### MATERIALS AND METHODS

## 2.1 Materials

### 2.1.1 Powder Classification

A morphological examination of the base powders GUR 412 and GUR 415 (Hoechst Celanese) used in the manufacture of ultra-high molecular weight polyethylene was performed. These powders are used in the manufacture of many UHMWPE materials including Poly Hi and RCH1000.

### 2.1.2 Stock Materials

Poly Hi and RCH1000 were the main materials studied. In addition, some aspects of the work were performed on a polyethylene from a batch known to have poor consolidation and numerous intergranular defects. Poly Hi is an extruded rod form of GUR 4150 and RCH1000 is a compression moulded form of GUR 4120.

### 2.1.3 Retrieval Materials

Retrieval materials examined in this study were chosen from a wide selection of designs from a database of over 350 retrievals. Prosthesis type, length of implantation and reason for removal were known for all components studied. Designs included in this study are AGC, Brigham, Insall Burstein, Kinematic, Marmor, Miller-Galante, PCA, St Georg Sledge and Total Condylar, with total knee and unicondylar designs examined.

## 2.2 Microscopy Methods

### 2.2.1 Light Microscopy

Specimens were prepared for light microscopy by cutting 50 $\mu$ m sections using a standard histological sledge microtome. Specimen thickness was checked with a micrometer. Retrievals were sectioned perpendicular to the wear track. Samples were viewed in transmitted and polarised light for the appearance of unconsolidated particles (fusion defects). In addition, residual deformation and wear in retrievals were studied. Polarised light was used to examine residual deformation within the polymer structure. Birefringence is observed when molecular orientation occurs, because the refractive index varies according to the direction of light propagation and the orientated of plane polarised light<sup>160</sup>. In the case of un-implanted materials this could be due to molecular orientation and/or moulding stresses caused by processing. In the case of

retrieval material this could be due to deformation of the bonds within the polymer producing molecular orientation.

### 2.2.2 Scanning Electron Microscopy

All materials were examined using a JEOL 35C scanning electron microscope (SEM). Specimens were sputter coated with gold prior to examination, since a poor conducting material such as UHMWPE, can produce charging of the specimen surface. This can result in reduced resolving power and difficulty in focusing, so is overcome by coating the surface with a very thin layer of high density and high electrical conductivity metal. This was done using a Polaron SEM coating unit (E5100). The thickness of the coating was calculated from the equation:

$$th=7.5It \quad th=\text{thickness}(\text{\AA}), I=\text{current}, t=\text{time at } 2.5\text{kV}$$

Specimens were typically coated for three to six minutes, corresponding to a thickness of 400-800\AA.

### 2.2.3 Transmission Electron Microscopy

Transmission electron microscopy (TEM - Phillips CM12) was used to investigate the ultrastructure of UHMWPE. Materials to be examined were mounted in an epoxy resin medium (Araldite CY212), then sectioned using a diamond knife to a thickness of 40nm, before observation. Alternatively, sections were taken on a cryomicrotome after mounting in 2% sucrose. In some instances materials were cut into small pieces approximately 0.5mm<sup>2</sup> and stained with chlorosulfonic acid (ClSO<sub>3</sub>H) for sixty minutes prior to embedding in the resin<sup>161</sup>.

## 2.3 Chemical Treatments

### 2.3.1 Chlorosulfonic Acid

Powder particles were treated with chlorosulfonic acid (CSA) to discern areas of high crystallinity. The treatment of materials with CSA was used as a qualitative technique to measure and monitor levels of oxidation. CSA was used by Li et al<sup>120</sup> to examine the relationship between crystallinity and oxidation resistance in retrieved and never implanted components. CSA is a strong oxidising agent and stains the polyethylene a brown/black colour in amorphous regions and also regions of oxidation. This technique was carried out in conjunction with FTIR analysis on several samples to confirm the affects of this acid<sup>161</sup>. Sections of 50\mu m thickness were immersed in CSA at 60°C. An elevated temperature was used to accelerate the reaction between polyethylene and acid. The time samples were treated for varied, but 60 minutes was

the most common duration. All specimens for qualitative comparison were the same thickness and treated for the same time period.

### 2.3.2 Heptane Treatment

Retrievals were treated with heptane to remove any adsorbed lipids after reports in the literature<sup>128</sup> indicated that FTIR data can be misleading due to adsorbed esterified fatty acids. Heptane treatment of sections was carried out prior to FTIR analysis and also CSA treatment to ensure staining of the polyethylene under the wear track was not due to adsorbed fluid products which had been forced into the material during articulation of the joint. Specimens were first washed in distilled water in an ultrasonic bath for one hour. The specimens were dried then placed in heptane in an ultrasonic bath for one hour. The specimens were finally washed for a further hour in distilled water in an ultrasonic bath.

### 2.3.3 Hydrogen Peroxide

Hydrogen peroxide solutions are often used in *in vitro* testing as they are known to produce oxidation of UHMWPE<sup>162, 163, 164</sup>. Sections of 50 $\mu$ m thickness were cut from each material and placed in a 2% hydrogen peroxide solution for periods of 3, 5, 8, 11 and 14 days, at room temperature or at 60°C. Solutions were changed every seven days. Once treated, sections were washed in water, then alcohol and dried. One section was CSA treated as a qualitative measure of oxidation. In addition to the treatment of thin sections, blocks of Poly Hi were cut (all dimensions >6mm) and placed in a 2% hydrogen peroxide solution for 5 and 10 days, with solutions changed every 5 days. Sections of 50 $\mu$ m thickness were then cut from the block and CSA treated. All specimens were viewed in a transmitted light microscope. FTIR analysis was carried out on a selection of sections to quantify levels of oxidation.

### 2.3.4 Xylene Treatment

Solvent etching experimentation was performed using hot xylene, as reported by Betts & David<sup>165</sup>. Sections 40 $\mu$ m and 75 $\mu$ m thick, cut from a selection of stock and retrieved materials were treated with xylene at 85°C for approximately 10 minutes. Hot xylene extracts the lower molecular weight constituents which exist after manufacture or can be formed due to irradiation.

## 2.4 Physical Treatments

### 2.4.1 Plasma Ashing

A Biorad (Polaron Division, E2000) plasma-asher was used to etch regions on a flat cut surface. This selectively removes amorphous regions since the crystalline regions possess a greater resistance to ion damage, resulting in the preferential etching of the amorphous regions<sup>139</sup>. The resultant morphology then reflects the lamellar organisation. This method was initially performed on blocks (approx. 1cm<sup>3</sup>) of stock materials to visualise fusion defects, but used later in the visualisation of spherulites in the SEM. Samples were etched in an oxygen plasma for 15-45 minutes, with a forward power of 100W.

### 2.4.2 Freeze Fracture

Samples from stock and retrieval materials were freeze-fractured and observed in the SEM in an attempt to visualise fusion defects, seen in the light microscopy examination of sections, and also reported in the literature<sup>166</sup>. Samples from materials were cut into small rectangular bars measuring approximately 30x5x5mm. These were then notched with a razor blade, immersed in liquid nitrogen and fractured between forceps.

### 2.4.3 Recrystallisation

Recrystallisation of the powder pre-cursors to UHMWPE material was carried out after reports in the literature<sup>166</sup> claimed to have observed spherulites in UHMWPE ram extruded material, and on the recrystallisation of the powder. Recrystallisation was performed by placing a thin layer of the powder on a glass slide and placing it in an oven at ~180°C until the powder melted. The slides were then viewed in transmitted and polarised light. Spherulites were observed in the SEM by examining freeze-fractured surfaces. Powder was also melted onto specimen stubs for viewing in the SEM, and both freeze-fractured and melted samples were additionally plasma-ashed before observation.

## 2.5 Material Analysis

### 2.5.1 Infrared Spectroscopy

Fourier transform infra-red (FTIR) microspectrometry was performed to determine oxidation and crystallinity with depth from the articulating surface. Sections 100µm

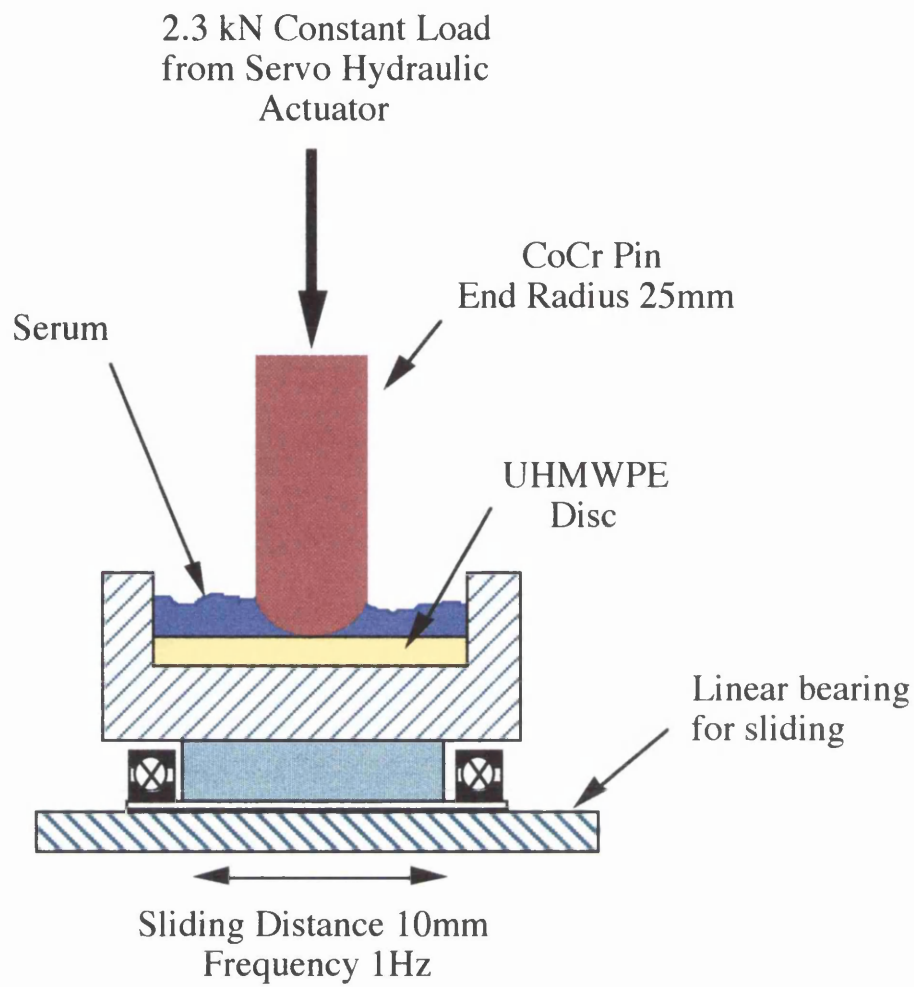


Figure 2.1 Schematic of the wear test configuration

thick were cut perpendicular to the articulating surface, as described previously. A Nicolet 740 FTIR spectrophotometer was used. This has a light microscope attached which allows alignment of the section and space-localised analysis, using a beam of diameter 200 $\mu\text{m}$ . Each spectrum was obtained with five hundred scans, with crystallinity measured according to Gueugnaut et al<sup>167</sup>, by measuring the absorbance bands at 1303  $\text{cm}^{-1}$  and 1894 $\text{cm}^{-1}$  (amorphous and crystalline peaks). The oxidation ratio of samples was calculated according to the method of Li et al<sup>120</sup> by comparing the heights of the absorbance bands at 1720  $\text{cm}^{-1}$  and 1740  $\text{cm}^{-1}$  (corresponding to carbonyl and ester groups) and comparing them to the peak at 3600 $\text{cm}^{-1}$ , which corresponds to polyethylene. Measurements were taken every 250 $\mu\text{m}$  from the articulating surface.

$$\text{Oxidation Ratio} = \frac{\text{height of peak at } 1720\text{cm}^{-1} + \text{height of peak at } 1740\text{cm}^{-1}}{\text{height of peak at } 3600\text{cm}^{-1}}$$

$$\% \text{ Crystallinity} = \frac{100}{1 + \left( \frac{\text{height of peak at } 1303\text{cm}^{-1}}{\text{height of peak at } 1894\text{cm}^{-1}} \right) * \left( \frac{6.2}{26.5} \right)}$$

## 2.6 Wear Testing

### 2.6.1 Materials

All tests specimens were machined from extruded rod GUR 4150 (Poly Hi). These were sterilised using gamma irradiation, using standard implant dose levels (25 kGrays). All specimens were tested within six months of sterilisation.

### 2.6.2 Test Configuration

A pin-on-plate test configuration was used as shown in figure 2.1. This test simulates the sliding conditions occurring at the knee joint. The machine consists of either six or twelve hydraulically loaded metal cylinders reciprocating on UHMWPE discs. The metal pins were cobalt-chrome with an end radius of 25mm, polished to a surface finish of 0.025 $\mu\text{mRa}$ . The hydraulic actuators were calibrated to an accuracy of 0.1% (BS1610.195). The cylinders are loaded to 2.3 kN giving an initial contact pressure (ignoring plastic deformation) of 71 MPa. This is designed to mimic the higher contact

stresses seen in less conforming TKR designs. The UHMWPE discs are reciprocated at a frequency of one Hertz along a track of length 10mm. All testing was performed at ambient temperature.

### 2.6.3 Lubrication

A serum lubricant was used in all tests. Bovine calf serum (Serolab, Crawley, Sussex) diluted to 50% with distilled water was used, with an addition of 0.8% sodium azide to prevent bacterial growth. Distilled water was added during the testing to replace water lost due to evaporation.

### 2.6.4 Frequency of Measurement

Tests were stopped every 200,000 sliding cycles. Pins and discs were washed, then dried in an oven for 24 hours. Weight loss was measured and the change in the wear track profile was determined using a Talysurf 10 (Taylor-Hobson).

### 2.6.5 Gravimetric Measurement

Specimens were dried for 24 hours at 37°C and weight loss measurements were made using a balance which could measure to an accuracy of 0.0001 grams, which was calibrated according to BS5750/ISO9002. Average values were taken from three test specimens (6 samples per test). Weight change for individual test samples were adjusted by subtracting the average weight change from three control discs (per treatment) of the same geometry as the test specimens. The soaked controls were not cyclically loaded. Average values were tested for statistical significance using a paired t-test. Significant differences were assigned when the P value was below 0.05.

### 2.6.6 Volumetric Measurement

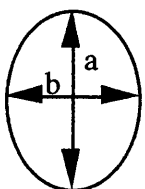
Volumetric change was estimated using a talysurf by taking profiles through the centre of the wear track perpendicular and parallel to the direction of sliding. The depth of the track could be estimated from these profiles along with the length and width of the wear track. The volumetric change could then be estimated using the equation<sup>168</sup>:

$$\text{Wear track volume} = \frac{2}{3}\pi(1/2a)(1/2b)c$$

where a = length of the track

b = width of the track

c = depth of the track





Comparisons were made using the students t test and significance was assigned at values below  $p=0.05$ .

### 2.6.7 Light Microscopy

Sections  $50\mu\text{m}$  thick were cut perpendicular to the wear track with a sledge microtome. These were examined under polarised light to determine the amount of residual deformation under the wear track. CSA treatment was performed on  $50\mu\text{m}$  sections at  $60^\circ\text{C}$  for 30 and 60 minutes.

### 2.6.8 Scanning Electron Microscopy

The wear track of specimens was viewed in the SEM to determine the type and extent of wear seen. Specimens sectioned perpendicular to the wear track were also examined for the presence of fusion defects and sub-surface cracking.

## 2.7 Mechanical Testing

### 2.7.1 Materials

All materials for the mechanical tests were machined to the required dimensions from the same piece of Poly Hi (GUR4150) UHMWPE. Specimens were manufactured at the same orientation relative to the processing direction. Compact tension specimens for crack growth rate measurements were additionally machined from RCH1000 (GUR4120). All testing was performed dry at ambient temperature. All machined specimens were sterilised using gamma irradiation (25 kGrays) prior to testing.

Methods were developed to artificially age polyethylene to produce levels of oxidation commonly seen in retrieved prostheses. These methods were employed to determine the affects of post-irradiation oxidative degradation on the material and mechanical properties of UHMWPE. The ageing regimes for materials are described in chapter five.

### 2.7.2 Tensile Testing

Testing was performed according to BS638-89. Specimens were tested in the as-irradiated condition and after 4, 6 and 8 days of simulated oxidation in the pressure vessel. Two cross-sectional geometry of specimen ( $9\text{mm}^2$  and  $3\text{mm}^2$ ) were tested to observe the affect of ageing on specimen thickness. Thirty three thick specimens and twenty thin specimens were tested. Tests were performed at room temperature using a Hounsfield biaxial testing machine, with an elongation rate of  $25\text{mm}/\text{min}$ . A 1000N load cell was employed and elongation and force measurements were recorded on a

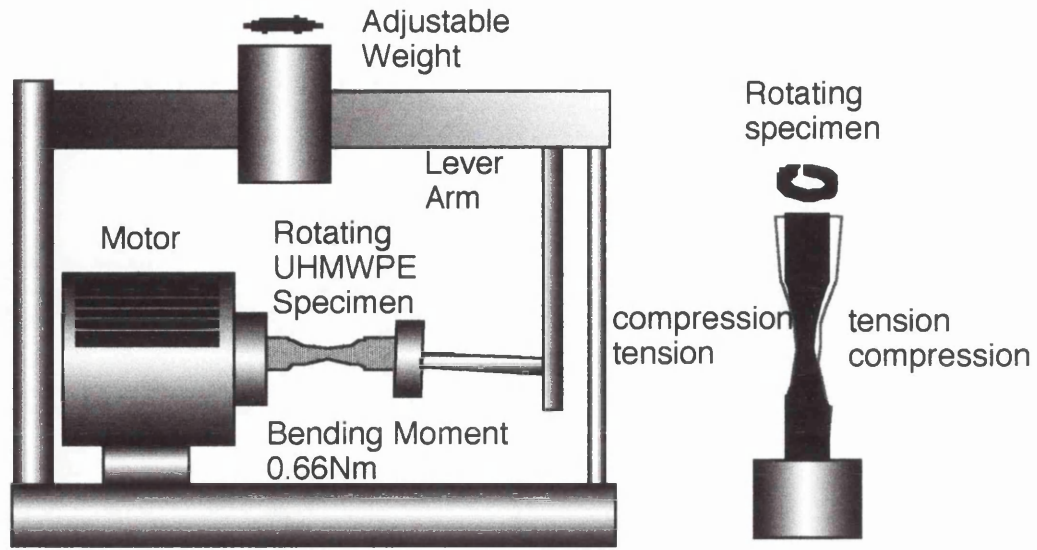
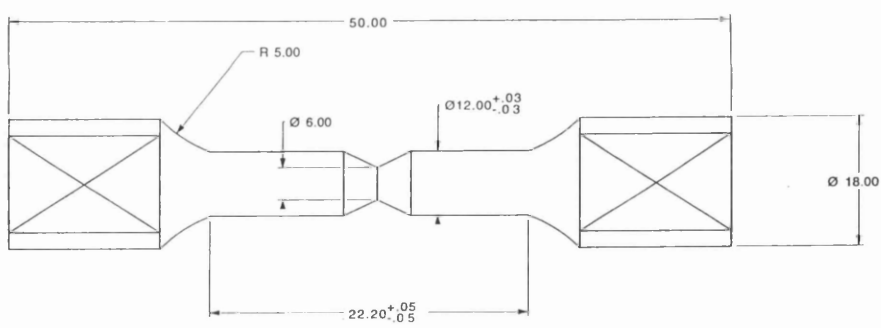


Figure 2.2 Schematic of the rotating beam fatigue machine



computer with software supplied by Hounsfield. Ultimate tensile strength and ultimate strain of the specimens were calculated. Specimens were retained after testing and fracture surfaces examined in a scanning electron microscope.

### 2.7.3 Rotating Beam Fatigue Testing

Testing was performed according to BS 3518, using a Wohler type apparatus (see figure 2.2). Specimens (total = 17) were tested in the as-irradiated condition and after 4 and 8 days of simulated oxidation in the pressure vessel. A constant bending moment of 0.66Nm was applied to all specimens and the number of cycles to fracture was determined. The moment was calculated to allow specimens with various oxidation levels to be comparatively tested under the same conditions. It should be noted that this constant moment will not produce a constant stress within the specimen and that the level of stress will depend on the fatigue cracks generated within the specimen. A frequency of two Hertz was used, in accordance with previous work which showed thermal fatigue was not implicated as a mode of failure. Specimens were retained after testing and fracture surfaces examined in a scanning electron microscope.

### 2.7.4 Crack Propagation Testing

Testing was performed in accordance with British standard E647-93. Specimens (total = 11) were machined into standard compact tension specimens, the notch being sharpened with a razor blade immediately prior to testing. Specimens were tested in the as-irradiated condition and after 4 and 8 days of simulated oxidation in the pressure vessel. Specimens were tested on a Hounsfield machine using a cyclic displacement of 1mm at a frequency of 0.93Hz. Parameters were controlled by the computer and chosen to allow comparison between materials with various degrees of oxidation. Measurements of crack length were made with a 10 power travelling microscope, as a function of the number of cycles.

For all mechanical testing, values were tested for statistical significance using the students t-test, with significance assigned for  $p < 0.05$ .

## CHAPTER THREE

# VARIABILITY IN 'MEDICAL GRADE' ULTRAHIGH MOLECULAR WEIGHT POLYETHYLENE

### 3.1 Introduction

The wear performance of total knee replacement is directly related to the material properties of the polyethylene used in its manufacture<sup>37, 43, 44, 121, 169, 170, 171, 172, 173</sup>. However, there are relatively few controls governing the manufacture or processing of this material. Specifications for 'medical grade' UHMWPE have been established by voluntary organisations such as ASTM (F648-96 for UHMWPE used in the orthopaedic industry). However, the specifications for chemical content and mechanical properties do not eliminate the possibility of large variations in properties, since the sampling and quality assurance specifications of this standard, are very general.

Recent research has recognised that manufacturing variables are a vital consideration in the longevity of UHMWPE implant materials. The physical and chemical properties of polyethylene and fabrication techniques that affect the microstructure of this material are critical considerations in minimising long-term wear<sup>3</sup>. The fabrication technique employed affects consolidation as seen in chapter one, and this in turn will affect material, mechanical and ultimately, wear properties. Some properties will affect surface wear, which is of a fine particulate nature and is applicable to all TJR, while other properties (especially fatigue strength and fracture toughness) will affect sub-surface crack propagation leading to delamination wear, which is more applicable to TKR.

Studies have identified a wide range of wear mechanisms and severity's in retrieved polyethylene components. However, limited research has been done to relate this to the morphology and microstructure of the as-manufactured material, and to identify the affect of different manufacturing and processing regimes, on material properties. The resin chosen for the manufacture of UHMWPE will depend on the final properties required. Different resins are available which will produce different molecular weight, material and mechanical properties in the final material. The quality of this powder is known to have a strong influence on the processability and final product properties<sup>174</sup>. There are also variations in the purity of medical grades of UHMWPE as some manufacturers add various fillers or additives<sup>170</sup>. Particle size is another potentially important factor since it may affect the packing ability and thus consolidation during manufacture. Pienkowski et al<sup>175</sup> found significant lot to lot variability in the sizes of micron sized particles and significant lot to lot differences in size and shape for sub-micron particles. Variability leads to questions about variations in polyethylene quality and *in vivo* wear performance. Duus & Li<sup>176</sup> carried out a systematic study of resin

type and manufacturing process, and found the properties of a single resin could be altered significantly by the processing conditions. Batch variations in the specific surface area of UHMWPE powder have been found and correlated to the processability of the resin by ram extrusion (with a lower surface area being harder to process)<sup>174</sup>. Different grades of virgin UHMWPE also display different thermal and thermo-oxidative behaviours, due primarily to their particle size, molecular weight and possible differences in polymerisation catalyst<sup>177</sup>. This will affect their ability to consolidate fully and highlights another variable between different resins which will produce differences in the final material.

It can be seen that the resin used in the manufacture of polyethylene can be utilised to produce the required properties in the final product, but that there are possibilities for variation from these desired properties. Processing controls during manufacture of the bulk material from the powder need to be stringent, since slight variations in processing parameters can lead to a material of different structural integrity. Bennett et al<sup>178</sup> found large variations in the physical properties of UHMWPE between different lots of the same resin, which had been extruded. Eyerer et al<sup>174</sup> found the presence of oxygen during the sintering process affects the physical and mechanical properties, both in free sintering and hot-pressing procedures. Ramani et al<sup>40</sup> found melt cooling rate to be the most important processing parameter, which can affect consolidation, crystallinity, modulus and strength. The highly porous nature of polyethylene powder has also been reported to continue once processed<sup>179</sup>. This microporosity can lead to detrimental wear in TKR, by initiating sub-surface cracks and delamination. Consequently despite recognition of the difficulties associated with the manufacture of ultra-high molecular weight polyethylene leading to poorly consolidated material, little has been done to improve manufacture or understand the effect of the variable nature of polyethylene.

Retrieval studies have generated ideas about material variability and its correlation to the wear properties seen *in vivo* and these will be discussed in greater detail in chapter four. However one of the most significant problems arising from manufacture is due to unconsolidated areas in the polyethylene known as fusion defects. Many authors have commented on these leading to weaknesses within the material. Landy & Walker<sup>43</sup> commented that the presence of fusion defects was a marker, indicating relatively weak bonding between all granules in a specimen and a subsequent tendency for bonding to decay under mechanical stress. Wrona et al<sup>44</sup> stated that fusion defects are an indication of considerable variation in the degree of consolidation of polyethylene, resulting in a material with quite variable fatigue resistance. Their hypothesis was that if the quality of the polyethylene, as assessed by the number and

location of fusion defects can be improved, perhaps the fatigue failures observed (and thus delamination) could be reduced. However, if the number of defects are not controlled, a wide range of wear behaviour should be expected, even in the absence of abrasive factors<sup>37</sup>.

The wear rate in *in vitro* simulations has been reported to vary dramatically for essentially identical prostheses but from different manufacturers<sup>37</sup>, which implies variable material consolidation. In early studies such as that by Rose et al<sup>37</sup> it was not known if such variability had concrete clinical consequence; today it can be clearly seen that it does. It has since been reported that the current concern for large-scale fatigue failure of polyethylene components is the result of a lack of sufficient understanding by some manufacturers of the importance of using high quality material from which components are to be fabricated<sup>45</sup>. Blunn et al<sup>169</sup> found numerous fusion defects in a particular unicondylar design and these were initiation sites for sub-surface cracks and delamination. Walker et al<sup>180</sup> found that UHMWPE containing defects had fatigue failure in the form of pitting, which was associated with the ends of the wear track.

In addition to the destructive nature of fatigue type wear mechanisms, there have recently been reports that the unconsolidated powder particles seen in both stock UHMWPE<sup>181, 182</sup> and retrieval material<sup>181, 183, 184</sup> may be released due to wear and fatigue processes in the body. It has been hypothesised<sup>175</sup> that sub-micron particles found in the tissues around prostheses, may in part originate from structures already present in virgin polyethylene powder. This is given credence by studies that have found features representative of flattened resin powder and nodules, confirming the hypothesis that the base resin flakes retain their identity through processes such as ram-extrusion<sup>182</sup>.

The hypothesis of this work was that different base resins and manufacturing processes will lead to a large variation in material properties of 'medical grade' ultrahigh molecular weight polyethylene. The aim was to examine the microstructure of material fabricated by different processes, from different resins, to examine the variability in consolidation, morphology and resistance to chemical attack, and suggest potential clinical implications of this variability.

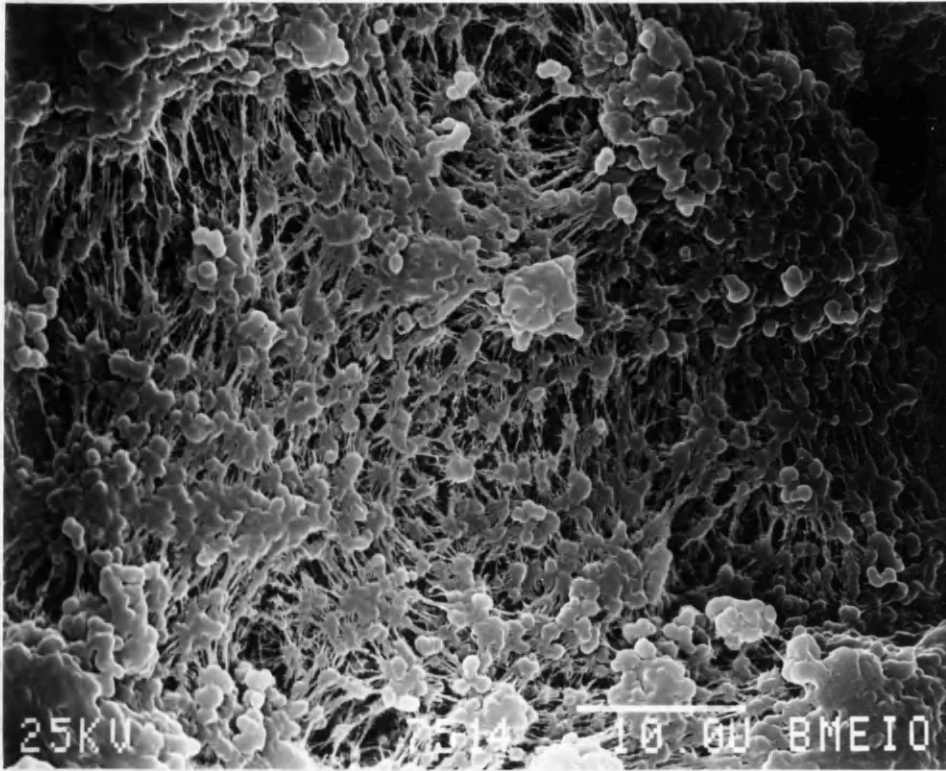


Figure 3.1a High power scanning electron micrograph of UHMWPE powder morphology

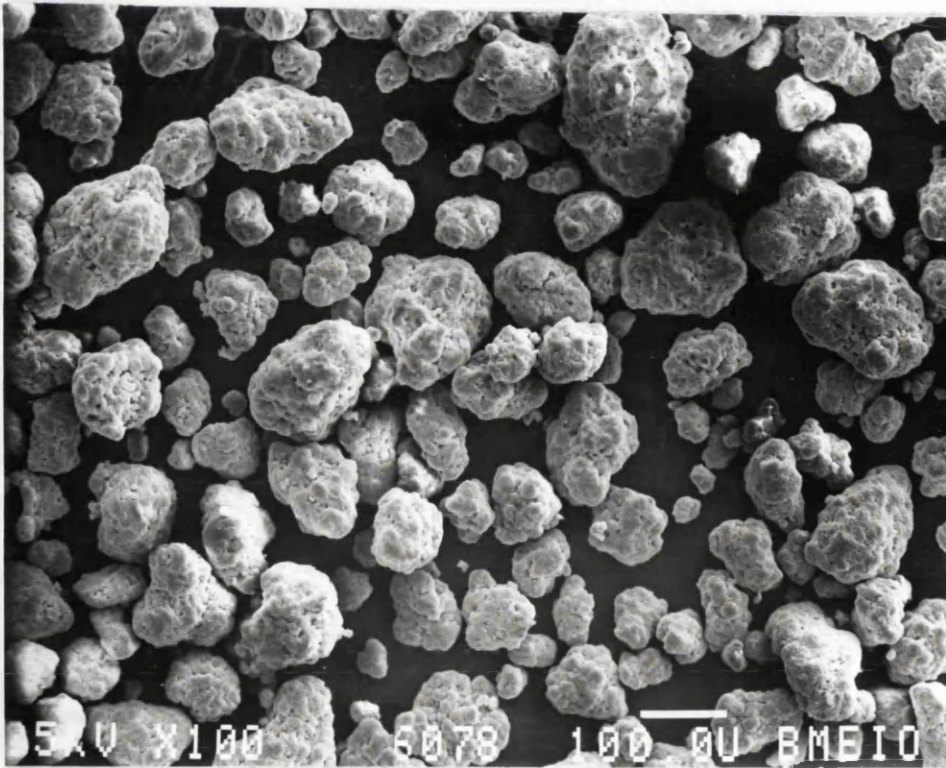


Figure 3.1b Low power scanning electron micrograph of UHMWPE powder morphology



## 3.2 Results

### 3.2.1 Powder Morphology

Examination of the powders GUR 4120 and GUR 4150 in the SEM showed both to have similar morphology. A hierarchical structure of the powder particles could be seen. Each particle consists of aggregated nodules connected by fibrillar ties (figure 3.1a). The particles were of varying sizes (50-250 $\mu\text{m}$ ), with some consisting of only several nodules and some of hundreds (figure 3.1b). Each nodule probably corresponds to the original catalyst which the ethylene molecules add onto in the reactor, until enclosed.

CSA treatment of the powders showed the nodules to be more pronounced, but the fibrillar ties seemed unaffected after 60 minutes at 60°C, however very few fibrillar ties could be seen after treatment for 48 hours at 60°C. Individual powder particles appeared to stain at variable rates when treated with CSA.

### 3.2.2 Stock Material Morphology

Examination of the stock materials in the light microscope showed UHMWPE obtained from one manufacturer and RCH1000 to have a propensity of fusion defects (with the former having approximately twice as many defects as RCH1000). Poly Hi however only had a few defects in a 1cm<sup>2</sup> area. SEM examination of materials after plasma ashing served to highlight these defects on the surface of all materials (figure 3.2). Freeze-fractured samples produced patterned surfaces (orthogonal shapes) which usually only covered approximately the first third of the fracture surface from the notch (figure 3.3). Depressions were observed on fracture surfaces where particles appeared to have been pulled out, and these had ductile type fracture surfaces. In some areas a structure consistent with that of UHMWPE powder was seen with unconsolidated material observed within grains.

TEM examination of materials allowed visualisation of crystal lamellae. Figure 3.4 is a micrograph showing lamellae of approximately 30 nanometres diameter. The pairs of dark lines of the lamellae correspond to their crystalline and amorphous boundaries, with their apparent thickness and length affected by their orientation to the electron beam<sup>152</sup>.

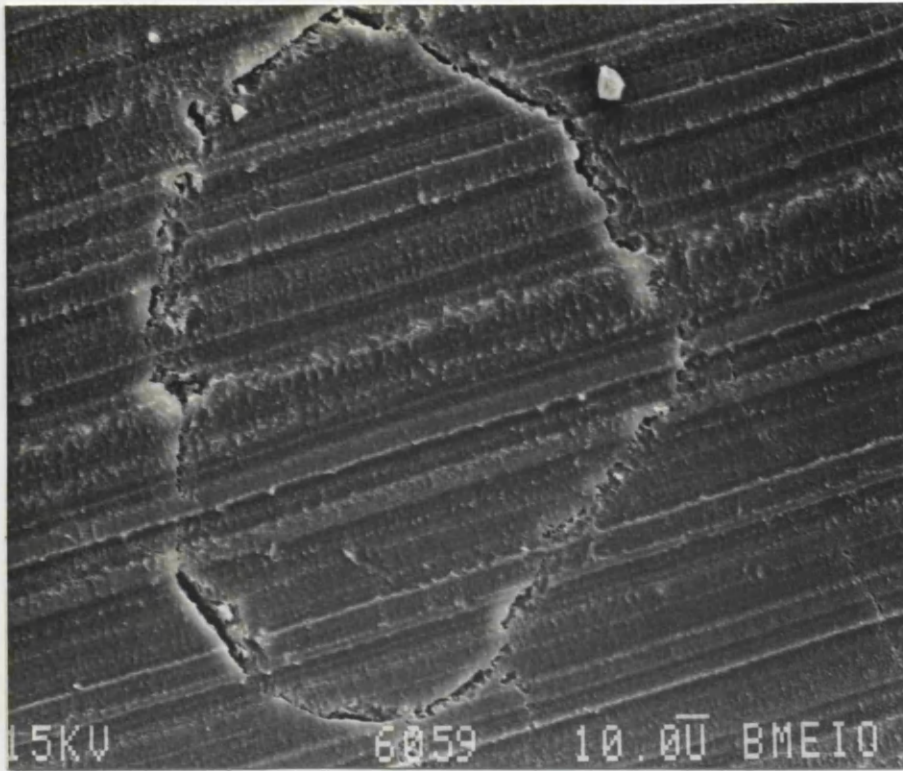


Figure 3.2 Low power scanning electron micrograph of a plasma-ashed fusion defect

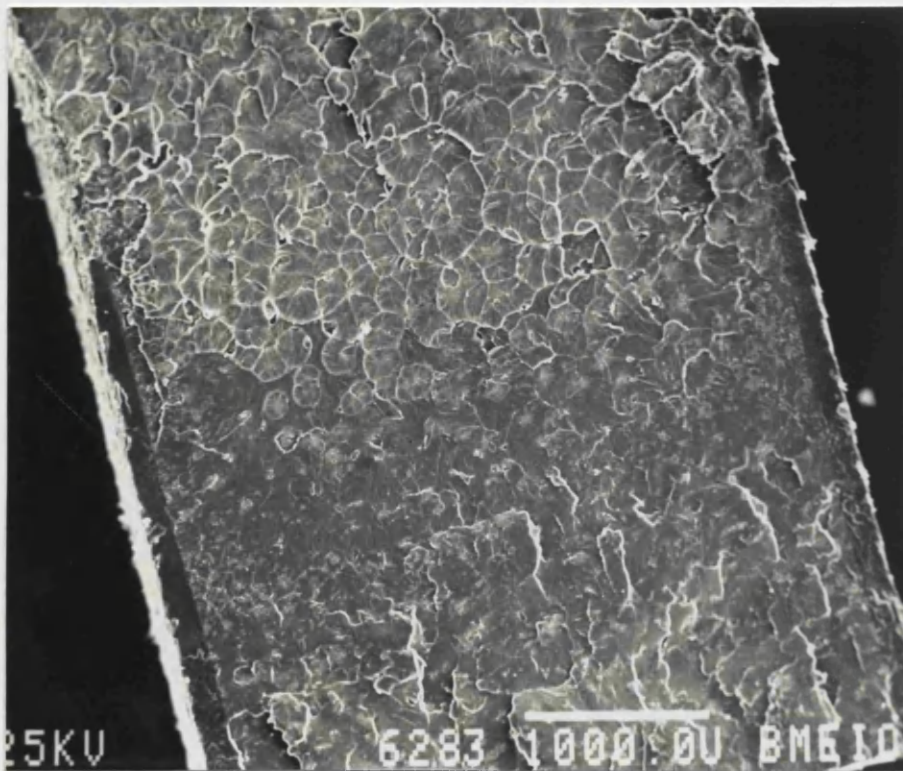


Figure 3.3 Low power scanning electron micrograph of freeze-fractured surface

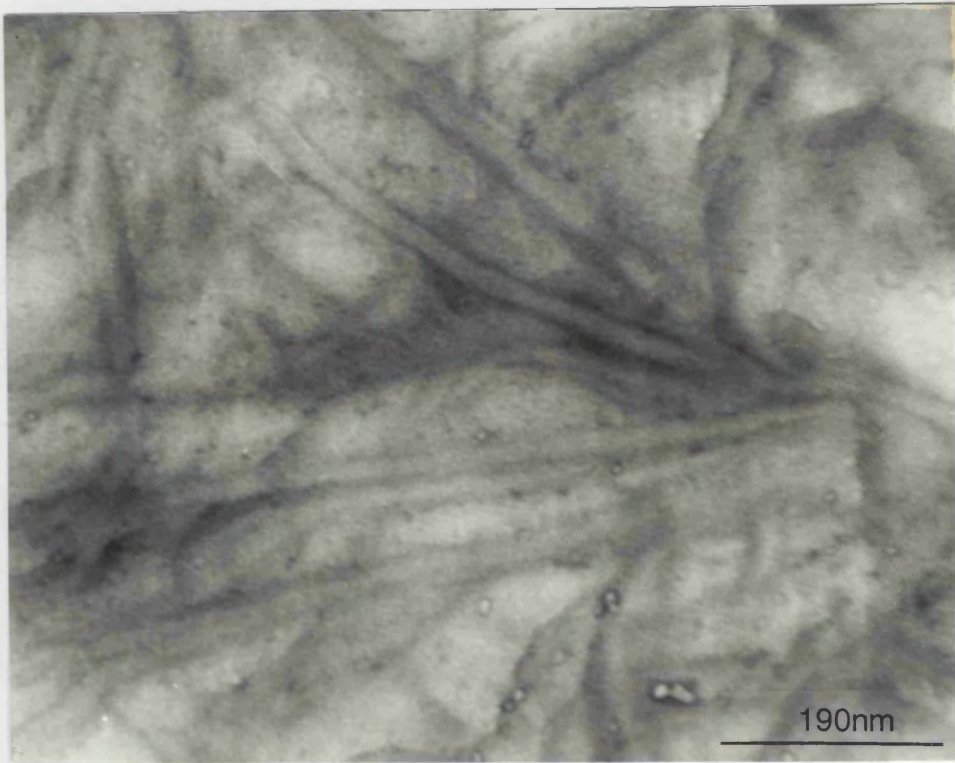


Figure 3.4 Transmission electron micrograph of UHMWPE crystal structure



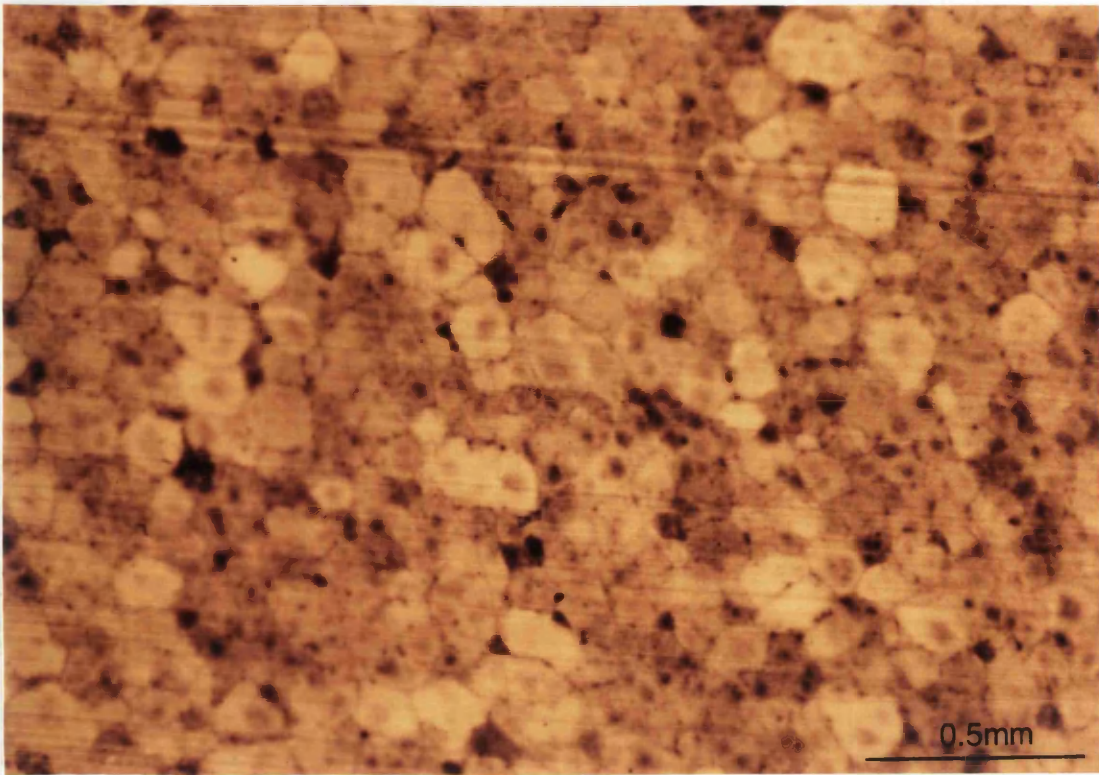


Figure 3.5 Chlorosulfonic acid treated Poly Hi

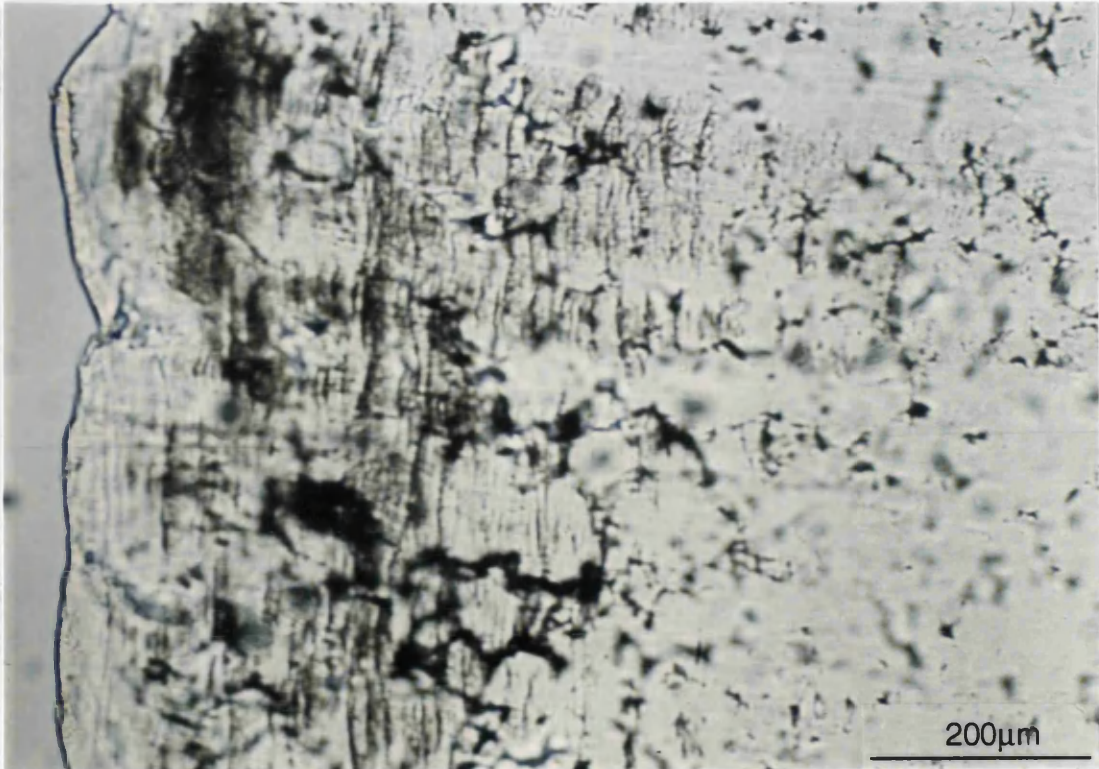


Figure 3.6 Xylene treated RCH1000

### 3.2.3 Resistance to Chemical Attack

#### 3.2.3.1 Chlorosulfonic Acid

The affect of CSA treatment was a general staining of the section a brown/black colour. The CSA could be seen to have highlighted grain boundaries and fusion defects in all materials (figure 3.5).

#### 3.2.3.2 Hydrogen Peroxide

Sections treated at room temperature had no noticeable change in oxidation levels, whereas specimens treated at 60°C showed increasing levels of oxidation with time.

Distilled water controls showed no signs of oxidation. CSA was used as a preliminary measure of oxidation of materials, prior to FTIR analysis. Poly Hi appeared to have a variable grain structure with a patchwork of light and dark grains evident. Sections of RCH1000 were not as affected, but a patchwork effect was still apparent. Poly Hi appeared less resistant to attack by hydrogen peroxide than RCH1000. Blocks of material after five days of H<sub>2</sub>O<sub>2</sub> treatment showed a distinct black border (after CSA treatment) approximately 0.2mm wide from the edge of the block. After ten days this oxidised band was approximately twice as thick.

