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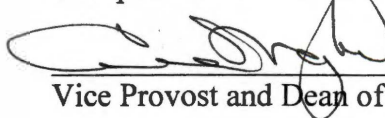


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Crosslinking Methods for Enhanced Tribological Properties of Ultra-High-Molecular-Weight Polyethylene for Total Joint Arthroplasty

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For the
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ABSTRACT

One of the primary life-limiting factors for modern total joint arthroplasty components is ultrahigh-molecular-weight polyethylene (UHMWPE) wear-debris-induced periprosthetic osteolysis, which leads to aseptic implant loosening and, ultimately, the need for revision surgery. Therefore, substantially reducing the wear rate of UHMWPE orthopaedic implant components is critical to extending the *in vivo* lifetime of these implants. This work is an effort to compare the wear performance of a novel radiation treatment, ultraviolet (UV) radiation, to that of other UHMWPE materials. The UHMWPE materials tested include conventional, unmodified, ram extruded (C-RE); gamma-irradiated (7.5 Mrads), ram extruded (G-RE); UV irradiated (100 J/cm^2), ram extruded (UV100-RE); UV irradiated (150 J/cm^2), ram extruded (UV150-RE); conventional, unmodified, compression molded (C-CM); and UV irradiated (150 J/cm^2), compression molded (UV150-RE). The UV irradiated material sets were exposed to UV radiation ($\lambda=248 \text{ nm}$) at various doses to induce crosslinking within the polymer.

Pin-on-disk wear tests were performed for a simulated 6 years of *in vivo* use and the amount of wear was quantified via profilometry. Wear tests were performed with UHMWPE disks against a Co-Cr-Mo (ASTM F799) pin at a contact stress of 3.45 MPa. Diluted bovine blood serum with additions of sodium azide (NaN_3) and EDTA was utilized as the lubricant to simulate synovial fluid. Fourier Transform Infrared Spectroscopy (FTIR) spectra in attenuated total reflectance (ATR) mode were also collected, when possible, before irradiation, after irradiation, and after shelf storage.

A total of 18 pin-on-disk wear tests were performed. Examination of the average wear rates and factors revealed that the unmodified, compression-molded (C-CM) polyethylene demonstrated the best wear resistance under the current test conditions. The UV-irradiated material (150 J/cm^2) also demonstrated increased average wear resistances. However, an analysis of variation revealed that the standard deviation in the majority of the material sets was large enough to result in statistically insignificant differences in average wear rates and factors. The only statistically significant differences in wear resistance were between the C-CM material and the UV150-CM material, the G-RE material, and the UV100-RE material. The average oxidation indices decreased slightly after irradiation. In addition, an analysis of variance showed that all oxidation indices increased by statistically significant amounts after storage in air. Finally, it is important to note that the range of wear factors calculated for the variety of materials tested on the UT pin-on-disk machine are within the range of wear factors reported in the literature.

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1. Introduction

Wear in ultra-high molecular weight polyethylene (UHMWPE) and the resultant wear particles appear to be the lifetime limiting factors for modern total joint replacements (TJR). Consequently, a great amount of research is currently focused on improving the wear properties of this material. Research has shown that the deformation and wear of UHMWPE articular surfaces not only degrades the mechanical stability and articulations of the artificial joint, but that the wear particles generated can induce adverse cellular reactions. During long term *in vivo* use, the accumulation of these UHMWPE wear particles can result in bone resorption and osteolysis.^{1,2} This degradation of the surrounding bone can ultimately lead to component loosening and revision surgery. The problem of wear particle accumulation in periprosthetic tissues and the resulting osteolysis and component loosening is the primary life-limiting problem in hip and knee arthroplasty today.³⁻⁷ Therefore, one approach to extending the service life of total joint replacements is dependent upon reducing the amount of wear debris that is generated in the use of the artificial joint.

UHMWPE crosslinked via exposure to ionizing irradiation and other means (chemical) has exhibited improved wear properties in laboratory tests and clinical use relative to the unmodified polymer.^{3,8} Irradiation of polyethylene via ultraviolet (UV) radiation has, thus far, not been studied extensively. Preliminary research by Hollis at The University of Tennessee has demonstrated a decrease in polyethylene wear upon exposure to an increasing UV dose.⁹ In this study, Hollis irradiated compression-molded samples of GUR 4150HP at various UV intensities in a vacuum. In order to evaluate the wear resistance of these crosslinked specimens, unidirectional pin-on-disk wear tests were performed on the wear machine utilized by the author. However, these samples were tested in physiological saline against a ruby sphere counterface. Furthermore, Ohan also investigated the same material.¹⁰ In this effort, nanoindentation provided a means for various material properties of the polyethylene to be examined as a function of depth from the UV treated surface. This effort demonstrated that UV irradiation resulted in increased hardness and modulus up to a case depth of approximately 140 nm.

The primary hypothesis for this research effort is that ionizing radiation, including UV radiation, will induce crosslinking in polyethylene. Preliminary data from UHMWPE exposed to ultraviolet (UV) irradiation in a vacuum has shown improved mechanical properties and wear resistance. Therefore, the objective of the proposed research is to verify the improved wear resistance produced via this novel method of crosslinking UHMWPE.

2. Significance of Materials Research to Orthopaedics

Arthroplasty is defined as “surgery to reshape or reconstruct a diseased joint.”¹¹ According to the American Academy of Orthopaedic Surgeons, there were approximately 245,000 total knee arthroplasties (TKAs) and 138,000 total hip arthroplasties (THAs) in 1996 in the United States. Furthermore, assuming there are no significant advances in preventative treatment, these numbers are projected to increase to 454,000 TKAs, an 85% increase, and 248,000 THAs, an 80% increase, by 2030.¹² In 1996, the market for hip and knee implants in the United States alone was \$1.6 billion. As evidenced by these statistics, the advances of materials research in the orthopaedics community are of great significance.

2.1 Purpose of Total Joint Arthroplasty

Total joint arthroplasty is performed to attain three primary goals. First, joint arthroplasty typically provides improved motion and stability in the joint. The range of motion and stability of the joint is of particular importance in the hip and the knee since these are weight-bearing joints. Second, arthroplasty is normally performed to relieve joint pain due to damaged articular surfaces. Finally, arthroplasty is commonly performed in order to correct deformities in the joint. Without correcting these malformations in the hip or knee, other problems can arise due to uneven loading of the joint.

2.2 Reasons for Total Joint Arthroplasty

Total joint arthroplasty is generally done when a person has a severe degenerative joint disorder such as arthritis in which the articular, or moving, surfaces of the joint deteriorate. These joint surfaces are covered with “a thin layer of smooth, elastic cartilage.”¹¹ This articular cartilage reduces friction and absorbs shock to the joint. A schematic diagram of a typical synovial joint is presented in Figure 1 (all figures are presented in Appendix B). According to National Arthritis Foundation estimates,¹³ arthritis is the number one cause of physical disability, affecting over 40 million Americans—more than 15 percent of the population of The United States. Two types of arthritis commonly occur: osteoarthritis and rheumatoid arthritis.

Osteoarthritis is the most common form of arthritis and is a result of mechanical degradation by which the joint articular surfaces gradually wear out.¹⁴ According to the Arthritis Foundation, osteoarthritis affects an estimated 15.9 million Americans.¹⁵ This may be due to aging, angular deformities, overuse or abuse of joints, or previous fractures or joint injuries. Rheumatoid arthritis is a chronic, systemic connective tissue disease that affects the synovium, the membrane that normally lubricates the joint.¹⁴ Inflammation of the synovial membrane results in pain and stiffness of the joint and the lack of normal joint lubrication results in the articular surfaces of the joint being destroyed. In either case, the articular surfaces of the joint are worn away and, with time, walking and other daily activities become difficult and painful.