#### 3.2.3.3 Xylene Treatment

Samples treated with hot xylene became opaque and slightly expanded after treatment. The xylene attacked from the surface of the samples, highlighting grain boundaries and enhancing inter-grain regions (figure 3.6). Poly Hi was much less affected by xylene than other materials examined.

### 3.2.4 Recrystallisation

Recrystallisation of GUR 415 produced spherulites, easily observed in polarised light due to the Maltese cross effect (figure 3.7). The effect is the result of the numerous crystals radiating from a central nucleus, with their chain axes perpendicular to the radius (i.e. across the radial fibrils), the refractive index is higher in the chain direction than in the perpendicular. This tangential orientation of chains leads to extinction in opposite quadrants if the spherulite is observed in polarised light, leading to the Maltese cross effect<sup>185</sup>. Some spherulites had a ringed appearance (concentric banding, figure 3.8), which is attributed to a regular twist in the crystals giving rise to a periodic change in refractive index. Once it had been shown that spherulites could be formed, further work was carried out to try to observe spherulites in the SEM. The most successful method for spherulite observation was the plasma-ashing of the powder recrystallised polyethylene onto a metal SEM stub (figure 3.9) and the freeze fracture of recrystallised powder, where the concentric banding pattern was seen (figure 3.10).



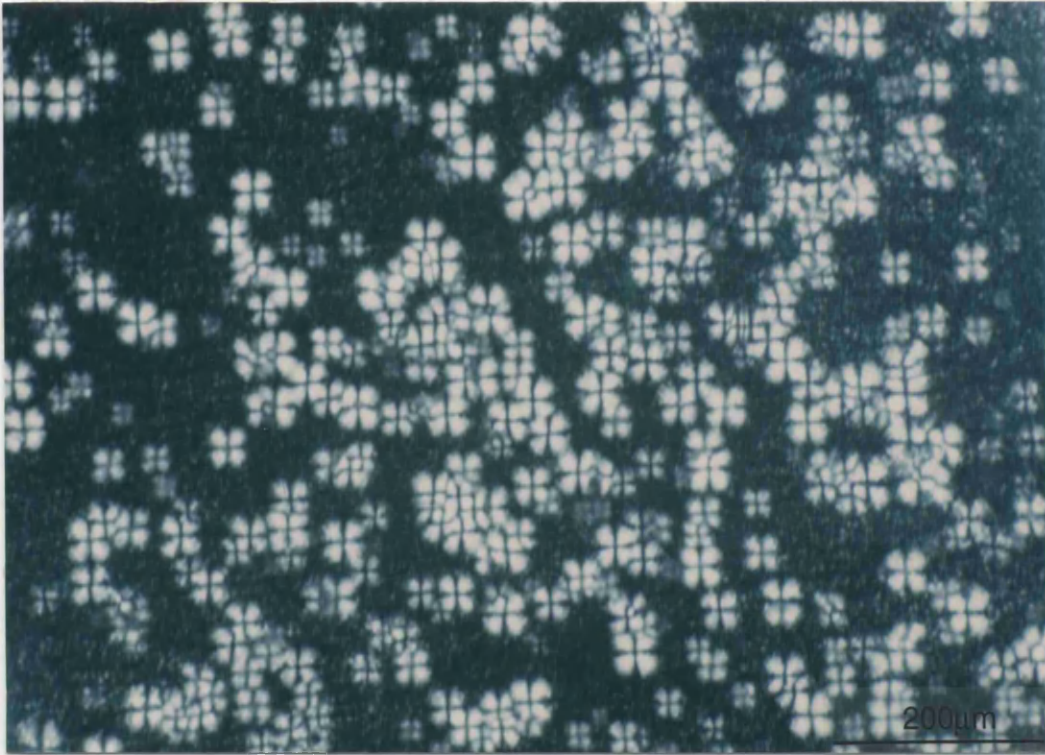


Figure 3.7 Spherulitic morphology produced on recrystallisation of GUR415 powder

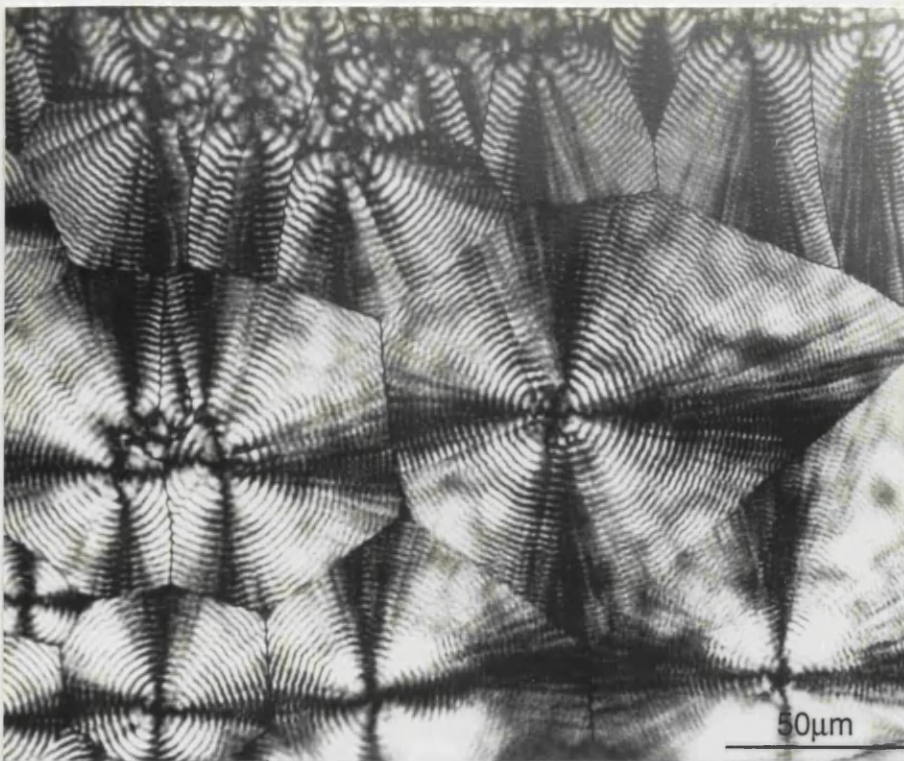


Figure 3.8 Spherulitic morphology exhibiting concentric banding



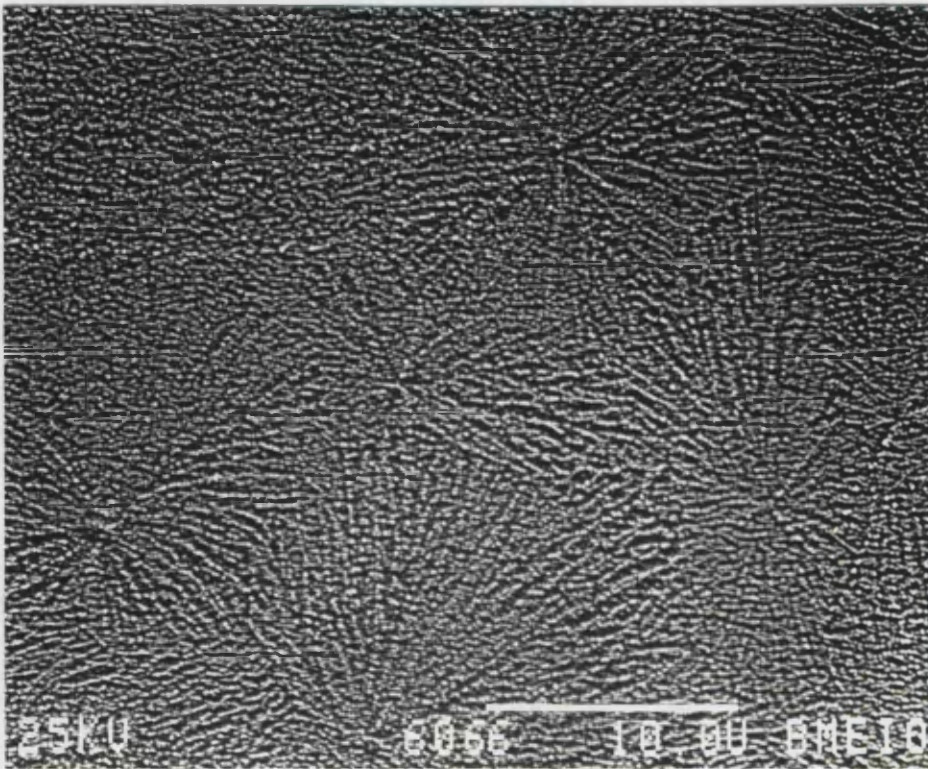


Figure 3.9 Scanning electron micrograph of spherulitic morphology

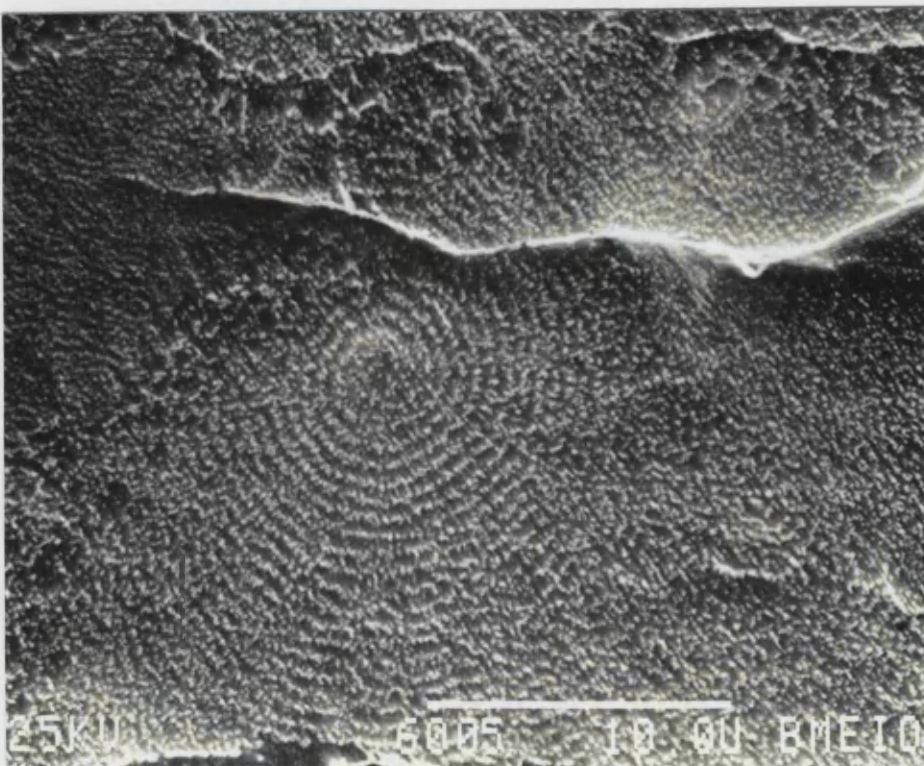


Figure 3.10 Scanning electron micrograph of spherulitic morphology exhibiting concentric banding

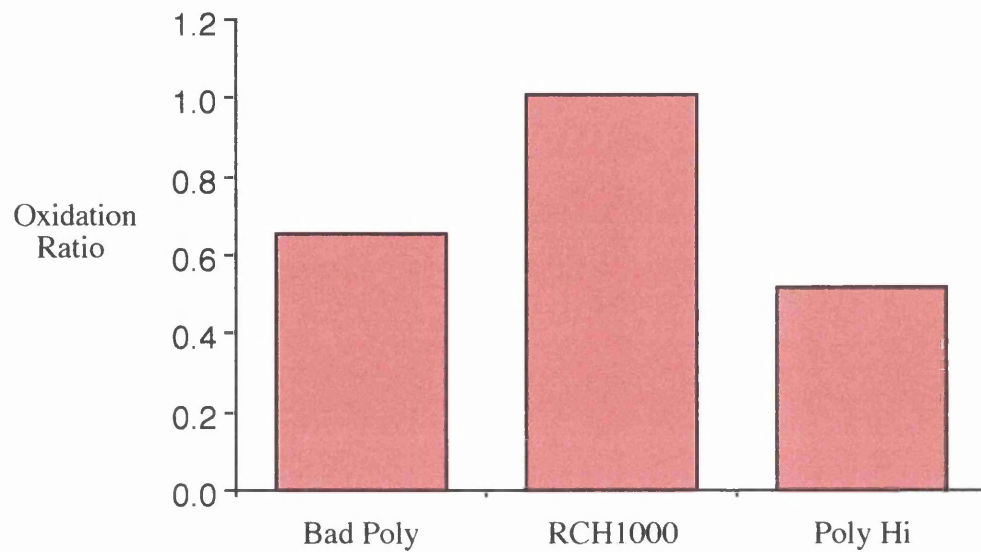


Figure 3.11a Oxidation ratio for stock materials

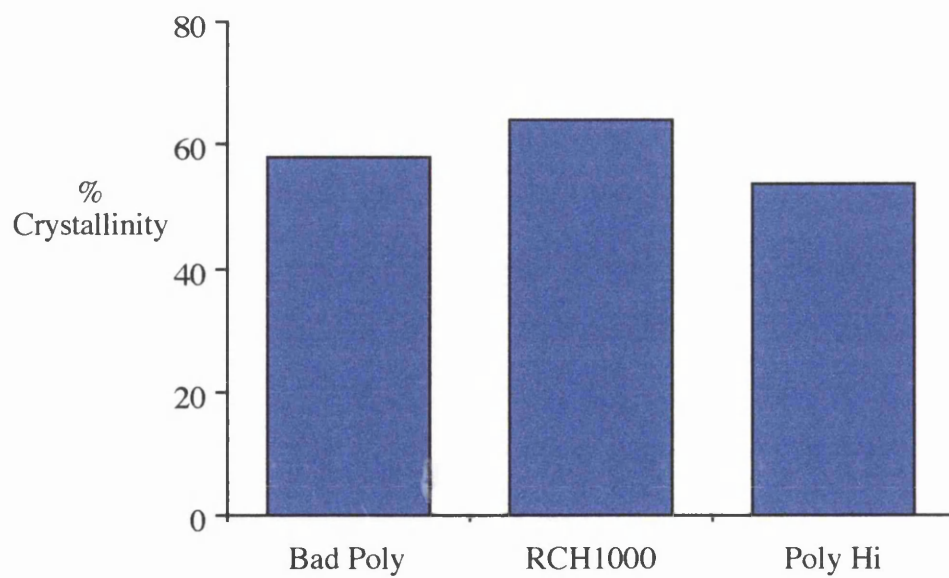


Figure 3.11b Percent crystallinity for stock materials



### 3.2.5 Infrared Spectroscopy

The results from the FTIR data are shown in table 3.1, with corresponding graphs in figures 3.11a&b. Crystallinity measurements ranged from 53-64%, in agreement with Rose & Radin<sup>42</sup>, with the exception of the recrystallised powder sample which had 41% crystallinity. A higher oxidation ratio obtained from FTIR data corresponded to the darker staining of a section by CSA.

Table 3.1 - FTIR data for a selection of stock UHMWPE materials

Material	% Crystallinity	Oxidation Ratio
Bad Poly	57.97	0.65
RCH1000	63.92	4.01
Poly Hi	53.45	0.52
R-415	40.61	2.40

### 3.3 Discussion

#### 3.3.1 Powder Morphology

Recent work has investigated the morphology of the powders used in the manufacture of UHMWPE<sup>37, 166, 175, 186, 187</sup>, and showed a hierarchical structure of the powder particles, but no work has been published involving the treatment of these powders with strong oxidising agents, such as chlorosulfonic acid. Treatment of powder with CSA was performed to obtain an indication of their crystalline nature, since it has been suggested that increasing crystallinity will improve the resistance to oxidation<sup>120</sup>. The possibility that the fibrillar ties seen between nodules/granules are crystalline in nature has been reported<sup>37</sup> and initial work with CSA seemed to confirm this. This is important because the tie molecules are responsible for the materials excellent toughness, impact and wear properties<sup>91</sup>. The CSA treated powders looked similar in morphological detail to untreated powders, with nodules more pronounced but with the 'ties' seemingly unaffected, indicating a crystalline nature. However, further treatment of powders has indicated a complete breakdown of fibrils, indicating their susceptibility to degradation under extreme conditions.

#### 3.3.2 Stock Material Morphology

The light microscope examination of Poly Hi and RCH1000 showed differing amounts of fusion defects. This could be accounted for by their manufacture from different base powders or by their different manufacturing methods. The observation that one sample which was moulded from the same powder used to manufacture RCH1000 had the greatest number of defects in any material, is in agreement with previous work stating fusion defects to be a result of manufacturing processes and not *in vivo* conditions<sup>44</sup>. Whether a combination of powder quality and manufacturing process lead to the particularly poor consolidation of this material could not be ascertained. This is in contrast to more recent work which suggests compression moulded material to have better consolidation than extruded materials<sup>188</sup>. It has also been reported that UHMWPE with a molecular weight between 2-4 million (GUR4120) has a greater molecular mobility which may enhance resin consolidation<sup>40</sup>. This was obviously not seen here with either RCH1000 or the 'bad poly'. It is probable that the process controls for compression moulded material have improved in recent years due to a better understanding of the problems associated with consolidation, thus avoiding the poor consolidation seen here. The increased use of directly moulded components, for which much more stringent process controls are possible, will also result in better consolidation materials in the future.

### 3.3.3 Resistance to Chemical Attack

The boundaries of fusion defects have been reported to be weaknesses in the material and strong evidence has been found that grain boundaries represent actual inhomogeneous properties in UHMWPE and that visible grain boundaries may be structurally weak, and may be regions of low molecular weight<sup>165</sup>. Treatment of the powders did not appear to stain them any quicker than a section of material. It therefore cannot be deduced from this work whether or not the grain boundaries are areas of unconsolidated material. CSA treatment of powders and stock materials proved a useful tool in the examination of these materials with the staining effect of this acid highlighting variations in polyethylene quality. Blackening of the polyethylene has been attributed to the oxidation of this material<sup>189</sup>. Highlighting of defects and grain boundaries in all materials indicates that these will be areas of weakness when exposed to oxidising agents within the body, since oxidation is known to be a phenomenon strongly associated with damage of UHMWPE<sup>120</sup>. In addition to this, other research<sup>133, 165</sup> has suggested that grain boundaries may facilitate oxidation, and possibly other chemical attack. This was shown upon exposing materials to xylene.

Treatment with hot xylene, caused an expansion of materials. The reason for this is unclear, but this phenomenon has been reported elsewhere<sup>133</sup>. Hot xylene dissolves low molecular weight products and this occurred at the inter-grain regions showing a weakness in the material structure since a low molecular weight is associated with reduced mechanical and wear properties. Low molecular weight products exist after manufacture or may be due to chain-scission, however the materials in this study were not irradiated. It has been reported that hot xylene extracts oxidation products<sup>124, 133</sup> and this supports the hypothesis that oxygen diffuses along the grain boundaries of the flakes of original resin.

Hydrogen peroxide treatment showed Poly Hi to be less resistant to oxidative attack by this chemical than RCH1000. It should be noted that these materials were unsterilised, therefore actual oxidation of this material *in vivo* due to hydroxy radicals may be different. Treatment of blocks of material indicated this is an unsuitable method to produce artificial ageing in wear test simulations due to the slow penetration of the fluid into the material, although this process would probably be increased under the cyclic loading. Other authors<sup>91</sup> have also found H<sub>2</sub>O<sub>2</sub> to have no significant affect on physical, chemical or mechanical properties.

This work on the resistance of commercially available UHMWPEs to chemical attack would have been improved by studying irradiated materials. This would have given a

more definitive view on their oxidation resistances, which is now known to be a major factor in the wear of polyethylene components.

### 3.3.4 Recrystallisation

It has been reported that UHMWPE is non-spherulitic<sup>152</sup> whereas Jasty et al<sup>166</sup> reported spherulitic organisation in ram extruded material and Weightman & Light<sup>172</sup> found spherulites in Hifax resin. The possibility of spherulite formation is potentially important, because the highly folded chains of the polymer molecules in spherulites can unfold when worn, leading to a decrease in wear resistance<sup>166</sup>. Spherulites produced by the heating of powder on a glass slide are not characteristic of bulk crystallised samples. One would not expect the clearly defined spherulites seen on melting of powder particles to resemble those seen in retrievals. Such spherulites are the outcome of a special heat treatment, and in this form will not be characteristic of bulk crystallised samples<sup>185</sup>. Thus spherulites produced by this method does not prove UHMWPE forms spherulites especially considering these experiments were performed in an atmosphere where oxidation of the polyethylene occurred. This was evidenced by FTIR results which showed high levels of carbonyl groups compared with normal UHMWPE. The highly birefringent nature of the recrystallised material indicates a high degree of orientation, but this does not imply high crystallinity, also evidence by the FTIR results. Although this work does not prove UHMWPE forms spherulites under the conditions that exist for manufactured material for prostheses, it does not disprove it either.

The orthogonal shapes seen on the freeze fractured surfaces were a form of fracture pattern, similar to craze patterns seen in other materials. This is in agreement with Atkinson et al<sup>97</sup> who commented that on examination of fracture surfaces from semi-crystalline polymers, the appearance was often closely reminiscent of the craze structure left on glassy polymer fracture surfaces. The radial lines seen on freeze fractured surfaces are due to initiation at the centre of particles. Such features are not seen in microtomed samples, due to preferential orientation imparted during the cutting process. Spherulitic structures have been reported<sup>166</sup> on freeze-fracture material but it is possible that these were not spherulites, but were these craze patterns. No photographs of their observations were given therefore this is only speculation. Inter-spherulitic fracture is not a general phenomenon, but examples have been found in semicrystalline polymers and trans-spherulitic fracture has also been observed<sup>160</sup>.

Other features seen on freeze-fractures surfaces included areas of persistent powder morphology, which has been reported by other authors<sup>181, 182, 190</sup>. The fractured surface was relatively flat, indicating a transgranular fracture and good consolidation of the material<sup>139</sup>.

### 3.3.5 Infrared Spectroscopy

Surprisingly, the crystallinity measurement for the recrystallised powder was only about 41%, possibly due to the lack of pressurisation of the material upon solidification. The reason is not fully understood, but the results are similar to those reported by Jasty et al<sup>166</sup> who stated that the powder resin (GUR 4150) had a crystallinity of approximately 60%, but on reheating the powder the crystallinity dropped to about 45%.

Oxidation and crystallinity measurements were performed to give an indication of values typically seen in non-implanted materials. Relatively high oxidation of RCH1000 is surprising since this had neither been irradiated nor implanted. Oxidation of stock material can occur during manufacture since polymers are normally protected by antioxidants but their use is forbidden in the case of implant materials. Crystallinity values were as expected for UHMWPE.

Overall, a high variation in un-implanted, non-irradiated stock materials gives an insight to the problems of analysis of retrieval specimens. Such variation prior to implantation will affect the wear performance *in vivo* and thus detrimental variations in the bulk UHMWPE need to be minimised. Large variations in material properties have been reported between different test centres for the same material<sup>178, 191</sup>. Collier et al<sup>192</sup> examined bulk medical grade UHMWPE from different orthopaedic suppliers and tensile test results indicated large variations in properties such as yield strength (23%), UTS (42%), elongation at break (>100%) and creep (>400%). These variations raise the concern whether marginal designs using thin polyethylene inserts will be at additional risk, due to the use of polyethylene with less than optimal properties.

It has been found that resin lots of the same grade, from the same supplier, processed in a controlled manner, yield consistent results<sup>191</sup>. In an attempt to reduce the variation in physical properties reported by different research groups, a global reference UHMWPE was manufactured. This material was donated to the Hospital for Special Surgery (HSS) and then supplied to any research facilities<sup>193</sup>, to try to produce comparative results, and thus limit variability seen in polyethylene properties due to testing of different batches and grades of material. Bennett et al<sup>178</sup> produced a paper characterising this material and deemed it a consistent material uniform along its length and thickness in physical and chemical properties. Although this is a step forward for the research community to allow comparison of test results, manufacturers have to take heed of the warnings in the literature and ensure tighter manufacturing controls.

All this work is essentially in agreement with Kilgus et al<sup>170</sup> who summed up the present problem, stating that UHMWPE is a material that varies greatly in its consistency and its physical properties, not only between different medical grades of

polyethylene, but also within single production runs of UHMWPE. The variations in properties will lead to variable performance *in vivo* in terms of surface wear, and sub-surface delamination wear. Hence some standardisation would be beneficial. If combinations of properties could be optimised, polyethylene wear rates could be reduced i.e. all components could be made with the 'best' polyethylene and maybe substantially reduce wear particles and delamination failures. Until research produces some guidelines for the manufacture of UHMWPE, to reduce some of this variability, it is unlikely that new designs of replacement knee joints will resist the fatigue failures seen today.

## CHAPTER FOUR

### OXIDATION AND DELAMINATION OF RETRIEVED TOTAL KNEE REPLACEMENTS

## 4.1 Introduction

The study of retrievals is of great importance for the evaluation of a materials behaviour to wear mechanisms and the *in vivo* environment, to determine the factors that influence degradation (chemical or physical) of the polyethylene insert. The problem encountered with such a study is to determine the extent of changes that have occurred, when there are often no records of the grade of material used, the processing conditions and there are no unimplanted (or time zero) components for comparison.

Early retrieval studies were concerned mainly with failures of fixation and design. Early failures in total knee arthroplasty were often a result of loosening of the prosthesis. This occurred due to many factors such as malalignment, poor initial fixation, stress on the prosthesis, prosthesis design, wear debris and bone stock<sup>194</sup>. These were then followed by a spate of reports concerning the failure of TKA implants caused by severe wear of the tibial polyethylene<sup>3, 8, 43, 195</sup>. These cited several potential reasons for their findings including conformity, polyethylene thickness and alignment. Overall, a number of factors have been suggested to affect polyethylene wear, including patient characteristics such as size, sex, level of activity as well as component factors such as accuracy of alignment, prosthesis design and implant materials. The latter group of factors is now recognised as being influential on the long-term efficacy of a TKR, since the wear of UHMWPE is one of the main factors dictating the success of a total joint replacement.

This chapter is concerned with the wear of TKR, particularly the material properties of the polyethylene used for the tibial bearing surface. As seen in the previous chapter, a variability exists in UHMWPE materials as a consequence of different base resins, additives and manufacturing processes. Once this material is machined or moulded to the required dimensions, a new set of defining parameters take effect, which are related to the design of the component. Variables such as the thickness of the polyethylene, metal backing and conformity of the condyles will affect the type and magnitude of wear observed on a retrieval, as discussed in chapter one. Consequently, there are many types of wear seen on retrieved tibial components, including deformation, abrasion, scratching, pitting and delamination. Delamination is the most catastrophic form of wear, leading to the loss of large flakes of polyethylene from the articulating surface. The other types of wear produce much smaller wear particles, which in the hip have been associated with osteolysis, loosening and ultimately the need for revision surgery.



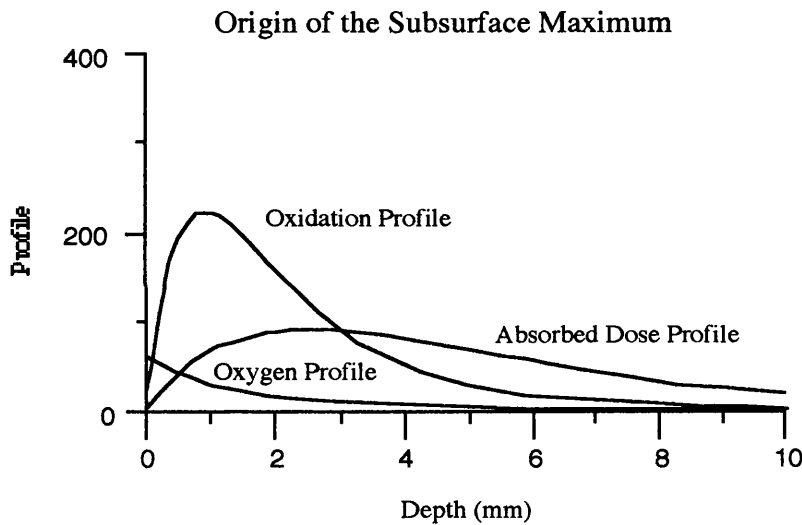
Delamination, being the most destructive form of wear, has been extensively investigated to determine its origins, even though this form of wear is only seen in a small proportion of prostheses. It is believed to be due to a fatigue failure of the material as a result of repetitive cyclic loading during every day activity. This failure is initiated by the development and propagation of sub-surface cracks which eventually connect with the surface releasing large flakes of wear debris<sup>169</sup>. Various factors effect the onset of delamination. The kinematics at the articulating surface are important with sub-surface crack initiation and propagation occurring during cyclic sliding rather than rolling<sup>196</sup>. Design of the implant is important, with delamination and catastrophic fracture related to high contact stresses and associated more with bearing surfaces of low congruity<sup>5, 13, 197</sup>. Misalignment of components also appears to be important with delamination and cracking occurring as a result of increased stresses particularly towards the edges of flat components and at the intercondylar notch where more conforming designs resist rotational movements<sup>6, 14, 17, 43, 170, 198</sup>. In addition to the geometry of the knee, a number of material factors appear to affect delamination of the plastic. Fusion defects have been linked with delamination as possible crack initiation and propagation sites<sup>43, 169, 180, 196</sup>. Walker et al<sup>199</sup> suggested that polyethylene with fusion defects has a low crack initiation time and that cyclic stresses will lead to crack initiation from defects particularly at depths of approximately 1mm below the surface, the area of highest von Mises stresses.

Another factor that will probably affect delamination of tibial polyethylene, which is investigated in this chapter, is the material changes initiated by gamma sterilisation. Gamma irradiation has been the most widely used sterilisation method for UHMWPE implants, but is now known to induce various chemical changes, including chain scission which can lead to oxidation<sup>66, 76, 90, 120, 200</sup>. Chain scission occurs during gamma irradiation with the formation of free radicals, which can subsequently cause either cross-linking or oxidation, depending on the atmosphere surrounding the material. The latter results when oxygen is present either at the time of irradiation, on the shelf or in the body.

The effects of gamma-irradiation on polymers and specifically polyethylene have been recognised for over two decades. In 1979, Nusbaum and Rose<sup>201</sup> investigated the effect of gamma sterilisation on UHMWPE and concluded that irradiation in air caused oxidative degradation as well as cross-linkage of the polyethylene molecules, and probably increased the materials susceptibility to damage caused by low level cyclic deformation. More recently the chain scission of polyethylene molecules has been reported to result in shorter molecular chains, thus altering abrasion resistance and material properties<sup>202</sup>. Gamma sterilisation in air has also been shown<sup>66</sup> to oxidise

UHMWPE, which results in chain scission, molecular weight reduction, and degradation *in vivo*.

The oxidation of UHMWPE has recently been shown to result in the time dependant development of a sub-surface band of more highly oxidised material<sup>125</sup>. The reason the peak is sub-surface is a culmination of several factors. When components are sterilised by irradiation the absorbed dose is none uniform through the sample and results in a maximum dose at approximately five millimetres from the surface. During shelf ageing and *in vivo* ageing, the oxygen profile within the material is determined by diffusion, with the oxygen concentration decreasing from the surface. The interaction of these two factors results in the peak of oxidation occurring at a depth below the surface of the component. The magnitude and depth of the sub-surface oxidation will depend on the radiation dose, the diffusivity of oxidants and the temperature.



(from Sun et al<sup>125</sup>)

The oxidised region is often referred to as the 'white band'. This is because upon sectioning a component, micro-cracking occurs in the oxidised band due to embrittlement, resulting in an opaque appearance. Since the oxidised region is embrittled, this represents a structural weakness within the material. Since delamination wear is known to result from sub-surface cracking, the hypothesis of this work was that delamination wear is initiated within this oxidised band. A selection of delaminated retrievals of a variety of designs with varying conformities and thus different stress levels *in vivo*, were examined. The aim of this work was to investigate a correlation between the development of a sub-surface oxidised band in retrievals and delamination wear.

## 4.2 Materials and Methods

### 4.2.1 Variability Study

A selection of components were chosen from a database of over three hundred retrieved tibial components, to analyse different designs and therefore materials and manufacturing methods, for variability in polyethylene quality. Fifty micron sections were examined in transmitted and polarised light for the presence of fusion defects, inclusions and voids in the microstructure. Oxidation was examined qualitatively using CSA staining. FTIR was performed to quantify both the bulk oxidation and crystallinity of the selected materials as well as performing depth profiles.

### 4.2.2 Oxidation and Wear Study

A selection of retrievals were analysed for the presence of wear damage, specifically delamination, to see if a correlation could be found between delamination and oxidation of the polyethylene. Thirty four retrievals were examined, the majority were St Georg Sledge and Kinematic designs which had been implanted for greater than six years. The study was expanded to introduce specimens which had been retrieved after shorter implantation times, and of several different designs. All the chosen components showed delamination wear. The reasons for removal were variable and are listed in table 4.1, with loosening the main reason for removal. All retrievals were scored for type and severity of wear damage. This was achieved using a modified form of that of Hood et al (1983) and used by Blunn et al<sup>6</sup>. Each condyle is divided into three equal areas with respect to anterior-posterior position. Each area is then rated from 0 (no wear) to 5 (most severe wear) for deformation(burnishing), pitting, abrasion, cement, scratching, bone, metal and most importantly delamination.

In order to assess the location and amount of oxidation, sub-surface failure and position of any residual stresses, the retrievals were cut transversely through the middle of the wear track. Fifty micron sections were cut perpendicular to the wear track. Specimens were viewed in transmitted and polarised light to qualitatively examine the position of residual stresses caused by deformation of the polyethylene. Sections were treated with chlorosulfonic acid. To verify the effect of this acid CSA treated sections were compared with sections from the same component which were analysed by FTIR. Treatment with hexane or heptane was carried out on sections prior to CSA treatment, due to reports of absorbed species giving misleadingly high oxidation levels<sup>128, 129</sup>.

Table 4.1 - Prosthesis type, number, duration and reason for removal.

Prosthesis Type	Number	Duration of Implantation (years)		Reason for Removal  (No. of prostheses)
		Range	Average	
Attenborough	3	3 - 12	8	Tibial loosening (2), Infection (1)
Freeman	1	15.5	-	Loosening (1)
Kinematic	14	2 - 10	6	Fractured tibial tray (3), Loosening (8), Infection (2), Polyethylene wear (1)
Minns Meniscal	1	7	-	Subluxation (1)
PCA	3	4 - 5	4.5	Loosening (1), Pain (1), Polyethylene wear (1)
Rota Glide	1	6	-	Loosening (1)
Sledge	10	6 - 14	10	Loosening (2) Infection (2), Ligament Instability (6)
Total Condylar	1	9	-	Pseudoarthritis (1)

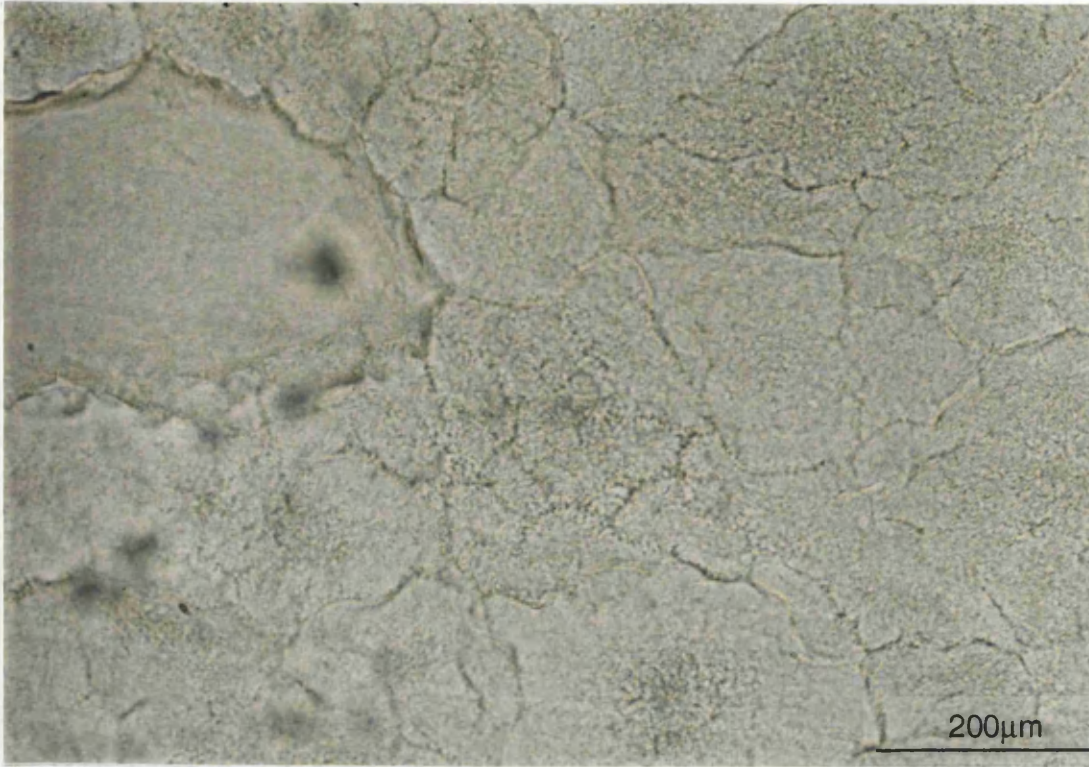


Figure 4.1 Grain boundary morphology

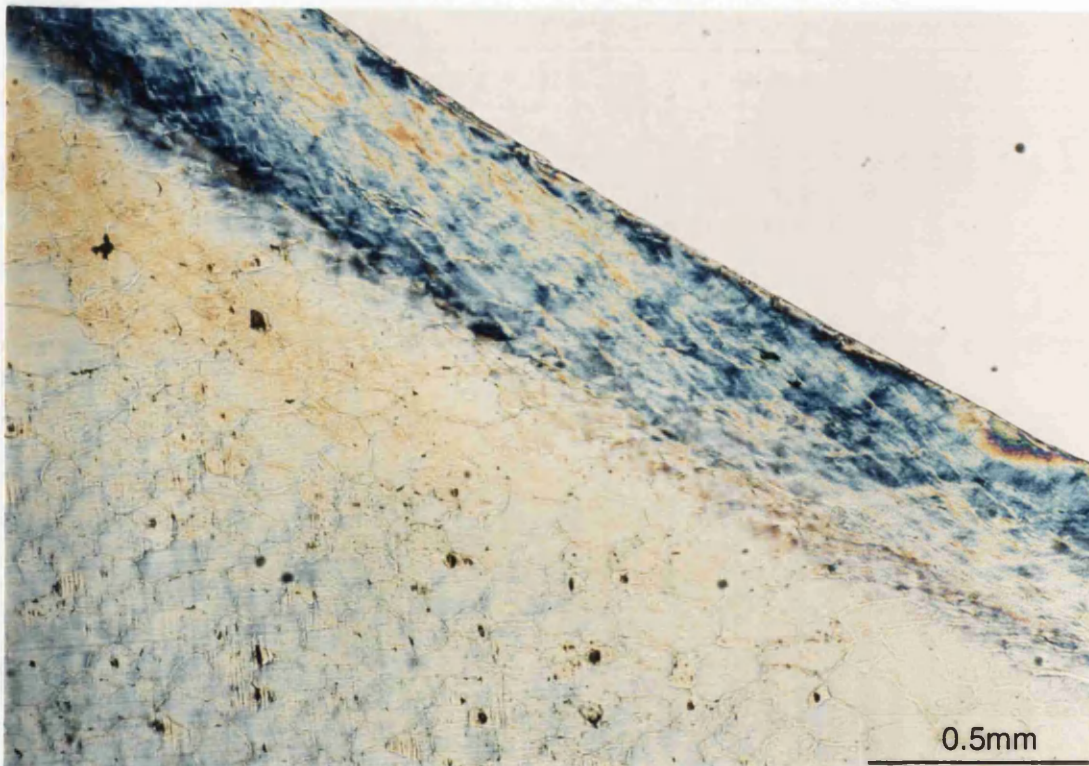


Figure 4.2 Polarised light micrograph showing high crystallinity in the demarcation zone of the hot pressed region of a PCA retrieval

## 4.3 Results

### 4.3.1 Variability Study

#### 4.3.1.1 Morphology

Examination of thin sections cut from retrieved prostheses showed variable microstructure both within and between components. Some sections had a well consolidated structure with few defects observed, whereas others had some grain structure visible, with this enhanced towards the bearing surface, and defects situated uniformly throughout the section. Variable microstructure within a single component was especially apparent in the Marmor, MG and AGC components. These components did not have any fusion defects, but grain boundaries were visible throughout the sections (figure 4.1).

The PCA component had a typical banded structure seen at a depth of approximately 1-2 mm from the articulating surface of the component, associated with the hot pressing of this surface. The demarcation zone could be seen more clearly in polarised light (figure 4.2) and was seen from FTIR data to have increased crystallinity.

The two Brigham unicondylar prostheses examined showed a variable microstructure, with fusion defects apparent. On one component, spherulites could be seen, as an unresolved birefringent mass under polarised light, in the region where the polyethylene interlocked with the tibial base plate (figure 4.3). This polyethylene component was excessively worn, in regions through to the metal base plate.

#### 4.3.1.2 Infrared Spectroscopy

FTIR analysis of the oxidation and crystallinity of the bulk material in selected components is shown in table 4.2 and figures 4.4 a & b. In addition the depth profiles for four retrievals are shown in figures 4.5 - 4.7. For the Marmor component shown in figure 4.5, it can be seen that the trends for oxidation and crystallinity are opposing, with an increase in one parameter occurring concurrently with a decrease in the other. In contrast for the Kinematic and PCA components shown in figures 4.6 & 4.7 respectively, the levels of oxidation and crystallinity increase and decrease together. For these components a peak in both oxidation and crystallinity occurred at 0.5 - 1 millimetre below the articulating surface. All components showed a decrease in crystallinity at the surface compared to the bulk material.



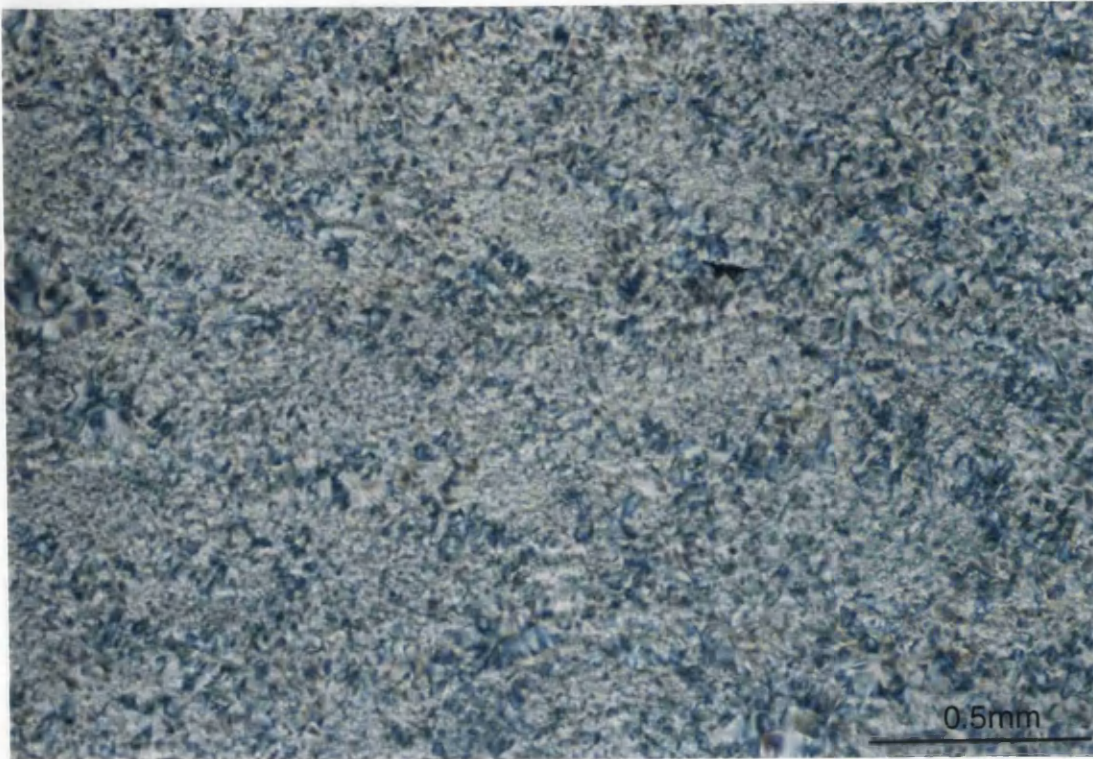


Figure 4.3 Spherulitic morphology in a retrieved St Georg Sledge prosthesis

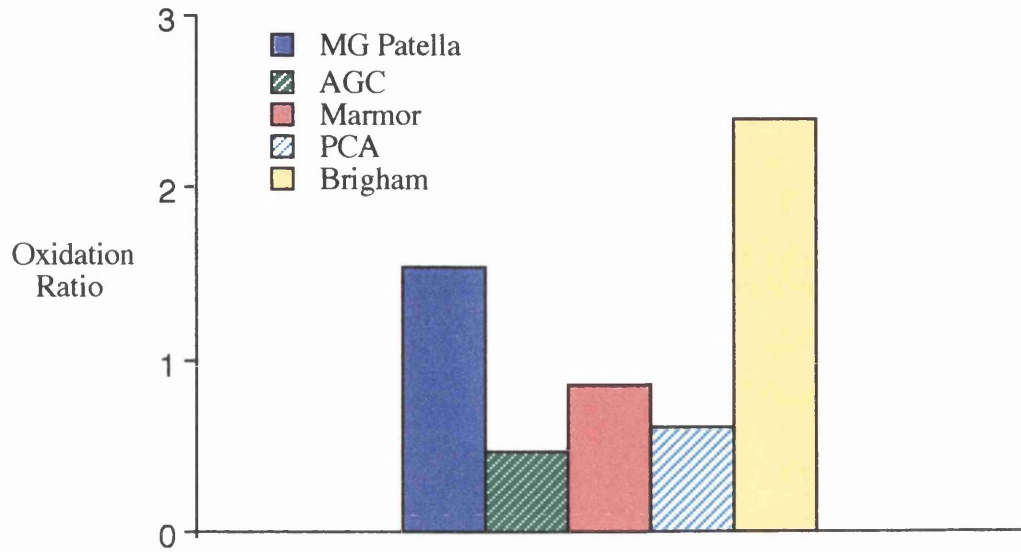


Figure 4.4a Oxidation ratio for selected retrievals

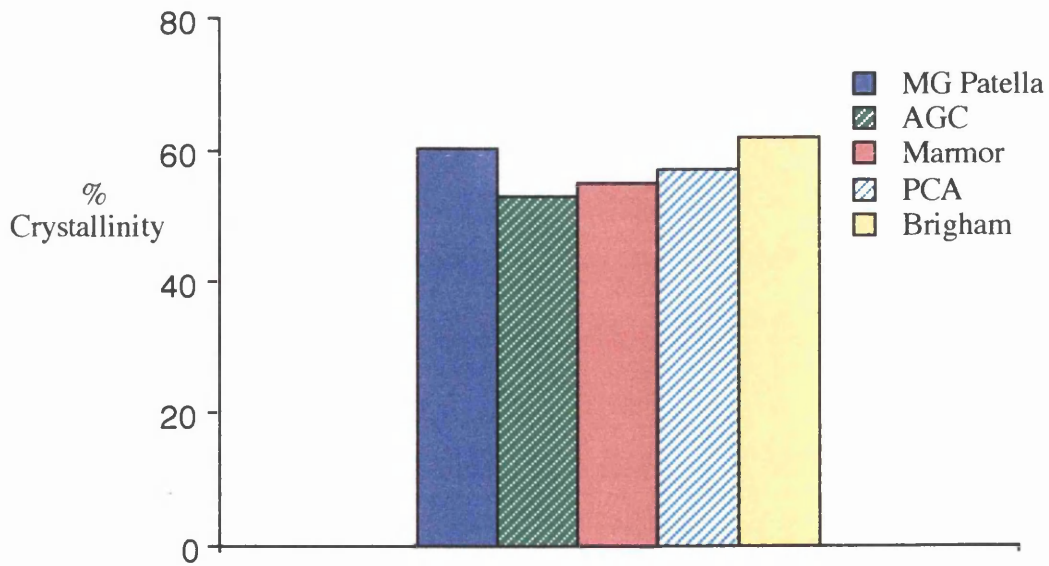


Figure 4.4b Percent crystallinity for selected retrievals



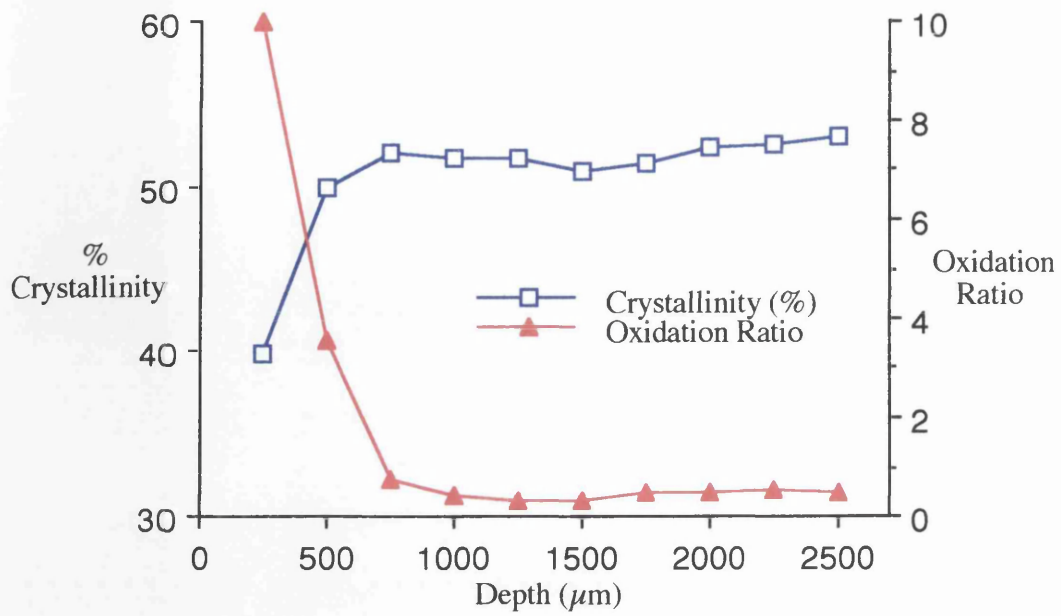


Figure 4.5a FTIR data for a Marmor retrieval

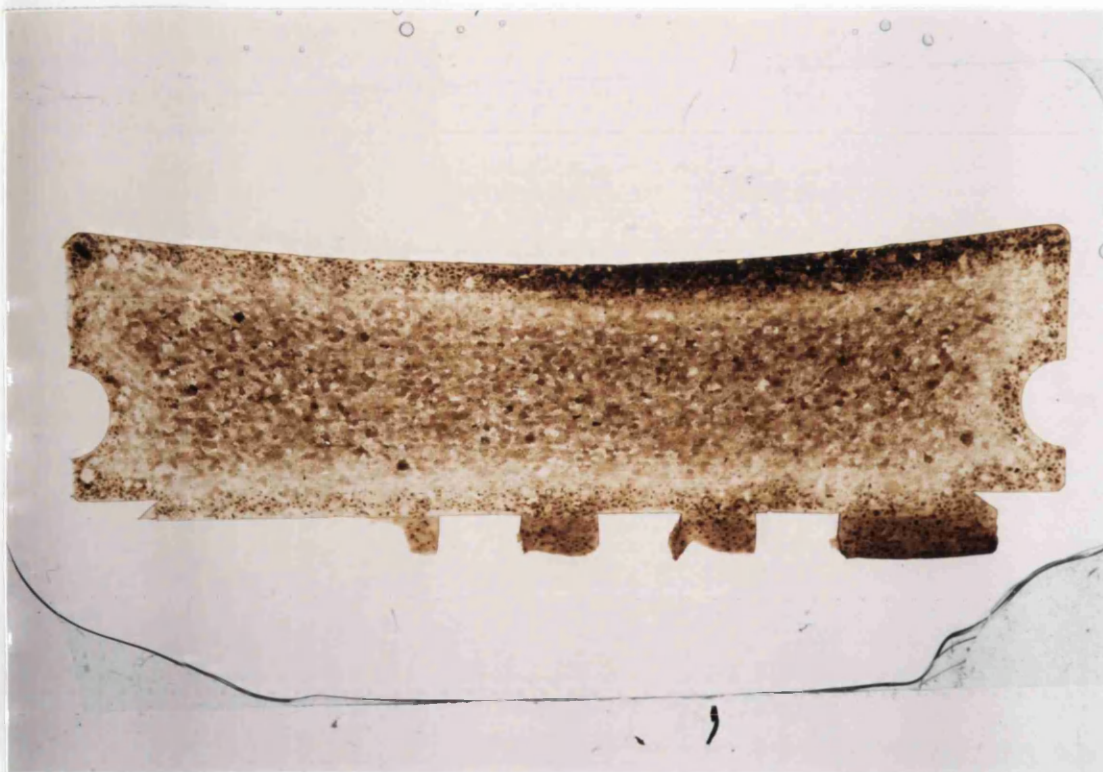


Figure 4.5b CSA stained thin section from a Marmor retrieval

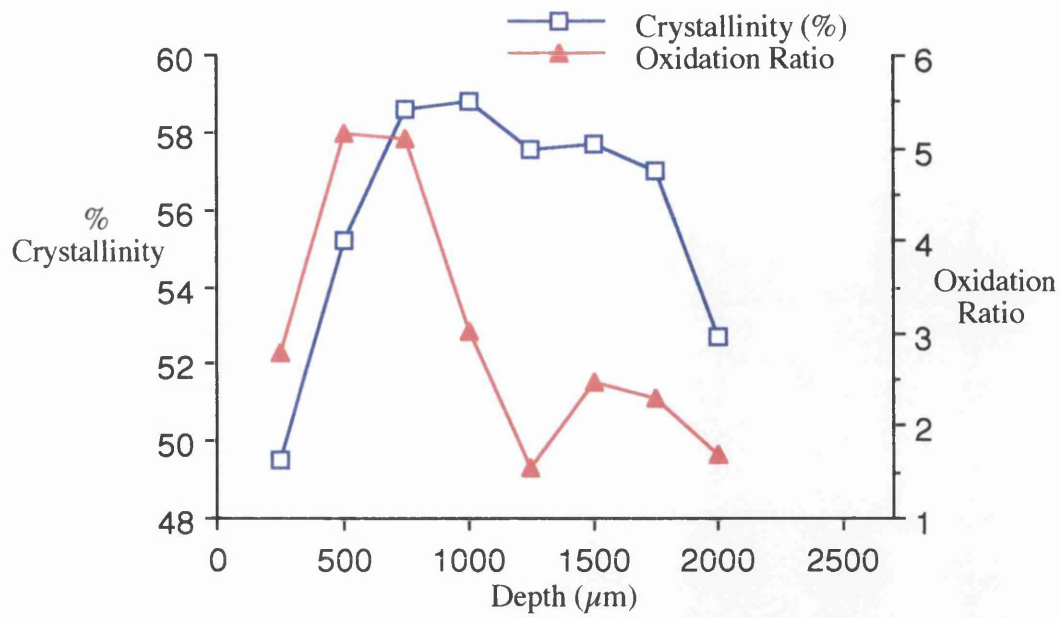


Figure 4.6a FTIR data for a Kinematic retrieval

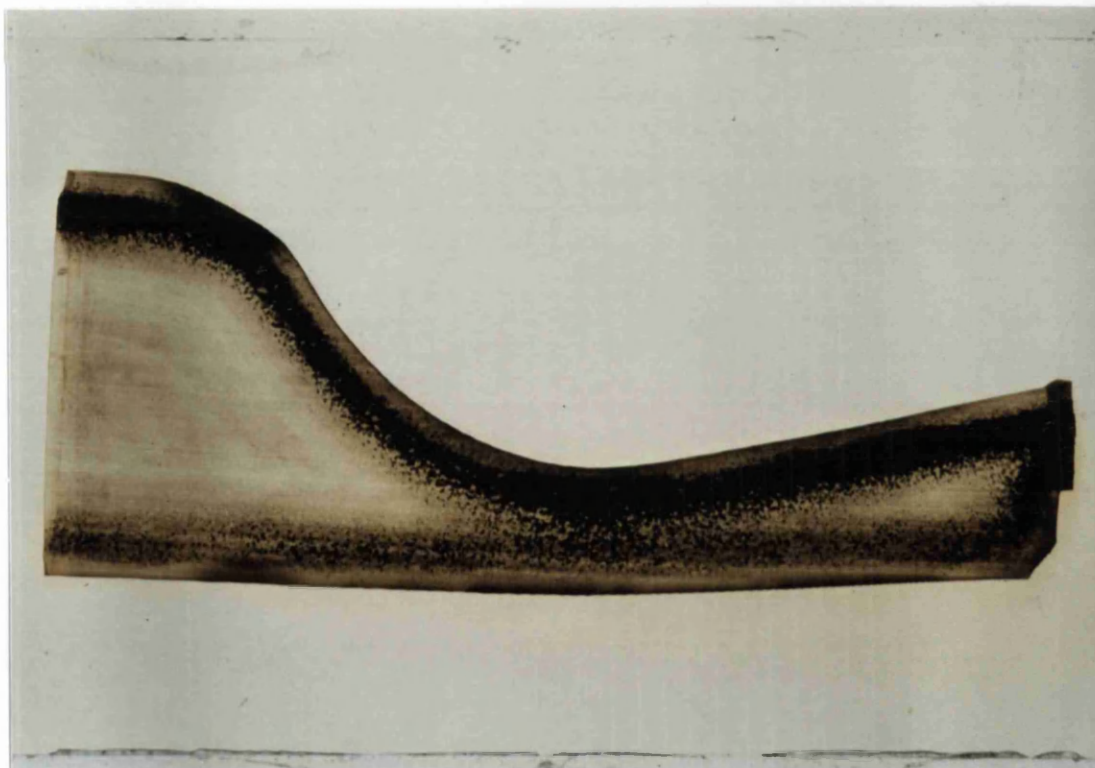


Figure 4.6b CSA stained thin section from a Kinematic retrieval

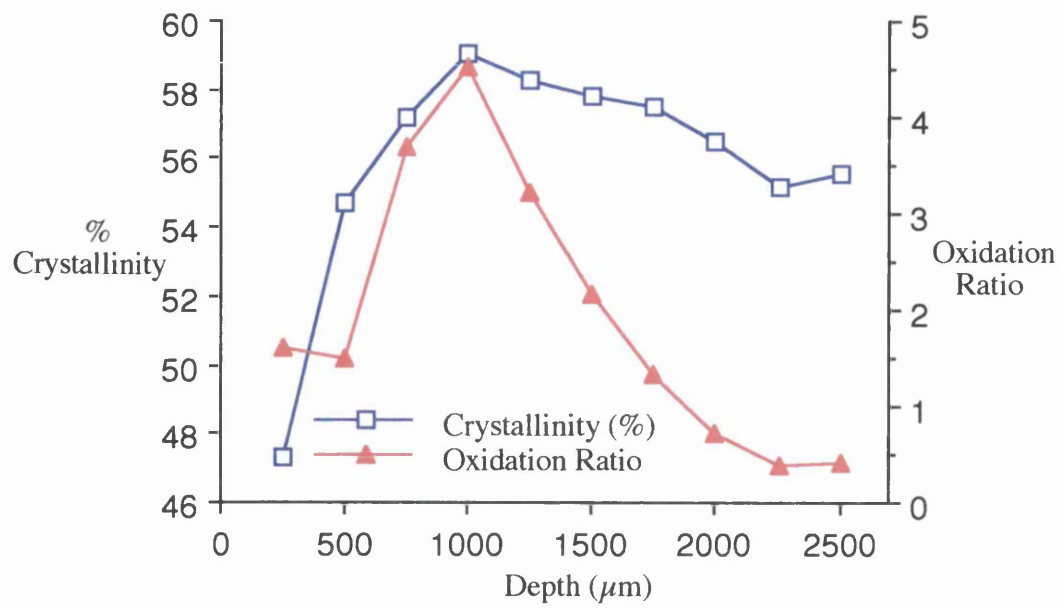


Figure 4.7a FTIR data for a PCA retrieval

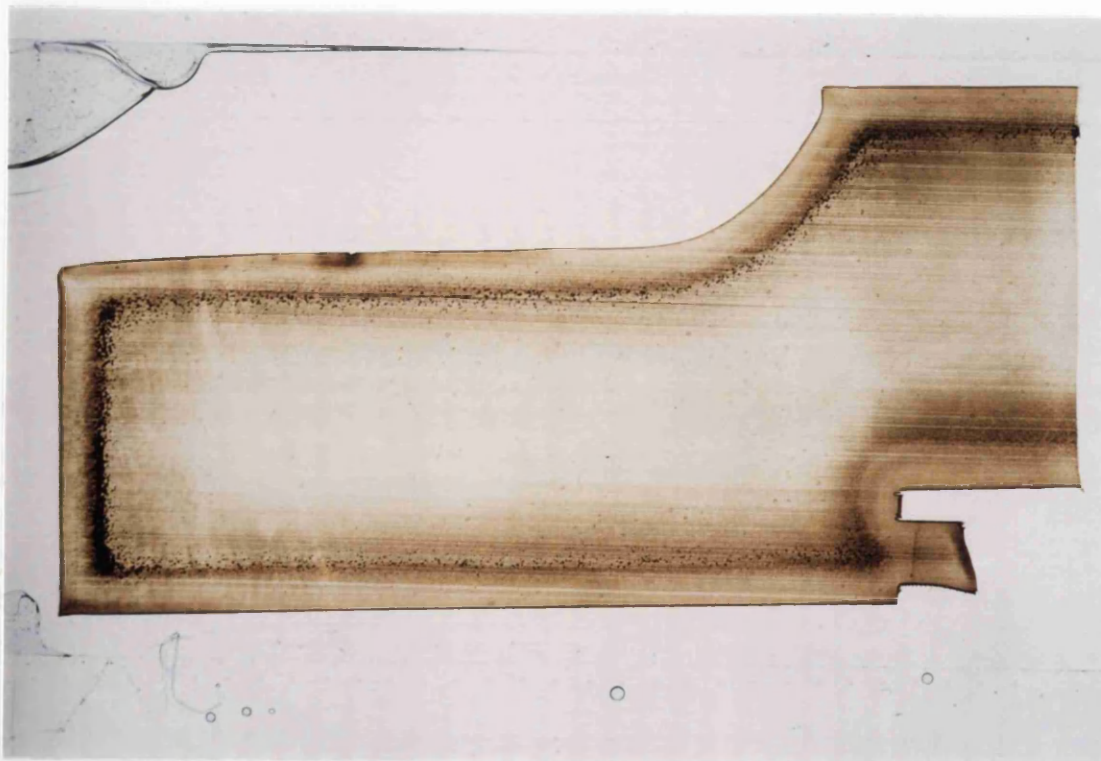


Figure 4.7b CSA stained thin section from a PCA retrieval

### 4.3.1.3 Resistance to Chemical Attack

CSA treatment highlighted defects, grain boundaries and the wear track on the articulating surface of all retrieval components by staining them black. Staining of the wear track indicates an alteration in the chemical and thus physical properties of these components at the bearing surface, relative to the underlying non-worn polyethylene and to the stock materials. Heptane treatment of sections prior to CSA treatment showed no reduction in the levels of staining by CSA compared to the untreated section. This indicated that adsorbed species did not produce any artefact with this staining method associated with either surface oxidation or the subsurface band.

The PCA, had a dark band which was seen to extend around the whole section at a depth of 1-2mm from the surface (figure 4.7b). This does not however relate to the hot-pressed region, as the band extends around the whole component and not just the articulating surface, but is related to oxidation of the polyethylene due to the sterilisation process.

The AGC component had very low wear and low surface oxidation. The oxidation of this material was the lowest of the selected retrievals and there was no sub-surface oxidation.

The MG tibial component had a dark band of constant thickness, along the bearing surface, associated with the wear track. The MG patella component showed oxidation at the worn surface, but also at the point of interlock with its metal backing (figure 4.8). The Brigham prosthesis also showed high oxidation in the bulk material as evidenced by FTIR and also high oxidation at the lower surface. Oxidation (as measured by CSA staining) at the lower bearing surface of these components decreased after heptane treatment.

Table 4.2 - Oxidation and crystallinity of selected retrieval materials

Material	Oxidation Ratio	% Crystallinity
MG Patella	1.534	60.05
AGC	0.459	52.86
Marmor	0.862	55.04
PCA	0.605	56.93
Brigham	2.400	61.89



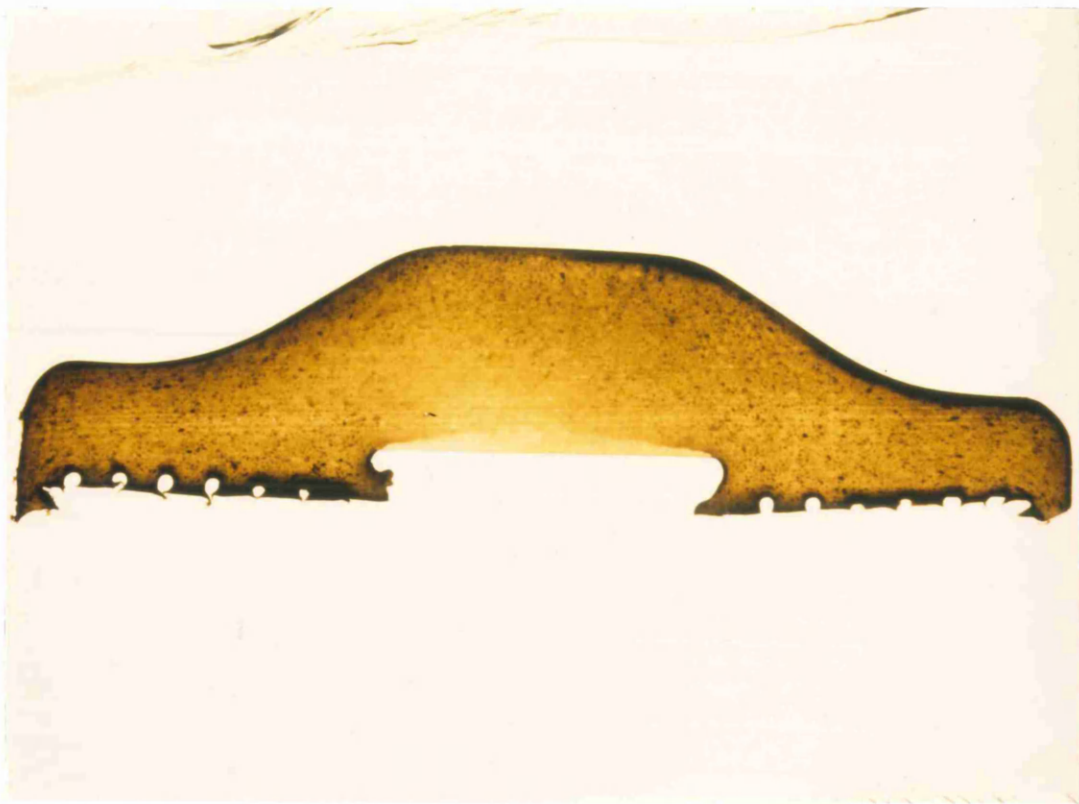


Figure 4.8 Wear track highlighted by chlorosulfonic acid

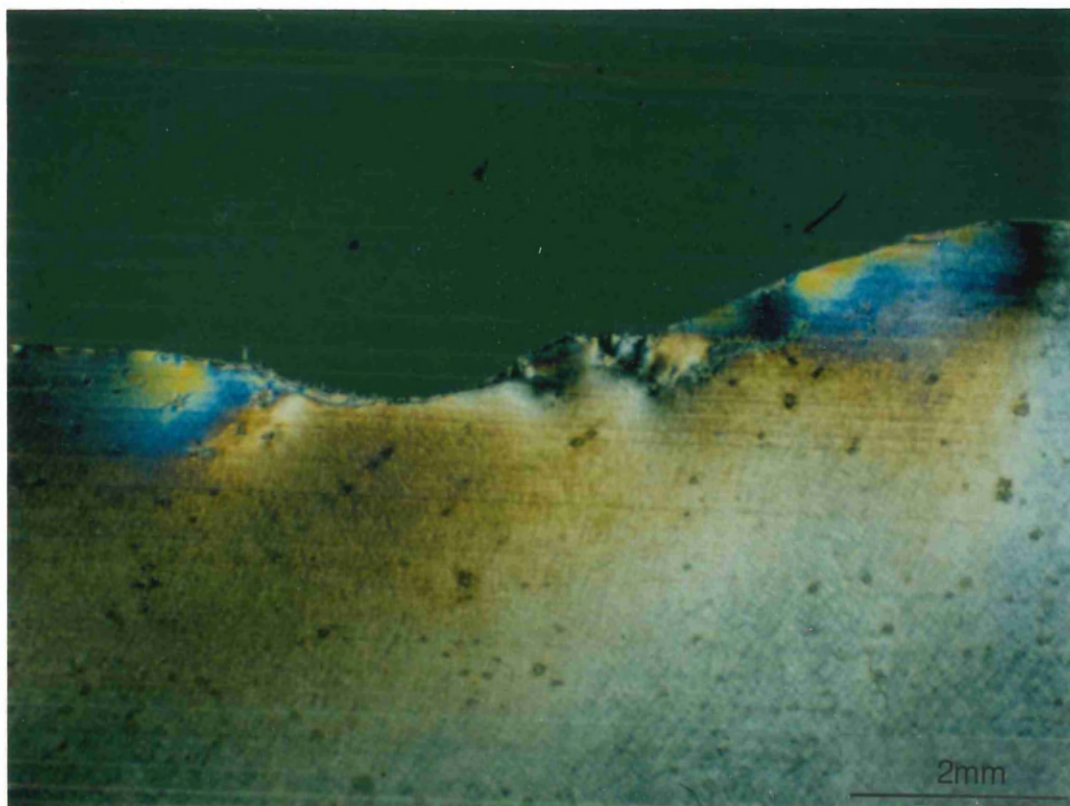


Figure 4.9a Polarised light micrograph of the wear track of a retrieval

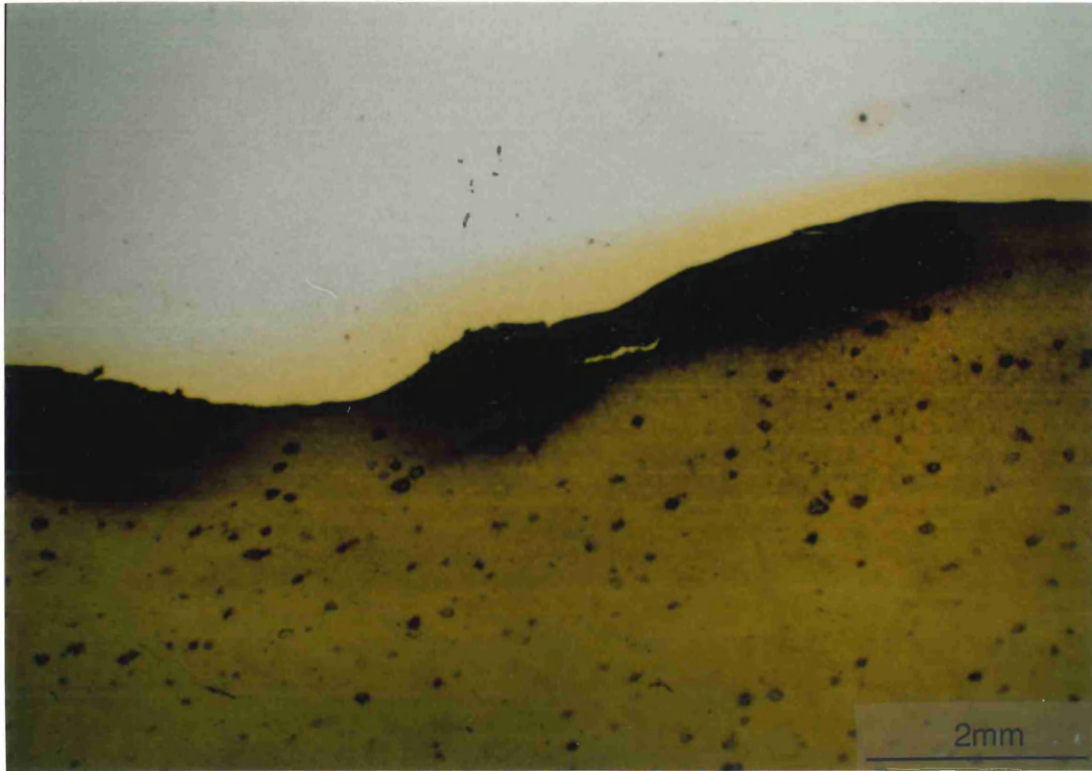


Figure 4.9b Chlorosulfonic acid treated wear track of retrieval in fig 4.9a

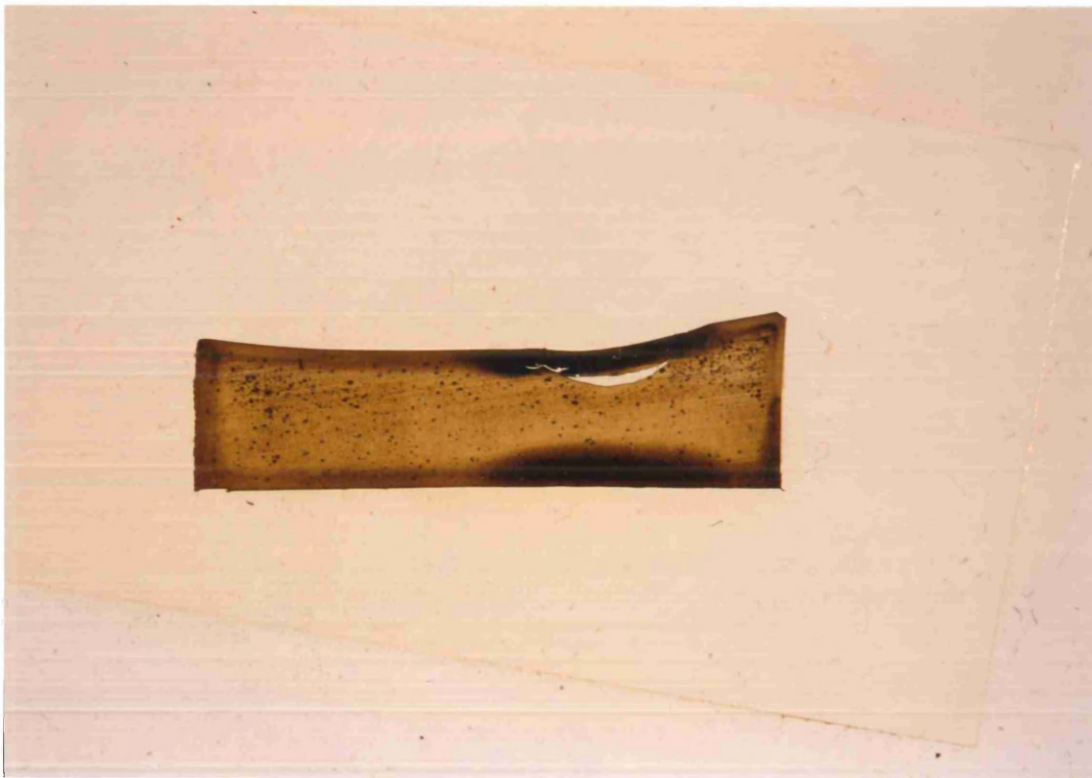


Figure 4.10 Chlorosulfonic acid treated delaminated retrieval

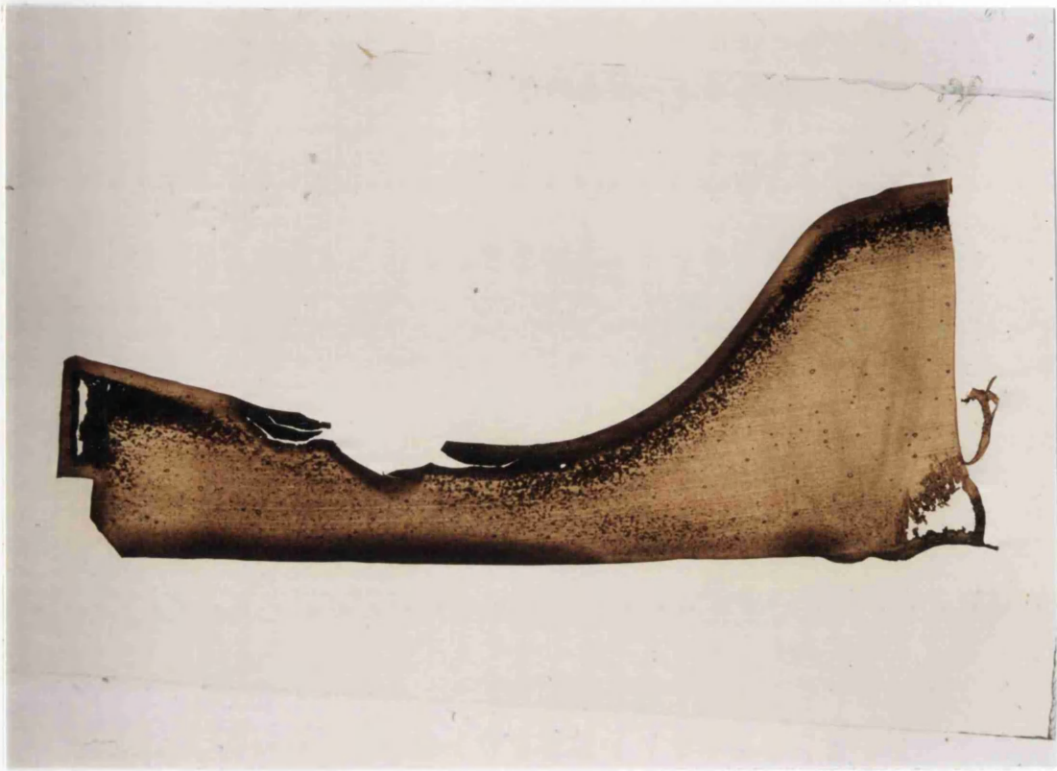


Figure 4.11a Chlorosulfonic acid treated delaminated retrieval

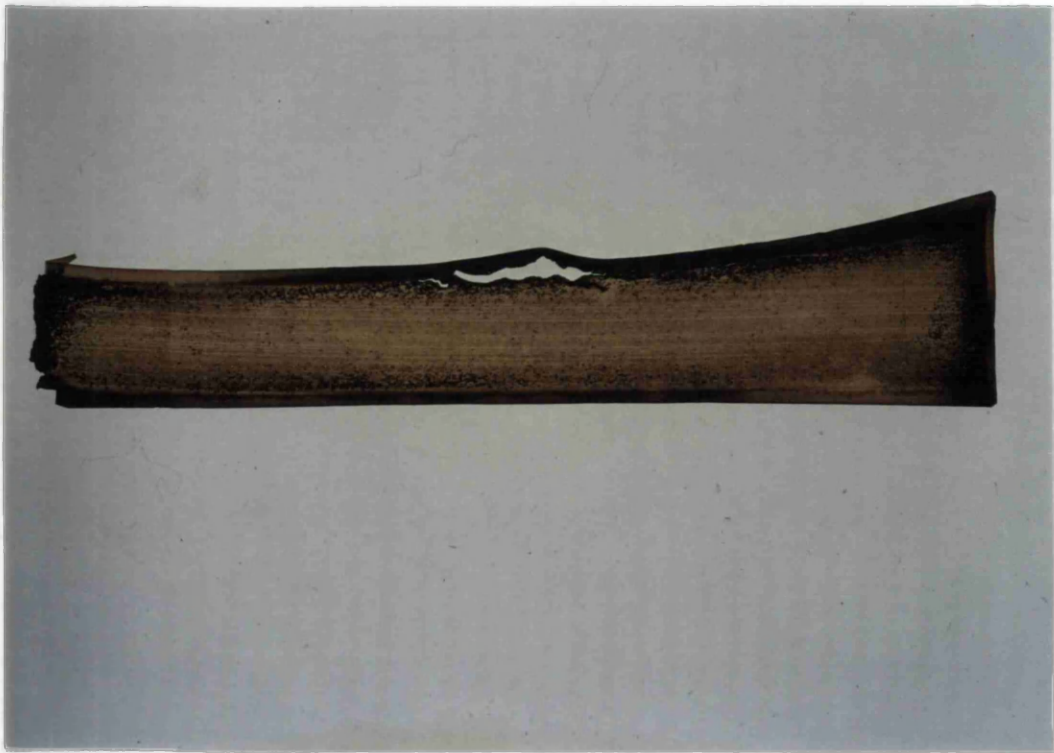


Figure 4.11b Chlorosulfonic acid treated delaminated retrieval

### 4.3.2 Oxidation and Wear Study

Numbers and type of each design were given in Table 4.1. Implantation times varied from 2-15 years, with a variety of revision causes including infection, wear and instability. Macroscopic and microscopic evaluation revealed all types of surface damage including pitting, abrasion, burnishing etc. with delamination seen on all components.

Examination of retrievals highlighted a widely variable microstructure of the polyethylenes, including fusion defects, impurity particles and cracking. These phenomenon were highlighted by CSA treatment which indicated in addition highly variable oxidation within the components examined. Treatment with CSA highlighted the sub-surface bands which were observed upon sectioning prior to staining. In some instances oxidised sub-surface bands were not evident prior to CSA treatment. Regions of polyethylene stained with CSA were also areas where high carbonyl and ketone groups were measured using FTIR.

From observations of CSA treated thin sections and residual stress analysis using polarised light microscopy, the regions of maximal stress and oxidation were coincident in several cases. This was seen at the articulating surface in the worn region of the polyethylene (figures 4.9 a & b).

Delamination was associated with high surface oxidation in one component (figure 4.10). However in the majority of delaminated tibial components, cracking was initiated within the sub-surface band of high oxidation (figures 4.11 a & b).



## 4.4 Discussion

### 4.4.1 Observations from the Variability Study

The variable consolidation and subsequent grain morphology viewed on most retrieved components can be attributed to the variability arising in the stock materials. CSA staining highlighted fusion defects and grain boundaries in some materials, but only in those in which they were already apparent using light microscopy, prior to staining. This indicates enhanced chemical attack of the polyethylene at the grain boundaries and highlights the weakness of this material. In some of the materials studied there was enhanced visibility of grain boundaries near to the articulating surface. This suggests an *in vivo* degradation mechanism related to the wear process. The weakness of grain boundaries particularly to chemical attack has also been reported by Dwyer & Bryant<sup>203</sup> who found mechanical and chemical weakness at inter-particle boundaries upon exposure to oxidising atmospheres. They concluded that this is likely to contribute to mechanisms of UHMWPE degradation in TJA.

General examination of different designs of TKR showed different observations for each design. Marmor components showed minimal wear, after as long as seventeen years. The reasons for this are unclear and quite surprising since the non-conforming geometry of this design will lead to high contact stresses. Landy & Walker<sup>43</sup> reported that Marmor components showed remarkably little overall wear, and suggested that the low profile of the Marmor makes it less susceptible to impingement or the trapping of particles between the bearing surfaces which leads to three-body wear. Blunn et al<sup>169</sup> also reported that the pitting wear seen on Marmor components was not associated with three body abrasion. It is probable that the lack of fusion defects seen in this study and in others<sup>169, 204</sup> has a beneficial effect on the long-term survival of these prostheses, especially since a lack of delamination for these components has been reported<sup>169, 204</sup>.

The AGC also had very low wear, however this would be expected due to its short *in vivo* duration (3 years). The AGC has been reported as having the lowest failure rate in the Swedish Knee Arthroplasty Register<sup>205</sup> and the AGC has also been reported to have a 98% survivorship at ten years<sup>29</sup>. This survival rate is similar to that seen with more congruent implants. Low wear was also seen on both the MG patella and tibial components and is also probably attributable to their short implantation times (2.5 and 0.5 years respectively) and their lack of fusion defects.

In addition to short implantation times, the delamination theory postulated by Walker et al<sup>199</sup> would account for the low wear seen in the non-conforming designs studied

here. There may however be another fundamental reason for the low wear in these non-conforming designs. The Miller-Galante and AGC are both manufactured from directly compression moulded Hifax 1900 resin. Recent research has claimed that polyethylene manufactured by compression moulding 1900 resin has a more consistent microstructure and lack of fusion defects. The absence of fusion defects has been attributed to a lack of calcium stearate in the production of this material, which has been associated with voids and weaknesses<sup>38, 41, 46, 47, 48</sup>. A resistance to oxidation for compression moulded 1900 resin has also been reported<sup>206, 207, 208</sup>. The reasons for this oxidation resistance are unclear. In light of the results of this study and the reports of improved wear performance of these and other directly compression moulded materials, work was performed to investigate these factors in greater detail (see chapter seven).

The Brigham prosthesis was the only component examined which exhibited spherulitic morphology. The possible affect of the spherulitic morphology on wear properties was difficult to discern with only one component to examine, but spherulitic morphology has been suggested to be detrimental to wear properties<sup>166</sup>. Unfortunately the duration of the Brigham prostheses was unknown so it is not possible to correlate the severity of the wear with implantation time. However the spherulitic morphology was not associated with the wear track so should not have affected the wear properties. This component also had high oxidation at the lower bearing surface which suggests a possible mechanical degradation of the material, since heptane extraction showed this not to be an artefact. This could be possibly due to micromotion against the metal base plate. A similar phenomenon was seen in the MG patella component, with high residual stresses and high oxidation at the point of interlock with the metal base plate.

PCA components observed in this study showed the typical demarcation zone of high residual stress beneath the bearing surface associated with the hot pressing of the surface of this design. High crystallinity was measured in this zone, which can result in high stress concentrations and weakness within the material. This zone is at a similar depth to that at which post-irradiation oxidation developed, which in conjunction with the pre-existing weakness at this depth, resulted in the catastrophic delamination of these components at very short duration's.

FTIR analysis showed a decrease in crystallinity for all components at the bearing surface, which has been also reported by others<sup>120, 169, 204</sup>. Increased crystallinity in load bearing areas has also been reported<sup>209</sup> which was attributed to denser packing of the polyethylene molecules under loading *in vivo*. Increased crystallinity associated

with ambulation<sup>171</sup> increases the elastic modulus and results in an increase in stress magnitudes associated with wear damage. There was an increase in crystallinity of retrievals compared to the unimplanted, unirradiated components examined in chapter three. This has been associated with the crystallisation of shorter chains which are a result of chain scission, which can occur either as a consequence of mechanical or chemical degradation.

FTIR depth profiling of these components showed two different trends. The Marmor showed a decrease in crystallinity with an increase in oxidation, whereas the Kinematic and PCA components showed a concurrent increase or decrease in both parameters. Other reports have also associated an increase in oxidation with an increase in crystallinity. Perhaps herein lies an advantage of the Marmor. If an increase in oxidation is associated with a decrease in percent crystallinity, there will be no associated increase in elastic modulus and stresses associated with accelerated wear damage. The potential reasons for an increase in oxidation with a decrease in crystallinity are outside the scope of this study, but warrants further investigation.

#### 4.4.2 Oxidation and Wear Study

Several studies have tried to correlate oxidation of polyethylene with an increase in the wear rate. Studies of retrieved acetabular cups have found a correlation between *in vivo* wear rate and embrittlement<sup>210</sup> or between the sub-surface band and cracking and delamination<sup>211, 212</sup>. However, reports of a linear penetration rate of the femoral head into the acetabular cup after the first one or two years<sup>115</sup> indicates that an increased wear rate due to a time dependant oxidation does not occur. Also Li et al<sup>213, 214</sup> found no correlation between the sub-surface band of oxidation and wear in acetabular cups. In contrast, in an earlier study of retrieved hips and knees, Li et al<sup>120</sup> found that oxidation generally followed the extent of damage. There has however been no correlation found between severity of wear and oxidation in TKR components. Other correlations have been found, such as between damage score and patient weight<sup>8, 12</sup> and also damage score and implantation time<sup>8, 12, 43</sup>. In addition a statistically significant correlation between duration of implantation and the extent of pitting, cracking, delamination, creep and overall wear has been found<sup>45</sup> as has a positive correlation between intensity of wear and level of contact stress<sup>13</sup>.

One of the difficulties in correlating wear and oxidation is that the oxidation of a component is not simply related to its *in vivo* duration. The extent of oxidation will depend on the sterilisation method and atmosphere, shelf-age time and atmosphere prior to implantation, *in vivo* duration and has also been shown to depend upon post

retrieval time<sup>110</sup>. Often one or more of these factors are unknown making it difficult to make correlations for components that have been *in vivo* for similar lengths of time. Even if these factors are known, reports of large variations in the oxidation level and depth in components from different manufacturers prior to implantation<sup>120</sup> complicates the analysis further. One factor that is now accepted throughout the industry is that oxidation of polyethylene post-irradiation is a time dependant process so shelf-life must be kept to a minimum. Another factor that is becoming apparent is that different designs manufactured from different materials, have varying oxidation resistances.

The oxidation of polyethylene is a result of chemical changes which occur during and after sterilisation by irradiation. The effects of ionising radiation on polymers are becoming better understood, with oxidation of polyethylene leading to the development of a sub-surface band of highly oxidised material with time. In this study (and in others) this region of highly oxidised polyethylene occurs at a depth of about half, to one and a half millimetres below the surface. The oxidation results in embrittlement of this region resulting in different material properties to the surrounding material. This is particularly important for knee replacements because the relatively high stresses imposed during everyday activity means that maximum shear stresses coincide with the region of maximum oxidation and embrittlement. With these factors in mind, the objective of this study was to discover whether the development of a sub-surface band of oxidation was correlated with delamination of tibial components.

Due to the alteration in properties and in particular the embrittlement, it was hypothesised that this would be a predetermining factor in the delamination of tibial polyethylene components, since when the zone of shear stress coincides with sub-surface embrittlement, fatigue fracture of the polyethylene would result in delamination. This study indeed showed that delamination cracking occurred through the highly oxidised sub-surface band, except in one case. This indicates a high correlation between the formation of an oxidised sub-surface band and delamination wear. In many of the retrievals examined the wear had occurred through to a depth that meant the peak of oxidation was at the surface. This has been reported by others<sup>198</sup> and is consistent with the delamination having occurred through to the sub-surface, highest oxidised region. In the case of the exception, the delamination cracking was sub-surface in nature, beneath a region of very high surface oxidation associated with the wear track. This component was a non-conforming unicondylar component (duration 7 years), a design which has previously been associated with delamination wear.

It can be seen from these results that the sub-surface oxidised band can be defined as a factor which will result in delamination wear. However, other contributory factors may influence the rate and extent to which the delamination occurs. As already seen in chapter one, particular designs such as those with a low conformity surface have been associated with an increased incidence of delamination wear<sup>13, 171, 215, 216</sup>. Related factors have included fusion defects and in the case of the PCA, hot pressing of the polyethylene surface. Tsao et al<sup>195</sup> found a 7% failure rate for the PCA due to severe polyethylene wear after an average time of 4.5 years. They concluded that the projected failure from polyethylene wear alone, would be more than 20% at six years. Bloebaum et al<sup>171</sup> found a 52% incidence of severe delamination in a study of 33 PCA retrievals within 4 years. When these values are compared with other literature reports of only a 2% incidence in non-heat pressed retrievals (<4 years)<sup>171</sup> or a 4% incidence of delamination in condylar type knee replacements within 4-5 years<sup>217</sup>, this implicates hot-pressing in the delamination of TKR components. However there was some controversy that this was actually the case and Lavernia et al<sup>218</sup> in an autopsy retrieval study of 28 PCA TKRs concluded that excellent long term function is possible with heat pressed UHMWPE. Engh et al<sup>215</sup> also suggested that heat pressing in conjunction with minimal congruency does not necessarily weaken the polyethylene to a point where delamination occurs. They suggested that higher contact stresses when combined with the deformation of thin polyethylene caused this threshold to be exceeded. Hot pressing has now been discontinued.

It is possible that this design of non-congruent component, with an induced band of weakness at approximately half a millimetre below the surface due to the heat pressing technique, was sufficient to produce early delamination in these components. In light of recent research, oxidative degradation will also play a significant role. The mechanism of delamination is similar for both of these phenomenon, since both produce a structural weakness at a depth associated with high shear stresses and fatigue wear mechanisms. It is impossible to predict the individual affect of each of these factors on the delamination rate, but both individually have the potential to result in delamination wear. In other retrieval studies any change in appearance sub-surface was probably attributed to hot pressing, so no comment about a 'white band' has been made. Photographs of the demarcation line in a paper by McDonald & Bloebaum<sup>219</sup> were the same as seen in 'white band' formation, with multiple fine cracks in the embrittled region, but no reference to these being related to irradiation degradation was made. It is possible in some retrieval studies that delamination occurred early in many of these components so there wasn't sufficient time for a white band to develop. However, with unknown shelf-ageing time prior to implantation, this cannot be determined. It is also possible that the chemical changes induced by the heat pressing

technique exacerbated the irradiation damage since these components were heat treated prior to sterilisation. Overall, the development of an oxidised band at the level of pre-existing structural weakness due to hot-pressing, resulted in the catastrophic delamination of these components at shorter implantation times than other designs of TKR.

In addition to oxidation being a result of post-irradiation ageing, it was found that oxidation can occur at the surface of the components in areas associated with the wear track. Residual stresses were observed at the articulating surface in polarised light, indicating a significant degree of molecular orientation at the worn surfaces. This has also been reported for acetabular cups<sup>134</sup>. These correlated with oxidation as highlighted by CSA treatment indicating a relationship between mechanical action due to the motions and stresses imposed during everyday activity.

Several authors have since found that the high cyclic loads that polyethylene is subjected to *in vivo* are responsible for the degradation in properties of the material near the articulating surface<sup>125, 198, 220, 221, 222</sup>. Heat generated during articulation<sup>223</sup> has been associated with accelerated oxidative damage at the surface and tissue exposure and friction have also been suggested to affect the level of oxidation and degree of crystallinity in retrieved hips<sup>224</sup>.