2.3 UHMWPE and Applications in Orthopaedic Implants

In orthopaedic applications, UHMWPE is primarily used in hip and knee joint prostheses. Harry Craven is credited as the first to study this material after polytetrafluoroethylene (PTFE) succumbed to high wear and creep rates in Charnley's hip implants.¹⁶ The first hip prostheses utilizing high molecular weight polyethylene (as UHMWPE is commonly termed in older literature) were implanted in 1962.¹⁷ Within the last 30 years, UHMWPE (to be referred to simply as polyethylene for the remainder of the paper) has become the standard material for use as an articular surface in orthopaedic joint replacements. The combinations and uses of biomaterials that have been utilized in total hip arthroplasty are presented in Figure 2.

Total hip arthroplasty typically involves resurfacing the acetabulum and replacing the head of the femur. In modern hip implants, the acetabular cup is typically machined or compression molded from polyethylene. Depending on the model, the acetabular cup can be all polyethylene or a polyethylene liner with a metal backing. The femoral component comes in a variety of materials. For the ball, Co-Cr-Mo is the most common alloy employed in the U.S. today. Some common total hip arthroplasty components are presented in Figure 3.

Total knee arthroplasty commonly involves resurfacing both the distal end of the femur and the proximal end of the tibia or the tibial plateau. A schematic diagram of the knee joint is presented in Figure 4. For knee implants, polyethylene on a Ti-6Al-4V backing commonly covers the tibial plateau and the femoral condyles are ordinarily covered with a Co-Cr-Mo alloy. Finally, a polyethylene "button" is ordinarily utilized to resurface the posterior surface of the patella. Some common total knee arthroplasty components are presented in Figure 5.

2.4 Significance of Wear

Wear of the articular surfaces of orthopaedic implants is one of the most common reasons for implant failure. Concerns about the wear properties of orthopaedic implants involve the structural integrity of the components as well as the biological effects of the wear debris.¹⁸ Revision surgery is necessary if degradation of the articulating surfaces due to wear is extensive. If significant loss of material occurs due to wear, the geometrical conformity of the components is altered and can result in increased stresses. In the past decade, the wear characteristics of the articular surfaces of joint replacement components have risen to the forefront of orthopaedic biomaterials research because the resultant wear particles have been shown to be a major cause of component loosening via bone resorption.¹⁹ According to many sources, immune response and bone resorption are a result of excessive amounts of wear particles, as opposed to chemical effects of the wear particles or mechanical degradation of the components.^{1,2}

It is for this reason that wear testing of orthopaedic candidate materials is important. A pin-on-disk wear-screening test provides a relatively quick and simple way to compare selected materials to each other under stable conditions of speed, load, and environment.

In addition, the wear characteristics of different combinations of materials can be quantified and compared via a value designated as the wear factor. The wear factor (k) is defined as follows:²⁰

$$k = \frac{V}{PX}$$

Where: V = volume loss (mm^3)
 P = load (N)
 X = sliding distance (m)

However, this common parameter (k) does not account for contact area and the resulting contact stress at the interface. Therefore, the author proposes the use of a modified wear factor (k^*) to be defined as follows:

$$k^* = \frac{V}{\sigma X}$$

Where: V = volume loss (mm^3)
 σ = stress (N/m^2)
 X = sliding distance (m)

Although this modified wear factor (k^*) is simply proportional to the traditional wear factor (k), inclusion of the stress instead of the load results in a parameter that is easily compared to results generated on different wear test devices. Therefore, this modified wear factor will be used in this text.

3. Review of Related Literature

In order to examine the relationship between structures, processing and wear properties, it is necessary to understand the fundamentals of wear and wear testing. This basic knowledge will be reviewed in the following sections.

3.1 Fundamentals of Wear

3.1.1 Types of Wear

Wear is defined as “the progressive loss of substance from the operating surface of a body occurring as a result of relative motion at the surface.”²¹ Tribology is the study of wear, friction, lubricants, lubrication and the interaction of materials with surfaces in relative motion.²² While the importance of friction and wear has been recognized since before recorded history, it was in the second half of the 20th century that the great technological importance of tribology was examined.²² Surface topography, friction and the common types of wear are better understood due to these advances.

Wear may take many forms depending on the nature of the surfaces involved (i.e. roughness, modulus, hardness, etc.), their relative motion, the contact forces, lubrication, and other environmental factors.^{21,23} In general, there are four primary types of wear. Bisson classified these four modes of wear as follows: adhesion, abrasion, corrosion or tribo-chemical, and surface fatigue.²⁰

Adhesive wear is a result of strong adhesive forces between two surfaces that result in what is commonly referred to as “cold welding” (Figure 6). These adhesive shear forces can become great enough to cause transfer of material from one surface to the other if an adequate tangential shear stress is applied. Materials that have experienced adhesive wear typically exhibit cones, flakes and pits on the worn surfaces.²¹

According to Salomon and Gee, abrasion is “wear by displacement of material from surfaces in relative motion.”²⁴ Abrasive wear can be subdivided into two modes: cutting wear or two body abrasion and third body abrasive wear.²¹ Cutting wear results from a hard surface rubbing against a softer surface where protuberances on the hard surface plow through or gouge out portions of the softer surface. Third body wear is the result of an abrasive particle being caught between the two articulating surfaces. If this particle is harder than one or both of the articulating surfaces, abrasive wear can occur. Abrasive wear is most prominent in artificial joints such as the knee and hip in which both typically employ a cobalt-chromium-molybdenum (Co-Cr-Mo) or titanium alloy surface that articulates on ultra-high molecular weight polyethylene (UHMWPE). These implants are commonly affixed with polymethyl methacrylate (PMMA) cement. Small particles of PMMA or bone debris can break off and become third body abrasive particles between the articular surfaces.

Corrosive wear is a result of a combination of corrosion and wear. First, corrosion takes place on the articular surfaces and results in an oxide scale. This oxide scale is then removed due to rubbing and friction. Once the protective oxide scale is removed, the corrosion reaction continues at the initial rate. As long as wear occurs, this cycle continues indefinitely and material is lost due to corrosion.²¹ In addition, third body abrasive wear can also occur if the corrosion product (oxide scale) acts as a third body wear particle.

The fourth type of wear is surface fatigue in which damage occurs from cyclic stresses particularly in rolling or sliding contact. Surface damage to articular surfaces is manifested in cracks and “local pitting or flaking.”²¹ This type of wear is also possible in polyethylene with high, cyclic loads and can result in delamination or cracking in the polymer. Fatigue wear is predominately a concern in knee implants where sliding and rolling occurs over a small contact area.

3.1.2 Types of Lubrication

Human joints are naturally lubricated by synovial fluid. Synovial fluid is an “ultrafiltrate of plasma” containing hyaluronic acid, which is a high molecular weight glycosaminoglycan.²⁵ Following total joint arthroplasty, synovial fluid progressively begins to lubricate the joint once again. Therefore, it is important to examine the different modes of lubrication when concerned with wear of polyethylene components. The most prominent factors affecting the mode of lubrication are presented graphically in the Stribeck curve (Figure 7). These factors that determine which lubrication mode is dominant include the friction coefficient (f) for the materials involved, the lubricant viscosity (η), the interfacial velocity (v) and the normal load (F_N). As indicated in the figure, there are three primary lubrication regimes that depend on the friction coefficient (f) for the materials involved, the lubricant viscosity (η), the interfacial velocity (v), the normal load (F_N), the geometry, surface roughness (R) and the separation distance (h) between the interfaces. The lubrication regimes are defined as follows: I. Hydrodynamic and elastohydrodynamic (EHD) lubrication, II. Mixed lubrication and III. Boundary lubrication.²¹

Hydrodynamic lubrication describes a regime in which the articulating surfaces are separated by a continuous, thick film of lubricant that maintains a surface separation distance (h) that is much larger than the surface roughness (R).²¹ Friction encountered in this regime is only due to shearing of the lubricant. Since the surfaces are not in direct contact under the hydrodynamic lubrication regime, wear cannot occur except under certain circumstances (surface fatigue wear). Elastohydrodynamic (EHD) lubrication is a more complex case of hydrodynamic lubrication in which the pressure at the lubricant/material interface deforms the surface elastically and can alter the lubricant viscosity.²¹