The *in vivo* environment is also likely to accelerate surface oxidative degradation since the formation of reactive sites due to mechanical and chemical events including cutting wearing and scraping has been reported<sup>225</sup>. Oxidation is also reported to be catalysed by transition metal salts (prosthesis metals) and *in vitro* studies have found that UHMWPE oxidises in solutions of physiological NaCl (found in body fluids) as well as other ions in body fluids (Ca, Mg, K)<sup>110</sup>. It has also been suggested that there is a generation of oxidising compounds *in vivo* as a result of the inflammatory response to implant debris<sup>224</sup>.

Similar findings of degradation at the articulating surface have been found in *in vitro* wear tests<sup>163</sup> and simulator studies<sup>131</sup>. Rimnac et al<sup>162</sup> found the mechanical and physical properties of irradiated polyethylene are affected both by loading and environment and that these effects are interactive. The only disagreement to these findings is that of Jahan et al<sup>59</sup> who found that the load bearing areas of retrievals (as indicated by peroxy radical content) had reduced oxidation levels. This was attributed to enhanced radical recombination through frictional heating in these areas.

For both shelf-ageing and *in vivo* ageing the increase in oxidation by wear has been shown by FTIR to be due to the formation of aldehyde (RCHO) rather than the more commonly observed ketone ( $R_2C=O$ ) groups<sup>125, 222</sup>. There should be some caution when examining the oxidation level of retrievals and *in vitro* test specimens by FTIR, to ensure oxidation levels are not artificially increased by absorption of contaminants from the surrounding fluid.

In conclusion it has been seen by examination of retrieved TKRs, that oxidation of UHMWPE can be caused by post-irradiation damage leading to a sub-surface band of oxidation, which is a major factor in the onset of delamination wear. Surface wear of components can also be enhanced *in vivo* by mechanical forces during loading, leading to surface oxidation and material degradation.

## CHAPTER FIVE

### ARTIFICIAL AGEING REGIMES AND THE EFFECT OF OXIDATION ON THE WEAR MECHANISMS IN TKR



## 5.1 Introduction

The interaction of gamma irradiation with the chemical structure of polyethylene has been studied for over twenty years, however it is only in the last few years that the affect of these interactions have been associated with an increase in wear of TJR. As seen in the previous chapter, the effects of post-irradiation oxidative degradation on the properties of UHMWPE are undesirable, resulting in an increase in delamination wear in TKR.

The extent of oxidative degradation depends on many factors, especially the length of time that the implant is stored between irradiation and implantation. This process is believed to occur both in shelf-stored and in implanted components, however there are conflicting views in the literature concerning the effects and extents of shelf ageing and *in vivo* ageing. Furman et al<sup>226</sup> found that oxidation of UHMWPE on the shelf is more extensive, severe and rapid than oxidation *in vivo*. Trieu & Paxson<sup>200</sup> found the oxidised surface layer became more oxidised and grew thicker with time during shelf-ageing (up to 83 months). Results indicating that *in vivo* exposure does not accelerate the oxidative process<sup>123</sup> reaffirms these findings. However in contrast to these observations Kurtz et al<sup>227</sup> found average density to increase linearly for the first 44 months after sterilisation, implying degradation rate is not altered by loading or differences between shelf and *in vivo* environments. Work by Liu et al<sup>228</sup> has suggested that oxidation of polyethylene does occur after implantation.

In addition to conflicting publications on the rate of oxidation on the shelf and *in vivo*, there have been reports of differences in oxidation products identified by FTIR between shelf ageing and *in vivo* degradation<sup>121, 127, 222, 229</sup>. These were described in chapter one. The concentration of different oxidation products has also been reported to vary with depth into the component<sup>222</sup>. Consequently, as concluded in a study by Furman et al<sup>226</sup>, it would appear that shelf ageing and *in vivo* ageing are two different processes and should be studied accordingly.

Several studies have investigated the affect of shelf ageing on the wear properties of UHMWPE. Kurtz et al<sup>89</sup> developed 3D FEA models with material properties which changed with depth from the articulating surface and found that shelf ageing had little effect on the sub-surface maximum shear stress distribution for acetabular and tibial models. However, within 1mm of the articulating surface, tensile stresses in tibial models were highly sensitive to changes in material property distributions due to ageing. Higher wear rates have been reported for shelf-aged polyethylene compared to

unirradiated or recently irradiated material<sup>108, 230</sup>, with the difference as great as a three fold increase for shelf-aged polyethylene over non-irradiated material<sup>108</sup>. It should be noted that in these studies that the polyethylene was machined from shelf-aged acetabular cups, to correspond to a depth of 0.5-1mm below the articulating surface, to represent the depth and position of the wear surface *in vivo*. Care has to be exercised in *in vitro* studies of the wear of shelf-aged components since the increase in wear rate associated with ageing has been eclipsed by surface roughness of the counterface material<sup>116, 231</sup>.

Although *in vitro* studies indicate an increase in wear with ageing, studies of polyethylene from retrieved prostheses have reported conflicting findings. Li et al<sup>213, 214</sup> found that the contribution of oxidation and the presence of bands was undetectable in the clinical performance of Charnley acetabular cups. However Liu et al<sup>228</sup> found a correlation between wear rate and severity of polyethylene embrittlement in retrieved acetabular components and Sutula et al<sup>211, 212</sup> found that the sub-surface oxidised band correlated with cracking and delamination.

The literature shows conflicting data from experimentation performed on shelf-aged and retrieval polyethylene and consequently methods of artificially ageing materials are now being investigated, to understand and evaluate the effects of post-irradiation oxidative degradation on the properties of UHMWPE. Artificial ageing regimes are also important for the evaluation of new materials and new processing regimes in simulated long-term testing. Short-term *in vitro* testing of a new material may achieve results indicating improved wear properties over conventional UHMWPE, but long-term results are vitally important. Artificial ageing regimes are not suitable for the prediction of the lifetime of an implant due to the large number of other variables involved, but it allows testing of the susceptibility of new materials to oxidative degradation, which is known to reduce the quality and lifetime of an UHMWPE implant.

Two principle methods have been developed to achieve accelerated ageing of UHMWPE. The first of these was developed by Sanford & Saum<sup>71</sup> (Depuy-Dupont). Their method of accelerated ageing employs elevated temperature and a nominally pure oxygen environment, which works by increasing both the thermal energy of the system and the oxygen concentration. Specimens are wrapped in a porous breather fabric then placed in a pressurised container of oxygen at five atmospheres pressure (0.5 MPa). This vessel is then heated to the required temperature (60°C or 70°C) where the temperature is held for a set time period (4 or 7 days). Temperature is monitored with a thermocouple and kept within a tolerance of 5°C. Results yielded a

significant increase in oxidation of all specimens irradiated in air at both temperatures. Specimens treated for seven days had oxidation levels equivalent to shelf ageing for 1.5 - 4.5 years (60°C) or 5 - 10 years (70°C). The development of a sub-surface peak of oxidation was achieved in specimens aged at 70°C.

The second method by Sun et al<sup>91, 221, 232</sup> involved the development of an accelerated thermal diffusion oxidative ageing (ADTOA) technique. This technique was developed to simulate oxidative degradation of UHMWPE after gamma irradiation, but is being studied for its applicability to other biomaterials. The generalised method for this technique is as follows. The sample undergoes a differential scanning calorimetry (DSC) heating run where the onset of melting is determined. A heating schedule is then devised to raise the temperature of the specimen to that required for ageing, ensuring adequate oxygen diffusion and thus minimising unwanted cross-linking reactions. Once the required temperature has been reached the sample is maintained at this temperature for the desired time period. This methodology<sup>91, 232</sup> was developed from an understanding of the thermodynamics which drive the oxidation reaction. The equations are as follows:

$$r=k[O_2][p.]; \quad k=Ae^{-\Delta H/T}$$

r is the oxidation reaction rate,

[O<sub>2</sub>] is the concentration of the oxidants (such as oxygen in air or in the body),

[p.] is the concentration of free radicals,

k is the rate constant and is determined using the Arrhenius equation,

A is a constant for the reaction, known as the Arrhenius constant,

ΔH is the activation energy, otherwise known as the heat of reaction or enthalpy change (heat absorbed by the system equals the change in enthalpy),

T is the temperature in Kelvin.

Sun et al<sup>91, 221, 232</sup> aged specimens for eleven and twenty-three day periods, using a temperature ramp of 0.6°C/min. After eleven days, property changes (crystallinity, oxidation, ultimate tensile strength and low molecular weight fraction) were equivalent to four to six years of shelf-ageing. The twenty three day period corresponded to changes in these properties of approximately seven to nine years. It was found that a slow heating rate produced higher oxidation and deeper penetration and that this method could produce surface or sub-surface oxidation depending on the ageing temperature and heating rate.

These two methods have subsequently been used and developed by other research facilities to achieve accelerated ageing of UHMWPE material. However, all processes

have a common factor, that of increased temperature. This is required to increase the rate of reaction since the reaction rate constant  $k$ , is small at room temperature. Also an increase in temperature will relax amorphous regions within the polymer allowing easier access for the oxidative species. In addition with all regimes, care must be taken with other parameters. There must be adequate oxygen present once the temperature is raised, otherwise cross-linking will occur. All regimes also have to ensure temperatures are not raised above 80°C, because at this temperature the onset of melting occurs<sup>91</sup> and changes in morphology and consequently properties may occur.

Consequently a method was developed to artificially age polyethylene to produce levels of oxidation commonly seen in retrieved prostheses, using a technique developed from that by Sanford and Saum<sup>71</sup>. The aim of this work was to discover the effect of accelerated oxidation on the material and mechanical properties of UHMWPE. It was hypothesised that the development of an embrittled sub-surface oxidised band would result in a reduction in fatigue life and result in a fatigue failure mechanism of wear in vivo. Mechanical testing was performed to determine how the extent of embrittlement affected fatigue properties. The affect of oxidation on the rates and wear mechanisms in a test which simulates the sliding motion of TKRs, was also investigated.

## 5.2 Materials and Methods

### 5.2.1 Materials

All specimens for wear testing were machined from ram extruded Poly Hi (GUR 4150), to discs of diameter 36mm and thickness 6mm. All specimens for the mechanical tests were machined to the required dimensions from the same piece of Poly Hi. Specimens were manufactured at the same orientation relative to the processing direction and scaled from the dimensions in the appropriate British Standards (see chapter two). Compact tension specimens for crack growth rate measurements were additionally machined from RCH1000 (GUR4120). All testing was performed dry at ambient temperature. All machined specimens were sterilised using gamma irradiation (Cobalt 60 source), using standard implant dose levels (25 kGrays).

### 5.2.2 Ageing

All ageing of wear test and mechanical test specimens was achieved by a method developed from that of Sanford and Saum<sup>71</sup>. The polyethylene specimens were placed in a pressurised container in nominally pure oxygen at a pressure of 0.5MPa. The vessel was placed in an oven at 80°C for a set time period. Specimens were removed from the vessel at time periods ranging from two to ten days and the degree of oxidation was assessed by FTIR and staining with chlorosulfonic acid. The specimens were removed over a time course to evaluate oxidation levels equivalent to varying times measured in retrievals.

Two pressurised devices were utilised in this study, the second device being a larger example of the first to allow more specimens to be aged at one time. Tests one and two used polyethylene oxidised in the small vessel, whereas test three used the larger vessel.

Additional experimentation was performed by placing specimens in an oven at 80°C for 48, 96 and 144 hours, to determine the effect of heating on oxidation of UHMWPE as opposed to heating and a pressurised oxygen environment.

### 5.2.3 Wear Testing

Three wear tests were performed with specimens aged for various time periods as detailed below. In addition for test two, specimens were cut from unworn areas of two retrieved tibial prostheses which were known to have delaminated *in vivo*. One specimen was from a Kinemax component which had been removed due to a fractured base plate after 6 years. The second retrieval was a Kinematic component which was retrieved for loosening after 8 years.

Test one: specimens aged for 0, 2, and 4 days

Test two: specimens aged for 6 and 8 days, and retrieval samples.

Test three: specimens aged for 4, 6 and 8 days.

Tests one and two were conducting using the standard protocol load of 2.3kN, which gives an initial contact stress (ignoring plastic deformation) of 71MPa. This figure corresponds to the higher range of contact stresses seen in non-conforming TKR. Test three was conducted using a load of 1.0kN and was designed to simulate a more congruent knee design. The aim was to examine the relationship between oxidation and contact stress and their relation to delamination wear, which is more often seen on designs of low conformity *in vivo*. It was decided to use a lower load rather than alter the geometry of the test specimens. Two specimens of each condition were tested.

#### **5.2.4 Short Term Testing**

An irradiated specimen and a four day aged specimen were wear tested for 2 hours to examine the initial wear rates of the two materials and to examine features of surface wear, which may be eliminated during longer periods of testing.

#### **5.2.5 Mechanical Testing**

Tensile testing, crack propagation and fatigue tests were performed as described in chapter two.

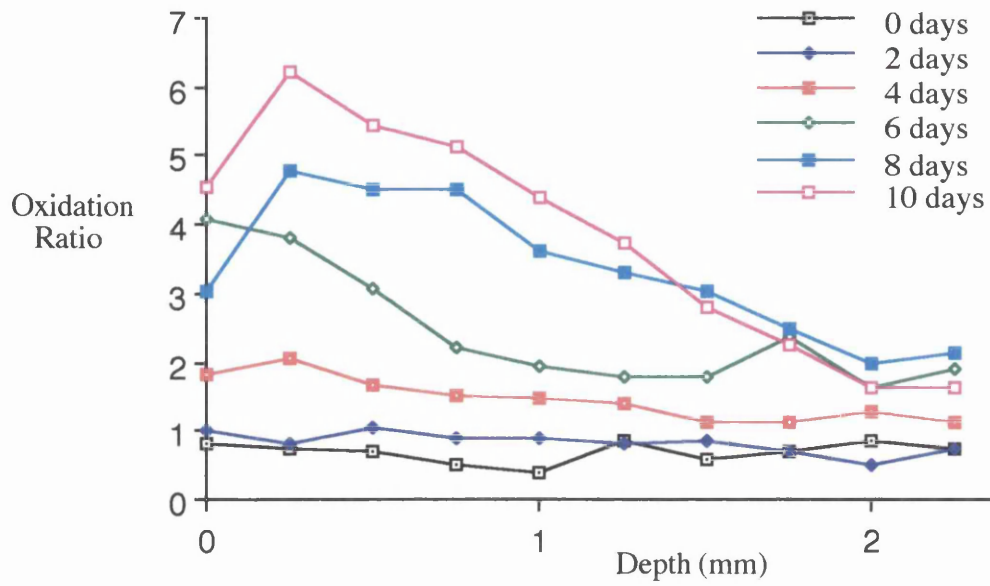


Figure 5.1 Oxidation ratio with depth for artificially aged UHMWPE

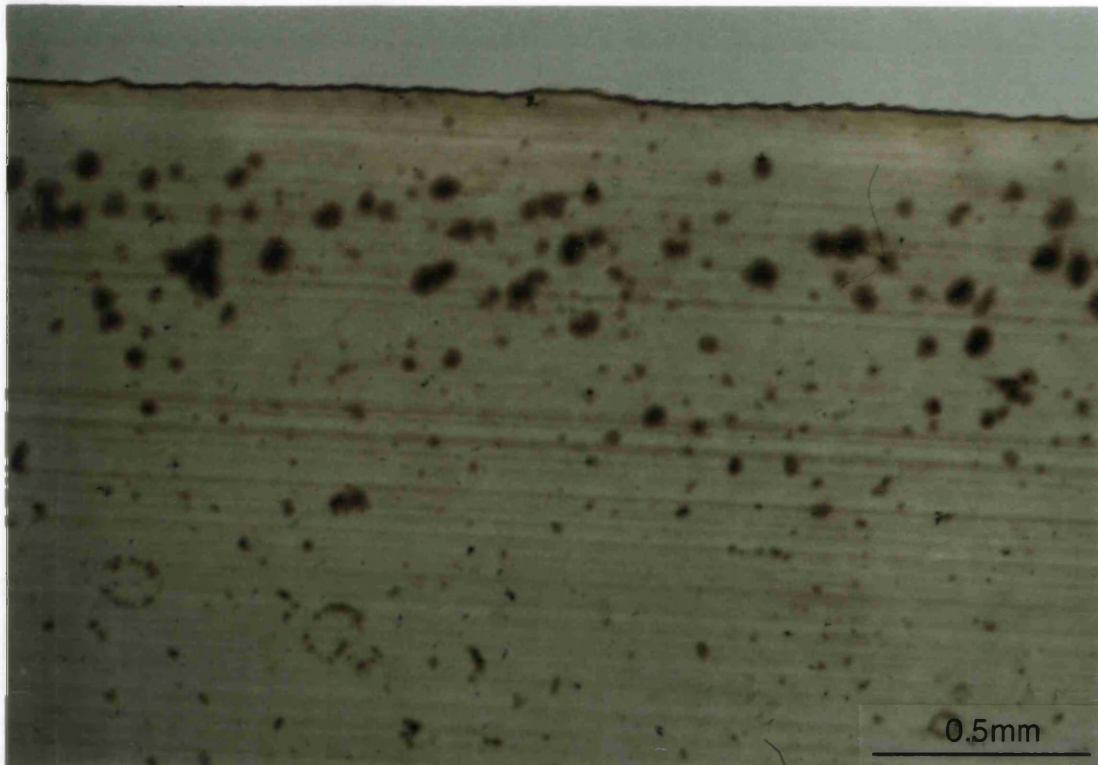


Figure 5.2a Chlorosulfonic acid treated six day artificially aged specimen

## 5.3 Results

### 5.3.1 Pressure Vessel Ageing

#### 5.3.1.1 Fourier Transform Infrared Spectroscopy

FTIR depth profiles of the oxidation of samples artificially aged for periods of between zero and ten days are shown in figure 5.1. Generally there was an increase in the degree of oxidation with increasing oxidation time, particularly at the surface of the specimen. The extent of oxidation and the depth of the maximum oxidation was dependent on ageing time. In these samples a sub-surface peak in oxidation only developed after ageing for eight and ten days. At the shorter ageing times of four and six days, the oxidation was highest at the surface. Ageing for two days produced effectively no oxidation compared to control samples.

Crystallinity for the specimens ranged from 54-58% at the lower range, to 62-67% maximum. Crystallinity trends approximately followed the peaks and troughs seen for the oxidation values, and there was a general increase in crystallinity for specimens associated with increasing ageing times.

#### 5.3.1.2 CSA Staining of Wear Test Samples

CSA treatment highlighted surface oxidation on samples aged for two and four days with minimal difference apparent between the different ageing times, and the control specimen. Specimens aged for six, eight and ten days showed the development of a sub-surface band of oxidation, which increased in size and intensity with increasing ageing time. These are shown in figures 5.2 a-c, after CSA treatment. For 6, 8 and 10 days specimens, treatment time was reduced from the standard sixty minutes to thirty minutes, to enhance visualisation of the sub-surface band.

The six day specimens showed a very mild sub-surface oxidation peak at a depth of 0.25-0.5mm. This was not seen on FTIR analysis (above) of a separate specimen aged for six days. This indicates that six days is the time taken for the beginning of development of an oxidised sub-surface using this ageing technique. Slight alterations in sterilisation dose, ageing atmosphere, time or temperature may account for this slight difference.

### 5.3.2 Oven Aged Specimens

All specimens showed surface oxidation, which appeared to extend to a greater depth within the material, than the specimens aged for the same time scale under pressurised oxygen. The specimen aged in the oven for eight days had comparable oxidation



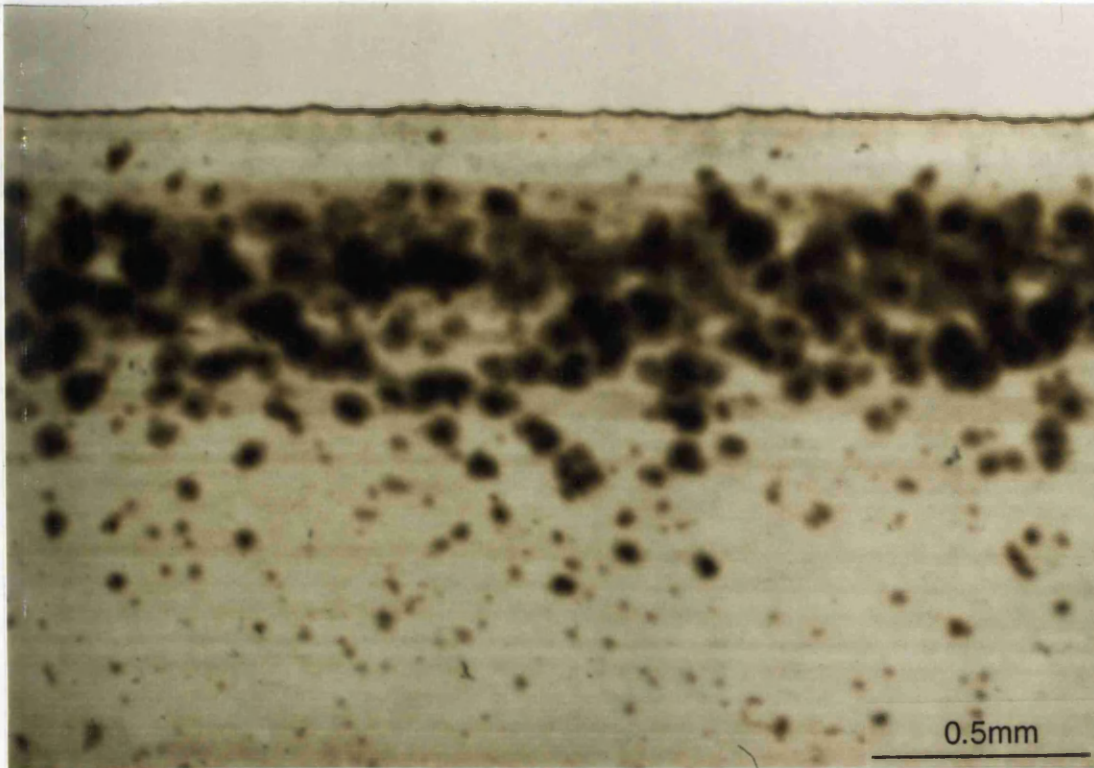


Figure 5.2b Chlorosulfonic acid treated eight day artificially aged specimen

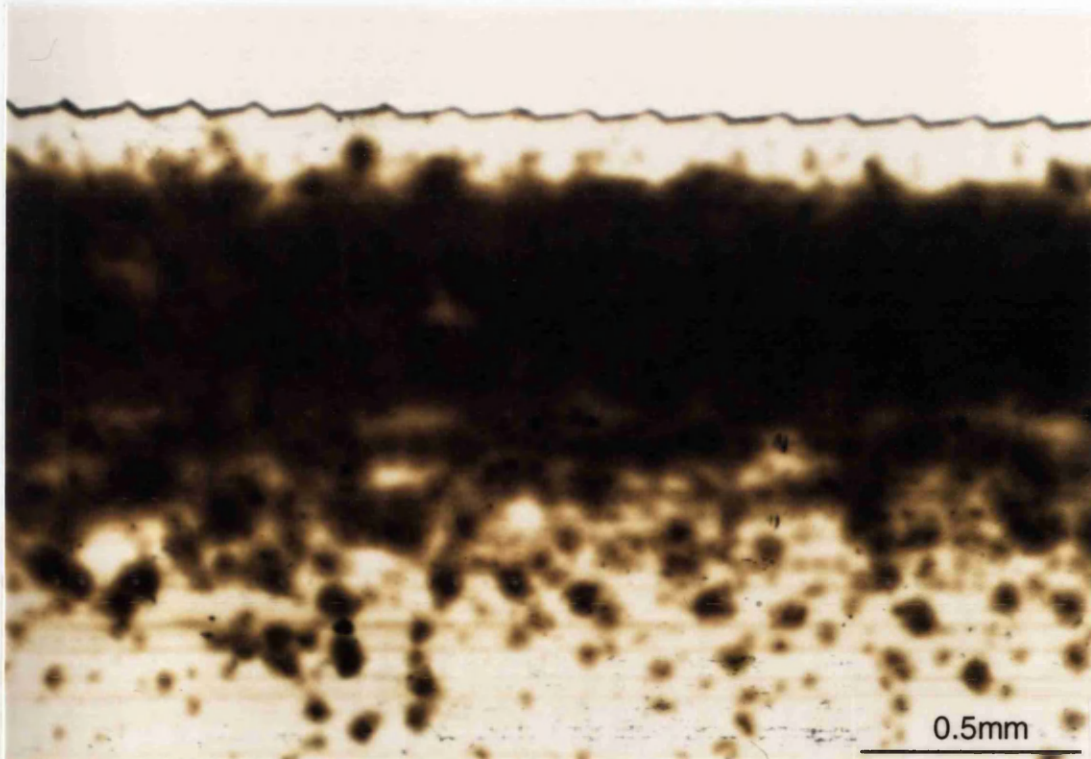


Figure 5.2c Chlorosulfonic acid treated ten day artificially aged specimen

the un-aged and four day pressured oxygen aged specimens. No sub-surface bands of oxidation developed at any time point with this method of ageing.

### 5.3.3 Retrieval Specimens

The retrieved samples showed sub-surface oxidation, which was of an extent in between that seen (by CSA) for the eight and ten day artificially aged samples.

### 5.3.4 Mechanical Testing

#### 5.3.4.1 Tensile Testing

Results from tensile testing of the 9mm<sup>2</sup> cross-section specimens are shown in figure 5.3a (UTS) and table 5.3b (ultimate strain). The results showed a significant decrease in ultimate tensile strength with increasing ageing. Specimens oxidised for 8 days were extremely brittle and broke without a region of plastic flow. A significant increase was seen for strain at break with 4 and 6 day aged specimens compared to non-aged specimens ( $p < 0.05$ ). The 8 day specimens had significantly lower strain at break than all other groups ( $p < 0.05$ ).

Results from tensile testing for the 3mm<sup>2</sup> cross-section specimens (figure 5.4a) showed a decrease in ultimate tensile strength associated with increasing levels of oxidation, but the results were only significant between the irradiated samples and the eight day aged specimens. The strain at break data (figure 5.4b) showed a significant increase for samples aged for eight days over the irradiated specimens, with greater elongation prior to failure.

The similarity in values for ultimate tensile strength and strain at break for the irradiated, four and six day specimens suggests cross-sectional area had no effect on these parameters at these similar oxidation levels.

#### 5.3.4.2 Rotating Beam Fatigue Tests

Rotating beam fatigue tests showed a significant reduction in fatigue life with increasing oxidation between all groups (figure 5.5). After eight days of ageing the fatigue life was reduced by two orders of magnitude from 240,000 to 2,300 cycles.

It should be noted that the loading in these tests was constant therefore as the crack propagated the stresses increased due to a smaller cross-sectional area, so this test had non-constant stress.

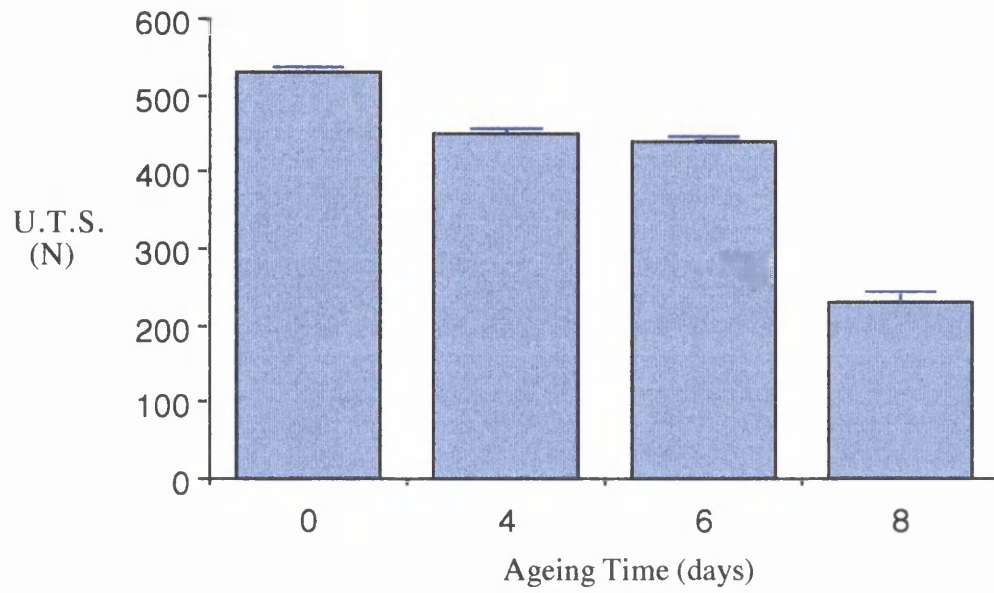


Figure 5.3a Tensile test UTS data for 9mm<sup>2</sup> specimens

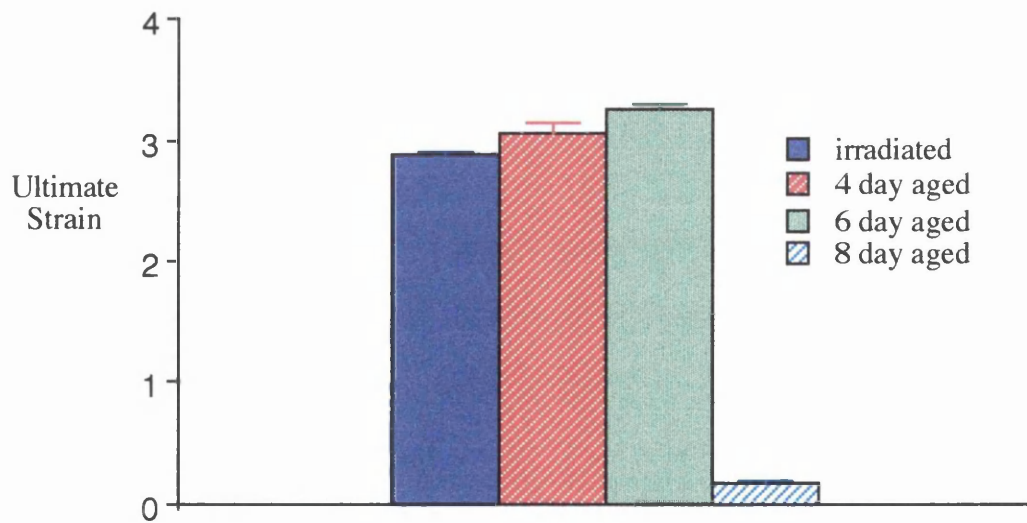
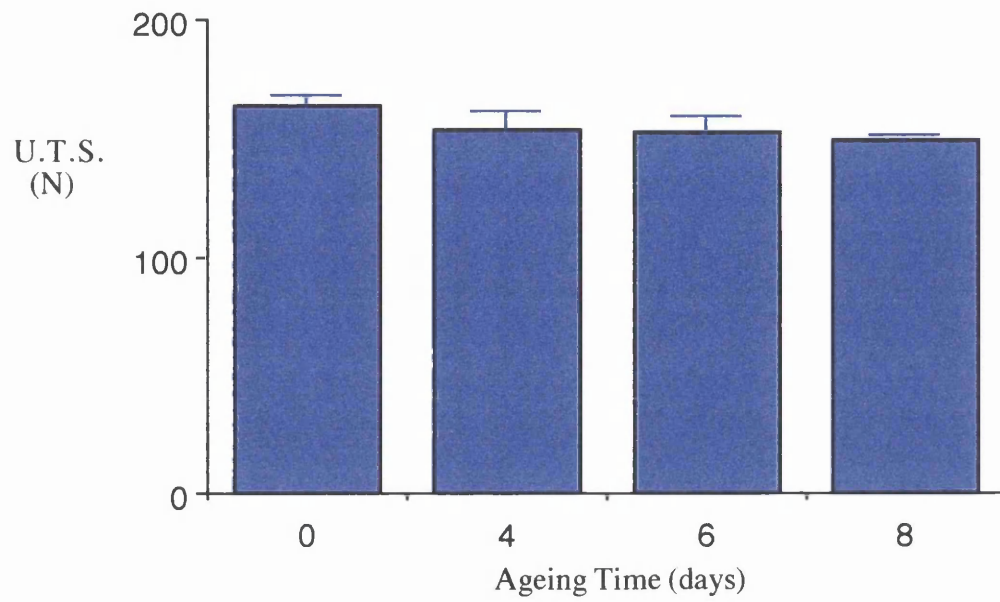
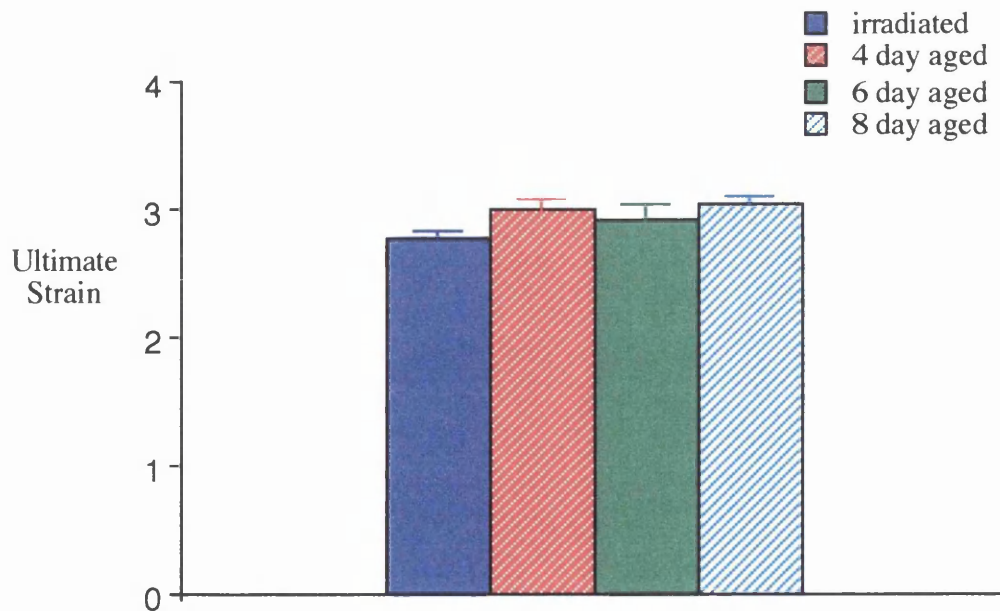


Figure 5.3b Tensile test ultimate strain data for 9mm<sup>2</sup> specimens



5.4a Tensile test UTS data for 3mm<sup>2</sup> specimens



5.4b Tensile test ultimate strain data for 3mm<sup>2</sup> specimens

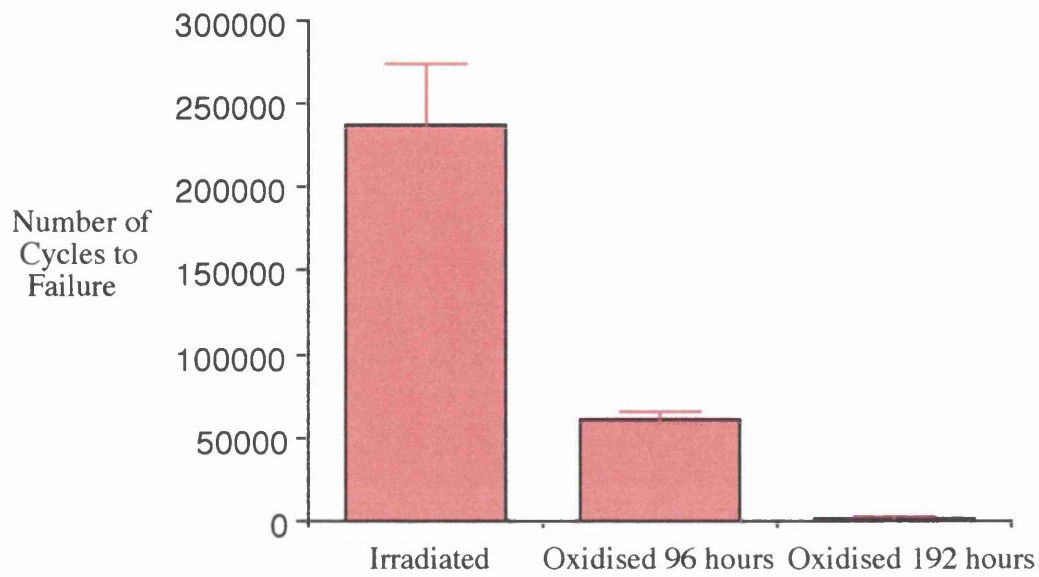


Figure 5.5 Rotating beam fatigue life for artificially aged specimens

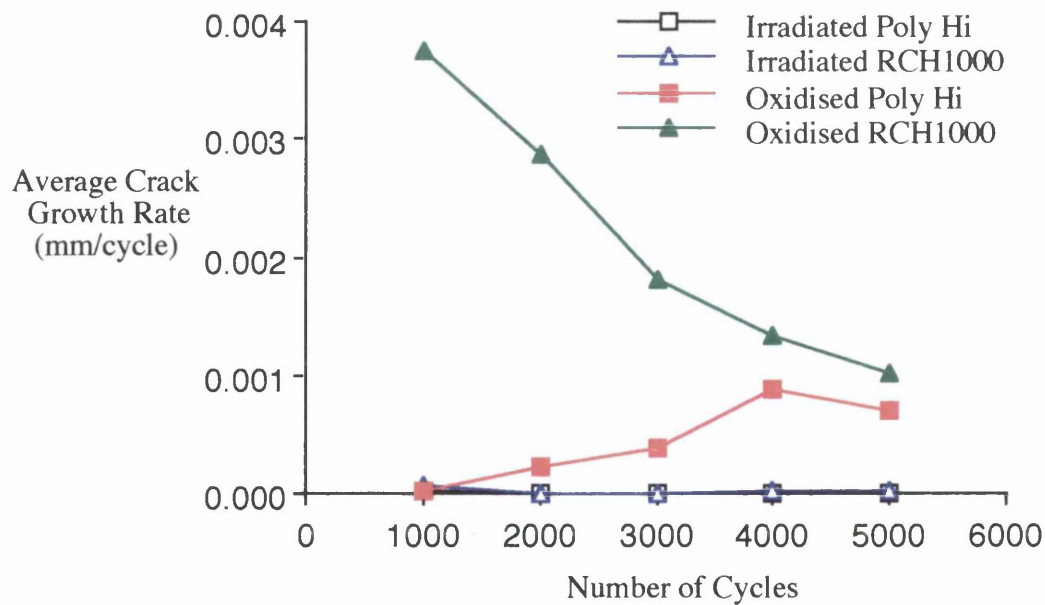


Figure 5.6 Fatigue crack growth rate graph for artificially aged specimens

#### 5.3.4.3 Fatigue Crack Propagation

Fatigue crack growth rates are shown in figure 5.6. Values could not be attained for the eight day oxidised specimens since they were so brittle they fractured at the point of loading. Comparison of irradiated and four day aged specimens showed a statistically significant increase in the crack growth rate for both Poly Hi ( $p < 0.026$ ) and RCH1000 ( $p < 0.006$ ) compared to non-aged control specimens. Comparing non-aged RCH1000 with non-aged Poly Hi showed the latter to have slower crack growth rate, although this result was not significant ( $p = 0.12$ ). The difference however was significant once specimens were oxidised, with Poly Hi having a crack growth rate approximately an order of magnitude less than that for RCH1000 ( $p < 0.016$ ). Oxidation of both materials produced a significant increase in crack growth rate, with the rate of RCH1000 being approximately 400 times that of the unoxidised specimens, compared to approximately ten times for oxidised compared to irradiated Poly Hi.

#### 5.3.5 Scanning Electron Microscopy

Both fatigue crack propagation and rotating beam specimens had similar morphological details for the irradiated and four day aged specimens. However, the fracture surfaces of the eight day aged specimens showed different fatigue and fracture mechanisms.

Rotating beam specimens had a typical fatigue failure appearance of fractured surfaces with multiple initiation sites, beach marks and overload regions evident for the irradiated and four day aged specimens (figure 5.7). The eight day aged specimens however were devoid of these and other morphological features and failed in a brittle manner.

The tensile test specimens aged for zero and four days showed ductile fracture mechanisms with stretched material in evidence. However eight day aged specimens showed a brittle fracture mechanism.

#### 5.3.6 CSA Treatment

CSA treatment of tensile test specimens and rotating beam specimens highlighted surface oxidation in the irradiated and four day aged specimens and a sub-surface band of oxidation in the eight day specimen.

#### 5.3.7 Fourier Transform Infrared Spectroscopy

Only tensile test specimens were evaluated using FTIR and the results are shown in figure 5.8. The degree of oxidation and the position of the maximum oxidation with reference to depth within the UHMWPE samples is dependent on ageing time. The irradiated specimen showed an oxidative peak at the surface of the sample, and



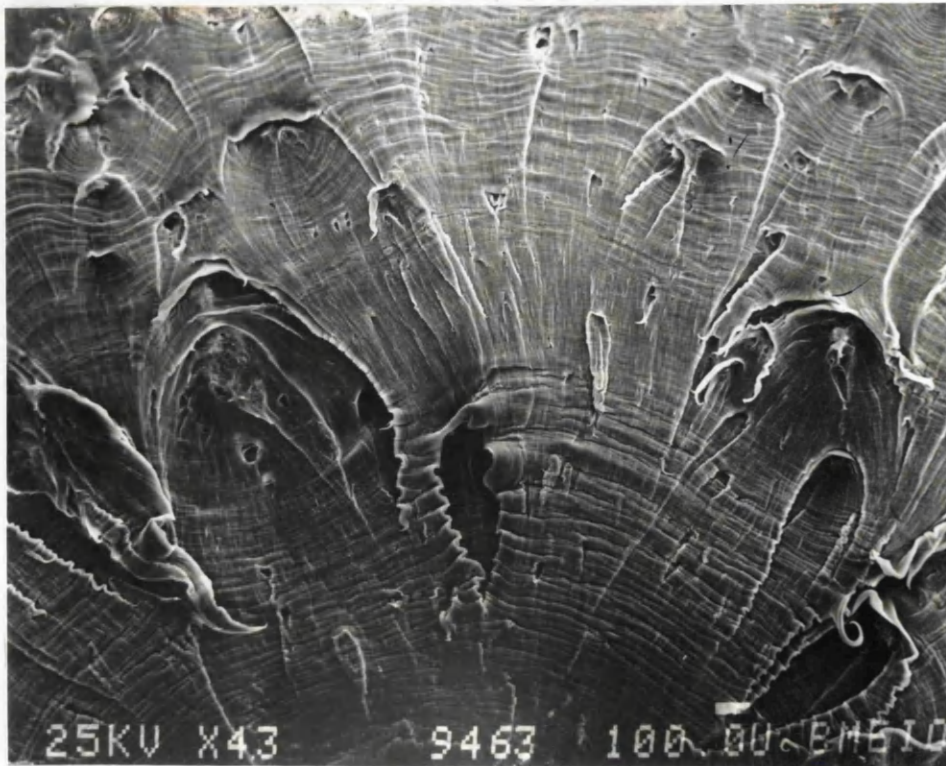


Figure 5.7 Scanning electron micrograph of a rotating beam specimen fracture surface

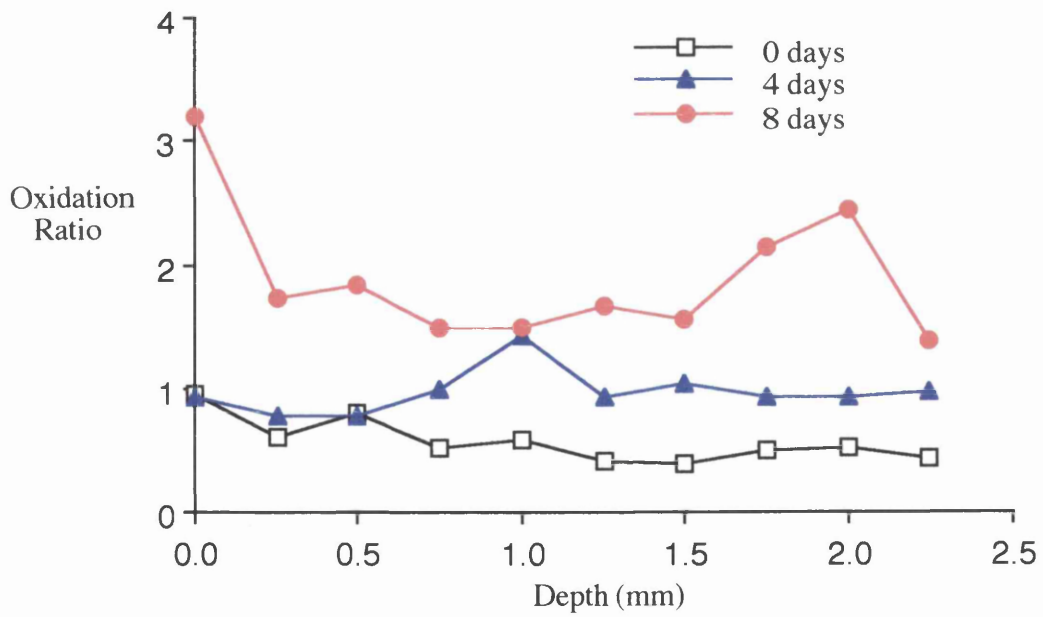


Figure 5.8 Oxidation ratio with depth for artificially aged tensile test specimens

crystallinity trends followed those of oxidation. The specimen aged for four days showed a sub-surface peak in oxidation and crystallinity at approximately 1mm. Trends between these two parameters were coincident. For the specimen aged for eight days, oxidation is maximal at the surface of the specimen, decreases with depth then increases again at approximately 2mm. However due to the cross-sectional area of this specimen, this depth from one surface corresponds to a depth approximately 1mm from the parallel surface. In contrast crystallinity is low at the surface and increases with depth into the specimen to a maximum about 2mm. Overall oxidation levels increase with ageing time. Crystallinity also increased with ageing time, with the averages being 57% (irradiated), 62% (4 day aged) and 69% (8 day aged). The corresponding average oxidation ratios are 0.57, 0.97 and 1.89 respectively.

### 5.3.8 Wear Test Results

#### 5.3.8.1 Gravimetric and Volumetric Data

The type and mechanism of wear seen for each specimen depended on the extent and position of the most oxidised region of the polyethylene.

The first test conducted with specimens oxidised for 0, 2 and 4 days showed no sign of delamination during the course of the test, however a significant increase in surface wear was apparent. Initially there was a significant increase in the surface wear rate as measured by weight loss for increasing lengths of ageing (figure 5.9). For aged specimens the initial high rate of wear reduces but never to the level of the control specimens (i.e. 0 days aged). The initial high rate of gravimetric wear can be attributed to the wear of the highly oxidised surface layer which is present in these specimens.

Volumetric change is shown in figure 5.10. For all specimens there is an initial large volumetric change with increasing ageing time. This can mainly be attributed to creep of the polyethylene. This is followed by a reduction in volumetric wear rate which can be attributed to the loss of material. Even so, after 200,000 cycles a significant difference in the volume of the wear track between control and samples aged for different lengths of time can be demonstrated. Volumetric change of the wear track is significantly larger with increasing ageing. Thin sections taken through the wear track at the end of the test showed an increase in oxidation associated with the wear track (figure 5.11).