Region II is commonly denoted as a mixed lubrication regime. This mode is encountered if the lubricant film decreases in thickness and the surface separation distance (h)

decreases. A decrease in the lubricant film thickness can result from a decrease in interface velocity or lubricant viscosity or an increase in load. In this regime, the surface separation distance (h) is approximately equal to the surface roughness (R) and contact between surface asperities is encountered. Friction in this regime is a result of both shearing of the lubricant and asperity contact between the surfaces. The lubricant film and the asperities in contact carry the load. In general, all four types of wear may be encountered in this regime of lubrication.²¹

The third region of lubrication is generally referred to as boundary lubrication. As the separation distance (h) approaches zero, the ratio of asperity contact area to total surface area approaches one. Therefore, the lubricant film thickness also approaches zero and the load is carried almost completely through asperity contact. At this point, the properties of the lubricant are not of great importance.²¹

3.2 Fundamentals of Wear Testing

3.2.1 Types of Wear Testing

In general, wear-testing devices can be categorized into one of the two following categories: screening devices and joint simulators. Screening devices, such as the pin-on-disk apparatus, utilize simplified sample geometry primarily to identify materials with sufficiently low wear rates to warrant additional evaluation. This type of wear test allows the researcher to rate candidate materials relative to other materials.²⁶ In addition, screening tests allow the researcher to vary certain test or material parameters and observe the effect on the wear rate in a relatively short amount of time.

Joint simulator tests are an attempt to test components *in vitro* under conditions similar to the actual service environment. This method of wear testing provides a much closer approximation to the *in vivo* conditions than screening tests. However, joint simulation is significantly more expensive and more complicated than screening tests and does not lend itself to testing a large number of experimental parameters.²⁶ Knee and hip simulators are common examples of joint simulator tests. The relative advantages of screening devices and joint simulators are presented in Table 1 (all tables are presented in Appendix A).

3.2.2 Methods of *In Vitro* Wear Evaluation

During and/or after wear testing, it is critical to be capable of measuring the amount of material lost during the wear test. This measurement is rather difficult due to the relatively good wear properties of polyethylene and the small amounts of wear that do occur. *In Vitro* wear tests typically involve one of four methods of wear measurement: sample weight loss measurement (gravimetric), wear debris isolation and analysis, constant dimensional measurement, and physical dimensional measurements of the sample surface before and after testing.²⁷ Each method has advantages and disadvantages that will be discussed.

The orthopaedic industry standard is gravimetric evaluation. This most common form of wear measurement is performed by weighing the sample before and after the wear test and calculating the amount of material lost due to wear testing. This method is complicated by the fact that polyethylene tends to absorb a small amount of liquid during testing. Typically, soak control specimens are utilized to monitor the fluid uptake. These control samples are weighed before testing, soaked in the lubricant and subjected to identical loads for the same duration as the test specimen and then weighed following testing. The weight gain of these soak control specimens can then be deducted from the post-test weight of the wear test specimen. In theory, the actual weight loss due to wear is the result. The primary difficulty with this method is the minute amounts of fluid absorption and wear. According to ASTM G99, the weight of the samples should be determined to the nearest 0.0001 g (0.1 mg).²⁸ The limitation of the weight loss methodology has been demonstrated in research by McKellop et al.²⁹ and Walker et al.³⁰ In these experiments, this wear measurement technique was utilized and resulted in a calculated net weight gain in several wear specimens after wear testing. Due to these errors, the wear was considered to be zero or the data from these samples was discarded, respectively. This wear quantification method is even more problematic with the advent of crosslinked polyethylene and the resultant low wear rates.

Second, the amount of wear can be determined by collection and isolation of the wear debris from the lubricant by digestion and filtering followed by particle analysis. If basic lubricants such as distilled water or saline are used, this method is rather simple. However, if serum is used, separation of the wear debris from the lubricant is more complicated. Several variations of a technique for wear debris separation from bovine blood serum through the aid of chemical digestion of the serum and proteins, filtration and wear volume estimation have been delineated in the literature.³¹⁻³⁵ These typically involve one of three techniques:³⁶ base digestion, acid digestion, and enzymatic cleavage. Campbell et al.³⁷⁻³⁹ described base digestion as a means of isolating wear debris from periprosthetic tissue. As the name implies, this method makes use of NaOH to digest tissue and qualitatively assess the amount of wear *in vivo*. The primary disadvantage of this methodology is the complex nature of the wear debris separation process that involves ultra-centrifugation and gradient filtration. Acid digestion and enzymatic cleavage are simpler processes that utilize HCl acid and proteinase K, respectively, to digest the serum proteins followed by filtration. Once the wear particles have been isolated, a SEM is used to image them and image analysis software is used to quantify the number and size parameters. The primary advantage of this technique is that it allows the morphology of the wear debris to be examined, which can lead to a better understanding of wear mechanisms. Niedzwiecki et al. verified all three of these techniques.³⁶

Third, wear measurement can be obtained via constant dimensional measurements during the test through the use of transducers. This technique provides a method of monitoring the wear rate as a function of test time without the test being stopped at certain intervals for measurement. On the other hand, dimensional measurement of a polymer wear surface is complicated by the viscoelastic nature of polymers. As presented in Figure 8, the

typical polymeric viscoelastic response produces a residual or unrecoverable deformation after stress relaxation is complete. Through the use of dimensional measurements, it is difficult to differentiate between wear and this residual deformation.

Finally, the amount of material lost due to wear can be evaluated by making dimensional measurements of the wear surface before and after wear testing. Through the use of profilometry, dimensional measurements can be made at numerous points on the surface of the virgin sample. After wear testing, profiles of the wear track can be made at numerous points and the average amount of material lost due to wear can be calculated. As in the aforementioned technique, the viscoelastic nature (creep and stress relaxation) of polymers complicates this method. However, allowing stress relaxation to occur before dimensional measurements are made can minimize this effect. Research performed by Dumbleton suggests that stress relaxation in polyethylene reaches an asymptotic value approximately 260-280 hours (10.8-11.7 days) after the load is removed (Figure 9).⁴⁰ Furthermore, it might be possible to separate the creep of the material from the wear via a thorough understanding of the viscoelastic properties polyethylene.

3.2.3 In Vitro Lubrication

Synovial fluid is not typically used as a lubricant for wear testing or simulation because it is expensive and not commonly available in sufficient quantities. Although synovial fluid progressively lubricates the artificial joint after total joint arthroplasty, research has shown that these fluids usually exhibit decreased levels of hyaluronic acid and increased concentrations of proteins (Table 2).⁴¹⁻⁴³ Therefore, synovial fluid after joint replacement is more comparable to blood serum in composition.⁴⁴ In addition, it has been determined that hyaluronic acid, the primary difference between synovial fluid and blood serum, contributes little to the lubrication of artificial joints.^{45,46} However, the proteins in the synovial fluid after joint replacement, and in blood serum, act as boundary lubricants and decrease the amount of wear.⁴⁷⁻⁴⁹

Comparison of wear rates, wear surface morphologies and wear debris of samples tested in bovine blood serum and distilled water or saline have demonstrated that only blood serum reproduces the type and quantity of wear seen in removed prosthesis.^{27,30,50-54} Furthermore, previous research has shown little or no difference in wear performance and wear debris morphology evaluated in bovine blood serum as compared to clinical (*in vivo*) observations.^{37,48,52,55-58} According to research by Wang et al., the protein concentration of the bovine blood serum is a major factor in the accuracy and validity of wear testing.⁵⁹ Human synovial fluids typically have a protein concentration of 10 mg/ml to 35 mg/ml.^{25,42,60} Therefore, the serum utilized as a lubricant for *in vitro* testing should be within this range.

3.2.4 Counterface Roughness

Multiple research efforts have studied the effect of counterface roughness on the wear of polyethylene. Weightman and Light examined the effect of surface finish of alumina and stainless steel on the wear rate of polyethylene.⁶¹ A six station pin-on-plate wear

screening apparatus was used to test alumina ($R_a=0.015\text{-}0.10\text{ }\mu\text{m}$) and 316S stainless steel ($R_a=0.020\text{-}0.078\text{ }\mu\text{m}$) discs against RCH1000 polyethylene pins in serum. The relationship between the wear factor and surface roughness was found to be approximately:

$$k = 1.5 \times 10^{-6}(R_a)^{1.37} [\text{mm}^3/\text{Nm}]$$

It was determined that the wear rate of polyethylene decreases as the surface roughness of both alumina and stainless steel decreases. This research also demonstrated that alumina possibly produces less wear at moderate surface finishes between 0.035 and $0.075\text{ }\mu\text{m}$.

Fisher et al. seemed to substantiate this finding with polyethylene tested against stainless steel counterfaces with an average counterface roughness from 0.014 to $0.078\text{ }\mu\text{m}$.⁶² Tri-pin-on-disc wear tests at interfacial velocities of 35 and 240 mm/s were performed in bovine serum at a contact stress of approximately 12 MPa . Similar to the aforementioned study, wear factors close to $10^{-8}\text{ mm}^3/\text{Nm}$ were found for $R_a < 0.05\text{ }\mu\text{m}$. However, higher wear factors were found for $R_a > 0.07\text{ }\mu\text{m}$.

Lancaster et al. investigated the effect of surface roughness of stainless steel, zirconia (ZrO_2), alumina (Al_2O_3) and a Co-Cr-Mo alloy against extruded GUR 415 polyethylene pins.⁶³ These pin-on-disk wear tests were conducted in bovine serum with an interfacial velocity of 240 mm/s and a contact stress of 12 MPa (1740 psi). The counterface disks were produced with surface roughness (R_a) ranging from $0.005\text{ }\mu\text{m}$ to $0.04\text{ }\mu\text{m}$. For differing materials with similar surface finish, there was no statistically significant differences in the polyethylene wear factors although all surface finishes exceeded the requirements of international standards ($R_a < 0.05\text{ }\mu\text{m}$). Therefore, Lancaster et al. suggest that there may be a surface roughness threshold below which there is little change in the wear factor. However, this research suggests that this threshold is below the current standard roughness value of $0.05\text{ }\mu\text{m}$. Based upon this data, the following relation approximated the wear factor dependence on surface roughness:

$$k = 7.69 \times 10^{-9}(R_a)^{0.37} [\text{mm}^3/\text{Nm}]$$

Lancaster et al. also examined the effect of surface roughness over a range of 0.04 to $0.10\text{ }\mu\text{m}$. The following exponential relation described the resultant wear factor dependence:

$$k = (6.29 \times 10^{-9})^{24.14 R_a} [\text{mm}^3/\text{Nm}]$$

Que and Topoleski seem to substantiate these results.⁶⁴ They performed reciprocating pin-on-disk wear tests with GUR 415 polyethylene against ASTM F799 Co-Cr-Mo of various surface roughnesses ($R_a=0.0047\text{-}0.0365\text{ }\mu\text{m}$). These tests were performed in bovine serum at 37°C at an interfacial velocity of 100 mm/s and a contact stress of 3.5 MPa (500 psi). The results indicated that polyethylene wear is independent of the

counterface surface roughness in the range from $R_a=0.0047\text{-}0.0125\text{ }\mu\text{m}$. In addition, Co-Cr-Mo components with a roughness greater than $0.0235\text{ }\mu\text{m}$ resulted in significantly greater wear.

Dowson et al. studied the effect of the surface finish of stainless steel against polyethylene in a reciprocating-pin-on-disk system with water lubrication.⁶⁵ This data suggested a wear rate/surface roughness relationship described by the following relation:

$$k = 4.0 \times 10^{-5}(R_a)^{1.2} [\text{mm}^3/\text{Nm}]$$

In a continuation of this research, Dowson et al. studied the effect of single scratches and imperfections on stainless steel counterfaces in the same aforementioned system.⁶⁶ The resultant data demonstrated that pile-up along a scratch in the counterface material is primarily responsible for increased polyethylene wear rates.

Essner et al. looked at the effect of counterface surface roughness on unmodified and crosslinked polyethylene.⁶⁷ Unmodified (EtO sterilized) and gamma-irradiated and stabilized GUR 4150 polyethylene acetabular inserts were subjected to hip joint simulator tests against Co-Cr-Mo femoral heads ($R_a=0.02$ and $0.20\text{ }\mu\text{m}$). These tests were performed in bovine calf serum for 1 million cycles. The results indicated that the wear rate of crosslinked polyethylene against “smooth” ($R_a=0.02\text{ }\mu\text{m}$) heads was 67% lower than the wear rate of unmodified polyethylene against smooth heads. The wear rate of crosslinked polyethylene against “rough” ($R_a=0.20\text{ }\mu\text{m}$) heads was 60% lower than the wear rate of unmodified polyethylene against rough heads.

Wang et al. utilized a hip joint simulator and a linear reciprocating wear test to examine the effect of counterface surface roughness.⁶⁸ Extruded GUR 4150 polyethylene was crosslinked with gamma radiation at 2.5 Mrad and tested in bovine calf serum against Co-Cr-Mo with a surfaces finish ranging from 0.01 to $0.85\text{ }\mu\text{m}$. For the reciprocating wear tests, the wear factor/surface roughness relationship was described by the relation:

$$k = 3.0 \times 10^{-5}(R_a)^{1.79} [\text{mm}^3/\text{Nm}]$$

Increasing R_a an order of magnitude from $0.01\text{ }\mu\text{m}$ to $0.1\text{ }\mu\text{m}$ resulted in a 60-fold increase in the wear factor (k). The wear factor increased by three orders of magnitude as a result of increasing R_a from $0.01\text{ }\mu\text{m}$ to $0.70\text{ }\mu\text{m}$. Once again, the wear factor was approximately independent of surfaces roughness below $0.05\text{ }\mu\text{m}$ R_a . For the hip simulator tests, the wear factor/surface roughness relationship was described by the linear relationship:

$$k = 8.68 \times 10^{-6}(R_a) + 1.51 \times 10^{-6} [\text{mm}^3/\text{Nm}]$$

In order to be consistent with other results, the hip simulator data was also fitted with a power function as follows:

$$k = 7.21 \times 10^{-6} (R_a)^{0.42} [\text{mm}^3/\text{Nm}]$$

The wear factor exhibited a 50% increase upon increasing R_a from 0.01 μm to 0.10 μm . In addition, the wear factor increased 600% over the surface roughness range tested (0.01 μm to 0.85 μm). From these results, Wang et al. concluded that, overall, surface finish has a weak influence on the wear rate of polyethylene.⁶⁸

Where possible, the data from the aforementioned literature was plotted to evaluate the degree of consistency (Figure 10). This comparison reveals that most of the surface roughness/wear factor relationships are consistent with each other, especially below an R_a value of 0.05 μm . The relation derived by Dowson et al. appears to be the model that does not agree. However, this disagreement might be expected because this model was derived from data based on wear tests in water while the other models were based on serum lubrication. As was previously discussed, water lubrication does not provide a wear model similar to the *in vivo* environment. Therefore, the model derived by Dowson et al. was removed from the data set. A graph of the remaining relations is presented in Figure 11. Overall, these experimental results appear to suggest that a counterface surface roughness of less than approximately 0.05 μm minimizes the roughness effect.⁴⁰ This data suggests that the range of typical prosthetic quality surface finish (0.01 $\mu\text{m} < R_a < 0.05 \mu\text{m}$) is satisfactory for minimizing polyethylene wear.