For the second test, specimens oxidised for 6 and 8 days (figure 5.12) delaminated. The 8 day oxidised specimens catastrophically delaminated after only 20,000 sliding cycles (equivalent to only five days duration in a fairly active person). In these specimens the plastic delaminated from both the articulating surface and the surface



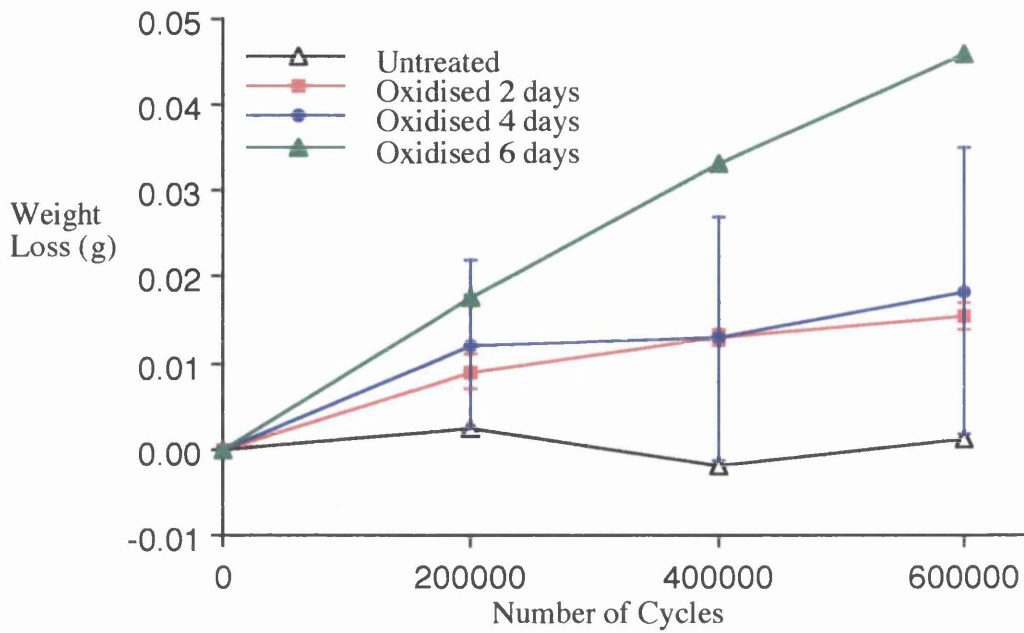


Figure 5.9 Weight loss graph for artificially aged specimens

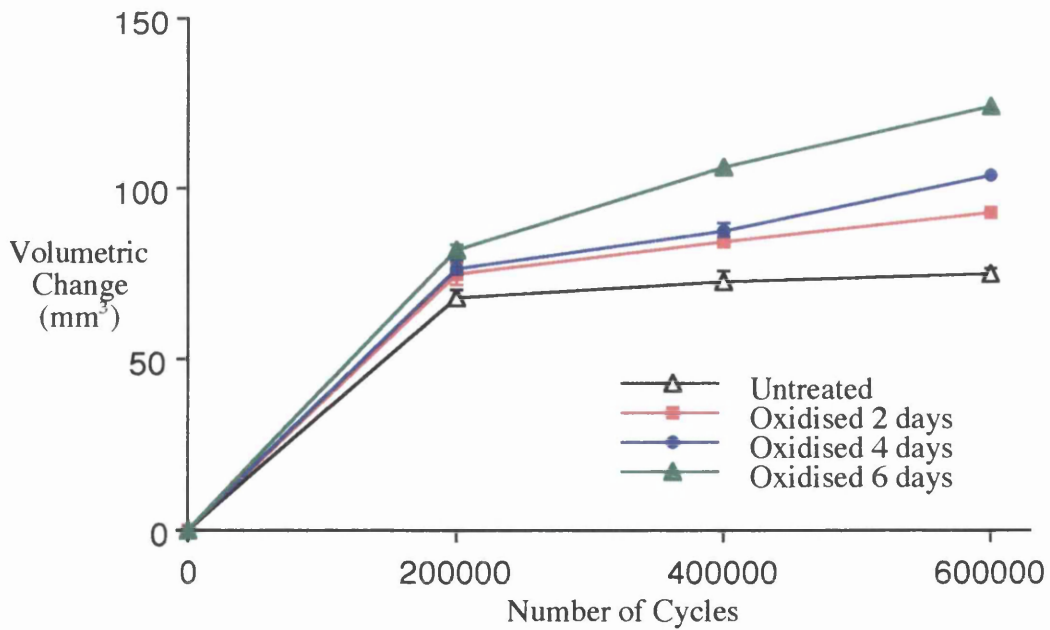


Figure 5.10 Volumetric change for artificially aged specimens

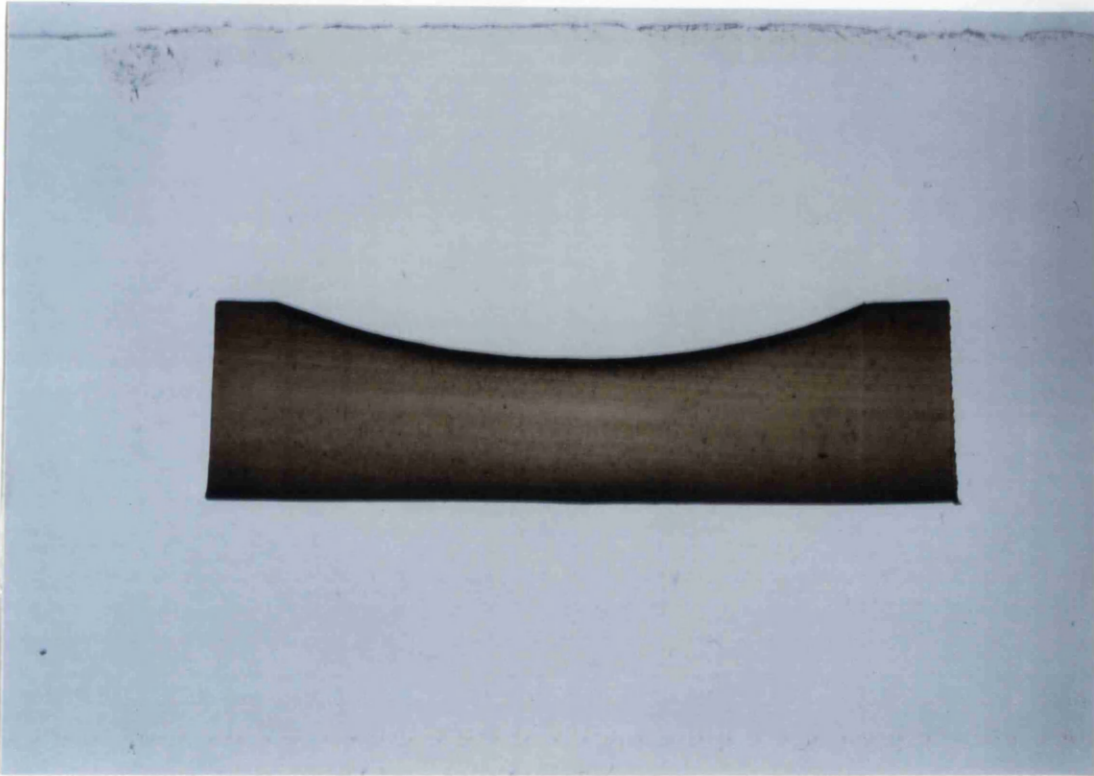


Figure 5.11 Chlorosulfonic acid treated thin section through the wear track

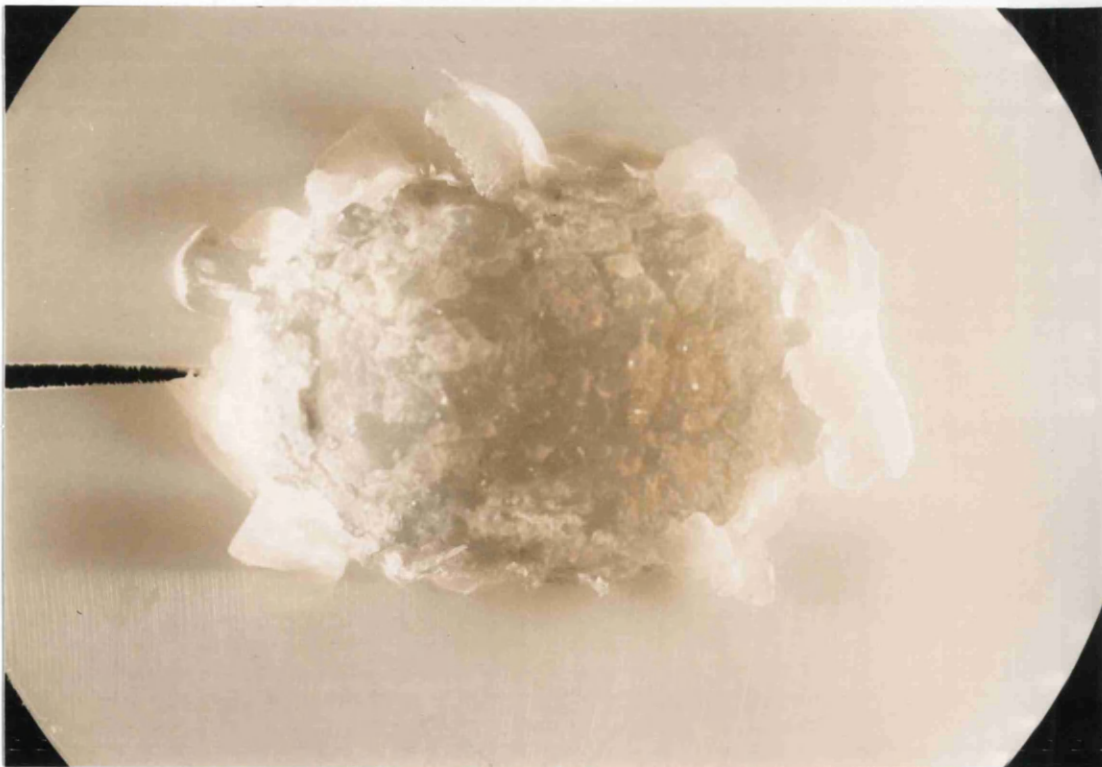


Figure 5.12 Delaminated wear test specimen (artificially aged 8 days)

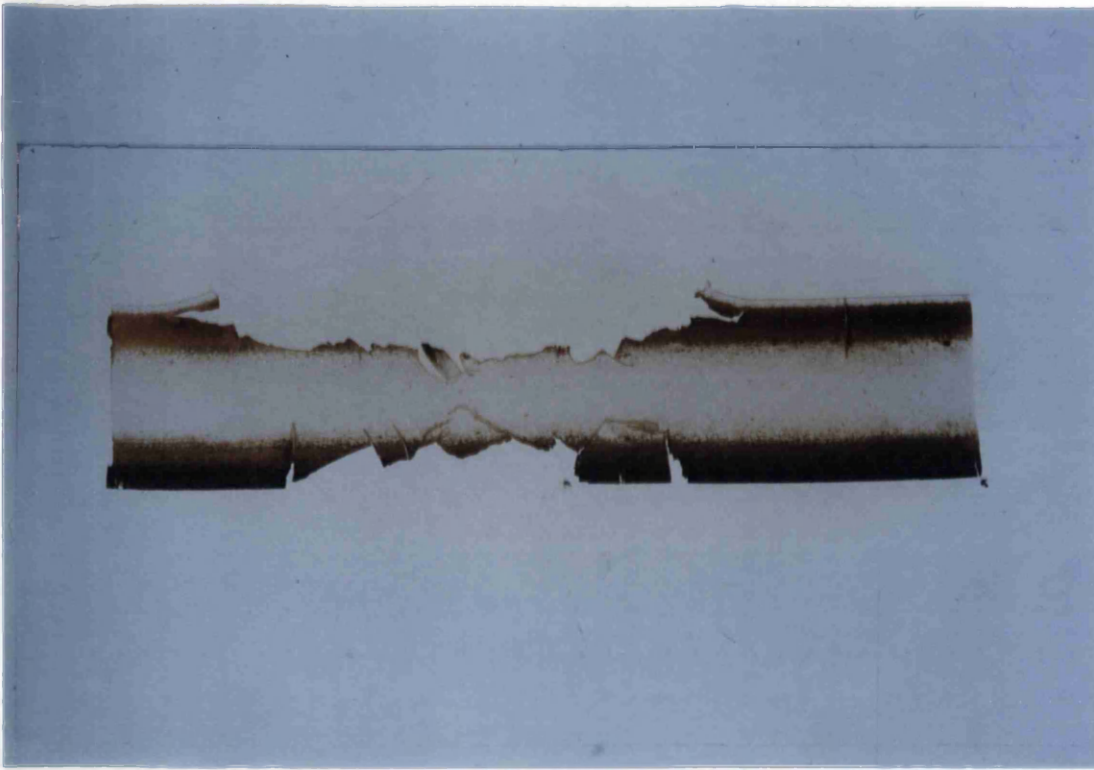


Figure 5.13 Chlorosulfonic acid treated thin section through delaminated specimen

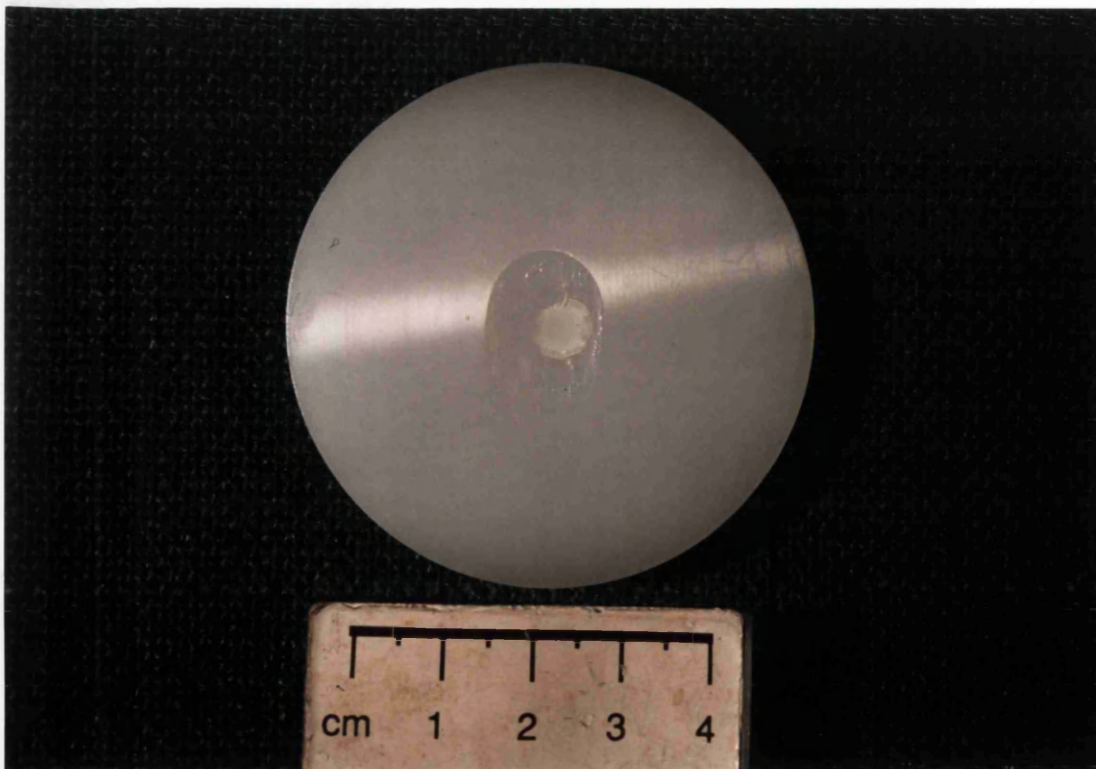


Figure 5.14 Delaminating wear test specimen

adjacent to the metal base plate. Cracks propagated through the sub-surface oxidised bands which were present on both upper and lower surfaces (figure 5.13). Six day oxidised specimens delaminated after an average of 200,000 cycles. Specimens aged for 6 days delaminated less catastrophically and small blisters similar to those seen on retrieved samples at the onset of delamination could be identified under the wear track (figure 5.14). Sections taken through the polyethylene perpendicular to the wear track showed sub-surface cracks which propagated through the oxidised sub-surface band which had not joined with the surface of the plastic (figure 5.15). The specimens cut from the retrievals failed catastrophically after only 20,000 cycles. This can probably be attributed to the lack of thickness of these specimens and oxidative embrittlement of the polyethylene.

For the third test, no delamination was observed after 600,000 cycles, so the test was extended to almost two million cycles. Specimens showed no overall trend between ageing time and amount of wear. All specimens showed an initial weight loss, followed by a weight gain to 600,000 cycles, followed by a further weight loss (figure 5.16). Volumetric data (figure 5.17) shows typical high initial change due to creep of the polyethylene, followed by a lower change attributable to the wear of the material. It can be seen that the least oxidised material had the largest volumetric change, although the results are not significant. This is probably due to lower creep resistance compared to the more oxidised materials.

### 5.3.8.2 Scanning Electron Microscopy

#### Test One

All discs demonstrated adhesive wear (figure 5.18) and the presence of polyethylene particles. Abrasion between the metal and the polyethylene was characterised by scratches in the plastic and the presence of cracks was noted associated with loose particles of polyethylene (figure 5.19). Adhesive wear was greatest at the ends of the wear track. Examination of sub-surface regions demonstrated no extensive cracking in the 0, 2 or 4 day samples. Fusion defects however were apparent in all samples, some with cracks emanating from them, parallel to the surface (figure 5.20).

#### Test Two

examination of the eight day oxidised specimens revealed extensive sub-surface cracking, as well as loss of flakes of polyethylene from the surface, propagating from the sub-surface cracks (figure 5.21). The six days specimens demonstrated similar morphological details, with clear sub-surface cracking occurring below the delaminated region.

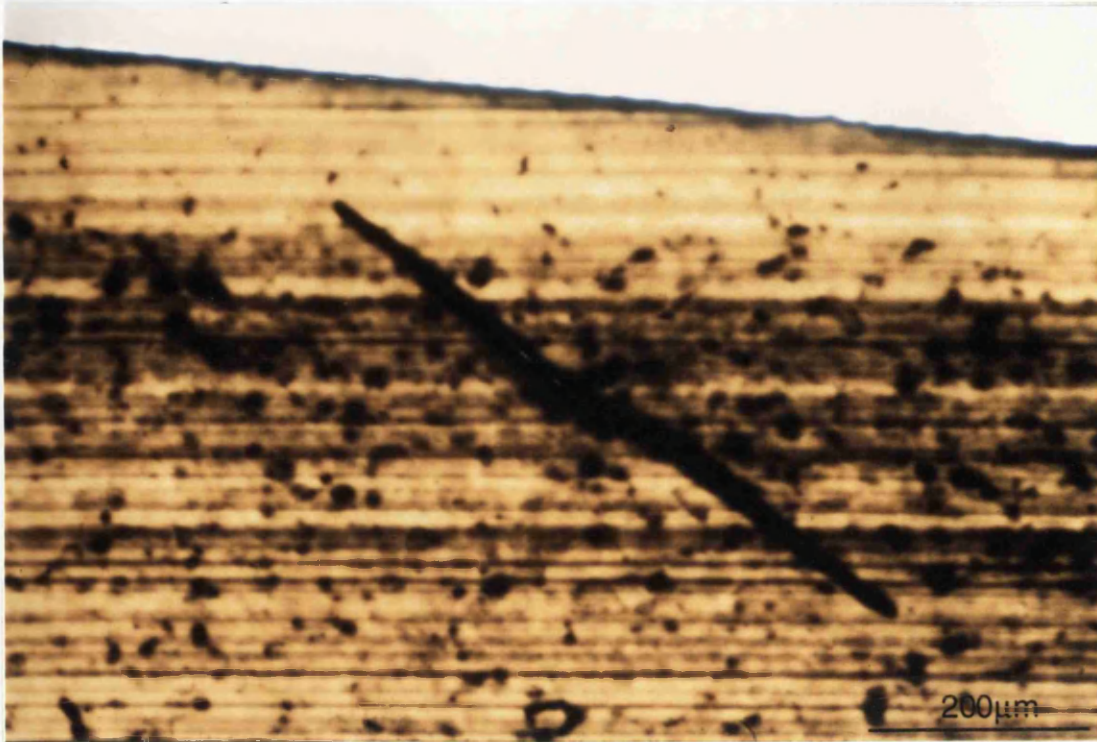


Figure 5.15 Chlorosulfonic acid treated section through delaminating wear test disc



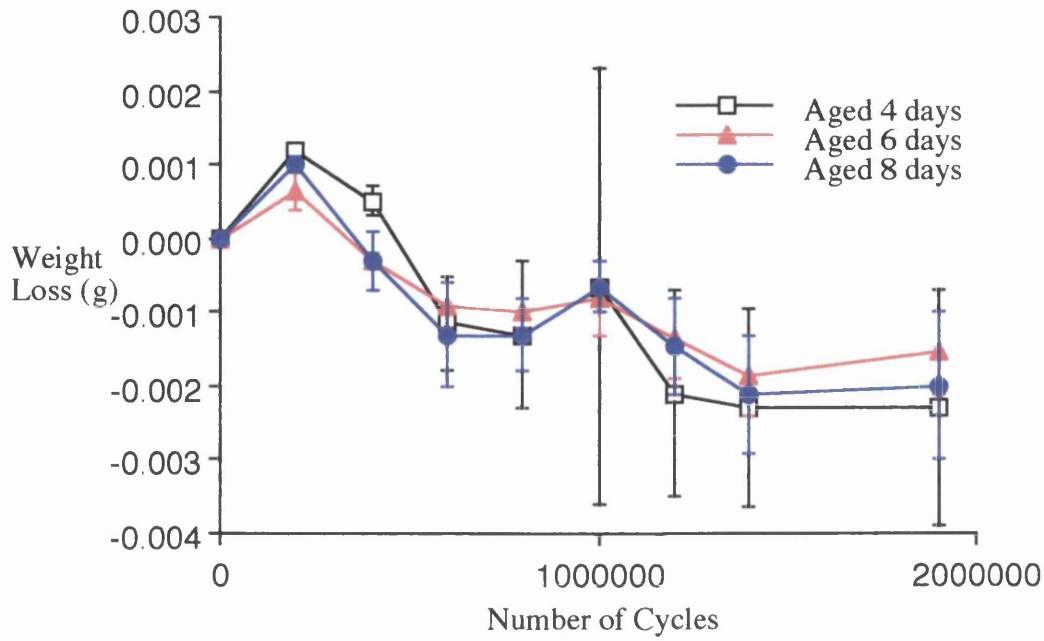


Figure 5.16 Average weight loss graph for 1kN wear test

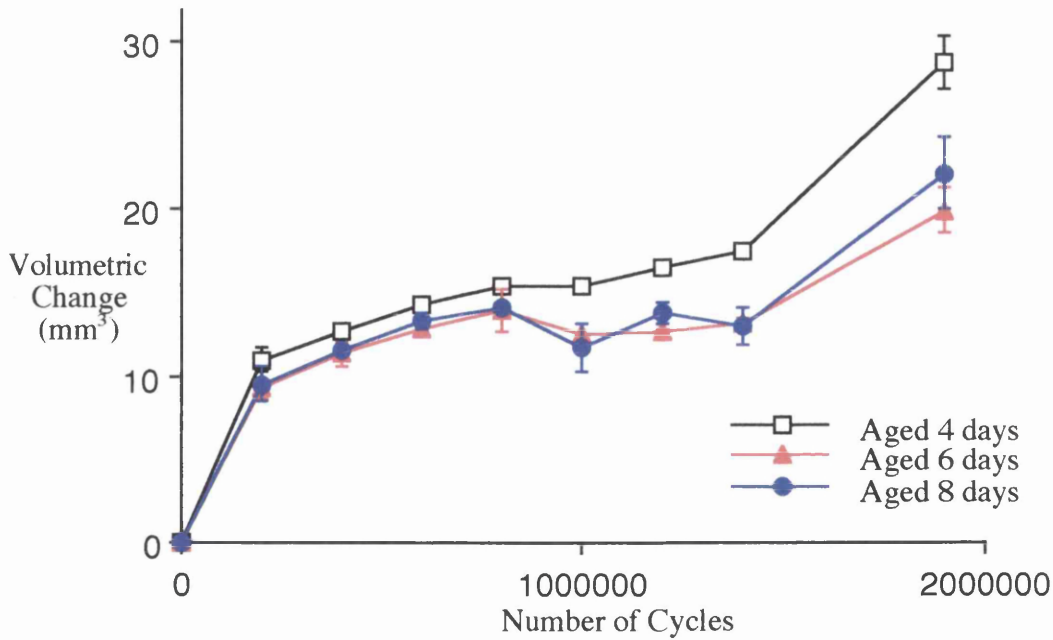


Figure 5.17 Average volumetric change for 1kN wear test

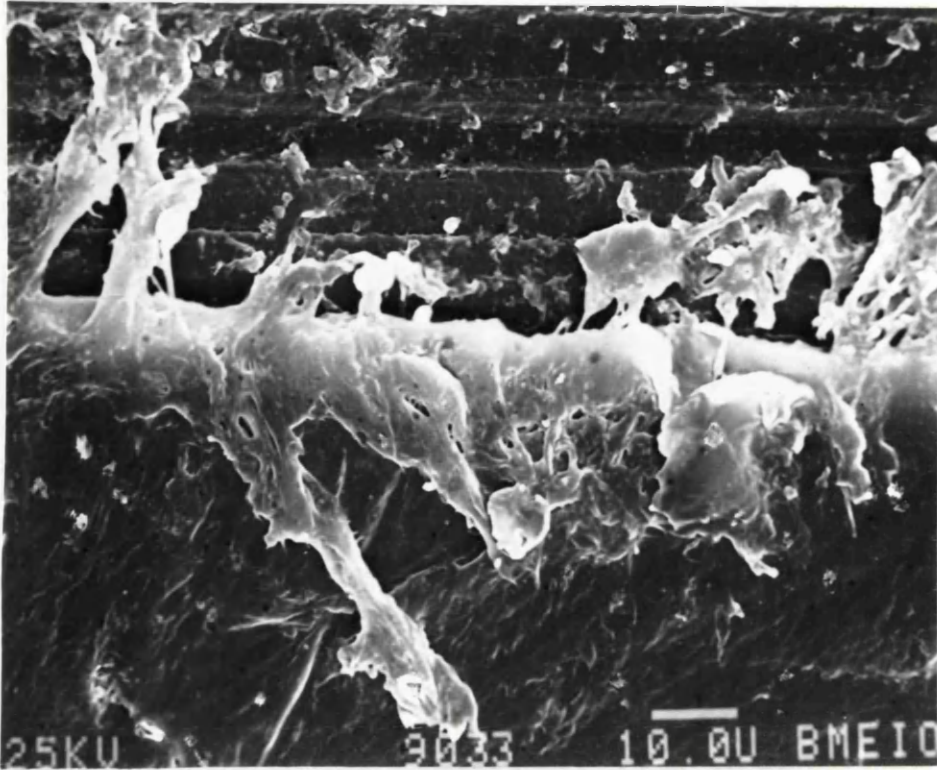


Figure 5.18 Scanning electron micrograph showing adhesive wear

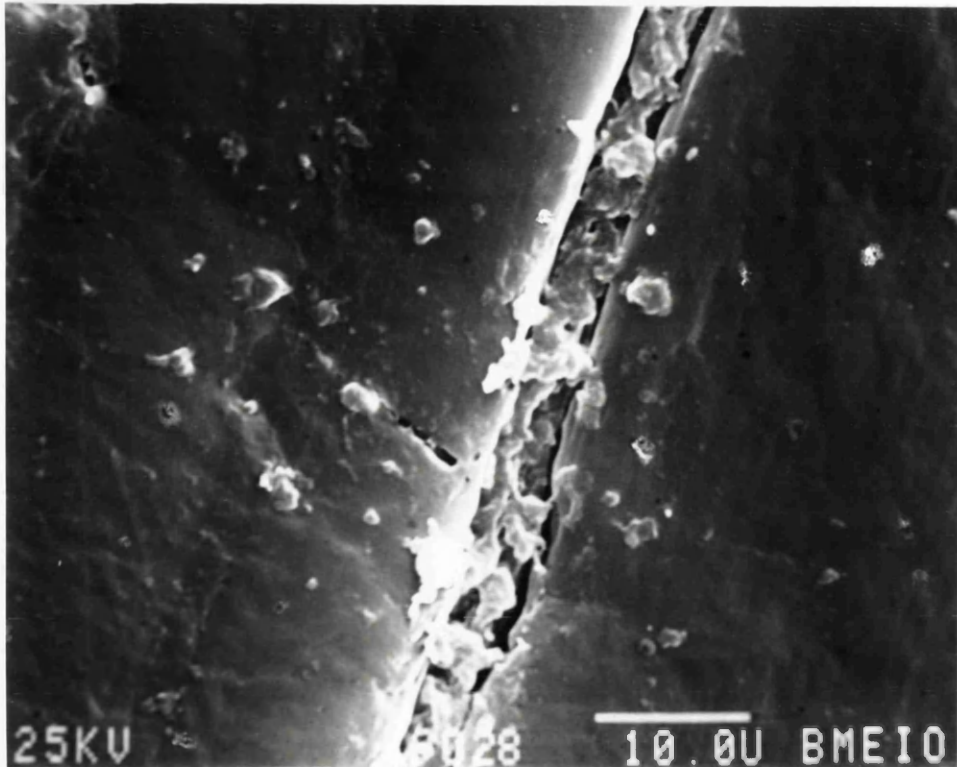


Figure 5.19 Scanning electron micrograph showing abrasion, cracks and embedded particles on the wear track

## Short Term Test

Machining lines were still apparent and more extensive on the un-oxidised specimen (figure 5.22) compared to the four day oxidised specimen, which showed more extensive adhesive wear and surface cracking (figure 5.23).



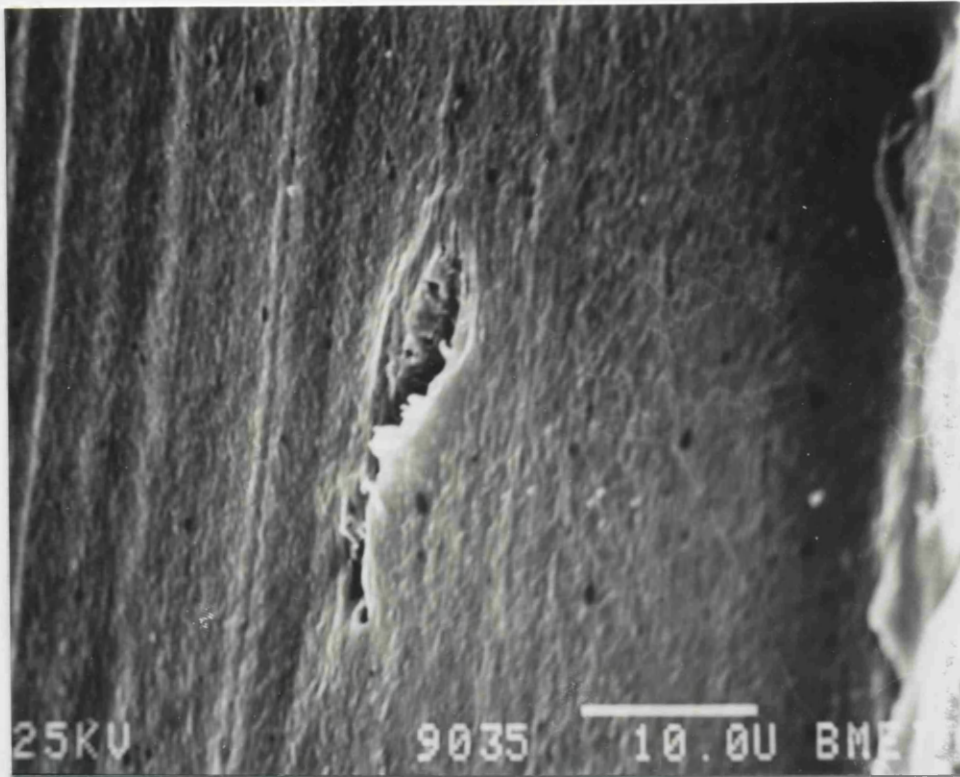


Figure 5.20 Scanning electron micrograph showing fusion defects parallel to the wear surface

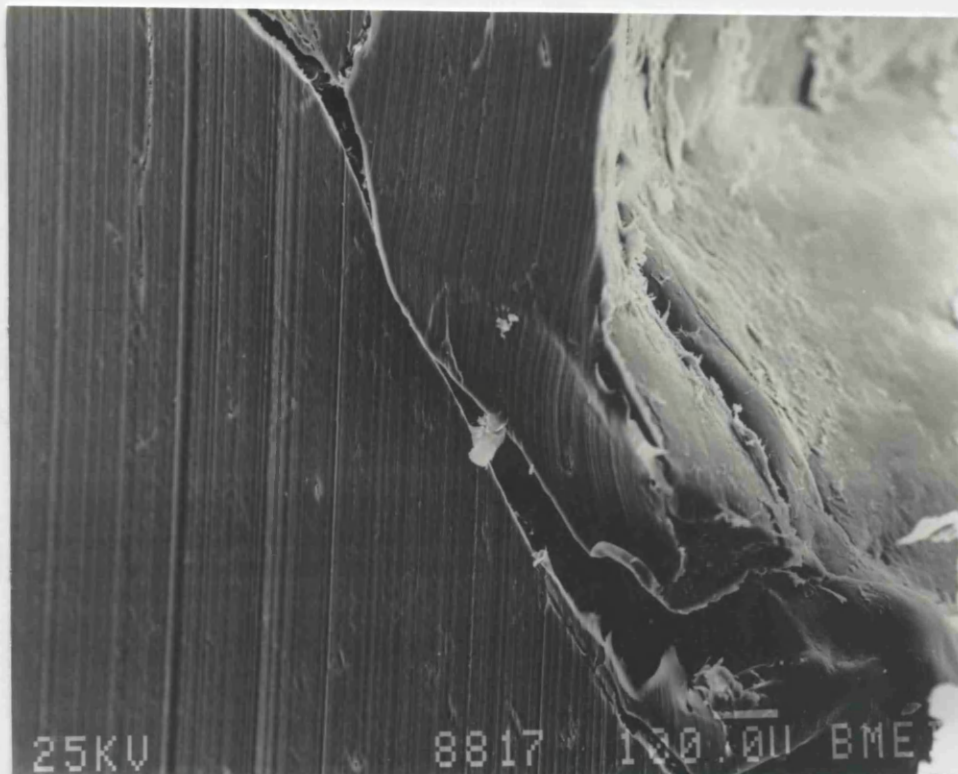


Figure 5.21 Scanning electron micrograph showing sub-surface cracking and delamination wear

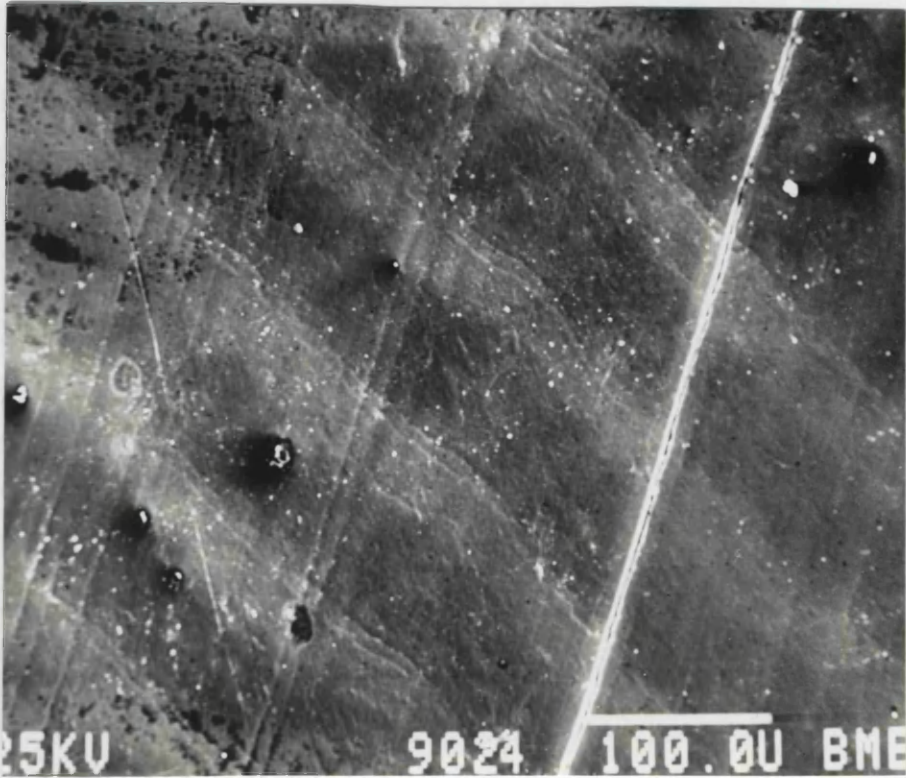


Figure 5.22 Scanning electron micrograph showing machining lines on an un-aged specimen

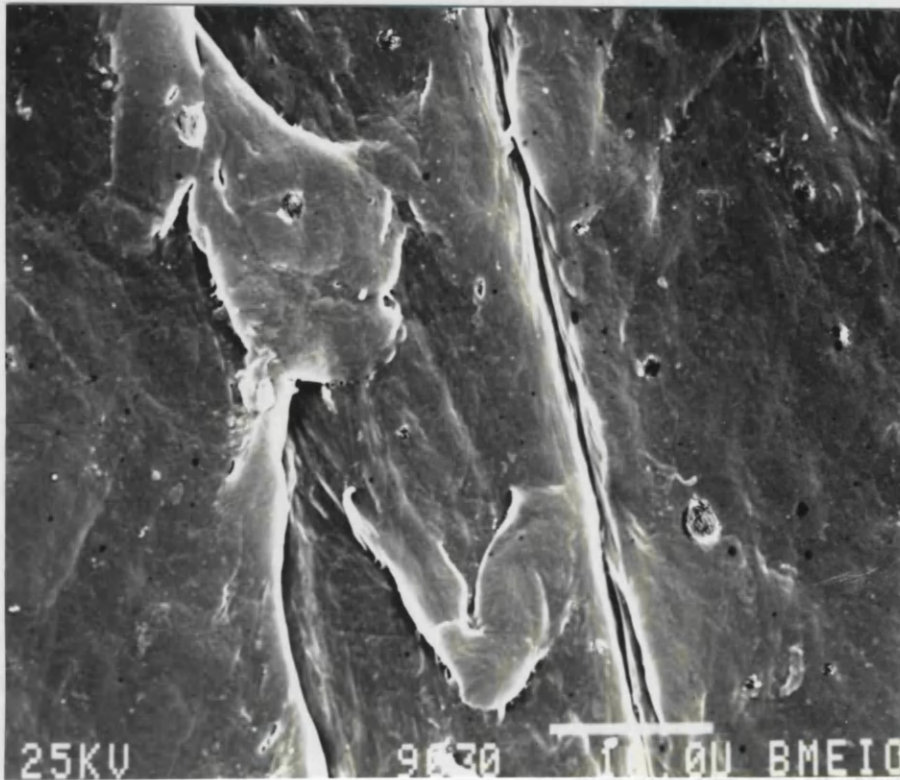


Figure 5.23 Scanning electron micrograph showing adhesive wear on a four day artificially aged wear test specimen

## 5.4 Discussion

Artificial ageing regimes have been developed to advance the understanding of the degradative processes which occur in ultra-high molecular weight polyethylene. Much of the degradation that occurs has now been linked with the chemical changes which result upon and subsequent to, irradiation sterilisation. This sterilisation method has not been discontinued since it can also lead to an improvement in the wear characteristics of polyethylene, due to cross-linking. Consequently artificial ageing regimes have been used to discover the affect of oxidative degradation on the wear properties of UHMWPE. They also have the potential to be used to discover factors affecting the rate and extent of degradation, and also with the development of improvements in manufacture and processing, to ascertain the oxidative resistance of any modified materials.

For the results of an artificial ageing regime to have any relevance to clinical data, the artificial ageing must be reliable and must produce consistent results in terms of the degree of oxidation and the depth profiles seen in both shelf-aged and retrieved components. There are conflicting reports about the extent and rate of oxidation on the shelf and *in vivo*, however generally the extent of post-irradiation oxidation has been reported to increase with time<sup>66, 76, 123, 200, 211</sup>. Therefore the development of a sub-surface band of oxidation is a time dependant process and its magnitude and depth will depend on the radiation dose, diffusivity of oxidants and temperature. Consequently, immediately post-irradiation, components have a surface peak of oxidation due to availability of oxidants, but with time this can develop into a sub-surface peak as diffusion allows oxygen deeper into the material, where it can react with long-lived free radicals. Thus the extent of oxidation (and crosslinking) changes with depth and time, leading to variation in wear properties, a phenomenon investigated in this study.

The artificial ageing regime employed (using elevated temperature and a pressurised oxygen environment) produced both surface and sub-surface bands of oxidation, depending on the time period used, thus enabling the range of oxidation levels seen in both shelf-aged components and retrievals to be replicated. These results are in agreement with the work of Sanford et al<sup>114</sup>. It has also been reported<sup>233</sup> that the ageing method of Sanford & Saum<sup>71</sup> (compared to that of Sun et al<sup>91, 221, 232</sup>) produces oxidation which is more typical of that seen in long-term retrieved implants. It was seen that the sub-surface band only developed after 6-8 days of ageing and that the rate of oxidation was not uniform over time. This was also reported by Sperling et al<sup>234</sup>, who found that oxidation occurs at a significant slower rate during the first few

days than after several days of artificial ageing. It should also be noted that the band of oxidation that developed was closer to the surface than seen in long-term clinical retrievals. An observation seen in other published work<sup>148, 221, 232, 233</sup>. Crystallinity could be seen to increase and decrease concurrently with oxidation, as seen in the retrieval samples in the previous chapter.

Once it was determined that the oxidation levels seen in shelf-aged and retrieved components could be replicated, mechanical testing was performed. Several types of test were used to investigate properties which are related to the materials *in vivo* behaviour. Tensile testing was performed as it provides a useful indicator as to whether any radiation interaction has taken place which may affect the polymer, even though pure tensile loading is rarely seen in articulating prostheses. Fatigue life is also a critical parameter determining the lifetime of an UHMWPE bearing surface, especially in TKR where fatigue is a well known failure mechanism. Fatigue crack propagation is also relevant even in a ductile material such as polyethylene which is highly resistant to crack initiation, since surface flaws caused by scratches, machining marks or defects within the material can act as sites of stress concentration and thus enhance the possibility of crack initiation. Once a crack initiates either at the surface or sub-surface, this will propagate under cyclic loading conditions and could result in pitting and delamination at the articulating surface<sup>235</sup>.

In this study the tensile strength of the polyethylene reduced with increasing oxidation, resulting in brittle fracture after eight days of ageing. This is in agreement with work by Swarts et al<sup>48</sup> who found artificial ageing (Sanford & Saum method, 7 days), resulted in the reduction of ultimate tensile strength for several types of UHMWPE. Strain at break was seen to increase with increased oxidation except for the eight day aged, 9mm<sup>2</sup> cross-sectional area specimen. However, the increasing strain at break with increasing oxidation is in contrast to the results of Nusbaum et al<sup>201</sup> who found a decrease in this value. Strain at break is an important property which indicates material ductility, and is thus related to toughness and has been found previously to be very sensitive to oxidation<sup>74</sup>. Tensile testing of thin sections (200µm) from bar stock and shelf-aged tibial components has also found that the white band produces markedly different mechanical properties with depth, effectively resulting in a composite material<sup>236</sup>.

FTIR data for the tensile test specimens was similar to that for the initial ageing analysis, although the eight day aged specimen only had a peak under one surface. Otherwise oxidation and crystallinity generally increased with increasing ageing time. The rotating beam testing showed a significant decrease in fatigue life upon artificial ageing which resulted in a near immediate catastrophic fatigue failure for specimens

aged for eight days. Unsterilised UHMWPE was not investigated here, but has been found to have a higher fatigue strength than gamma irradiated specimens<sup>68</sup>. It has also been found that unsterilised and gamma sterilised ram-extruded polyethylene have similar low cycle fatigue strengths but after ten million cycles, the gamma sterilised material had a significantly lower fatigue strength<sup>237</sup>. This implies that gamma radiation reduces the resistance to cyclic loading and may contribute to fatigue related failures. The results in this study also show how with time, the fatigue strength reduces further due to oxidative degradation, eventually resulting in catastrophic failure.

Fatigue crack propagation has been implicated as a mechanism for pitting, delamination and fracture of UHMWPE components<sup>43, 238</sup>. Both materials in this study (Poly Hi, RCH1000) showed a significant decrease in the resistance to crack propagation upon oxidation. This result however, was more apparent in RCH1000, which had a higher crack growth rate in the irradiated state than Poly Hi. This is in contrast to work by Pruitt et al<sup>239</sup> who found that compression moulded polyethylene showed a superior resistance to crack initiation than ram extruded polyethylene. The higher crack growth rate for RCH1000 may be explained by the greater number of fusion defects present in this material. Other research has shown high crack growth rates associated with fusion defects<sup>44, 199</sup>.

The resistance to the propagation of fatigue cracks has been reported to improve with increasing crystallinity<sup>142, 152, 201</sup>. The increase in crystallinity in this study with an increase in ageing time was over-ridden by the degradative effect of the oxidation, leading to an increased susceptibility to damage by cyclic deformation. The fatigue crack propagation testing used was not ideal since loading was controlled using constant displacement, so the load decreased as the crack extended. This is of significance since the rate of crack propagation is extremely sensitive to small changes in loading conditions. However this is still a valid test for comparison of the materials and oxidation states studied here.

The results of the wear testing showed that an artificially induced sub-surface band of oxidation resulted in delamination of polyethylene, in wear tests which simulate the sliding conditions of total knee replacements. Delamination only occurred where sub-surface bands had formed and the delamination cracks propagated through this zone. In samples where there was development of oxidised polyethylene at the surface (in specimens aged for shorter time periods) there was an increase in surface wear, without delamination.

The delamination occurred at only 20,000 cycles for the eight day aged specimens and also for the samples cut from retrievals. This indicates that the level of oxidation achieved after eight days of ageing is equivalent to that seen *in vivo*. It should be remembered that this level of oxidation *in vivo* develops over a much greater period of time so would not result in delamination within days, but would take months or years. The six day aged specimens delaminated after an average 200,000 cycles. This is closer to the results of Cristante et al<sup>111</sup> who found fatigue failure and delamination after only 600,000 cycles on a wear test machine for components gamma irradiated and shelf stored (~54 months). This suggests that the ageing produced by six days of ageing is closer to that seen in shelf-aged components after three years.

Results from the lower load wear test (1kN) showed only surface wear up to 1.9 million cycles, even after eight days ageing. This suggests that high conformity knee replacement designs have an increased resistance to delamination wear, as has been reported in the more congruent acetabular components<sup>213, 214</sup>.

There was a significant increase in the wear of artificially aged material over plain irradiated material at most time points. Other studies have found a five fold increase<sup>114</sup> or a 100% increase<sup>113</sup> in wear rate of aged air irradiated UHMWPE (Sanford & Saum method, 14 days). The initial high wear rates seen for all test samples can be attributed to surface oxidised polyethylene generating initial high rates of wear, since the artificial ageing method always produced high surface oxidation, even when the peak was sub-surface. This was then followed by a lower wear rate which has been reported to be associated with cross-linking<sup>114</sup>. Associated with the initial high wear rates, all specimens had an initial large volumetric change with increased with increasing ageing time. The volumetric change would be expected to decrease with increasing oxidation, due to an increase in creep resistance, but this was not seen in the 2.3kN test, due to early high surface wear as a result of high surface oxidation generated by this ageing technique. Early surface wear was demonstrated in the short-term test which showed greater surface wear for the aged compared to the un-aged material. The oxidised surface layer has been shown previously to be less resistant to material removal by abrasion<sup>200</sup>. However, the 1kN test did show a decrease in creep with increasing oxidation, although this was not significant.