3.2.5 Interfacial Velocity

Fisher et al. have estimated the typical physiological velocity in the hip joint to be approximately 0 to 60 mm/s (2.4 in/s)⁶² while Dumbleton estimated that this velocity ranges from 0 to 75 mm/s (3 in/s).⁶⁹ In addition, Dumbleton estimated the typical physiological velocities of the knee to be approximately 0-300 mm/s (11.8 in/s). Since it is desirable to accelerate wear testing to reduce the time required per sample per test, it is pertinent to examine the effect of interfacial velocity on the amount of wear in polyethylene. Fisher et al. compared the wear factor of polyethylene against a stainless steel counterface in a tri-pin-on-disc apparatus at velocities of 35 and 240 mm/s (1.4 and 9.4 in/s).⁶² This research demonstrated that sliding velocity, within this range, had little effect on the wear of polyethylene in bovine blood serum for counterfaces with an average surface roughness (R_a) of less than 0.05 μm .

3.3 UHMWPE Modification

In general, total joint replacement components are typically sterilized via exposure to gamma radiation. In the past 30 years, it has been recognized that ionizing radiation such as γ -radiation alters the physical structure of polymers such as polyethylene. Crosslinking of the polymer chains can result from exposure to radiation and can lead to improved wear resistance and other mechanical properties. It is due to these positive aspects of

crosslinking that this practice is now common in artificial joint components today. However, the detrimental aspects of this practice are still not well understood.

3.3.1 Modification Methods

Currently, polyethylene is crosslinked by a variety of methods. These include gamma irradiation from a ^{60}Co source, chemical means (benzoyl peroxide) and electron beam irradiation.

Multiple investigations have demonstrated that crosslinking induced by electron beam⁷⁰ and gamma irradiation^{71,72} is beneficial to the wear rate of polyethylene. Grobbelaar et al. examined the relationship between radiation dose and atmosphere on the degree of crosslinking, tensile strength, impact strength, and abrasion resistance of polyethylene.⁸ In this study of Hostalen RCH 1000C, samples were exposed to gamma-irradiation in a range from 0-80 Mrads in a nitrogen atmosphere, acetylene or an equimolar mixture of acetylene and chlorotrifluoroethylene (CTFE). The degree of crosslinking was determined via Soxhlet extraction. The resultant data showed that the degree of crosslinking increases with increasing radiation dose below 40 Mrads. The acetylene and CTFE atmosphere resulted in the greatest degree of crosslinking within this range. In addition, tensile strength and bulk surface hardness increased with increasing radiation dose. Once again, the acetylene and CTFE atmosphere produced the greatest values for both. On the other hand, the impact strength of the crosslinked specimens decreased drastically with increasing radiation dose. Furthermore, the resultant data seems to suggest that impact strength is virtually independent of the irradiating atmosphere. In order to avoid the dramatic degradation of the impact strength, it was suggested that radiation doses not exceed approximately 15 Mrads. Finally, a limited study of the abrasion resistance of unirradiated and irradiated (15 Mrads in acetylene atmosphere) samples was performed. The crosslinked samples exhibited a 30% decrease in weight loss as compared to the unirradiated samples.

Nusbaum and Rose investigated the effect of gamma-irradiation in air on the mechanical properties and structure of polyethylene.⁷³ All samples were irradiated with a ^{60}Co gamma ray source with a 2.5 Mrad dose. This research demonstrated that radiation sterilization of polyethylene in air causes both crosslinking and oxidative degeneration. Hydrophilic carbonyl groups formed upon oxidation result in increased fluid uptake as well as discolorations (yellowing) and an increase in density due to this fluid absorption. Nusbaum and Rose also concluded that no “immediate change in the deformation or wear behavior” should occur *in vivo*. Furthermore, irradiating in air did not improve the mechanical properties but increased the susceptibility of cyclic deformation damage.

3.3.2 Oxidation

As previously discussed, ionizing radiation breaks bonds within the polymer chain. Although the molecular structure of polyethylene is relatively simple, oxidation as a result of ionizing radiation is a complex process.⁷⁴ A summary of this degradation pathway is presented in Figure 12. Bond scission can occur at the carbon-carbon (C-C)

bonds along the polymer chain, end-type scission, or at the carbon-hydrogen (C-H) bond, chain-type scission (denoted in the figure as “Scission A” and “Scission B,” respectively).

In the Scission A scenario, two primary macroalkyl radicals (I) are formed due to scission of the C-C bond (reaction 1). Due to their large size and resultant low mobility, recombination can occur (reaction 2) whereby the C-C bond is reformed and the original macromolecule results. However, these primary macroalkyl radicals (I) could extract a H atom from a second polymer chain to form a secondary macroalkyl radical (II) and a new chain with a CH₃ end-group (reaction 3). This new chain has a lower molecular weight than the original and results in a decrease in average molecular weight. In addition, these chain-type macroalkyl radicals (II) are relatively stable and can remain for long periods of time. As a result, free-radicals can remain in the system and can participate in oxidative degradation long after sterilization and even *in vivo*.⁷⁴ Radical (I) can also bond with oxygen and form a primary peroxy radical (reaction 4). Furthermore, a second radical (I) might combine with this primary peroxy radical to form a peroxide (reaction 5). Finally, the primary peroxy radical could combine with a H atom (reaction 6) however, this reaction is not likely due to the non-reactivity of peroxy radicals.⁷⁴

In the Scission B scenario, a macroradical (II) and a highly mobile H atom are formed due to scission of the C-H bond (reaction 7). Due to the high mobility of the H atom, recombination (reaction 8) is unlikely. However, it is more plausible that the H atom would extract a second H atom from another polymer chain to form H₂ and result in the formation of a secondary macroalkyl radical (II) (reaction 9). If a free radical exists on an adjacent methylene, a double bond or crosslink is formed in addition to the H₂ atom (reaction 10). Crosslinking can also occur if two adjacent secondary macroalkyl radicals are at least as close to each other as the C-C bond length. Both of these reactions are dependent upon the absence of oxygen in the polymer. If oxygen is dissolved in the polymer, radical (II) can react with it to form a secondary peroxide (reaction 11). It is probable that this secondary peroxide will extract a H atom from another polyethylene molecule (reaction 12) to form a secondary hydroperoxide and a radical (II) that can then further propagate the oxidation cycle. Finally, the O-O bond in the hydroperoxide is weak and its scission can result in the formation of ketones, acids, esters and alcohols (reaction 13).⁷⁴

The dominance of one reaction scenario over the others is dependent upon, among other things, the environment in which the irradiation is performed and the time of exposure. Irradiation in the presence of oxygen (air) appears to promote oxidation and chain scission⁷⁴⁻⁷⁷ while irradiation in an inert environment such as nitrogen promotes radical recombination and crosslinking.⁷⁸⁻⁸¹ Following irradiation, unreacted free-radicals tend to be trapped in crystalline regions and migrate to amorphous regions with time.⁸² If the irradiated sample is not stored in an inert environment, these free-radicals can combine with oxygen molecules and increase the amount of oxidation with time.^{83,84} Furthermore, evidence suggests that post-irradiation oxidation also proceeds *in vivo* via long-lived free-radicals.⁸⁵⁻⁸⁷ Research has shown that post-irradiation oxidation reaches a maximum in

the near-surface region of an polyethylene component.^{88,89} This is seen through examination by fourier transform infrared spectroscopy (FTIR) as well as visually as a subsurface white band.^{86,90,91} These typical relationships between oxidation and crosslinking as functions of distance from the surface are presented in Figure 13. Electron spin resonance (ESR) has also revealed that long-lived free-radicals exist in the polyethylene following irradiation.⁹² If exposed to oxygen at any time in the future, peroxy radical formation will continue at an accelerated rate.^{78,93} Additional research focused on tribological properties has verified that post-irradiation oxidation is detrimental to the wear resistance of polyethylene.⁹⁴

In the past, it has been hypothesized that compression-molding of polyethylene can exacerbate oxidation and degrade crosslinking due to oxygen trapped in the polymer upon processing. On the other hand, several studies have indicated that compression-molded polyethylene possesses a resistance to oxidation and therefore promotes crosslinking upon and after irradiation.^{95,96} Methods such as post-irradiation annealing in an inert environment have also revealed an ability to further reduce the quantity of free-radicals and increase the degree of crosslinking.⁹⁷⁻⁹⁹ Annealing is based upon the theory that increasing the temperature in an inert environment extinguishes free-radicals and maximizes crosslinking while minimizing oxidation.

3.4 Clinical (*in vivo*) Wear

Evaluation and measurement of *in vivo* wear performance of polyethylene joint replacement components is primarily performed in one of three ways. These include: radiographic evaluation, retrieved component evaluation (*ex vivo*) and periprosthetic wear debris recovery.

3.4.1 Radiographic Evaluation

Traditionally, wear assessment has been accomplished through radiographic studies of hip prostheses. For metal-on-plastic prostheses, the wear of the metal ball is considered to be negligible compared to the polyethylene. With this in mind, radiographs can be used to approximately determine the amount of penetration of the metal ball into the polyethylene acetabular cup. These measurements are taken from points of reference in the joint region and provide a measure of the linear wear of the articulating surfaces. Charnley and Halley described this specific technique in 1975.¹⁰⁰ With this method of clinical evaluation, it must be recognized that the degree of penetration is due to a combination of both wear and creep. However, it has been shown that creep in polyethylene decreases as a function of time. Therefore, it can be assumed that a majority of the deformation after the first year is primarily due to wear.¹⁰¹

Hernandez et al. measured polyethylene wear in 231 porous-coated, uncemented acetabular cups via radiographs at 3-5 years post-operative.¹⁰² These components were divided into two primary groups based upon the fixation method of the femoral component: cemented or press-fit (uncemented). The mean linear wear rate for acetabular cups with cemented femoral components was 0.22 mm/year as compared to 0.14 mm/year

for uncemented femoral components. The mean volumetric wear rates were determined to be 92 mm³/year and 139 mm³/year, respectively. However, it should be noted again that these values represent both creep and wear and are better referred to as penetration rates.

Cates et al. examined the radiographic wear in 233 cemented hip arthroplasties.¹⁰³ The wear rates of 134 metal-backed polyethylene acetabular cups were compared to 99 non-metal-backed, all polyethylene cups. The calculated mean penetration rates for the metal-backed and all polyethylene cups were 0.11 mm/year and 0.08 mm/year, respectively. Furthermore, the mean volumetric wear rate was 66.2 mm³/year for the metal-backed components and 48.2 mm³/year in the all polyethylene cups.

Overall, the average rate of penetration observed via radiographic evaluation of total hip components has been in the range of 0.1-0.4 mm/year.^{100,104,105}

3.4.2 Retrieved Component Evaluation

The second method of evaluating *in vivo* wear performance is to examine removed prosthetic components after revision surgery or autopsy (*ex vivo*). Isaac et al. examined 100 Charnley cemented acetabular cups (78 had the associated femoral stems) obtained after revision surgery for mechanical problems.¹⁰⁶ Six categories of damage were observed on the acetabular cups: socket erosion or “back side wear”, rim wear due to femoral stem neck impingement, PMMA cement ingress resulting in embedded particles in the polyethylene, discoloration or yellowing most likely due to oxidation, cratering or pitting, and scoring or scratching due to abrasive wear. Of the examined acetabular components, 34% exhibited back side wear, 48% rim wear, 60% PMMA cement ingress, 30% discoloration, 89% pitting, and 100% roughening of the polyethylene due to abrasive wear. The articulating surfaces of the femoral stems demonstrated evidence of surface roughening *in vivo*. The average roughness (R_a) of these components ranged from 0.013 to 0.4 μm with a mean of 0.053 μm . Out of the 100 examined, 54 (76%) were rougher than 0.025 μm and 24 (33%) had a roughness greater than the standard maximum roughness of 0.05 μm . The mean penetration depth of the femoral component into the polyethylene acetabular cups was 1.69 mm with a range from 0.2 mm to 4.3 mm. The average penetration rate was 0.21 mm/year with a range from 0.005 mm/year to 0.6 mm/year. Isaac et al. plotted the service life as a function of penetration rate as presented in Figure 14. It is important to recognize that this data demonstrates that the service life of the component is dependent upon the penetration and wear rates. Isaac et al. found no acetabular components that demonstrated both a high penetration rate and long service life.¹⁰⁶ In other words, wear appears to be the dominant factor in limiting the life of polyethylene components.

Dowling examined 23 Charnley acetabular cups removed from patients with a service range between 1 and 14 years.¹⁰⁷ This study revealed that *in vivo* wear was confined to the superior portion of the socket due to the loading direction and geometry of the hip joint. For “normal” use conditions, a deep wear scar was visible with the naked eye in this region after approximately 7-8 years of use. In addition, physical examination suggested

that adhesive wear was the dominant wear mechanism initially. After about 7 years of use, surface fatigue wear seemed to predominate. The penetration rates observed in this study ranged from 0 to 0.4 mm/year. This large range was due to the differing activity levels of the patients.

James et al. compared the clinical wear rates of 63 retrieved acetabular components.¹⁰⁸ Specifically, 19 components were directly compression molded from calcium stearate free, polyethylene (Himont® 1900 resin) and 44 were made from machined, ram extruded, calcium stearate containing polyethylene (GUR 4150). All components had been implanted for a minimum of 4.26 years and an average of 8.34 years. The amount of volumetric wear was measured via fluid displacement. Overall, the mean volumetric wear rate was determined to be 60 mm³/year and 140 mm³/year for the compression molded and machined components, respectively.

Based upon evaluation of retrieved components, the average penetration rate of femoral heads into Charnley acetabular cups is estimated to range from 0.07 to 0.22 mm/year.¹⁰⁹

3.4.3 Wear Debris Recovery

Information concerning in vivo wear performance can be obtained by examining the size, amount, distribution and morphology of wear products. Multiple researchers have examined and described the morphology of polyethylene wear particles from periprosthetic tissue.^{32,37,110-115} Several methods have been developed for digestion of the tissue in order to isolate the wear debris.

Maloney et al. examined the wear debris from 35 soft-tissue membranes from the implant-bone interfaces of failed femoral components in total hip arthroplasties.¹¹¹ The particles were isolated via digestion of the soft tissue following revision surgery and were characterized through the use of optical light and scanning electron microscopy as well as x-ray and automated particle analysis. The mean sizes of the polyethylene and metallic particle wear debris were 0.5 µm and 0.7 µm, respectively, as determined by scanning electron microscopy. According to automated particle analysis, the mean particle diameter was 0.63 µm and an average of 1.7 billion particles per gram of tissue was estimated. Maloney et al. concluded that the particulate implant debris in periprosthetic tissues surrounding failed femoral components without cement are predominantly sub-micron in size and present in density of greater than one billion particles per gram of tissue.

Hirakawa et al. isolated and quantified wear debris from 123 tissue samples obtained adjacent to failed total hip implants from 88 patients.¹¹⁶ The resultant data demonstrated a particle density range of 8.5×10^8 to 5.7×10^{11} wear particles per gram of tissue and the concentration was highest near the proximal femoral membrane. The mean wear particle diameter was calculated to be 0.8 µm.

3.5 Results of *In Vitro* Wear Testing

Multiple research efforts have focused on examining the wear performance of polyethylene through *in vitro* testing. These studies have been performed via simple screening tests such as pin-on-disk and reciprocating pin-on-plate wear test devices as well as on complex knee and hip simulators to compare the wear resistance among unsterilized, gamma irradiated, electron beam irradiated, gas plasma sterilized and ethylene oxide (EtO) sterilized samples. In addition, different atmospheres (air, vacuum, nitrogen and argon) for irradiation and packaging have been examined as previously discussed. Furthermore, many studies also have examined different static loads and dynamic loading profiles, interfacial velocities, counterface materials, counterface roughness, resin types, processing methods, lubricants, additives (calcium stearate), annealing protocols and aging on different test devices.