The results of the wear testing also consolidated the phenomenon of increased oxidation associated with the wear track. This was seen in the retrievals in the previous chapter, associated with residual stresses and is due to the wear action facilitating oxidation at the surface.

In conclusion it can be seen that the artificial ageing regime developed here from the method of Sanford & Saum<sup>71</sup> produced oxidation levels equivalent to those seen in



retrieved UHMWPE tibial components. Our results have shown that increasing oxidation by artificial ageing reduces the fatigue life of polyethylene. Without the development of a sub-surface peak of oxidative degradation, delamination does not occur in wear tests. However, from the fatigue results it is still possible to induce fracture in non-oxidised components. This suggests that in terms of delamination failure, oxidation of the polyethylene reduces the operational limits of the material. In addition, tensile strength of the polyethylene is reduced with increasing oxidation, due to the significantly embrittled material. Previous work has shown that UHMWPE manufactured by different processes propagates cracks at different rates<sup>241</sup>. In addition, this study shows that different UHMWPEs may be more susceptible to oxidation resulting in increased fatigue crack propagation and reduced life in some materials. This is a potentially important finding reinforced by work by Furman et al<sup>208</sup> who found that compression moulded components from 1900 resin appeared to be more resistant to 'on-the-shelf' ageing than other resins. A finding seen in chapter four and thus investigated further in chapter seven.

As previously mentioned, although irradiation results in oxidative degradation, it has not been abandoned as a sterilisation technique since the crosslinking which also results is beneficial to wear properties. However, several studies have investigated other methods of sterilisation which will reduce the oxidation of polyethylene in the long term. These methods are based either on alternatives methods of sterilisation, or on alternative atmospheres for gamma sterilisation. For, example gamma irradiation in an inert atmosphere or under vacuum has been shown to reduce oxidation of UHMWPE<sup>65, 67</sup> compared to air irradiation. However it has also been reported that specimens irradiated in nitrogen and air showed a similar oxidation rate, under artificial ageing regimes<sup>71</sup>. Alternatives such as gas plasma and ethylene oxide are also being investigated. These methods may well reduce the development of this sub-surface oxidised band in polyethylene, which would probably mean a reduction in the incidence in delamination wear in tibial components in the future. Indeed the fatigue life of gas plasma sterilised samples has been found to be virtually unchanged after ageing, whereas gamma irradiated samples (air and inert gas) had a significant reduction in fatigue life of about three orders of magnitude<sup>94</sup>. Thus future research will probably shift from the prevention of delamination wear, to the reduction of surface wear. These problems may well be similar to those faced in the development of total hip replacements.

## CHAPTER SIX

### OXIDATION AND WEAR OF UNTREATED AND STABILISED POLYETHYLENE



## 6.1 Introduction

As has been seen in previous chapters, oxidative degradation of ultra-high molecular weight polyethylene occurs as a result of irradiation sterilisation. Despite this, irradiation is still the preferred method of sterilisation by many companies due to the improved wear characteristics imparted by cross-linking, which also results from this method of sterilisation. Other methods of sterilisation such as gas plasma or ethylene oxide are now being used as these do not result in the formation of free radicals and subsequent oxidation. However, they do not result in crosslinking either.

Generation of free radicals during irradiation and their subsequent oxidation is of critical importance to the wear performance of UHMWPE implants. Although irradiation in an inert atmosphere reduces the possibility of oxidation, due to the elimination of oxygen during sterilisation and during storage, it does not eliminate the free radicals<sup>66, 68, 76, 79, 102, 242</sup>. These radicals are long-lived as found by Trieu et al<sup>107</sup> who discovered primary radicals in shelf-aged, nitrogen packaged UHMWPE tibial liners, and concluded that these have the potential to cause long-term oxidation. This is because the free radicals remain in the polymer matrix and will subsequently react when in contact with oxidants, leading to a delayed oxidative degradation mechanism. Streicher<sup>202</sup> also concluded there was no difference in the amount of post-irradiation oxidation when comparing specimens irradiated in air and in nitrogen, because the amount of trapped radicals is the same. These findings are backed by those of Ries et al<sup>102</sup> who found UHMWPE irradiated in an argon atmosphere did not eliminate gamma radiation induced oxidation (due to air trapped within the polymer). However, others<sup>243, 244</sup> have found that gamma irradiation sterilisation in a nitrogen atmosphere reduces post-sterilisation oxidation. However these studies were performed immediately post-irradiation, so subsequent ageing may contradict these findings. It has also been suggested that unless impermeable packing is used, the inert environment will be contaminated with oxygen which will permeate the packaging material after sterilisation<sup>74</sup>. This will obviously reduce the advantage obtained by delaying oxidation due to inert gas packaging and sterilisation.

The effect of sterilisation atmosphere has been investigated in terms of mechanical properties and wear performance as well as post-irradiation oxidation. Fatigue crack propagation testing has been reported not to show significant changes for UHMWPE packaged and irradiated in an argon environment as opposed to air<sup>96</sup>. However, a decrease in fatigue life of an order of five has been reported for air irradiated polyethylene compared to irradiation in an inert atmosphere<sup>94</sup>. Streicher &

Schaffner<sup>115</sup> in a study of retrieved polyethylene found that the physical properties of polyethylene deteriorate during irradiation sterilisation, storage and implantation. This was found to have a negligible effect on clinical wear rate, however they advocated the use of inert gas irradiation since this dramatically reduces the amount of damage to the polyethylene structure and properties.

Wear testing using a pin-on-ring test set up has shown an increased wear resistance for nitrogen and vacuum packaged samples compared to air irradiated specimens<sup>78</sup>. Hip simulator testing has also shown a statistically significant reduction in wear rate for vacuum sterilised as compared to air sterilised polyethylene<sup>245</sup> and also for polyethylene irradiated with an oxygen scavenger compared to air irradiated components<sup>105</sup>. In the latter study it was noted that testing occurred within six months of sterilisation, thus eliminating late oxidation of residual free radicals which could affect long-term wear rates. It is probable that other studies have neglected to consider long-term oxidative degradation when advocating inert atmosphere irradiation to improve UHMWPE performance related variables. Consequently, the use of an inert atmosphere during irradiation and subsequent storage is generally believed to lead to reduced oxidation and reduced wear rates (*in vitro*) compared to air irradiated polyethylene. However, this is only a short term phenomenon and not a solution to the oxidation problem, as free radicals are still available for oxidation, and inert gas packaging can be permeable to oxygen.

By way of a solution, one orthopaedic company has produced a modified polyethylene to try and overcome these problems. Stabilisation is a process whereby an UHMWPE is produced which has an increased oxidation resistance. The stabilisation process has been patented by Howmedica (Rutherford, New Jersey, USA, International patent No. PCT/IB94/00083) and involves processing and irradiation in an inert atmosphere followed by an annealing regime. The aim of this process is to reduce the number of free radicals by recombination reactions during the annealing stage. Annealing or hydrogen treatment has been found by others to reduce the number of allyl/alkyl and peroxy free radicals in vacuum irradiated specimens<sup>240</sup>.

Consequently the aim of this work was to compare the oxidation levels of untreated and stabilised polyethylene, using two simulated artificial ageing treatments. In standard polyethylene, the first method induces oxidation to a level equivalent to that typically seen in retrievals after five years and the second reproduces oxidation levels seen in retrievals after 8-10 years, with the production of a sub-surface band of oxidation. It was hypothesised that by crosslinking the free radicals and chain scission products of irradiation, oxidative degradation of the stabilised polyethylene would not

occur, resulting in an improvement in wear properties. The first ageing regime was then used to determine its affect on the wear of untreated and stabilised polyethylene under conditions that simulate the sliding motion of total knee replacements.

## 6.2 Materials And Methods

### 6.2.1 Materials

Untreated, stabilised and stabilised then aged polyethylenes were examined in this analysis. Materials were stored in distilled water in sealed polyethylene bags prior to testing. Untreated polyethylene refers to ram-extruded Poly Hi (GUR 4150) which has been gamma irradiated in air (25 kGray).

### 6.2.2 Stabilisation Process

The stabilisation process has been patented by Howmedica. The resin used in its manufacture is stored in a sealed container from which most of the oxygen is removed. This can be achieved by several processes including vacuum, using an absorbent species or flushing with an inert gas. The vessel is then repressurised with an inert gas.

Rod or bar stock is manufactured by transferring the resin to an appropriate mould, where the resin is melted and formed in an oxygen reduced atmosphere. Once the material has been formed it is annealed and sealed in an oxygen reduced atmosphere in an airtight package. Radiation sterilisation is performed, then the material is annealed for a predetermined time and temperature which is sufficient to form cross-links between the free-radicals in neighbouring polymeric chains. The heat treatment to allow free radicals to cross-link lasts for at least 48 hours at a temperature between 37-70°C. Annealing is usually performed for 144 hours at 50°C. An elevated temperature is used to allow free radicals to migrate.

### 6.2.3 Ageing (Howmedica method)

All wear test specimens were aged according to the Howmedica method (Sun et al<sup>91, 221, 232</sup>) of treatment at elevated temperature as described in chapter five. Specimens were aged for eleven days at 80°C with a heating rate of 0.2°C/min as the initial ramp.

### 6.2.4 Ageing (BME method)

The method developed in the previous chapter was used to assess the ability of the stabilised polyethylene to prevent oxidation under a more aggressive methodology. Samples were aged for six days at 80°C, in oxygen at 0.5 MPa.

### 6.2.5 Wear Test Methodology

The wear test configuration is described in chapter two. Three wear tests were performed in total, as follows:-

Test one: Stabilised vs. untreated polyethylene, to approximately two and a half million sliding cycles.

Test two: Untreated then aged vs. stabilised then aged polyethylene, for over two and a half million sliding cycles.

Test three: Stabilised vs. untreated polyethylene, for four million sliding cycles.

Gravimetric and volumetric analyses were performed as described in chapter two. Wear mechanisms were examined using transmitted light and the scanning electron microscope. Oxidation of specimens was evaluated using chlorosulfonic acid treatment and FTIR. Three specimens of each condition were tested.

### 6.2.6 Determination of Short Term Wear

Soaked control discs of untreated, aged and stabilised then aged polyethylene were taken after their final gravimetric measurements and a short wear test performed. This test only lasted for three hours and was used to investigate the wear track morphology and wear mechanisms of the specimens at the beginning of the test.

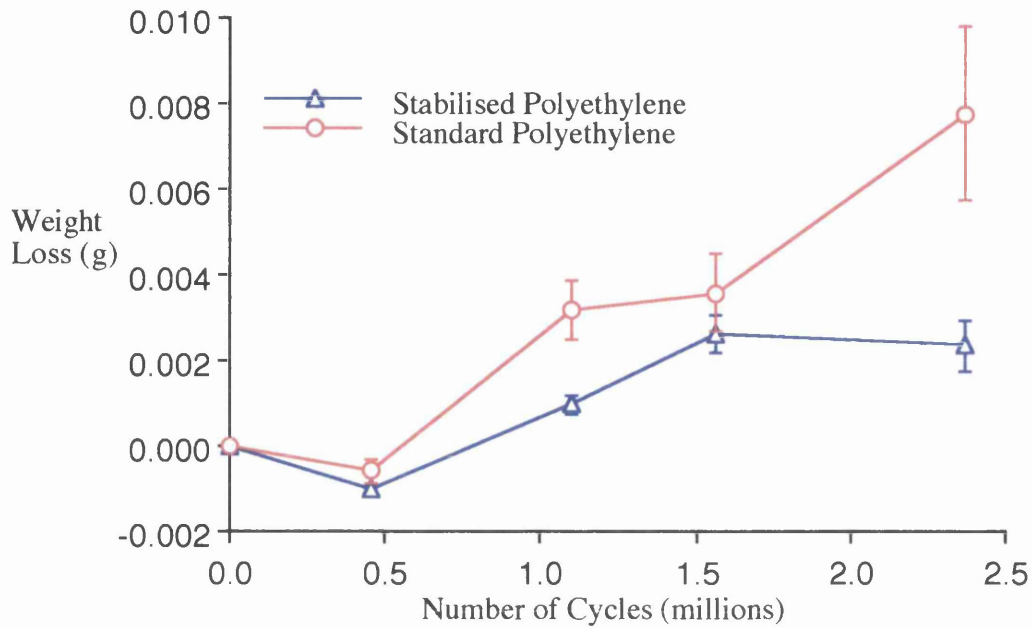


Figure 6.1 Weight loss for test one: stabilised vs. untreated polyethylene

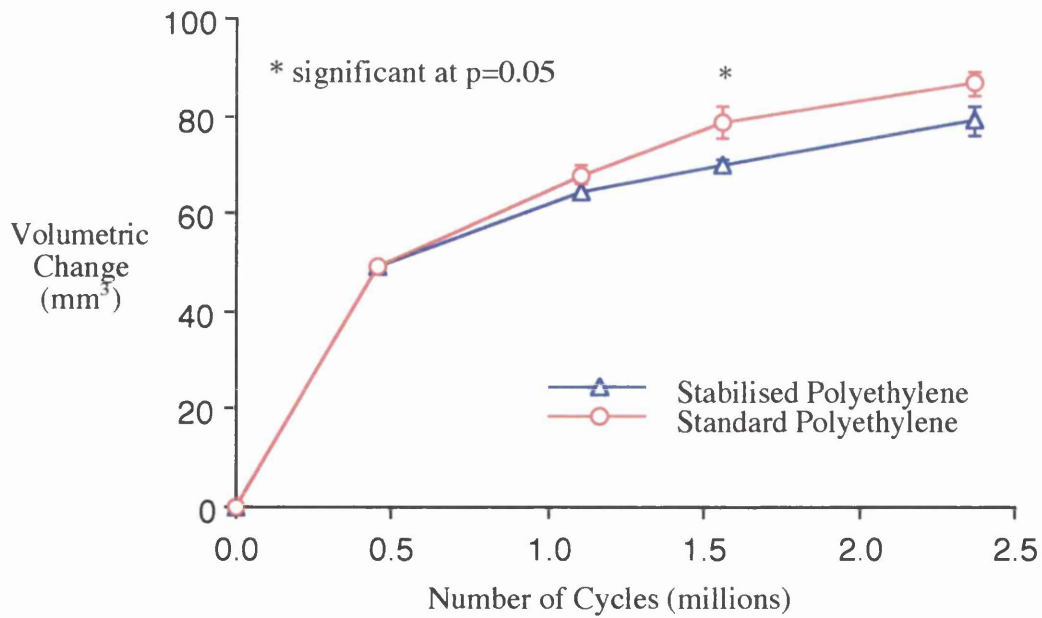


Figure 6.2 Volumetric change for test one: stabilised vs. untreated polyethylene

## 6.3 Results

### 6.3.1 Wear Test Results

#### 6.3.1.1 Test One: Stabilised vs. untreated polyethylene

Weight loss data showed no significant difference between the two materials (figure 6.1). It can be seen from the graph that at half a million sliding cycles there is a weight gain of the discs. This is probably due to fluid uptake related to the cyclic load action, relative to the soak controls. However, a significant difference between the average wear track volume on stabilised versus untreated polyethylene was seen after 1.5 million sliding cycles (figure 6.2), with the wear tracks on the stabilised polyethylene being smaller in size. Both materials showed an initial high volumetric change which is attributed to creep of the polyethylene.

#### 6.3.1.2 Test Two: Stabilised vs. untreated polyethylene, after simulated ageing.

Weight loss results (figure 6.3) show a significant reduction in wear rate of the stabilised/aged material compared to the untreated/aged material, after only half a million sliding cycles. After three million sliding cycles there is a six fold increase in wear of the untreated polyethylene compared to the stabilised material. Wear rates for the stabilised/aged material are also lower throughout the test compared to the untreated/aged polyethylene. The wear rates seen for the stabilised/aged material was  $2.6 \times 10^{-5} \text{ g/km}^{-1}/\text{kg}^{-1}$ , followed by a secondary wear rate of  $5.7 \times 10^{-5} \text{ g/km}^{-1}/\text{kg}^{-1}$ . The wear rate for untreated/aged polyethylene was  $4.7 \times 10^{-4} \text{ g/km}^{-1}/\text{kg}^{-1}$ . A significant difference was also found between the wear track volumes (figure 6.4) for these two materials, with stabilised/aged polyethylene having a reduced volume compared to the untreated/aged material, and also a reduced volumetric wear rate.

#### 6.3.1.3 Test Three: Stabilised vs. untreated polyethylene.

This repeat of the first test showed a significant reduction in weight loss for stabilised compared to untreated polyethylene after two and a half million cycles (figure 6.5). After four million sliding cycles the untreated polyethylene wore twice the amount of the stabilised polyethylene. A significant reduction in the volume of the wear track and was seen after three million sliding cycles for the stabilised polyethylene compared to the untreated polyethylene (figure 6.6).

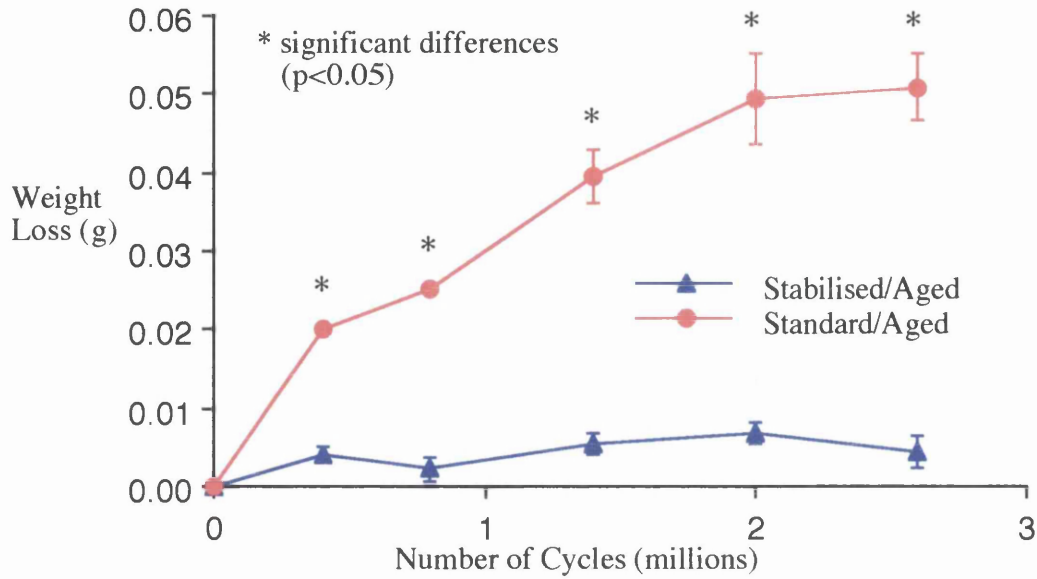


Figure 6.3 Weight loss for test two: stabilised/aged vs. untreated/aged polyethylene

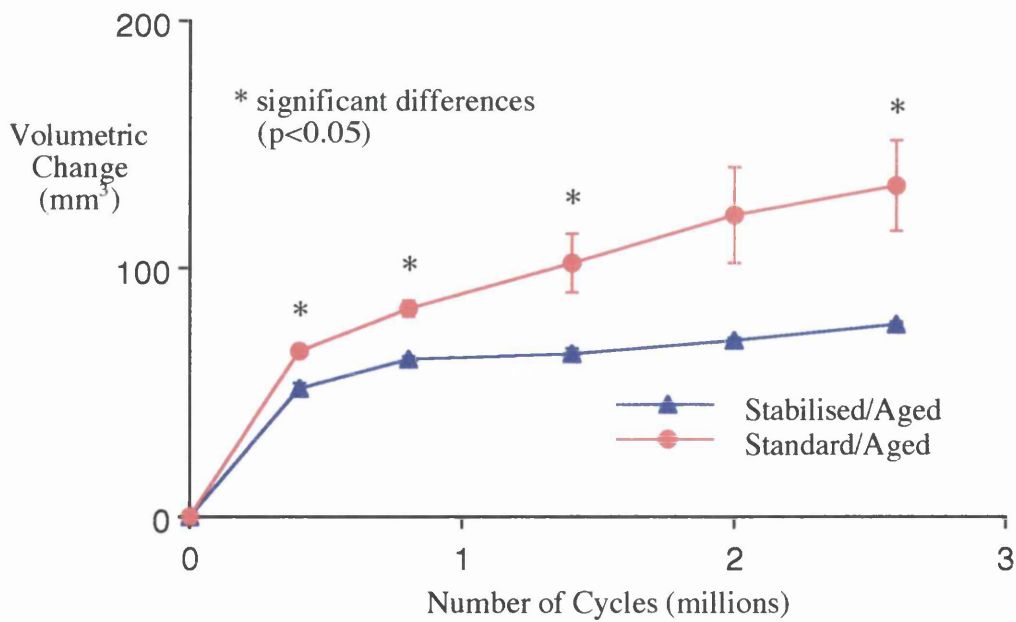


Figure 6.4 Volumetric change for test two: stabilised/aged vs. untreated/aged polyethylene



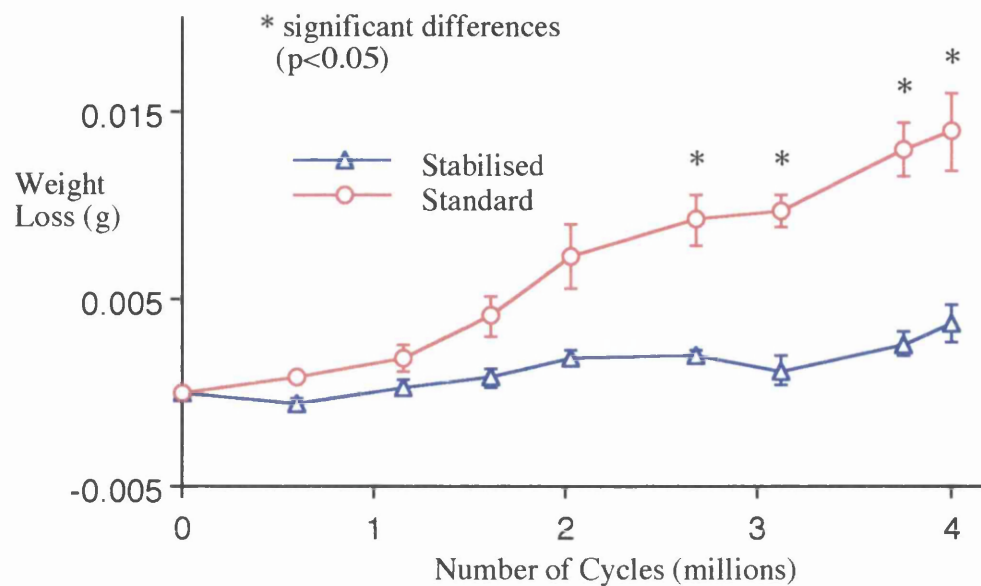


Figure 6.5 Weight loss for test three: stabilised vs. untreated polyethylene

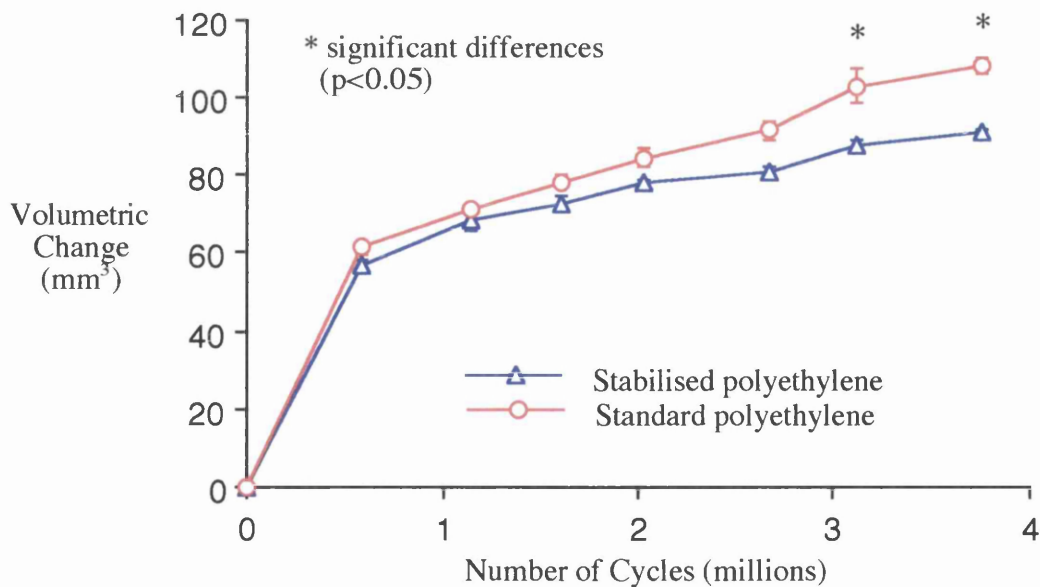


Figure 6.6 Volumetric change for test three: stabilised vs. untreated polyethylene

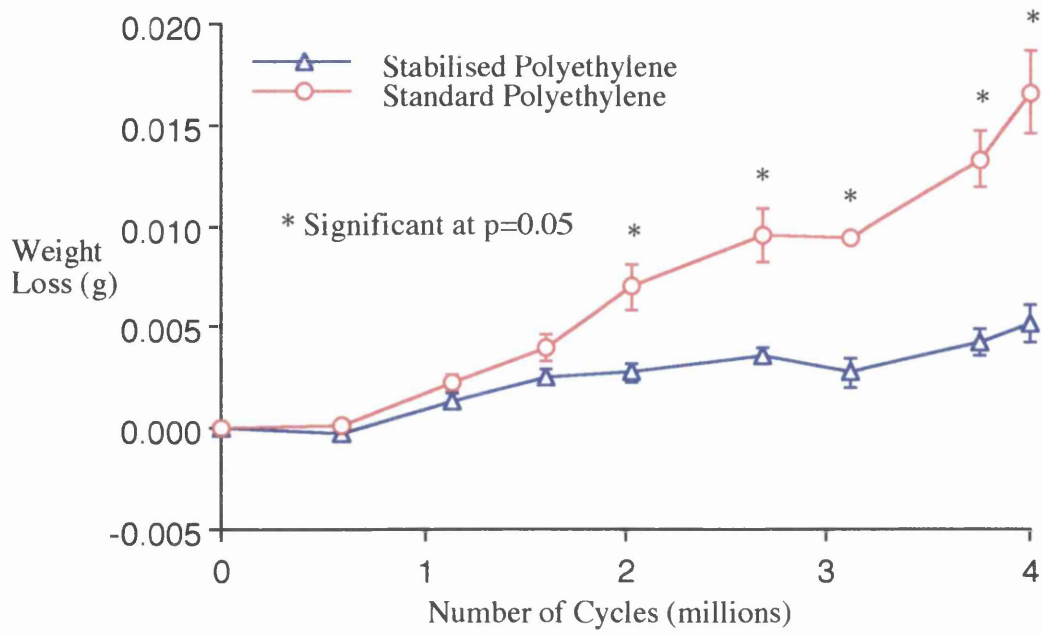


Figure 6.7 Combined weight loss data for tests one and three

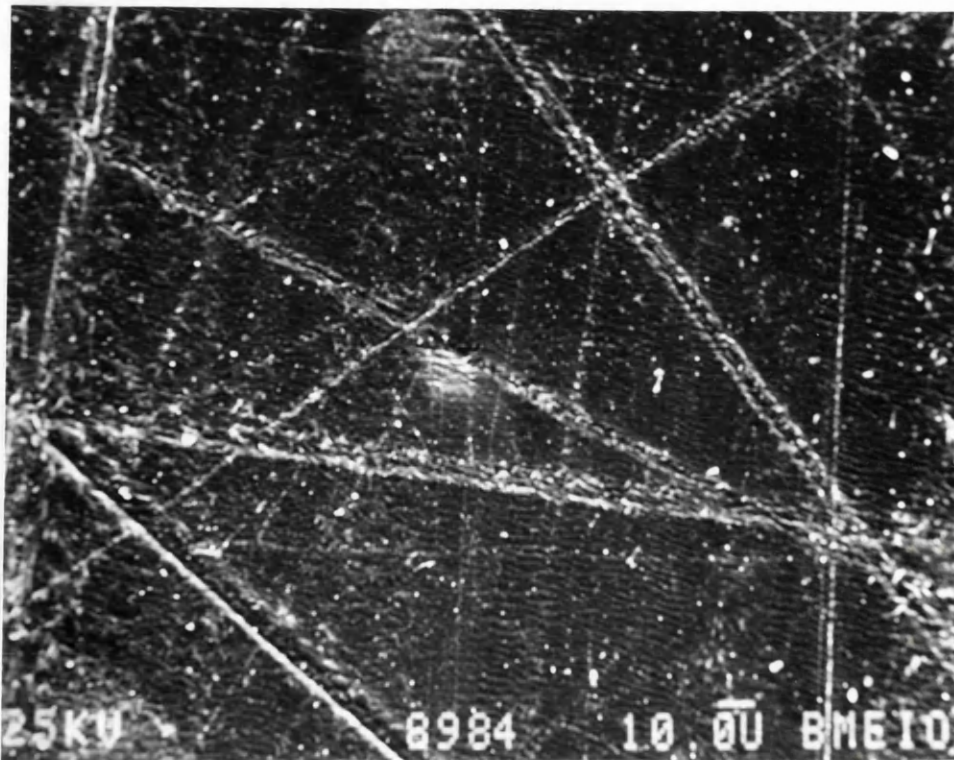


Figure 6.8a Scanning electron micrograph showing scratches on the polyethylene surface

A combination of weight loss data from tests one and three is shown in figure 6.7. It should be noted that the time intervals for data points for tests one and three were not the same, so the data from test one was transposed to the points taken in test three. This does not appear to affect the overall result. The weight loss between the stabilised and untreated polyethylene became significantly different after two million cycles.

### 6.3.2 Scanning Electron Microscopy

#### 6.3.2.1 Stabilised vs. untreated polyethylene, test three

Similar wear mechanisms were seen on these materials with scratching and adhesive wear evident. The wear track of the untreated polyethylene is shown in figure 6.8 a & b and that of the stabilised polyethylene in figure 6.9. A surface rippling with a periodicity of under  $1\mu\text{m}$  was seen on both materials, perpendicular to the direction of sliding. This effect however was more extensive on the untreated material, as were adhesive wear mechanisms. This adhesive wear produced sheets of polyethylene ( $\sim 10\mu\text{m}$ ) which were drawn from the bearing surface. This phenomenon has been seen on all previous tests of this type.

#### 6.3.2.2 Stabilised vs. untreated polyethylene, after ageing, test two

Similar wear mechanisms were seen on these materials with scratching and adhesive wear evident. However, adhesive wear in the form of shreds and sheets was more prevalent on the untreated/aged material (figure 6.10a) compared to the stabilised/aged material. The untreated polyethylene also exhibited cracking of the surface (figure 6.10b). In some regions of the stabilised/aged material it was difficult to discern areas of adhesive wear (figure 6.11).

An additional test performed to evaluate the early stages of wear showed adhesive wear and cracking on the aged material (figure 6.12a) whereas the stabilised/aged material still had machining marks clearly apparent (figure 6.12b). These observations tie in with the weight loss data seen in figure 6.7. The minimal surface wear seen on the stabilised polyethylene corresponds to the low initial wear rate seen for this material. In contrast the high level of surface wear seen on the untreated/aged polyethylene in the SEM corresponds to the high wear rate seen for this material.

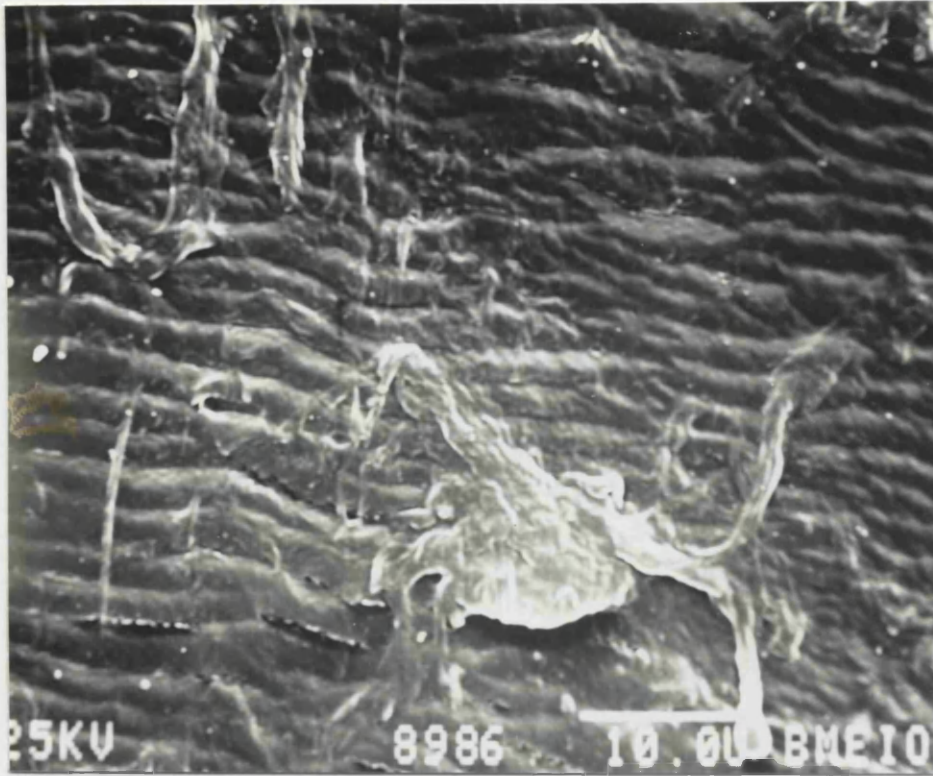


Figure 6.8b Scanning electron micrograph showing the ripple pattern on the polyethylene surface and shreds of polyethylene



Figure 6.9 Scanning electron micrograph showing the ripple pattern on the stabilised polyethylene surface and sheets of polyethylene



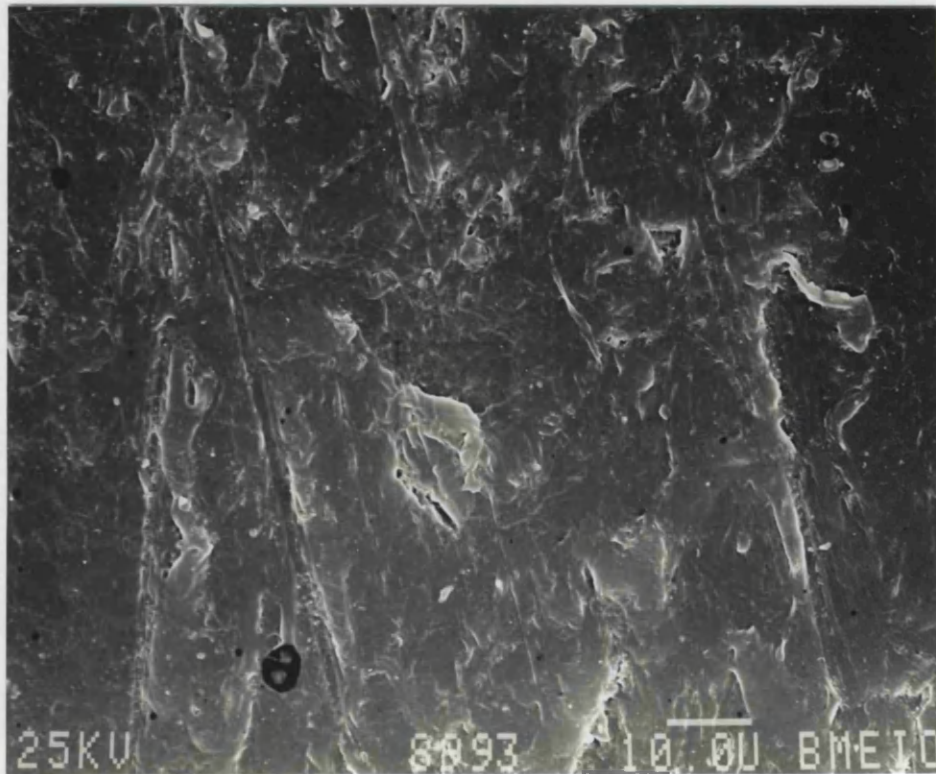


Figure 6.10a Scanning electron micrograph of aged polyethylene showing scratches, adhesive wear and polyethylene shreds

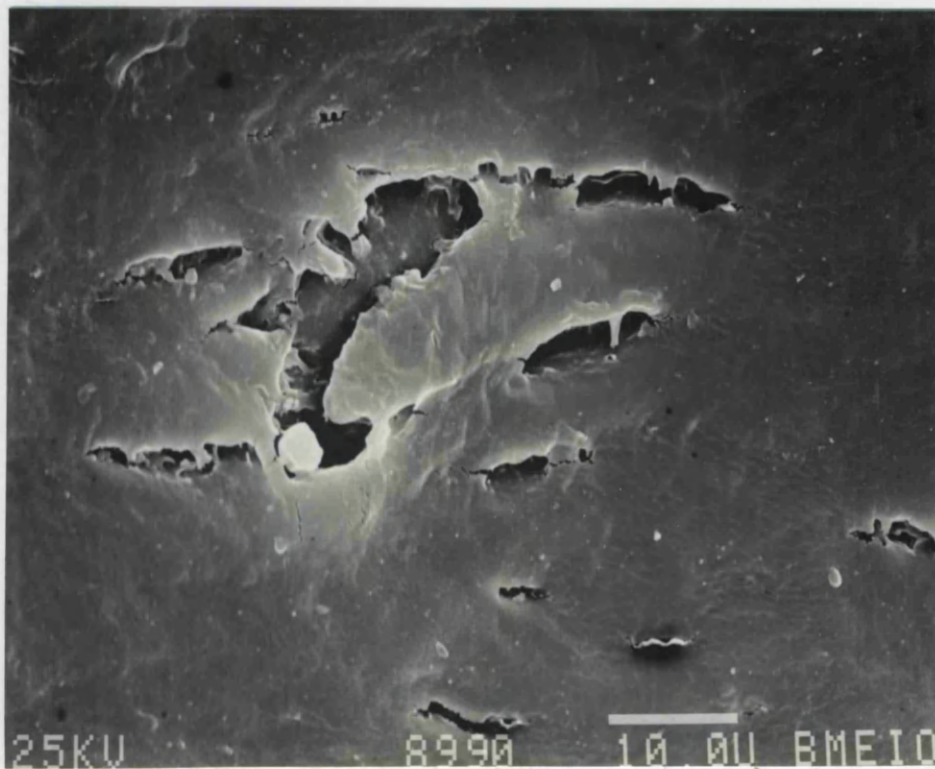


Figure 6.10b Scanning electron micrograph of aged polyethylene showing cracking of the polyethylene surface

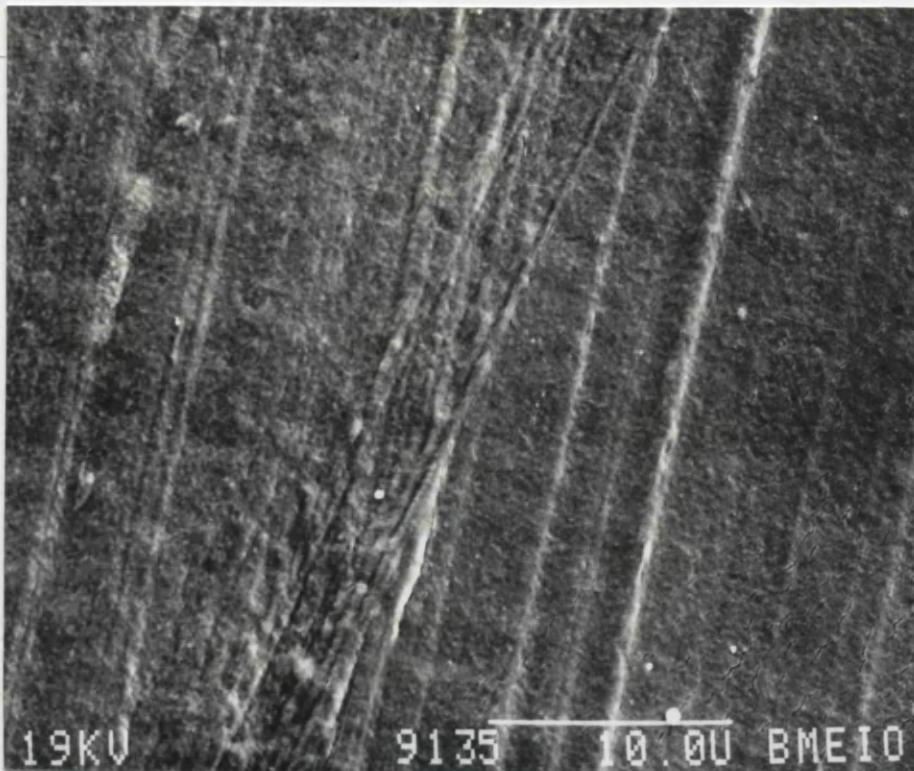


Figure 6.11 Scanning electron micrograph of stabilised/aged polyethylene showing the finely textured surface appearance

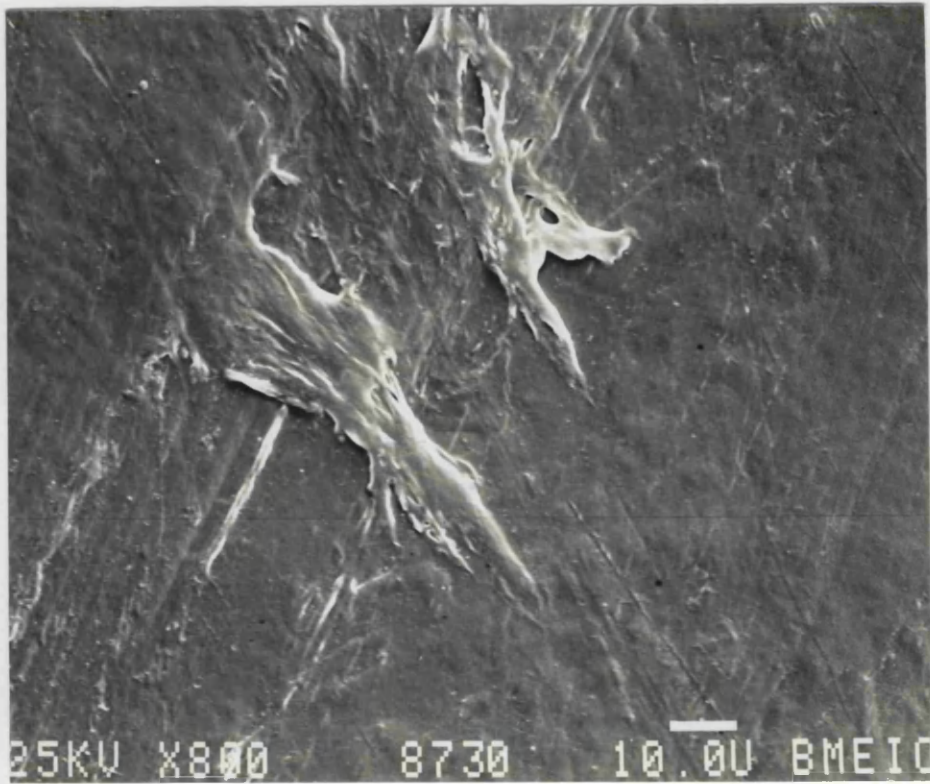


Figure 6.12a Scanning electron micrograph of aged polyethylene showing adhesive wear and cracking

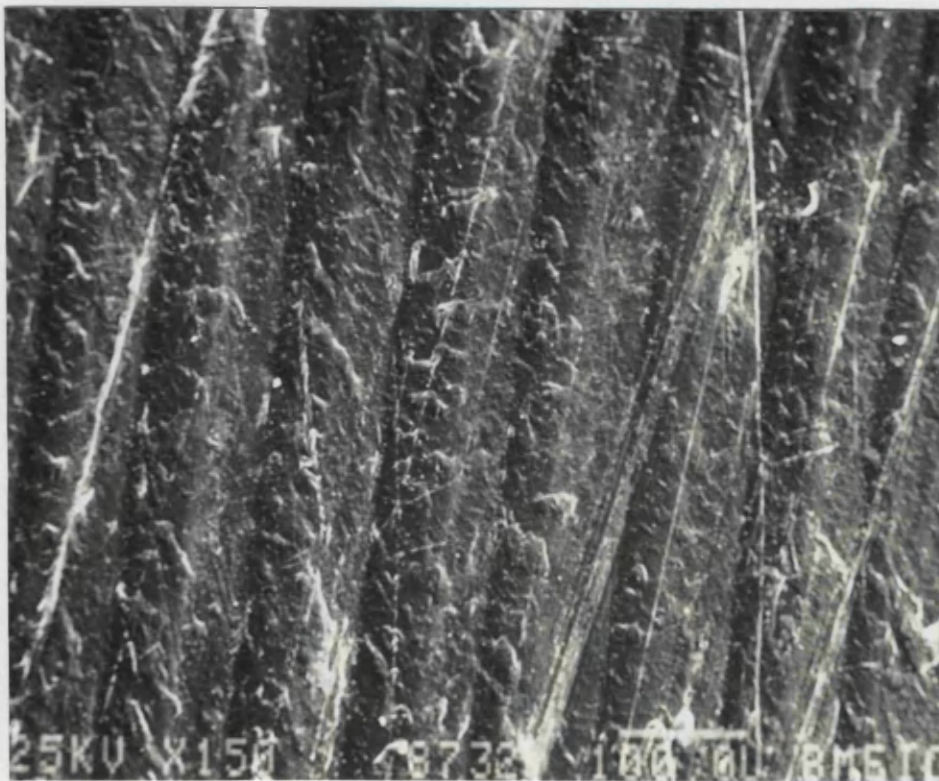


Figure 6.12b Scanning electron micrograph of stabilised/aged polyethylene showing the presence of machining marks



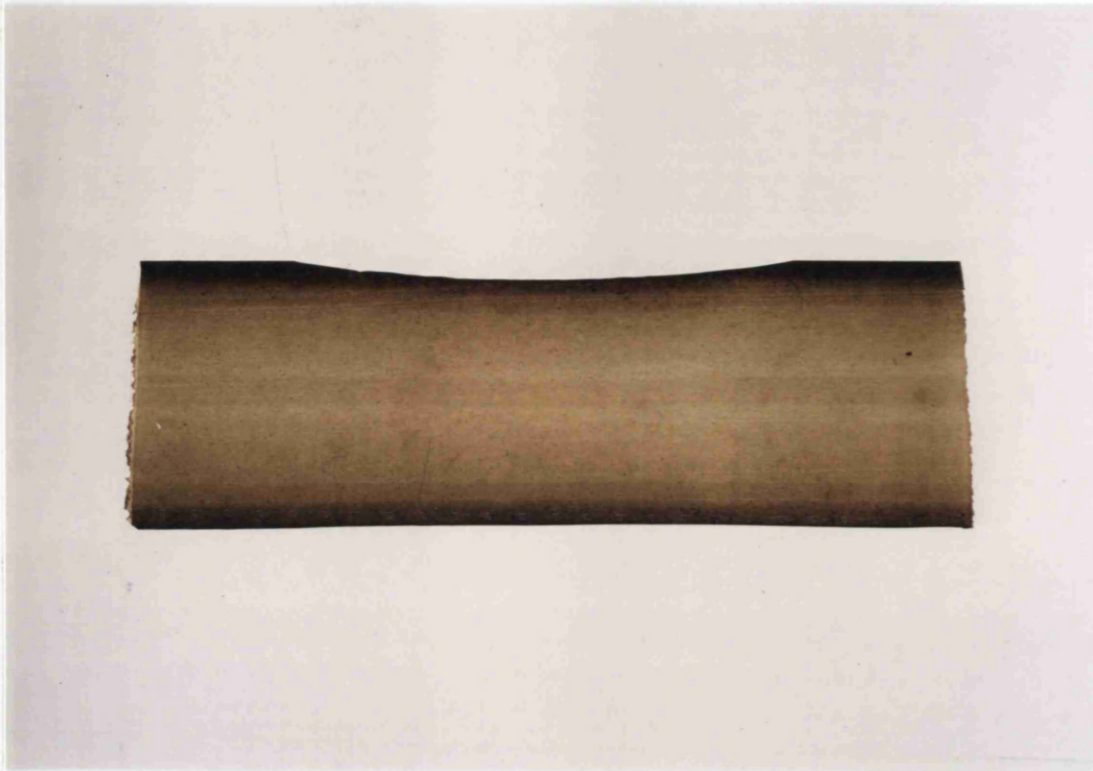


Figure 6.13 Chlorosulfonic acid treated thin section through the wear track of an untreated/aged specimen

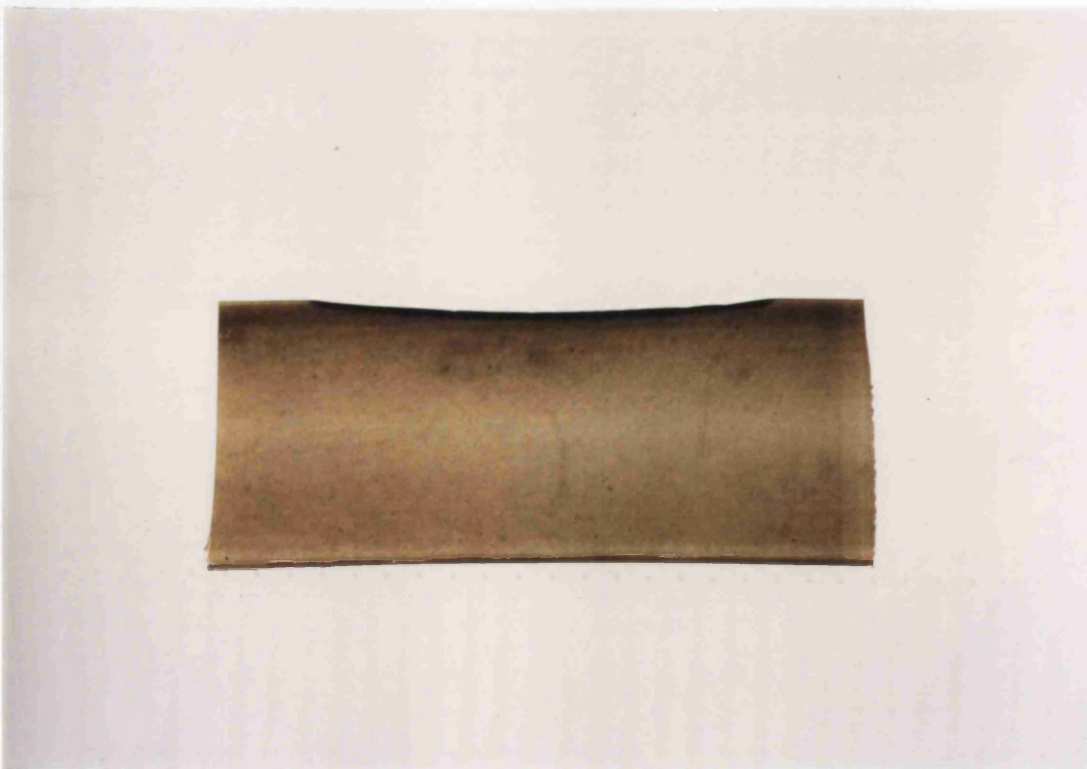


Figure 6.14 Chlorosulfonic acid treated thin section through the wear track of a stabilised/aged specimen



### 6.3.3 Light Microscopy

#### 6.3.3.1 Test two: Stabilised vs. untreated polyethylene, after ageing.

For the untreated/aged polyethylene a zone of oxidation which measured less than 0.5mm was visible on the surface, as a darkly stained band after CSA treatment (figure 6.13). This would indicate that at the end of the test the zone of oxidation had not worn through. However, the CSA staining technique shows oxidation to be high at the surface and gradually diminishes with depth into the material. For the stabilised/aged polyethylene a zone of oxidation could be observed at the wear track surface which was not apparent on the unworn surfaces, (figure 6.14) indicating an oxidative mechanism as a consequence of the wear action.