General trends in polyethylene wear resistance are evident although the results of various research efforts are not comparable, in general, due to the large number of differing variables. In general, wear factors determined through screening wear testing (i.e. pin-on-disk, reciprocating, etc.) reported in the literature are in the 10^{-6} to 10^{-9} mm³/Nm range.^{62,68,117} Overall, it is evident that the wear resistance of polyethylene improves as the crosslinking density increases.¹¹⁸⁻¹²⁰ Muratoglu et al. specifically concluded that the average molecular weight between crosslinks (M_c) is the variable that defines the wear resistance.⁷⁰ As discussed previously, irradiation and/or storage in an environment containing oxygen seems to inhibit crosslinking and promote degradation through oxidation and chain scission, which leads to reduced wear resistance.^{94,121-124} Therefore, irradiation and/or storage in an inert environment seems to correlate with improved wear resistance.^{94,118,119} Research has shown that sterilization via EtO gas does not alter the physical structure or properties of polyethylene.^{72,121}

Conflicting conclusions on the effect of several variables on the wear rate of polyethylene are evident upon inspection of the literature. The wear resistance is generally believed to increase with increasing average molecular weight of the resin.¹²⁵ However, one study has provided evidence that demonstrates a lack of influence of molecular weight.¹¹⁸ The presence of calcium stearate, a polyethylene additive, has also been suspected of inhibiting particle fusion and leading to a reduced wear resistance. Again, wear tests by McKellop et al. supported the lack of influence of calcium stearate on wear resistance.¹¹⁸

4. Materials

Wright Medical Technology (WMT, Arlington, TN) donated and machined ultra-high molecular weight polyethylene (UHMWPE) disks of Ticona 1050 ram-extruded (RE) bar stock from Poly Hi Solidur, Inc. (Fort Wayne, IN). Thirty-five disks or pucks with a thickness of 6.35 mm and a diameter of 38.1 mm were machined to an arithmetical average surface roughness (R_a) of 1.3 μm (50 μin). Five of the samples provided were machined from Ticona 1020, conventional, unmodified, compression molded (C-CM) sheet stock also fabricated by Poly Hi Solidur, Inc. The Co-Cr-Mo (ASTM F799) pin was machined at The University of Tennessee from rod stock manufactured by Carpenter Technology Corporation (Wyomissing, PA) and donated by WMT.

Five of the conventional, unmodified, ram-extruded polyethylene samples were used as control specimens (C-RE). Five of these ram-extruded, unmodified polyethylene samples were gamma-irradiated with 7.5 Mrads (G-RE) on April 16, 2000 by SteriGenics (Gurnee, Illinois). Following irradiation, the samples were packaged in a nitrogen environment for storage. Approximately 10 weeks later (June 28, 2000), these gamma-irradiated samples were annealed by WMT at 150°C for 2 hours (heated at 2 C°/min and cooled at 1 C°/min) to minimize the amount of residual free-radicals. Once annealed, the samples were stored at room temperature in air.

Eight samples were exposed to ultraviolet (UV) radiation. The source of the radiation ($\lambda=248$ nm) was a Lambda Physik LPX305i pulsed KrF laser (Goettingen, Germany). Through the use of optics and mirrors, the beam was expanded to an area of approximately 102 mm x 76 mm to expose one side of the entire sample surface to the beam pulses. Prior to sample exposure, the average energy density per beam pulse was measured with a Scientech Astral AD30 calorimeter (Idaho Falls, ID) and determined to be approximately 14.8 mJ/cm². This average value was then used to calculate the number of pulses required to obtain a given total energy dosage per sample.

Eight samples were irradiated with 248 nm UV radiation. Three extruded, unmodified polyethylene samples were exposed to total dosages of 100 J/cm² (UV100-RE). Three extruded, unmodified polyethylene samples were exposed to total dosages of 150 J/cm² (UV150-RE). Two compression-molded, unmodified polyethylene samples were also exposed to a total dose of 150 J/cm² (UV150-CM). These irradiation dosages were obtained at a laser pulse frequency of 10 Hz while the samples were contained in a chamber filled with nitrogen to minimize oxidation.

5. Experimental Methods

Various analytical methods and tests were utilized to evaluate the unmodified (control) and modified polyethylene samples. A brief summary of each technique and use will follow.

5.1 Pin-on-disk Wear Test

Prior to testing, polyethylene disks were soaked in distilled, deionized water for a minimum of 5 days to minimize liquid absorption during testing. A pin-on-disk (POD) wear apparatus that was designed and built at The University of Tennessee was utilized for these tests. The polyethylene disks rotated in a horizontal plane on the end of a vertical shaft. The Co-Cr pin, screwed into the end of a horizontal arm, made contact with the disk on the upper surface. The majority of the normal force was generated by the suspension of a lead weight from the bottom of the arm. Fine adjustments in weight were made with lead shot contained in small cups attached on top of the arm. A cup on the opposite side of the pivot point from the pin was used to counter-balance the arm so that the normal force was generated from the lead weight and lead shot only, not from the weight of the arm or pin.

Based upon previous research, sterile, filtered blood serum (Sigma B-2771) was utilized as the lubricant for these tests. According to Sigma literature, bovine blood serum has a protein concentration of approximately 60 mg/ml to 85 mg/ml as received. Therefore, the blood serum was diluted with distilled, deionized water (40% serum, 60% water) to produce a lubricant with a protein concentration of 24 mg/ml to 34 mg/ml that corresponds to the concentration typically found in human synovial fluid. In addition, 0.2 wt.% sodium azide, NaN_3 (Fisher S227I-25), and 20mM ethylenediaminetetra-acetic acid, EDTA (Fisher LC13910-1), was added to retard microbial degradation of the bovine blood serum and prevent precipitation of calcium phosphate,¹²⁶ respectively. The serum was stored at -20°C , thawed before testing and replaced following each test. Tests were performed at room temperature (21°C) with the disk and pin tip submerged in a reservoir containing approximately 650 mL of this serum solution. The temperature of this lubricant solution was not controlled and heating effects due to friction were considered to be negligible due to the large reservoir volume. During testing, lubricant lost due to evaporation was replaced with distilled, deionized water.

Dumbleton estimated the average contact stress in a typical hip implant to be approximately 3.45 MPa (500 psi) with peak stresses of approximately 6.90-10.35 MPa (1000-1500 psi).⁶⁹ Based upon this approximation, the current wear screening tests were conducted with a contact stress of 3.45 MPa (500 psi). The interfacial velocity for all wear tests was 150 mm/s and is well within the range examined by Fisher et al.⁶²

A 1.59 mm diameter Co-Cr (ASTM F799) pin was used as the counterface surface in these wear tests. The pin tip geometry was a flat end so that the surface contact area and the contact stress remained constant throughout the test. Prior to each test, the pin tip was

metallographically prepared to a final 0.05 μm alumina slurry surface finish. The mean surface roughness (R_a) of the pin tip before wear testing was determined to be 0.03 μm .

Prior to performing a wear test, each sample was cleaned via a protocol commonly used in the literature to remove all contaminants and debris. This cleaning protocol is presented in Appendix C. A similar cleaning protocol was followed after the wear test to remove all wear debris and lubricant residue from the surface. Following wear testing, all samples were stored at room temperature in desiccators.

Wear tests were conducted for an estimated equivalent of 6 years *in vivo* use, or 64.2 km, assuming an average of 10.7 km per year for a typical total hip prosthesis as calculated by Clarke.¹²⁷ The average wear rate and wear factor were calculated for each material set.

5.2 Profilometry

Profilometry data for the polyethylene samples were collected via a Taylor Hobson Talysurf 10 profilometer (Rank Taylor Hobson, Inc.; Rolling Meadows, IL) in conjunction with Dr. Peter Blau and Dr. Ron Ott at The High Temperature Materials Laboratory, Oak Ridge National Laboratory. Four profiles across the wear track were made randomly 90° apart. An example of a wear track profile before analysis is presented in Figure 15. The wear track area was calculated by fitting 4th or 6th order polynomials to the wear track and unworn (machined) surface data, subtracting the former from the latter, and integrating the difference within the limits of the wear track. An example of a wear track profile after fitting polynomials to the wear track and unworn surface is presented in Figure 16. This method estimated the amount of material (μm^2) removed from the wear track at that location and accounted for lips, or pile-up, on the edges of the wear track. An average of these four values was then obtained for each sample. The average wear volume for each sample was then determined by multiplying the average wear track cross-sectional area by the circumference of the wear track (94.2 mm).