### 6.3.4 Fourier Transform Infrared Spectroscopy

#### 6.3.4.1 Test two: Stabilised vs. untreated polyethylene, after ageing.

FTIR data (figure 6.15) demonstrates that oxidation of the untreated/aged polyethylene is high at the surface and reduces with depth into the material to a depth of about 2mm. The level of oxidation for the stabilised polyethylene is low and consistent with depth. Therefore the different wear rates for these two materials may be associated with the differences in the degree of oxidation with depth.

### 6.3.5 Aggressive Oxidation of Howmedica Specimens

This method was used to assess the ability of the stabilised polyethylene to resist oxidation under a more aggressive methodology. CSA staining of the stabilised polyethylene was reduced compared to the untreated material (figure 6.16 a & b). In addition the zone of maximum oxidation was at a greater depth in the stabilised material and of less thickness.

The FTIR oxidation depth profile shows a low level of oxidation at the surface of the stabilised material (figure 6.17). As expected the oxidation is higher after this method of oxidation as compared with the method employed by Howmedica. It is worth noting that the oxidation level of both materials is at approximately the same level after a depth of about 1mm, and actually higher in the stabilised material between 2-2.5mm.

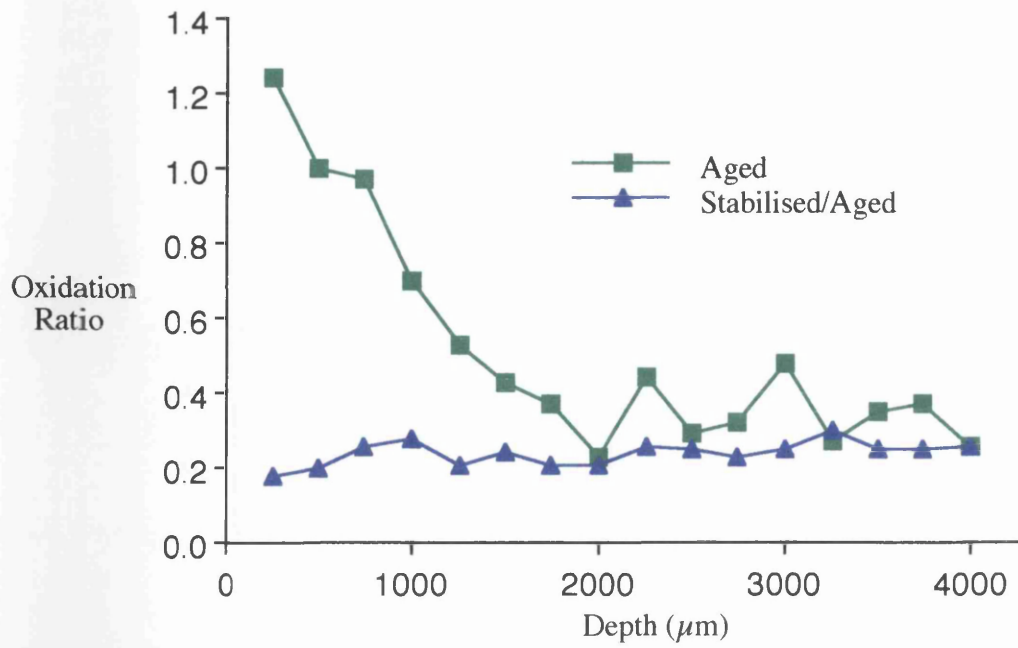


Figure 6.15 Oxidation ratio with depth for untreated/aged and stabilised/aged materials

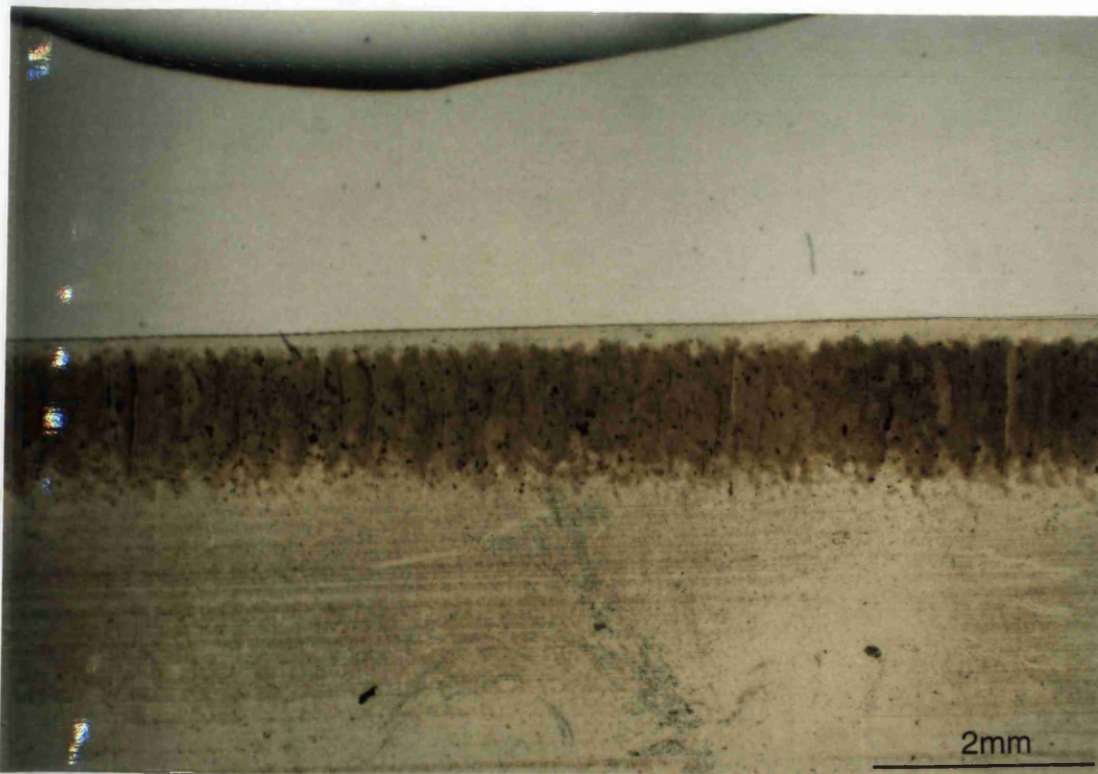


Figure 6.16a Chlorosulfonic acid treated thin section through an untreated/aged specimen showing a sub-surface oxidised band

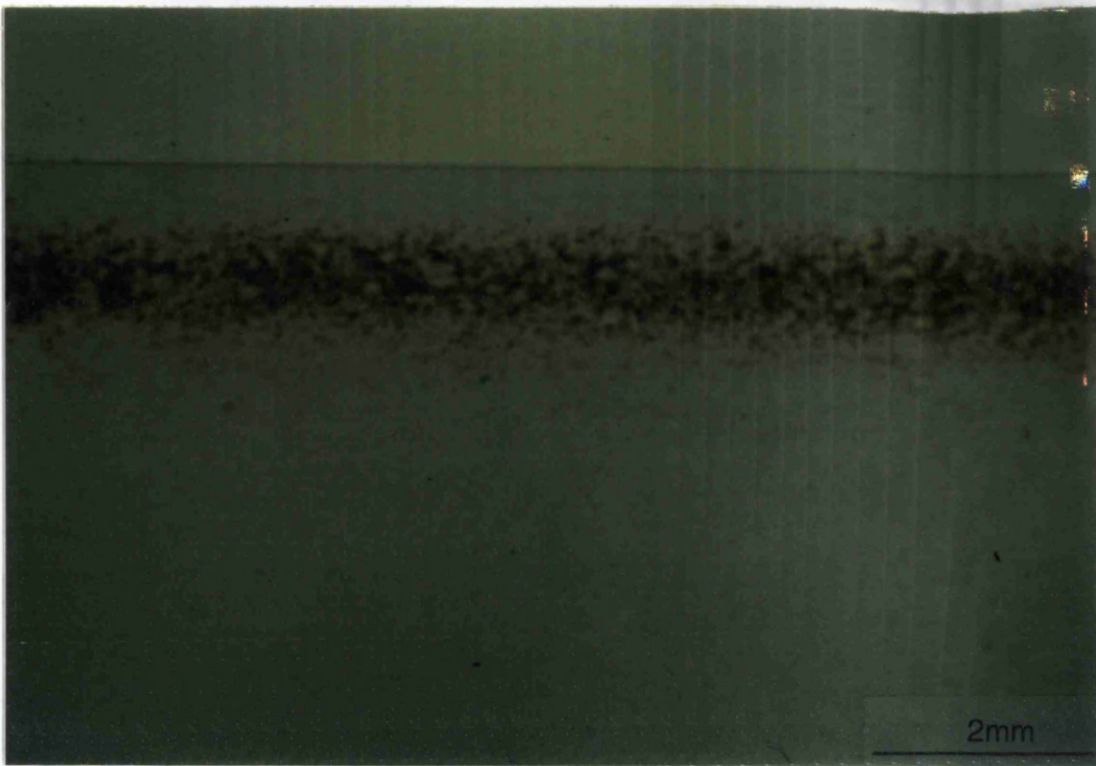


Figure 6.16b Chlorosulfonic acid treated thin section through a stabilised polyethylene specimen, after BME artificial ageing, showing a sub-surface oxidised band

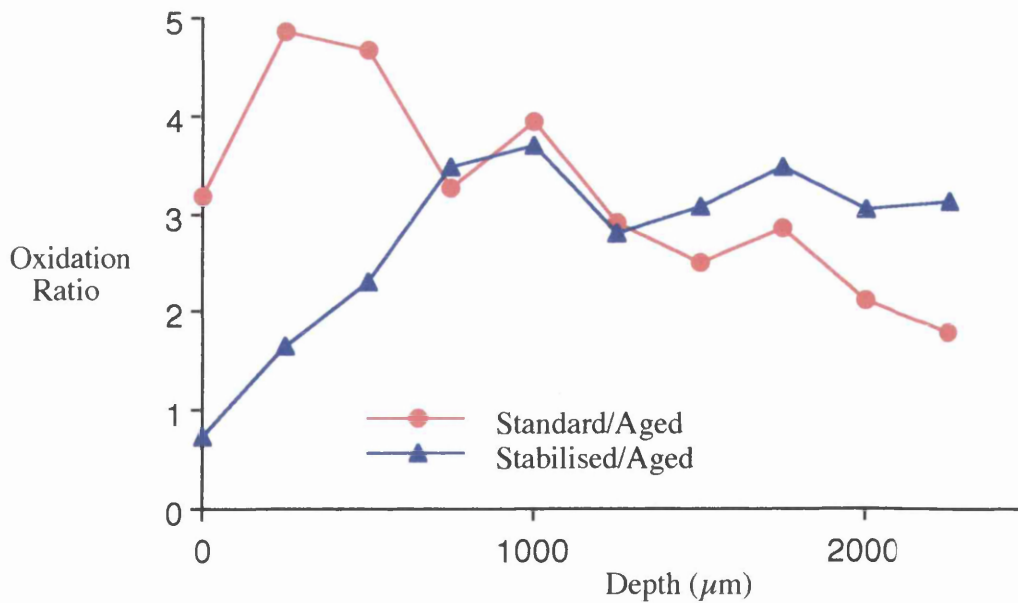


Figure 6.17 Oxidation ratio with depth for untreated and stabilised polyethylene, after BME artificial ageing

## 6.4 Discussion

The results of this study show that the stabilisation process is beneficial, with reduced oxidation and reduced wear compared to standard, untreated polyethylene. The wear rate of the untreated polyethylene was approximately twice that of the stabilised material under non-aged conditions (tests one & three), with significant differences occurring after two million sliding cycles. If this wear pattern was repeated *in vivo* then the wear rate of the stabilised material would be significantly lower and differences would be seen after only one year.

The difference between these two materials was amplified after ageing (test two). The untreated polyethylene appeared to have two wear rates. Initially the wear was high, probably due to the loss of the surface oxidised material. The second wear rate then corresponds to the wear of the less oxidised polyethylene beneath this surface layer. The FTIR data however indicated that the oxidised surface layer had not worn completely through. Therefore there may possibly have been a third lower rate of wear once this material had worn away. The stabilised/aged polyethylene appeared to have an increased oxidation along the wear track, compared to the unworn surface. This is due to the wear action which has been seen in the previous chapter and in other published work<sup>177, 232</sup> to cause an oxidative mechanism at the wear track. This result is in contrast to that of Yu et al<sup>131</sup> who found higher surface oxidation ratios after hip simulator testing for several types of sterilisation and atmosphere, except stabilised polyethylene. In contrast to the CSA results, the FTIR data does not show a peak of oxidation at the articulating surface for the stabilised wear test specimen. This is probably due to the first measurement being sub-surface and therefore below this oxidised region.

Scanning electron microscopy demonstrated that the wear on all specimens was surface in origin, with adhesive wear and scratches evident. The stabilised polyethylene had less adhesive wear than the untreated polyethylene, before and after ageing and no delamination occurred in any of the tests.

Comparison of stabilised polyethylene before and after ageing (Howmedica process) shows that the stabilisation process can effectively combat the effects of ageing. Others have also published work showing stabilised polyethylene to have negligible oxidation after artificial ageing<sup>83, 104</sup>. Even under the more aggressive ageing conditions employed (BME ageing methodology), oxidation was lower than a simultaneously aged, untreated sample. However, the oxidation was only reduced at

the surface of this material, implying that the stabilisation process is only reducing free radicals at the surface of the material and not at greater depths. This was shown when the aggressive oxidation method produced sub-surface bands of oxidation similar to those seen at retrieval after a long duration of implantation. This observation is in agreement with work published by Taylor et al<sup>243</sup> who found that a 50°C post sterilisation treatment (as used in the Howmedica annealing process) had no apparent effect on crosslinking compared to sterilisation and storage in nitrogen. They therefore advised that higher annealing temperatures would be more beneficial. However, Polineni et al<sup>104</sup> examined various sterilisation treatments in hip simulator testing and found stabilised polyethylene improves the tribological properties of UHMWPE while controlling any increase in oxidation levels, even after ageing.

It must be stressed that the oxidation which has been identified in retrieved samples is probably a combination of shelf ageing and time in the body. Shelf ageing can be reduced by storing in an inert atmosphere and manufacturers now tend to keep storage times to a minimum due to an awareness of the potential shelf-ageing problem. Consequently with the new understanding of the generation of free radicals during irradiation and possible recombination reactions in inert atmospheres using the stabilisation process, this should lead to a reduction in free radicals and oxidation in the future.

The results of this study are in agreement with subsequently published hip simulator testing. These have shown stabilised polyethylene to have a significantly lower wear rate than air-irradiated polyethylene<sup>83, 104, 105</sup> and also EtO sterilised polyethylene<sup>83, 104</sup>. A significantly lower average wear rate and volumetric wear rate has also been shown for stabilised versus air irradiated polyethylene after six months shelf-ageing<sup>246</sup>. The stabilisation process has also been reported to show long-term improvements in oxidation resistance, extent of crosslinking, molecular weight retention, UTS, impact strength, creep and wear resistance<sup>95</sup>. Thus *in vitro* test results indicate improved properties for stabilised UHMWPE, but clinical trials are required to see if these improvements are borne out *in vivo*.

## CHAPTER SEVEN

### OXIDATION AND WEAR RESISTANCE OF DIRECTLY MOULDED POLYETHYLENE

## 7.1 Introduction

Oxidation of ultrahigh molecular weight polyethylene is of considerable importance because it leads to higher wear and has been shown in the previous chapters to be correlated with delamination in TKR. Current sterilisation processes have been altered by some manufacturers to try and eliminate the problem. Sterilisation by irradiation in an inert atmosphere is now the method of choice for several companies. However there are concerns that this will only delay oxidation, due to latent free radicals within the UHMWPE. The alternatives are non-irradiation techniques such as ethylene oxide or gas plasma but these do not impart increased wear resistance due to crosslinking as seen in gamma irradiated materials. Research Institutions and manufacturers are also developing 'modified' polyethylenes to overcome oxidation. Although some materials, such as the stabilised polyethylene investigated in the previous chapter show an improvement in oxidation resistance, it is clear that the oxidative degradation process may still occur, albeit after longer time periods.

Although 'modified' polyethylenes are being developed it has become apparent that not all the presently available 'medical grade' polyethylenes are the same, especially in terms of the resistance to oxidation. It was seen in chapter four that directly compression moulded polyethylenes (such as the AGC and Miller Galante) had excellent wear properties and good oxidation resistance. The good consolidation and thus quality of directly compression moulded components has been reported by many authors from *in vitro* experimentation and retrieval studies. One of the most important gauges of how successful a particular design is (and by inference the material from which it is manufactured) are survivorship rates. Knutson et al<sup>205</sup> in their report on the Swedish Knee Arthroplasty Register found that knees manufactured from directly moulded polyethylene (AGC) had the lowest failure rate of all the knees studied. Ritter et al<sup>29</sup> found a 98% survival rate at ten years in a directly moulded flat-on-flat design, which is comparable to more congruent designs in which the stress levels are lower.

Early examination of compression moulded material, indicated greater numbers of fusion defects compared to their extruded counterparts. Recently however, directly compression moulded material has been deemed the preferred material. There are several reasons for this, including improved processing which has resulted in improved consolidation. In addition, the absence of calcium stearate in compression moulded materials has been reported to virtually eliminate grain boundaries and fusion defects<sup>47</sup>. The improved consolidation compared to other manufacturing methods has been shown in retrieval data. Landy & Walker<sup>43</sup> found that compression moulded

prostheses which had been in patients for similar periods of time to extruded components showed reduced wear, but were unsure of the reason why. They<sup>43</sup> also reported that many of the compression moulded components did not delaminate or crack. Bankston et al<sup>1247</sup> found that acetabular components machined from extruded bar had significantly greater wear than directly compression moulded polyethylene components, in a well-matched clinical series. They suggested that compression moulded all-polyethylene acetabular components may be optimal for reducing wear in THR. James et al<sup>188</sup> have also reported significant differences in wear rates between direct compression moulded and machined ram extruded acetabular cups. The compression moulded material had better consolidation and in addition, the ram extruded material was reported to have machining induced embrittlement at the surface of the cups.

With the recent interest in the relationship between oxidative degradation and wear, the resistance of polyethylenes to oxidation is being thoroughly investigated. The Insall Burstein TKR has proved a useful design for comparative evaluation since the design has not altered but the manufacturing method for the polyethylene has changed. The IBI was directly moulded from 1900 resin whereas the IBII is made from polyethylene machined from extruded bar (GUR 4150). Furman et al<sup>206</sup> in a study of retrieved IBI and IBII components found no sub-surface oxidised bands in directly moulded components compared to bands in three out of eight machined components for prostheses with comparable *in vivo* durations. They also found a much lower incidence of pitting in the IBI compared to the IBII. Collier et al<sup>13</sup> examined a limited number of Insall Burstein prostheses (it was not stated whether these were IBI or IBII) and commented that these presented an absence of cracking and delamination, although there were some large (2-4mm) shallow pits. They attributed these findings in part to the thickness of the components, as they were all greater than the recommended minimum of 6-8 mm.

One issue presently being debated is the affect of calcium stearate on the oxidative degradation of polyethylene. This is particularly relevant to compression moulded materials as most are manufactured from calcium stearate free material. Some grades of polyethylene have always been manufactured from non-stearate containing UHMWPE powder, however both European and American companies are switching from stearate containing to non-stearate materials in light of recent findings. Calcium stearate is added as an anti-oxidant for the manufacturing moulds however Premnath et al<sup>157</sup> reported that calcium stearate may possibly increase the number of free radicals in the UHMWPE. If this is indeed the case then it could adversely affect the oxidation resistance of polyethylene. It has also been reported that calcium stearate may increase



the mobility of oxygen within UHMWPE (under artificial ageing conditions), also potentially lowering its oxidation resistance<sup>35</sup>. This was attributed to increased mobility and activity of oxygen at the boundaries between resin particles. These resin boundary grain boundaries are enhanced in calcium stearate containing material. Findings by Johnson et al<sup>318</sup> support this hypothesis since in artificially aged materials they found superior tensile properties in non-stearate containing directly moulded polyethylene compared to extruded GUR4150.

The affect of the machining process and the stresses induced in components is another issue related to the wear and oxidation resistance of polyethylene which is presently being debated. Milling can cause internal stresses, which in turn can propagate internal cracks. This kind of machining also leaves a rough surface, which will lead to the release of a large number of very fine particles once the joint articulates, as the surfaces begin to wear. The magnitude of stresses induced depends on the size of the cutting tool. It is therefore worth noting that in the manufacture of acetabular cups, machining stresses should not be such an issue since much smaller cutting tools are used and in continuous cuts. Wrona et al<sup>44</sup> found highly significant differences between defect rating and thin section flaking for machined components (significantly higher) compared to moulded components, indicating fabrication techniques may be responsible for the phenomenon observed. Oxidation has also been reported to be affected by machining, since the heat damaged surface has a greater permeability for oxygen<sup>248</sup>. Thus, potential reasons for the improved properties of directly compression moulded material have been published.

Despite previous studies which have recognised excellent wear properties and oxidation resistance of directly moulded material, no long-term simulator testing has been performed to directly relate the oxidation and wear of polyethylene components manufactured by different methods. Simplistic pin-on-disc testing has been performed such as that by Huber & Plitz<sup>36</sup> who found that for GUR 1150 polyethylene, the pressed material had a better wear behaviour than extruded material in ring-on-disc tests. These results showed the deleterious effects of the existence of material inhomogeneities due to the extrusion process. There is however a need for simulator testing to replicate the complex kinematics of human gait to obtain a true picture of the wear of a particular device and to systematically test designs without the variation of patient variables confusing the results. There have been some hip simulator studies<sup>249</sup> which have found lower wear for directly moulded material than extruded polyethylene. However knee simulators are more appropriate to the current oxidation problem, since delamination is predominately a problem associated with TKR and has been shown to be related to the formation of an oxidised sub-surface band. Such

simulators have recently been designed and have been shown to reproduce some of the wear mechanisms seen on retrieved tibial components, with tibial wear patterns and wear debris similar to those reported in the literature<sup>250, 251</sup>.

A particular compression moulded material was chosen for this study. This is made by Biomet and manufactured using their 'Arcom' process. This can be used to produce both moulded bars from which components are machined, or can be directly moulded. The material is manufactured by isostatic pressing under vacuum. The resin Montell 1900H is initially cold compressed in a urethane sleeve. This is then packaged in a foil wrap, which is flushed with argon and then evacuated. This is then moulded at 4.8 MPa to form a rod of material. The microstructure of this material is very consistent, with no fusion defects and virtually no voids within the material. A similar process is used to directly mould components, but in this case the resin is placed in an appropriate shaped die.

The excellent survivorship rates for prostheses manufactured from directly moulded polyethylene lead to the hypothesis that the apparent oxidation resistance of this material was the reason for its excellent long-term wear behaviour. Directly moulded components were examined when recently irradiated, after artificial ageing and after shelf-life durations of up to fourteen years. These components were compared with equivalently aged materials manufactured by other methods. The aims of this work were to discover if directly moulded 1900 resin is oxidation resistant and if so, how this affects the wear of this material in a knee simulator.

## 7.2 Materials and Methods

### 7.2.1 Materials

A selection of shelf-aged components were obtained. These included components which had been manufactured from Montell 1900H resin by direct moulding, components that were machined from extruded bar (GUR 415 resin) and one component that was machined from moulded sheet (GUR 412 resin). Shelf-age times and sterilisation atmospheres for all components are shown in table 7.1. Specimens were sectioned and examined for the formation of a sub-surface oxidised band.

Type	Number	Designation	Shelf Age Time	Resin Type	Manufacturing Process	Sterilisation Environment
AGC	3	SA1	13	Montell 1900H	directly moulded	air
		SA2	13			
		SA4	12			
		SA6	12			
Acetabular Liner	3	SA7	12	GUR 415	extruded bar machined	air
		SA9	12			
		SA10	12			
Stanmore Cup	1	SA11	12	GUR 412	moulded sheet machined	air
Tibial Plateau	2	$\gamma$ O $\gamma$ O aged	0	1900	directly moulded	air
Tibial Plateau	2	$\gamma$ R $\gamma$ R aged	0	1900	directly moulded	argon

Table 7.1 - Component type, manufacturing method and sterilisation method for components examined

### 7.2.2 Infrared Spectroscopy

FTIR was performed as described in chapter two, to quantify oxidation and crystallinity. This was performed on specimens SA 1, 4, 6, 7, 8, 10, 11

### 7.2.3 Density Measurements

Density of polyethylene sections taken at different depths parallel to the plastic surface were measured using a calibrated density column. The column was set up with isopropanol and water to allow measurement in the range of 0.938 - 0.96. This was done according to British Standard BS 2782, method 620D. A set of eight calibrated floats were obtained (Martin Instrument Company) and were immersed in isopropanol

prior to being gently introduced into the column. The column was left to settle for 24 hours prior to any measurements. Each section was individually shaped for easy identification within the column and immersed in isopropanol prior to introduction into the column. Samples were introduced in sets of three samples and left to settle for ninety minutes to avoid unnecessary disturbance of the column. Any air bubbles were removed by manipulation of a thin wire. Once all samples had been introduced the column was allowed to settle for a further 24 hours before readings were taken.

Densities were calculated using the equation:

$$\epsilon_{sx} = \epsilon_{f1} + \frac{(x-y)(\epsilon_{f2} - \epsilon_{f1})}{(z-x)}$$

where  $\epsilon_{f1}$  and  $\epsilon_{f2}$  are the densities of two standard floats bracketing the system

x is the height of the specimen within the column

y and z are the heights of the two floats.

#### 7.2.4 Artificial Ageing

Artificial ageing was performed as described in chapter five by heating samples at 80°C in a sealed pressure vessel at 70psi in a nominally pure oxygen environment for eight days. This has previously been shown to reproduce levels of oxidation seen in retrievals after approximately ten years<sup>197</sup>. Directly moulded components recently sterilised in air or argon were artificially aged and their oxidation ratios were compared. (70 Psi  $\approx$  0.5 Mpa).

#### 7.2.5 Knee Simulator Testing

A four station force input knee simulator was used to compare the wear performance of non-aged, shelf-aged and artificially aged components manufactured by direct moulding and machining from extruded rod.

Test one investigated the wear of air irradiated Kinematic and Insall Burstein (I) components. The Kinematic components were stored for two years and the Insall Burstein components for one year, prior to testing. The test was run for nine million cycles then one of each design was then artificially aged for six days. At eleven million cycles the artificially aged Kinematic was replaced with an artificially aged Kinemax component, which had been aged for eight days.

Test two investigated the wear of four directly moulded AGC components which had been recently irradiated in argon (stored 6 months). Two of these were artificially aged for eight days. The test ran for ten million cycles.

Test three investigated the wear of two shelf-aged Kinematic (6 and 8 years) and two shelf-aged AGC components (11 and 14 years). All components were air irradiated and the test run for five million cycles.

Test four investigated the wear of four eight year shelf-aged AGC components, which were irradiated in air. Two of the components in this test had a minimum polyethylene thickness of 4.5 millimetres and the other two components had a minimum thickness of 16.5 millimetres. This test was run for five million cycles.

Test five investigated the wear of two shelf-aged Kinemax components (7.5 and 8.5 years) which were air irradiated. This test was run for 3.2 million cycles. A summary of these tests is shown in table 7.2.

The four station force input simulator input the flexion-extension angle, the axial compressive force, the anteroposterior (AP) shear force and the internal and external torque. The motion was applied using a servo-motor and gearbox, whereas the forces were applied using pneumatics, all under computer control using Labview (National Instruments Corporation, Austin, TX). The force and motion data are specified in the ISO standard (ISO/CD 14243-1) walking cycle, which includes a double-peak loading curve, with a maximum load of 2.3kN. Lubrication was 50% bovine serum (see section 2.6.3). Standard test measurements were performed approximately every one million cycles, as described in chapter two. For test one however, it was not possible to determine weight loss of the directly moulded components, therefore the penetration depth was used as a measure of wear for these components. Values were tested for statistical significance using the students t-test, with significance assigned for  $p < 0.05$ .

Test Designation	Component Types	Shelf Age Durations	Test Duration
Test 1	2 Kinematic 2 Insall Burstein(I)	recently irradiated (aged at 9M cycles)	11 million cycles
Test 2	4 AGC	recently irradiated (2 then artificially aged)	10 million cycles
Test 3	2 Kinematic 2 AGC	6 and 8 years 11 and 14 years	5 million cycles
Test 4	4 AGC	all 8 years	5 million cycles
Test 5	2 Kinemax	7.5 and 8.5 years	~3 million cycles

Table 7.2 - Summary of simulator wear tests

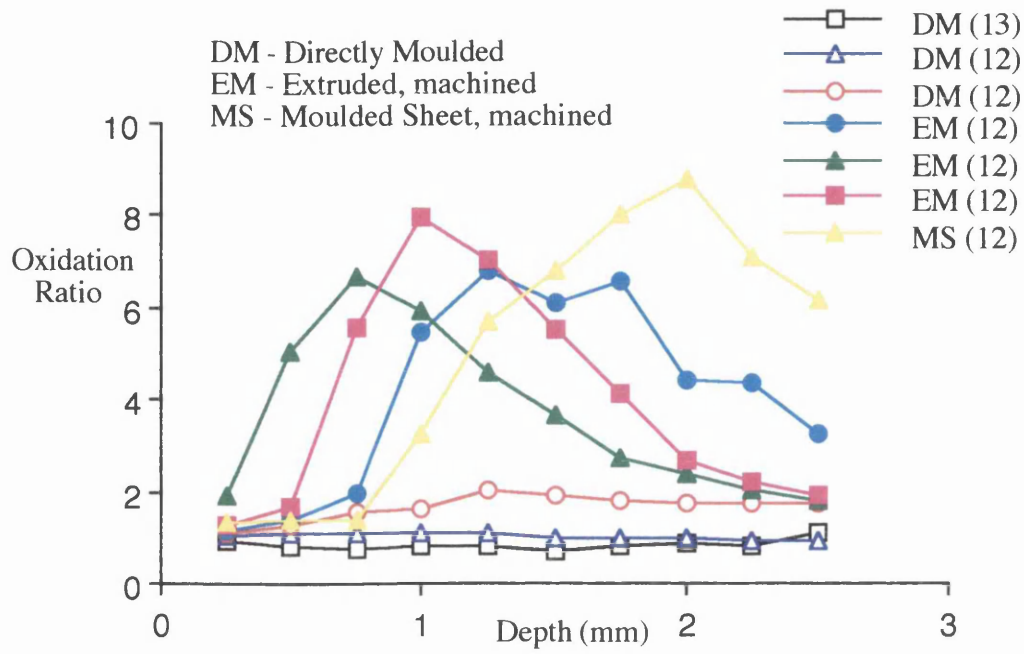


Figure 7.1 Oxidation ratio with depth for shelf-aged components (figure in brackets denotes shelf-aged time in years)

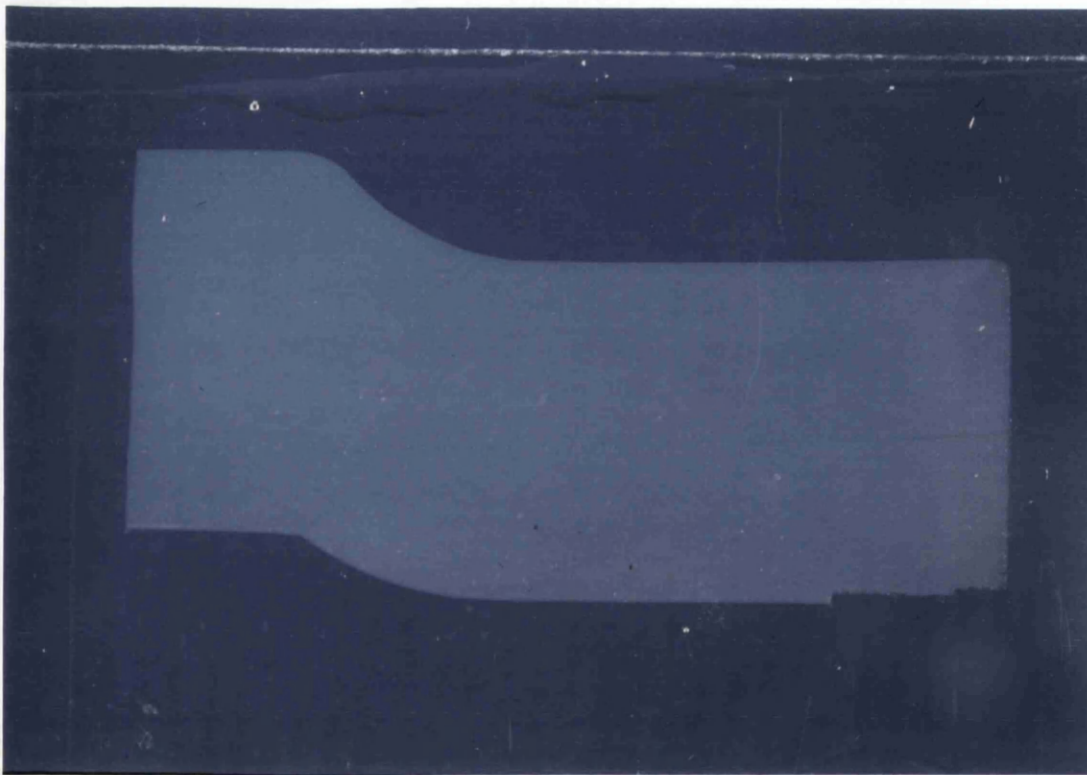


Figure 7.2a Thin section through a thirteen year shelf-aged directly moulded component, illustrating an absence of a sub-surface 'white band'

## 7.3 Results

### 7.3.1 Infrared Spectroscopy

The oxidation ratios for the shelf-aged components showed that directly moulded components did not develop a sub-surface peak of oxidation, whereas components machined made from extruded and sheet moulded polyethylene developed sub-surface bands of oxidation (figure 7.1). The oxidation peak in machined components was 1-2mm below the articulating surface. Thin sections through these components showed no evidence of sub-surface oxidation for the shelf-aged directly moulded components (figure 7.2a) whereas the shelf-aged machined components clearly exhibited a sub-surface 'white band' extending around the entire component (figure 7.2b). The machined component also showed cracking adjacent to the 'white band' which was induced during microtoming.

The oxidation ratio versus depth for directly moulded components which had been recently irradiated in air and argon are shown in figure 7.3, together with the oxidation ratios from artificially aged components. Artificial ageing of the air irradiated component produced a mild sub-surface peak of oxidation. This level is much lower than that typically seen in artificially aged, air irradiated, non directly moulded components. This is illustrated by the scale on the vertical axis which represents the level of oxidation seen in an equivalent shelf-aged machined component (from figure 7.1).

Artificial ageing resulted in a slight overall increase in oxidation level throughout the material for the argon irradiated component but this component did not develop a sub-surface band of oxidation and showed no alteration in oxidation with depth. Morphologically, the artificially aged directly moulded components showed a 'clear zone' below the surface upon staining with CSA (figure 7.4a). This finding has also been seen in CSA stained shelf-aged specimens that had been directly moulded from 1900 resin (figure 7.4b).

### 7.3.2 Density Measurements

Density measurements for shelf-aged components are shown in figure 7.5. These results showed higher density for the machined components, with a peak at the surface of over  $0.97\text{g/cm}^3$ , which decreased with depth. In contrast the directly moulded components showed no significant change in density with depth.



Figure 7.2b Thin section through a twelve year shelf-aged extruded component, showing a sub-surface 'white band'

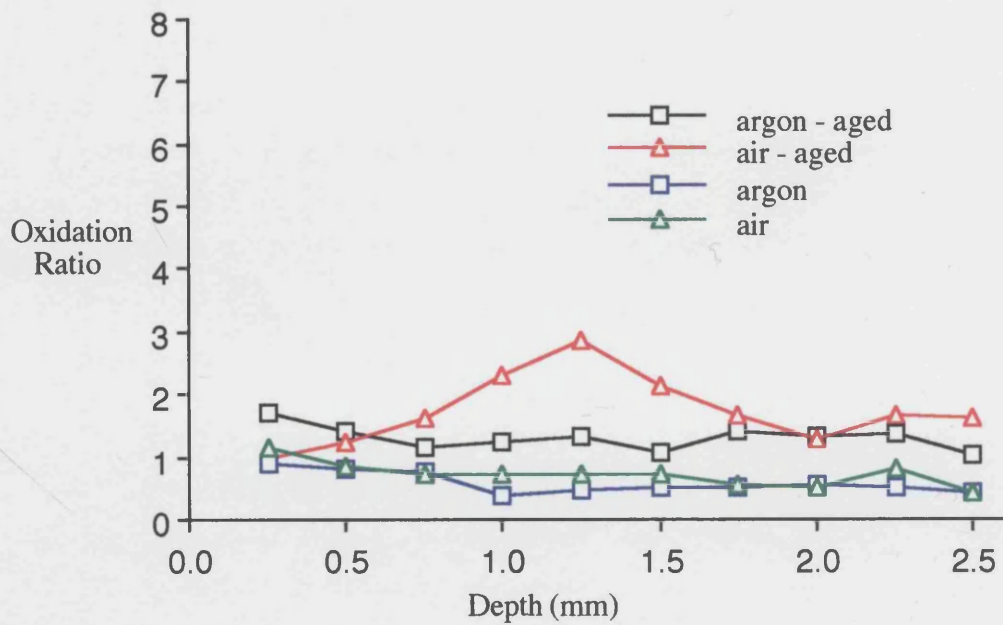


Figure 7.3 Oxidation ratio with depth for recently irradiated non-aged and artificially aged directly moulded components



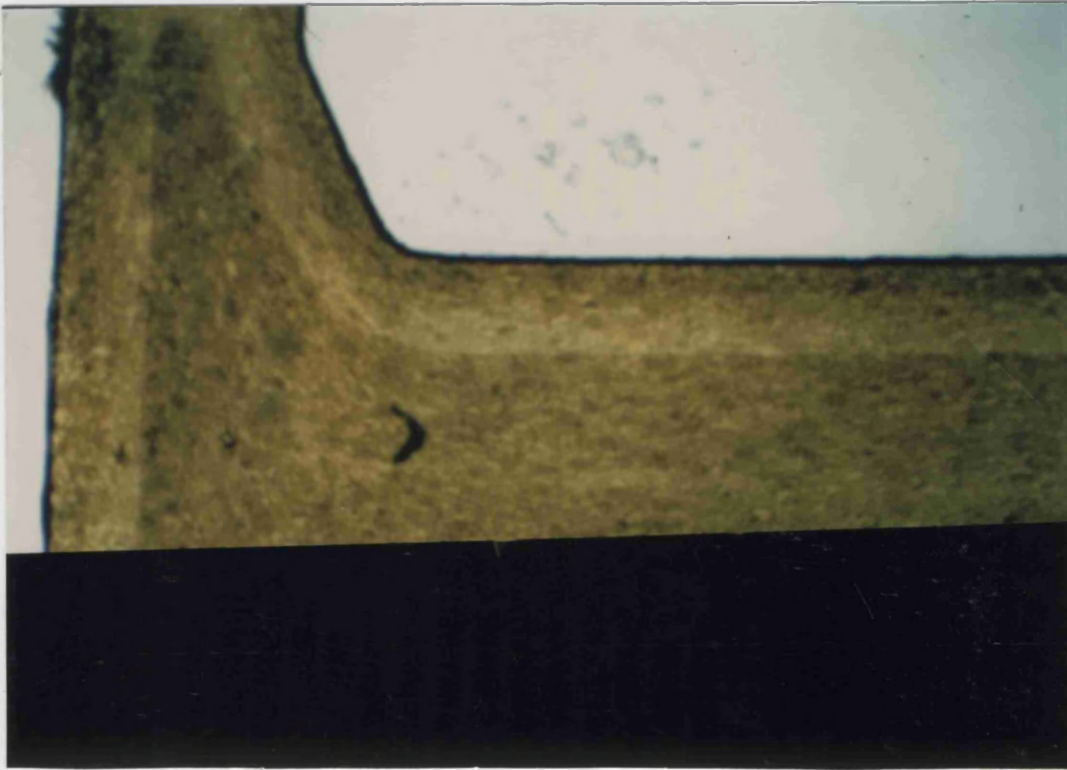


Figure 7.4a Chlorosulfonic acid treated thin section through an artificially aged directly moulded component, showing a 'clear zone'

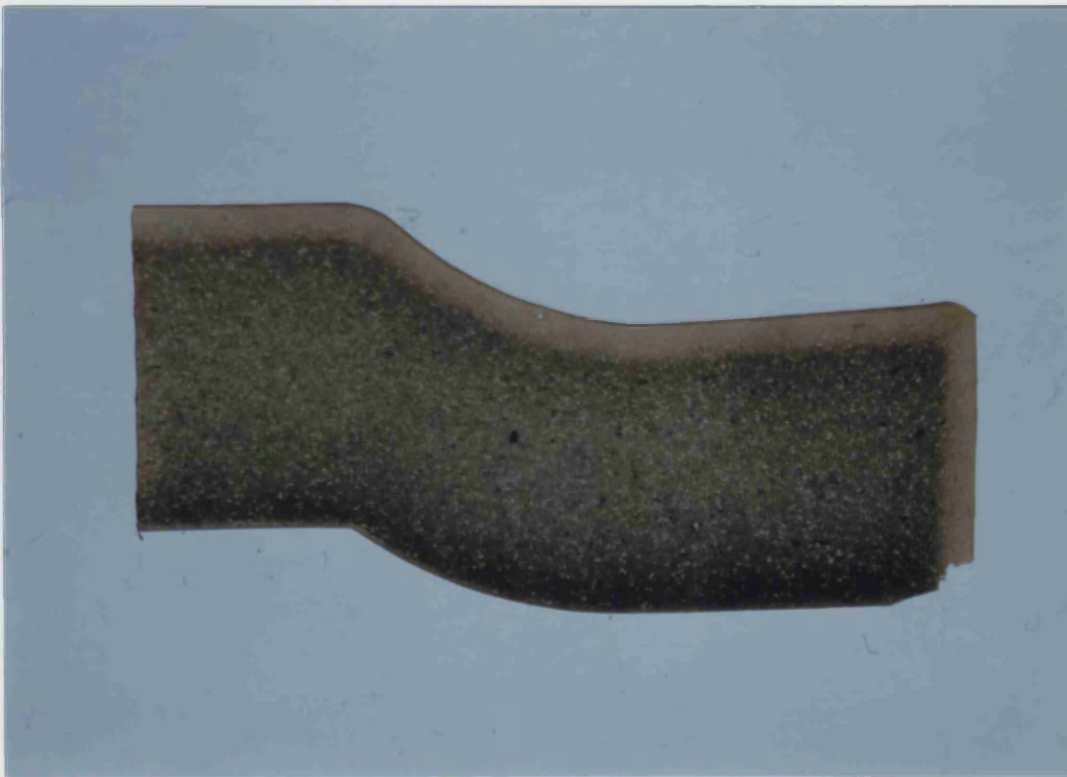


Figure 7.4b Chlorosulfonic acid treated thin section through a shelf-aged directly moulded component, showing a 'clear zone'

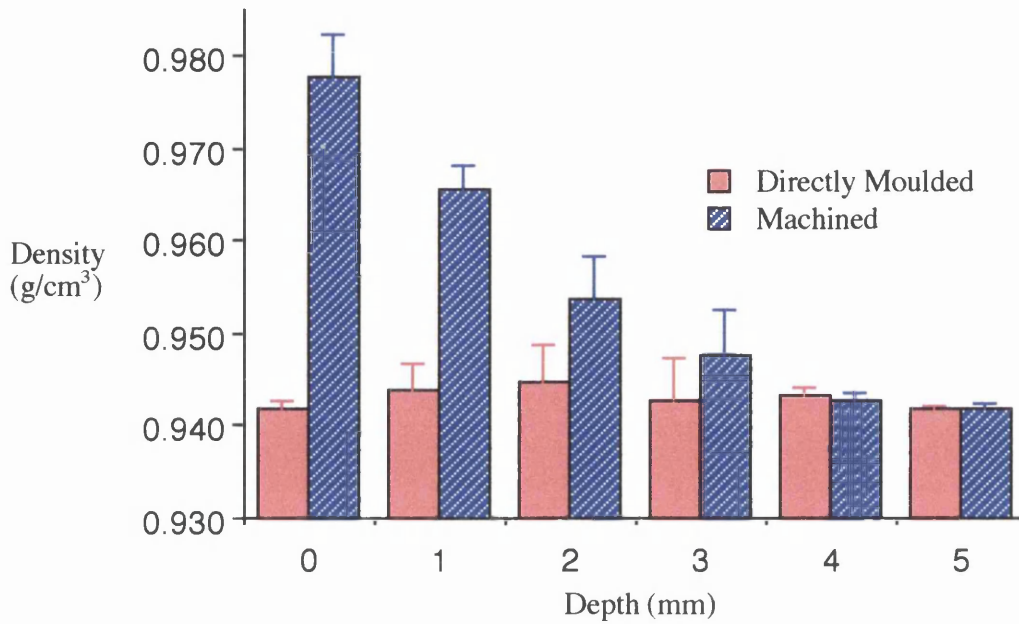


Figure 7.5 Density profile for shelf-aged machined and directly moulded components

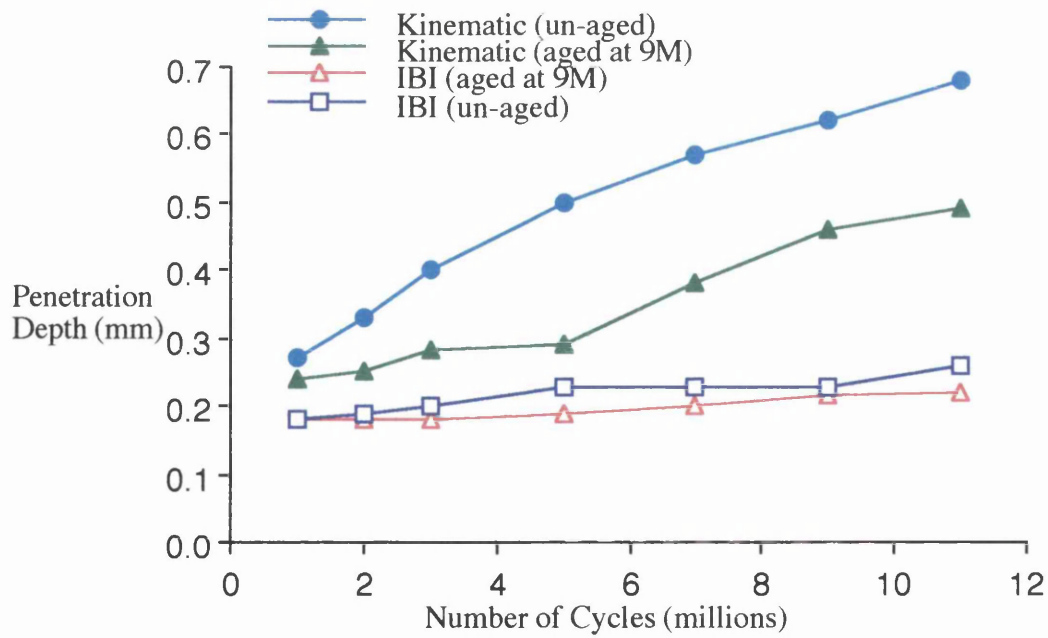


Figure 7.6 Penetration depth data for simulator test one

### 7.3.3 Simulator Wear Results

#### 7.3.3.1 Test One

Penetration depth data showed greater wear for the extruded Kinematic than for the directly moulded Insall Burstein (figure 7.6). This occurred in both artificially aged and non-aged specimens. Delamination of the Kinematic occurred at eleven million cycles, subsequent to the artificial ageing carried out at nine million cycles (figure 7.7). There was however no delamination of the equivalent aged Insall Burstein. The artificially aged Kinemax component which replaced the Kinematic, delaminated after only 600,000 cycles (figure 7.8). This ageing level was equivalent to that used in chapter five which produced delamination in a pin-on-plate test after 200,000 cycles.

#### 7.3.3.2 Test Two

Simulator results for non-aged and artificially aged directly moulded AGC components showed no significant difference in wear (figure 7.9). Wear for all components was surface in origin and there was no delamination at ten million cycles. The FTIR data for these components showed that the directly moulded components did not develop a sub-surface band of oxidation with artificial ageing and that the oxidation ratios with depth for both components were similar (figure 7.10). The oxidation levels were very low as illustrated by the scale of the vertical axis which is comparable to figure 7.1.

#### 7.3.3.3 Test Three

The eight year shelf-aged Kinematic component delaminated at 1.9 million cycles, with cracking occurring through the oxidised 'white band' (figure 7.11). At five million cycles, none of the other three samples showed wear other than surface deformation and scratching. FTIR data for these components (figure 7.12) showed high oxidation at the delaminated surface of the Kinematic, which then decreased with the depth. The oxidation ratios for the AGC components were much lower, with no sub-surface peak of oxidation.

#### 7.3.3.4 Test Four

Weight loss for the shelf-aged AGC components generally showed greater wear for the 16.5mm components than the 4.5mm components (figure 7.13a). However, fluid trapped between the polyethylene and the tibial tray produced highly variable weight loss data. Penetration depth (figure 7.13b) clearly shows greater penetration for the thicker components, especially during the first million cycles. At five million cycles, none of the samples showed delamination and wear was predominately surface deformation and scratching.



Figure 7.7 Photograph of the delaminated Kinematic (test one)

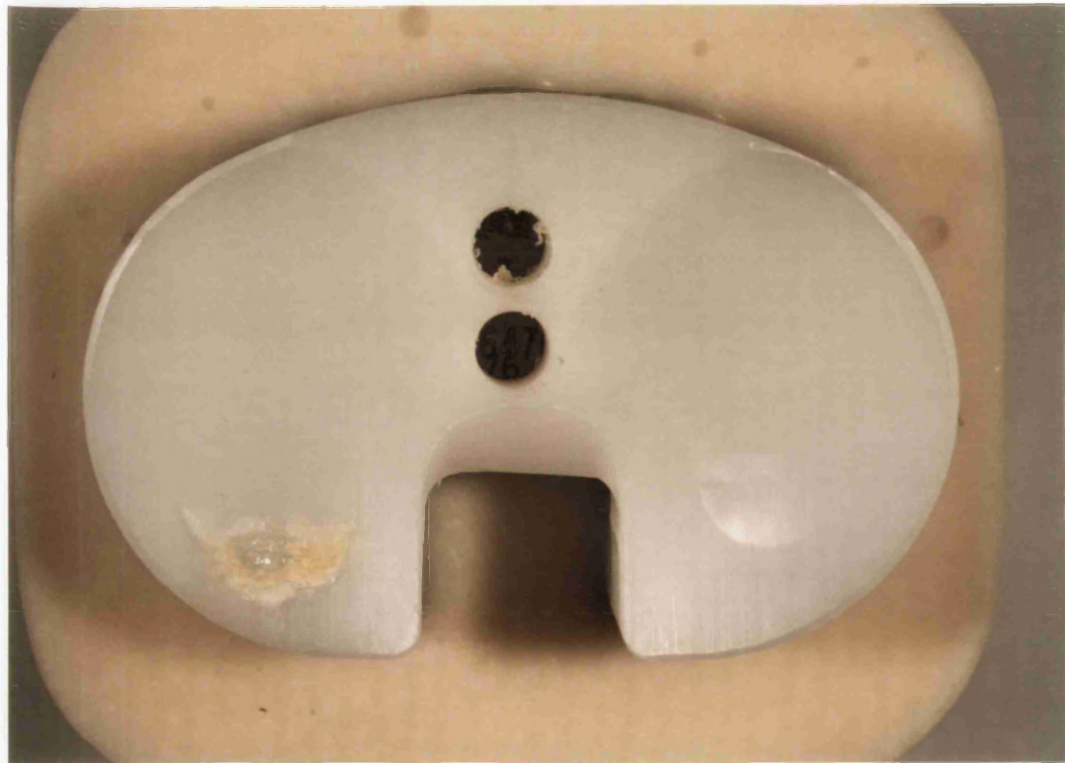


Figure 7.8 Photograph of the delaminated Kinemax (test one)

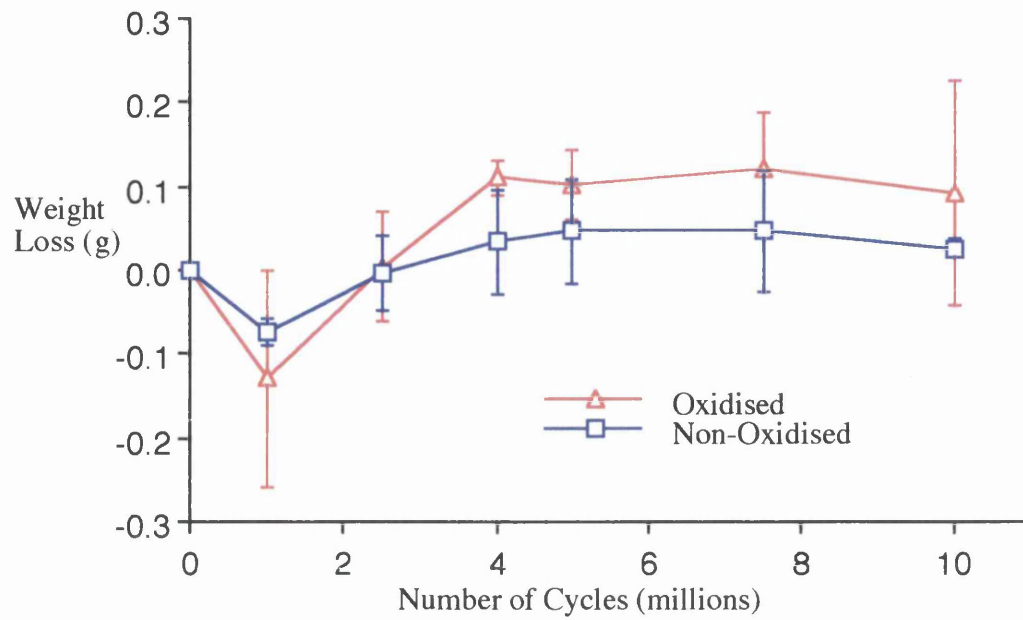


Figure 7.9 Weight loss for non-aged and artificially aged directly moulded components (test two)

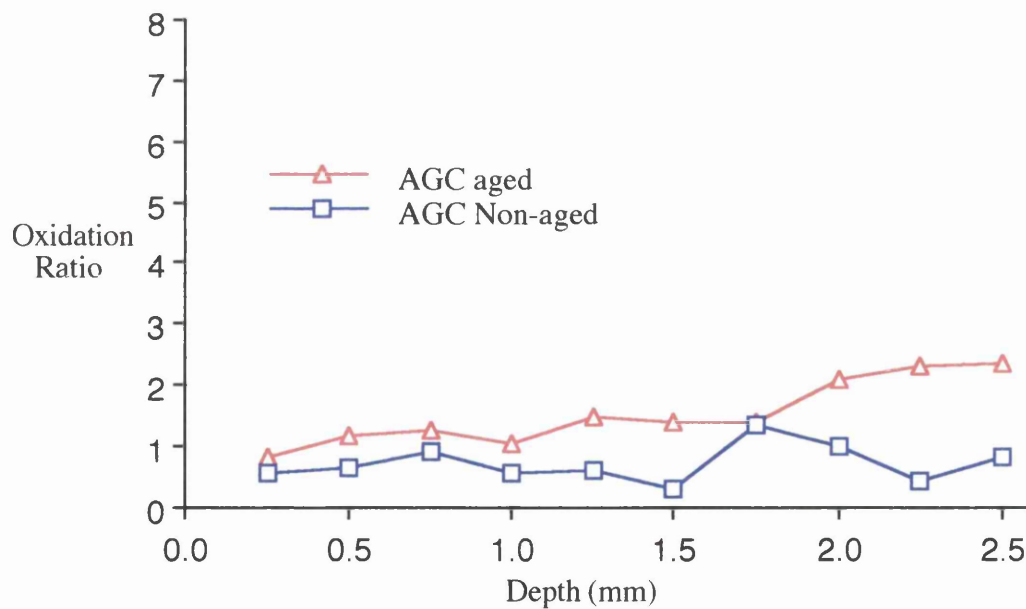


Figure 7.10 Oxidation ratio with depth for non-aged and artificially aged directly moulded components

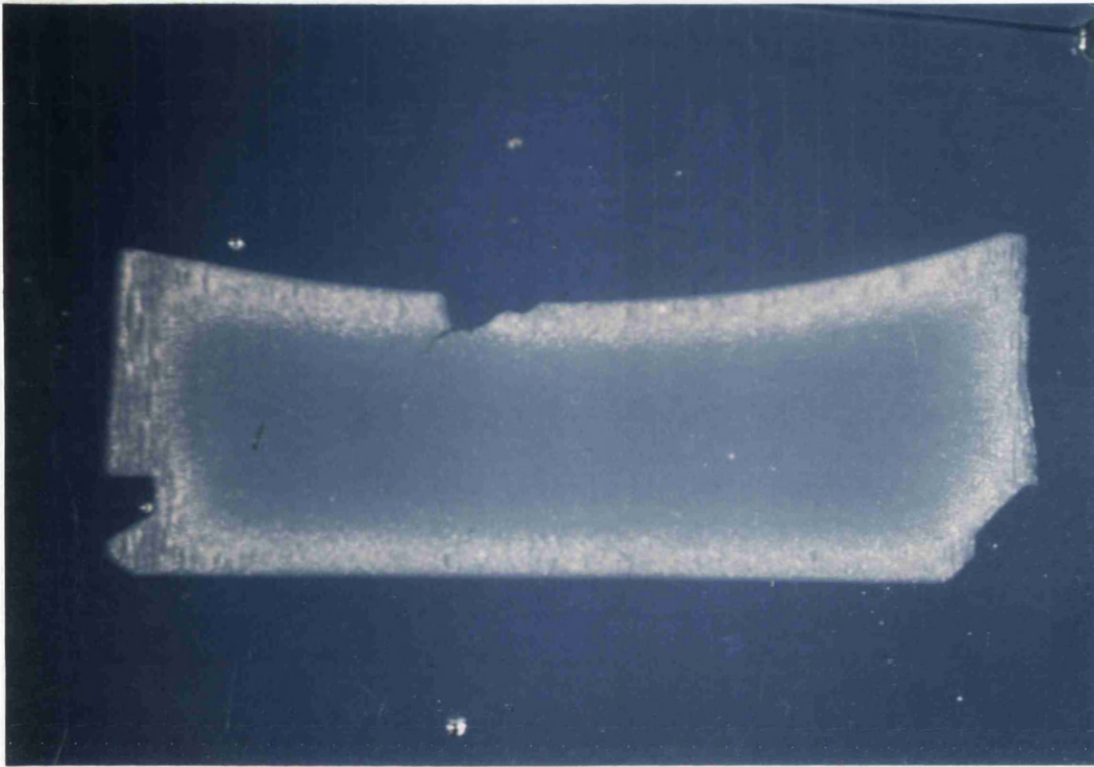


Figure 7.11 Photograph of delaminated Kinematic component (test three)

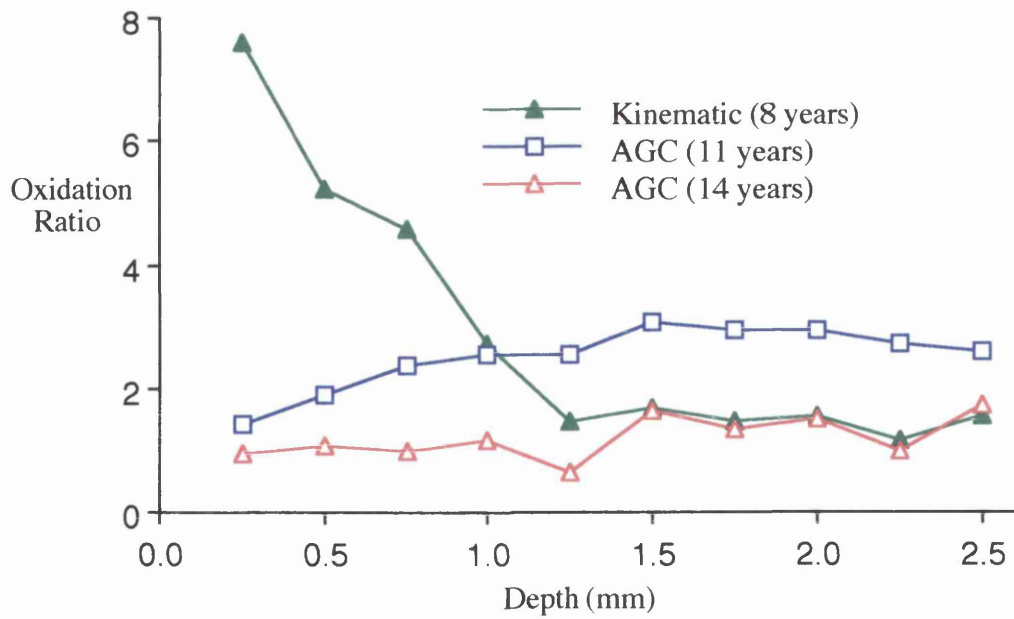


Figure 7.12 Oxidation ratio with depth for shelf-aged components (test three)



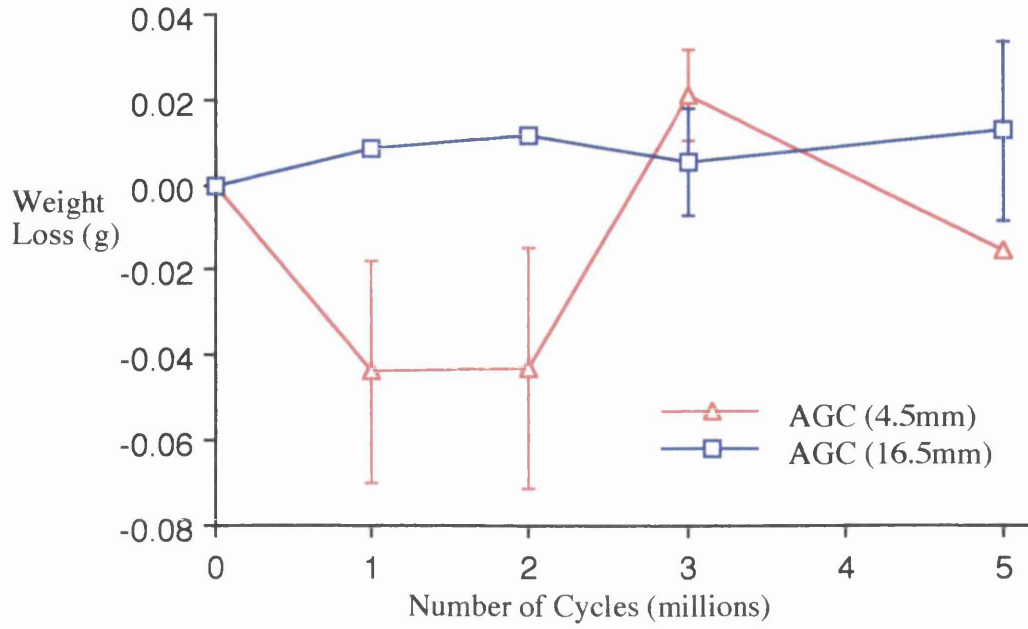


Figure 7.13a Weight loss for shelf-aged components (test four)

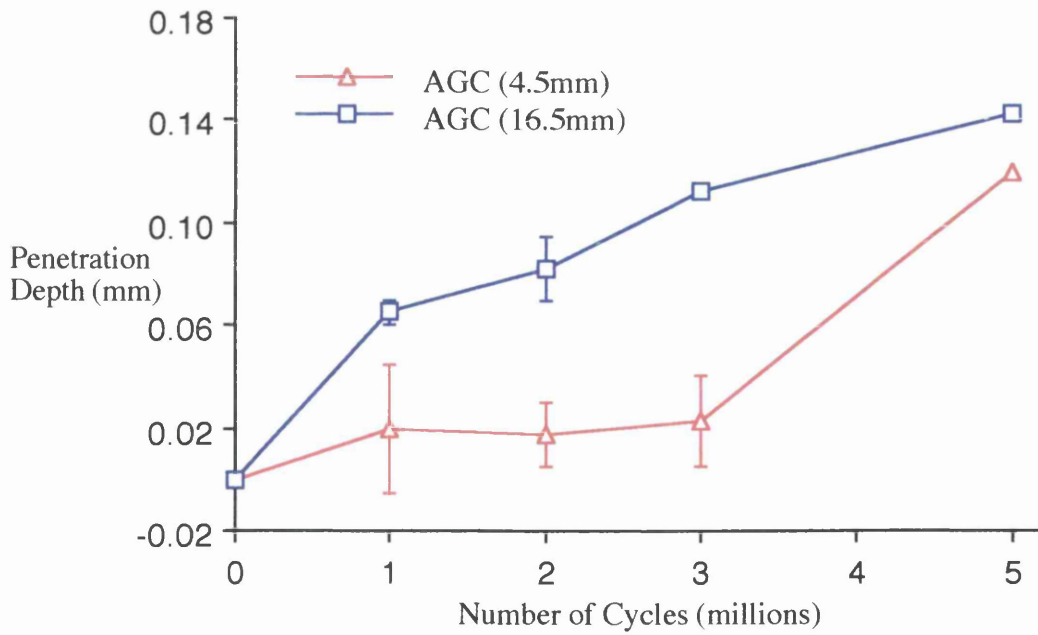


Figure 7.13b Penetration depth for shelf-aged components (test four)

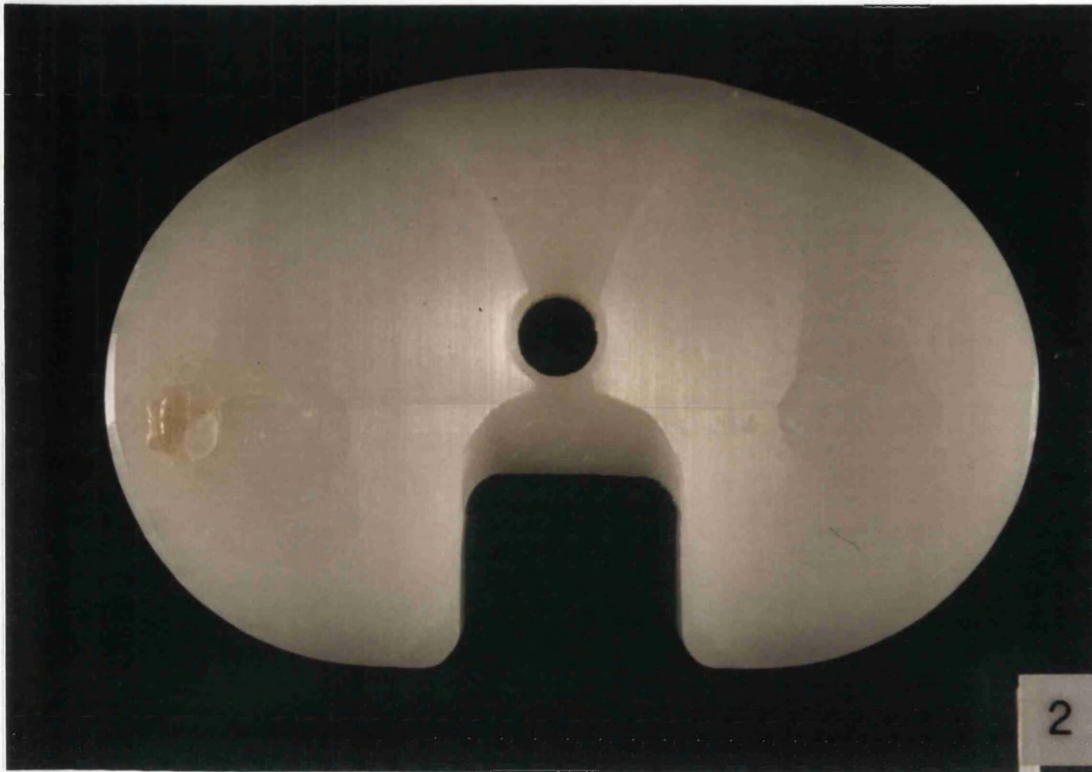


Figure 7.14a Photograph showing the onset of delamination in the Kinemax component (1.8 million cycles)

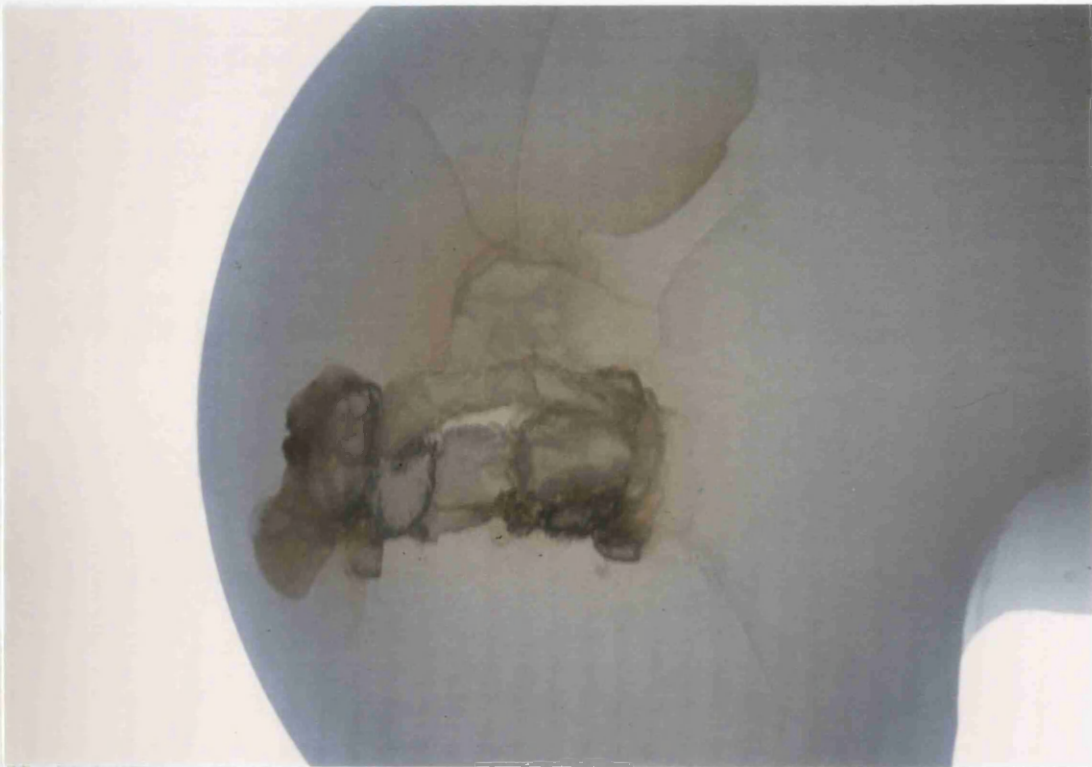


Figure 7.14b Photograph showing the delaminated Kinemax component (2.3 million cycles)



### 7.3.3.5 Test Five

Wear testing of the shelf-aged Kinemax components resulted in delamination for both components. This occurred at 1.8 million cycles for the 8.5 year aged component and at 3 million cycles for the 7.5 year aged component. Figures 7.14 a & b shows initiation of the delamination blister at 1.8 million cycles (for the 8.5 year shelf-aged specimen) and how this progresses to 2.3 million cycles, when the specimen was removed from the test. The FTIR data for these components once again showed high sub-surface peaks of oxidation on shelf-aged components machined from extruded polyethylene (Figure 7.15).

Wear as measured by penetration depth for the shelf-aged components was greater for extruded material than directly moulded polyethylene (figure 7.16). It should be noted that the all these components were shelf-aged for a similar length of time.

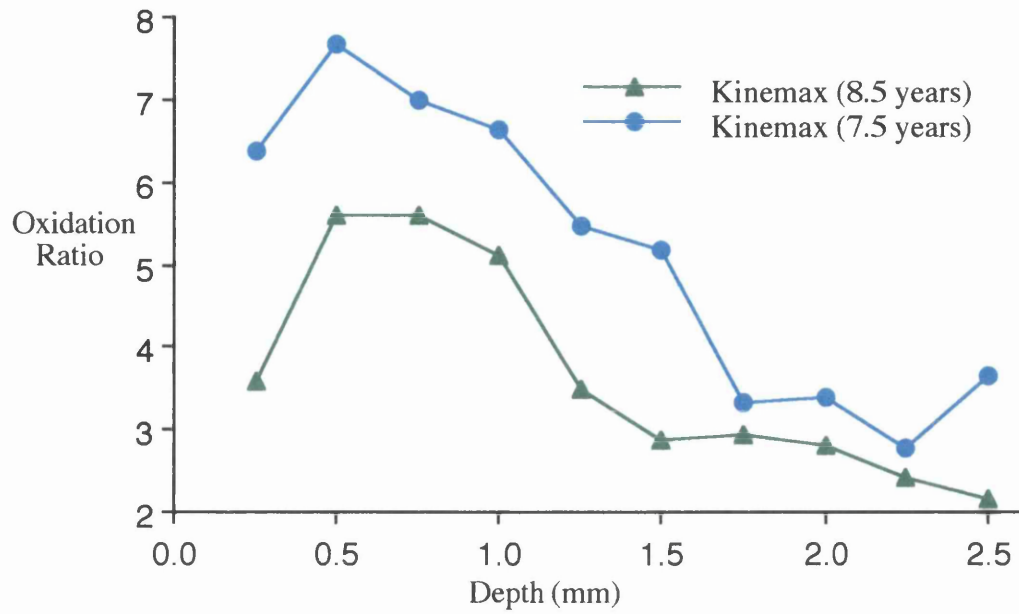


Figure 7.15 Oxidation ratio with depth for delaminated shelf-aged components

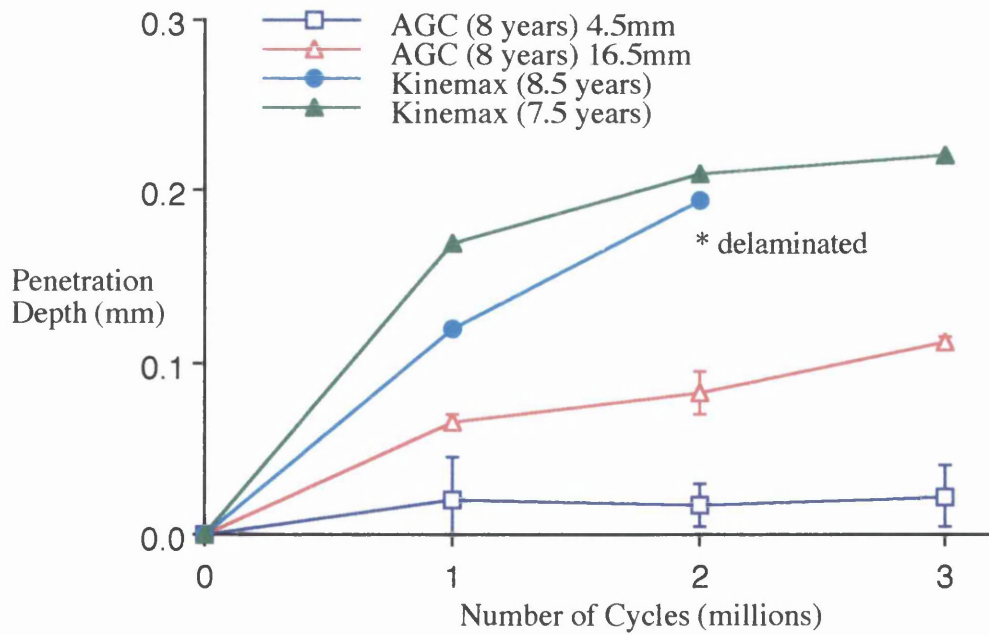


Figure 7.16 Penetration data for tests four and five combined

## 7.4 Discussion

Recently published work investigating retrieved implants has suggested that components directly moulded from 1900 resin have excellent survivorship rates<sup>29, 32, 205</sup>. This resin was also implicated in the success (due to lack of delamination wear) of a particular unicondylar design in a study by Blunn et al<sup>169</sup>, as early as 1991. Thus survivorship rates and retrieval studies have reported no delamination and low oxidation levels for components directly moulded from 1900 resin. However, the success of this material has not been attributed to one specific parameter, with opinion being split on the influence of the resin type and the moulding process.

Recently published work has indicated that components directly moulded from 1900 resin appear to be more resistant to 'on the shelf' oxidation, than machined components manufactured from other resins<sup>206, 207, 208</sup>. However other authors have published contrary findings. Sun et al<sup>252</sup> found a white band around the edge of directly compression moulded products. The study incorporated ram extruded, compression moulded and directly moulded components, but white bands were only found in the directly moulded components. The ram extruded material did exhibit a local maximum of crystallinity, oxidation and density at approximately 2mm below the surface, which was attributed to gamma irradiation. However, an additional maximum found in the directly moulded components at a depth of 4-6mm, was attributed to the moulding process itself, and possibly a result of residual stresses caused by a cooling differential in the material post-manufacture. McKellop et al<sup>130</sup> found brittle zones approximately 2mm below the surface in shelf-aged (17 years), gamma irradiated in air (2.5-7.5 Mrads), directly moulded and machined from extruded bar specimens (both 1900 resin), which corresponded to the region of greatest oxidation.

Due to conflicting results from retrieval studies, artificial ageing regimes have been employed to investigate the oxidation resistance of polyethylenes manufactured by different methods to discern differences under controlled conditions. Poggie et al<sup>35</sup> found compression moulded sheet was more oxidation resistant than ram-extruded rod (same resin and manufacturer), when artificially aged. Johnson et al<sup>38</sup> found superior tensile properties in compression moulded material compared to extruded polyethylene (after artificial ageing). Swarts et al<sup>48</sup> also found that compression moulded material retained higher mechanical properties for both shelf and simulated ageing than ram extruded material. However, care must be taken when interpreting results from artificial ageing studies alone<sup>234</sup>.

In this series of air irradiated components, oxidation of the shelf-aged AGC components was low compared with components made from sheet moulded or extruded polyethylene. In addition, well developed sub-surface bands of oxidation were evident for both extruded and moulded sheet components, however sub-surface bands of oxidation were not evident in shelf-aged directly moulded components. Irradiating then artificial ageing the directly moulded components showed that high sub-surface peaks of oxidation did not occur and overall levels of oxidation were not elevated above the non-aged material. However, irradiating then artificially ageing components manufactured by other methods resulted in formation of a sub-surface oxidised band.

It was outside the scope of this study to determine why the directly moulded components have excellent long-term oxidation resistance and do not develop the characteristic 'white band' seen in other irradiated, shelf-aged materials. As previously discussed, potential causes for oxidation have included machining of the surface resulting in increased residual stresses in the material. Machining will also result in a distorted surface which will produce less tortuous paths for oxygen diffusion. It has been found by Muratoglu et al<sup>133</sup> that preferential oxygen diffusion occurs along the grain boundaries between the flakes of the original polyethylene resin. Consequently, this could account for the lower oxidation seen in fully consolidated materials i.e. directly moulded material.

FTIR data showed no trends in crystallinity for these materials. Bellare et al<sup>84</sup> found an increase in crystallinity of shelf-aged, compression moulded sheet 1900 resin, which resulted in a maximum 1-2 mm below the surface. No increase in crystallinity associated with the upper 2mm was seen in this study. This could have accounted for the 'clear zone' seen upon CSA treatment, since CSA attacks amorphous regions of the polyethylene. It is possible that this region of material is not highly crystalline but highly crosslinked. Measurement of crosslinking was outside the scope of this study however, this would have been advantageous. This would have allowed a better understanding of wear properties of the material as a function of irradiation dose and atmosphere, and post-irradiation treatments such as annealing. It may also have lead to an understanding of the 'clear zone' present in directly moulded materials and its affect on wear properties.

Density with depth from the articulating surface was constant for directly moulded components, but machined components exhibited peaks of density near the articulating surface. The density of the machined components was very high and more akin to that seen in HDPE ( $0.96\text{g/cm}^3$ )<sup>208</sup>. This will result in a lower molecular weight and thus

decreased wear resistance, as was seen in the simulator testing of extruded then machined components.

In the wear tests, recently irradiated components indicated greater surface wear for machined than directly moulded components. Although no other knee simulator testing has been performed on these materials, hip simulator testing such as that by Clarke et al<sup>249</sup> has found a reduction in wear for isostatically moulded, argon irradiated polyethylene over gamma irradiated in air, extruded bar specimens. Greater surface wear was also seen in the machined, shelf-aged components, even though this extruded material had similar shelf-age durations to the directly moulded material. This indicates the excellent long-term on-the-shelf oxidation resistance of directly moulded materials as reported elsewhere<sup>206, 207, 208</sup>.

The use of penetration depth for the determination of wear is not ideal. However it was necessary in this study due to the variation seen in weight loss data for some directly moulded components, due to fluid entrapment between the tibial tray and the polyethylene. Initial creep of the material will have a large affect on the overall penetration depth. However, the subsequent rate of penetration does give an indication of comparative wear. All components in this study were moderately conforming, resulting in comparative stress levels. The AGC components were the least conforming, thus experiencing the highest stress levels, but produced the lowest wear rates of all the components tested. It can therefore be seen that the excellent quality of the polyethylene used in the AGC resulted in low wear rates under more severe loading conditions. This is also the case for the AGC components in test four, which had a minimum thickness of only 4.5mm, well below the minimum recommended thickness of 6-8mm.

Artificial ageing of machined components resulted in a sub-surface peak of oxidation and delamination after a short time. No sub-surface peaks of oxidation occurred in artificially aged directly moulded components and no delamination occurred, even at 10 million cycles. This clearly shows that the sub-surface band of oxidation is a major factor in the delamination wear of TKR. There was also no difference in wear between artificially aged and non-aged directly moulded polyethylene, showing superior oxidation resistance results in superior wear performance.

Shelf-aged extruded components had high sub-surface peaks of oxidation and such components delaminated after periods of 1.8 to 3 million cycles. This corresponds to some of the very short *in vivo* durations reported for some TKR components<sup>6, 43, 151, 169</sup>. Shelf-aged directly moulded components did not delaminate (even after 14 years

of shelf ageing) and showed no elevation of oxidation levels over recently irradiated materials.

These results show that components directly moulded from Montell 1900H resin are oxidation resistant, particularly to the development of a sub-surface band of oxidation. The reasons for this are unclear at present but probably are due at least in part to the process associated with directly moulding. The reasons for the high success rate of this material warrants further investigation to determine the source of its oxidation resistant nature. Polyethylene manufactured by direct moulding has been shown to result in a reduction in surface wear, both when recently irradiated and after long periods of shelf-ageing. Importantly, no delamination wear occurred for the directly moulded components, even under more severe conditions than those resulting in delamination in non-directly moulded components. This data is consistent with the empirical data in retrieved knees. Hence the direct moulding process could prolong the useful life of TKR components.

## CHAPTER EIGHT

### GENERAL DISCUSSION AND CONCLUSIONS

## 8.1 General Discussion

The aim of my study was to understand the relationship between the material properties and wear of polyethylene in total knee replacements. The hypothesis of this work was that manufacturing, processing and sterilisation techniques of ultrahigh molecular weight polyethylene result in a variability in material properties, oxidation resistance and wear performance.

The material classed as 'medical grade' UHMWPE covers polyethylene with a potential range of molecular weight from 2-6 million. Over five different base resins are available and there are several different methods of manufacturing the final product. Consequently it was hypothesised that the combination of different base resins and manufacturing methods available for the production of UHMWPE, would lead to a variation in material properties. In chapter three of this thesis, examination of stock materials found variable material consolidation between different commercially available UHMWPEs. This was highlighted by a novel staining technique which was developed, using chlorosulfonic acid. This acid attacks amorphous polyethylene, staining the plastic. This highlighted weakness to chemical attack along the grain boundaries, especially in the less consolidated materials. Poor consolidation and the presence of fusion defects are important parameters which have been linked to increased wear rates<sup>43, 169, 180, 196</sup>. A difference in the oxidation resistance of these materials was also discovered, even though they had not been irradiation sterilised.

In chapter four, material variability and oxidation resistance of retrieved polyethylene tibial components were studied to determine their effect on wear. Retrievals of different designs with delamination wear were also examined to determine if there was a correlation between delamination and post-irradiation degradation of polyethylene. It was hypothesised that the development of a sub-surface oxidised band due to post-irradiation ageing, would act as the initiation site for a fatigue failure mechanism, resulting in catastrophic delamination wear of the implant. Retrievals were found to have variable oxidation resistance, with some highly oxidised after short *in vivo* durations and others showing low oxidation after seventeen years *in vivo*. Delamination wear was clearly linked with the presence of a sub-surface oxidised region in the polyethylene. In some specimens, delamination was also linked to high residual stress and surface oxidation, indicating that other factors also play a role in the delamination process.



With the realisation that oxidation of polyethylene resulted from post-irradiation damage, researchers developed artificial ageing techniques<sup>71, 91, 221, 232</sup>. In chapter five, it was found that using the artificial ageing conditions described in my study, that the development of a sub-surface band was time dependant, only occurring after 6-8 of days of ageing. This band was similar in level of oxidation and depth from the articulating surface to shelf-aged and retrieved components. Shorter ageing times produced only surface oxidation.

This ageing technique allowed the investigation of the degradation effects of oxidation with time on the material properties of polyethylene. Tensile testing showed a decrease in UTS with increasing oxidation levels, and how the development of a sub-surface oxidised region resulted in loss of elongation and brittle fracture. Fatigue life also significantly reduced with increasing oxidation. Even in the absence of a sub-surface band, oxidation produced a statistically significant reduction in the fatigue resistance of UHMWPE. The fatigue crack propagation results also showed this, with four day ageing resulting in a 10-400 times increase in propagation rates over recently irradiated materials. These results clearly show the adverse effect of oxidation on the fatigue properties of polyethylene. Since fatigue is the most catastrophic wear mechanism in TKR, these results show that oxidation of polyethylene needs to be prevented.

Artificial ageing was also used to study the delamination process. The retrieval study showed delamination was linked to the sub-surface oxidised band, but the extent of oxidation associated with delamination wear could not be determined in chapter five. It was hypothesised that delamination would only occur in the presence of a sub-surface oxidised band. It was found that delamination occurred at oxidation levels associated with six to eight days of artificial ageing, when the sub-surface oxidised band was evident. Shorter ageing times resulted in surface oxidation only, and this produced increased surface wear compared to recently irradiated material. The articulating motion of the pin on the disc was found to induce surface oxidation. This work demonstrates the importance of the sub-surface zone of oxidation in the onset of delamination in polyethylene components, under conditions which simulate total knee replacement. Consequently the results of this study are in agreement with recently published work<sup>113, 114</sup> showing that increasing oxidation by artificially ageing components results in increased wear and reduces the fatigue life of polyethylene.

These results show the importance of oxidation of polyethylene and this has been shown to increase with time from irradiation<sup>53, 96, 123, 130, 132, 200, 211, 222</sup>. Consequently, many companies have reduced the shelf-life of components to five years. Considering the extent of reduction in fatigue properties at oxidation levels associated with five years of shelf-ageing, this may not be enough to prevent delamination failures.

Irradiation in inert atmospheres is only expected to delay oxidative degradation, due to trapped free radicals within the polymer<sup>66, 68, 76, 79, 102, 242</sup>. However, with the long-term impermeability of packaging materials questionable, oxidative degradation may be initiated prior to implantation.

In light of the understanding of the potential degradative effects of gamma irradiation on UHMWPE, modified materials are being developed to avoid this degradation process. In chapter six, one such material developed by an orthopaedic company, was tested. It was hypothesised that annealing polyethylene after gamma irradiation, would crosslink the free radicals, preventing oxidative degradation, and leading to an improvement in wear properties over 'standard' UHMWPE. A three times reduction in wear was achieved compared to 'standard' polyethylene. However, a greater than ten times reduction in wear was found once these materials were artificially aged. This shows the potential benefit of this material for long-term *in vivo* use. However, using artificial ageing techniques this material did oxidise, so delayed oxidative degradation may be seen in the long-term.

Alterations in sterilisation processes for polyethylene, leading to irradiation in inert atmospheres along with a combination of storage and annealing in an inert atmosphere, should reduce oxidation of UHMWPE. This will hopefully result in reduced cases of delamination wear and also in the amount of surface wear in TKR. The development of new 'modified' polyethylenes, especially highly crosslinked polyethylenes should reduce surface wear further, although these materials are potentially better suited to application in the hip. However caution should be noted since 'modified' polyethylenes may not bear out initial *in vitro* testing results, as has been seen previously with materials such as Hylamer.

Despite the developments of new modified UHMWPEs, it has become apparent from follow-up studies<sup>29, 384</sup> that a particular standard polyethylene, manufactured by direct moulding has resulted in excellent long-term survivorship and wear rates. In chapter seven, knee simulator testing found that recently irradiated directly moulded components had lower wear than extruded components. This was also seen after artificial ageing and shelf-ageing. Sub-surface oxidised bands were found in non-directly moulded components with a shelf-life of greater than seven years, which resulted in the delamination wear of these components. In contrast, no sub-surface oxidised bands were found in directly moulded components, even after fourteen years of shelf-ageing. Artificial ageing resulted in sub-surface oxidised bands in extruded components and subsequent delamination wear. However, artificial ageing did not induce oxidation in directly moulded components, resulting in no significant

difference in wear compared to recently irradiated components, and no delamination wear, up to ten million cycles.

This work has shown that a UHMWPE has existing for over two decades which has superior oxidation and wear resistance to standard polyethylene. An in depth study to determine the effect of resin type and moulding parameters needs to be performed, to determine why this material has performed so well *in vivo*.

In conclusion, my study has demonstrated differences in 'medical grade' polyethylene manufactured by different techniques. This results in variable material consolidation, oxidation resistance and wear performance.

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