The average surface roughness (R_a) of the Co-Cr pin tip was measured via a Rodenstock non-contact laser profilometer in addition to the contact Talysurf 10 for comparison. Both methods revealed an R_a value of 0.03 μm before wear testing.

5.3 Infrared Spectroscopy

Infrared (IR) spectroscopy is a method used to examine the vibrations between bonded atoms in organic compounds. The vibrational frequency of each bond is related to the interatomic bond and is dependent upon masses of the bonded atoms and the type of bonding (ionic, covalent, double and triple bonds). If the frequency of the incident radiation exactly matches the natural vibrational frequency of the organic molecule, a net transfer of energy occurs, which results in a change in the amplitude of the molecular vibration and absorption of the radiation. Since each type of atomic bond has a distinctive frequency of vibration, a particular atomic bond is associated with the absorption of a particular light frequency. In other words, the nature and quantity of atomic bonds within

a material can be determined by examining the intensity of light absorbance as a function of frequency. The Fourier transform infrared spectrometer (FTIR) is a modern version of the traditional IR spectrometer in which the source is split into two beams whose path lengths can be varied to give interference patterns. Data can be obtained through measurement of transmitted or reflected light.^{128,129}

The wear surfaces of the polyethylene samples were examined via attenuated total reflectance (ATR) in the bulk form (Bio-Rad FTS6000; Cambridge, Massachusetts). Mid-infrared spectra (4800-900 cm^{-1}) were collected at four locations along the radial direction as indicated in Figure 17. Two hundred fifty-six scans were performed at each location to improve the signal-to-noise ratio. An oxidation index (OI), a qualitative measure of oxidation, was determined in order to compare the relative amount of oxidation in the samples. The oxidation index is a ratio of peak area (absorbance) for the carbonyl peak (1720 cm^{-1}) to the CH_2 peak (1370 cm^{-1}). The CH_2 peak is a result of wagging of CH_2 groups within the carbon chain in the amorphous region of the polymer.¹³⁰ Therefore, a low OI denotes a lack of oxidation in the polymer and a high OI denotes a greater amount of oxidation.

When possible and applicable, FTIR spectra were collected for samples before irradiation (C-RE, C-CM, UV100-RE, UV150-RE and UV150-CM), post-irradiation (G-RE, UV100-RE, UV150-RE and UV150-CM), and post-storage (C-RE, C-CM, G-RE, UV100-RE, UV150-RE and UV150-CM). Post irradiation spectra were collected within 6-8 hours of irradiation with the exception of the G-RE samples, which were irradiated by SteriGenics (Gurnee, Illinois) prior to machining and shipping to The University of Tennessee. In this case, the post-irradiation spectra were collected approximately 9 months after irradiation. Post-storage spectra were collected after shelf-storage of approximately 1 year from the date of irradiation.

5.4 Statistical Data Analysis

In an effort to correctly interpret the meaning of the data collected, statistical data analysis was employed. Standard deviation of the data sets was determined through the following equation:

$$\text{Standard Deviation} = \sqrt{\frac{n \sum x^2 - (\sum x)^2}{n(n-1)}}$$

Where: n = number of data points
 x = value of data point

One-way analysis of variance (ANOVA) was utilized to determine whether differences between data sets were statistically significant. Analysis of variance was calculated with WebStat 2.0 software. The software calculates the probability (p) that two or more sample sets are statistically equal. For instance, $p = 0.02$ means that there is only a 2% chance that the data sets are statistically equal (statistically insignificant difference).¹³¹

6. Experimental Results and Discussion

6.1 Pin-on-disk Wear Test

A total of 18 pin-on-disk wear tests were performed, with each test corresponding to an estimated 6 years of simulated *in vivo* use. A minimum of 2 (UV150-CM) and a maximum of 4 (C-CM) tests were conducted for each sample set. Three POD wear tests were conducted for the remaining materials sets. A summary of the wear data is presented in Appendix D. The average calculated wear rates and modified wear factors as a function of material type are presented in Figures 18 and 19, respectively. The error bars on the data represent the standard deviation of the sample set. It is important to note that the wear rate and modified wear factor (k^*) are proportional to one another. The modified wear factor simply takes into account the stress of loading as a means of comparison between laboratories.

Examination of the average wear rates and factors reveals that the unmodified, compression-molded (C-CM) polyethylene demonstrated the best wear resistance under the current test conditions. In fact, the C-CM material exhibited an average 50% decrease in wear rate as compared to the unmodified, ram-extruded material (C-RE). The UV-irradiated material (150 J/cm^2) also demonstrated a decreased average wear rate. The UV irradiated, compression-molded material (UV150-CM) and UV irradiated, ram-extruded material (UV150-RE) exhibited average 27% and 20% decreases in wear rate, respectively, as compared to the C-RE material. Under these test conditions, the 7.5 Mrad gamma-irradiated material (G-RE) and the lower UV dose material (UV100-RE) exhibited wear rates similar to the C-RE material.

However, a statistical analysis of variation (ANOVA) revealed that the standard deviation in the majority of the material sets is large enough to result in statistically insignificant differences in average wear rates and factors ($p > 0.05$). The only statistically significant differences in wear resistance were between the C-CM material and the UV150-CM material ($p = 0.03$), the G-RE material ($p = 0.03$), and the UV100-RE material ($p = 0.02$).

From the results of these wear tests, it appears that UV irradiation of compression molded polyethylene results in a higher wear rate. However, this conclusion might not be warranted. In the case of all the UV irradiated samples, with the exception of the UV150-CM samples, wear tests were performed within 7-10 days after irradiation. In contrast, wear tests on the UV150-CM samples were performed approximately three months following irradiation due to time constraints. Therefore, it is possible that the increased wear rate demonstrated by the UV150-CM material group is a result of this extended time between irradiation and testing when oxidation and degradation could have occurred.

The large standard deviation in the wear data is primarily due to the relatively small amount of wear that occurred with the polyethylene and the resultant difficulty in measuring this wear. UHMWPE has been used in orthopaedic devices for the last 20+ years because of its tremendous wear resistance. Therefore, a balance must be attained

between performing wear tests for a reasonable amount of time and producing a consistently measurable amount of wear. In this study, testing of one sample at a time was a major disadvantage in the time required per test. Due to these time limitations, tests were run for the minimum amount of time required to produce a visible amount of wear when evaluated by profilometry. Furthermore, the use of profilometry as a means of wear quantification requires the experimenter to determine the location and width of the wear track within the profile. This task was made difficult in most cases due to the lack of consistent, identifiable wear tracks within the wear test time and parameters. As a result, the quantification of wear was too dependent upon the evaluator's discretion to determine the location and width of the wear track within the profile. It is believed that this resulted in inconsistent results and the large spread in data evidenced by the standard deviation.

Finally, it is important to note that the range of wear factors (Appendix D) calculated for the variety of materials tested on the UT pin-on-disk machine ($10^{-7} < k < 10^{-8}$) are within the range of wear factors reported in the literature (Section 3.5). In fact, the range of wear factors determined through the current testing protocol falls in the middle of the range predicted by the equations discussed in Section 3.2.4 for an average counterface roughness (R_a) of 0.03 μm . Therefore, the UT pin-on-disk test apparatus appears to produce wear factors for polyethylene similar to those reported in the literature.

6.2 Infrared Spectroscopy

The average oxidation indices (OI) for all material sets before irradiation, post-irradiation and post-storage are presented in Figure 20. In general, it is evident that the average oxidation indices decreased slightly after irradiation. It is suspected that the decrease in average oxidation indices after irradiation was a result of the UV/polymer interaction at the surface of the samples. In addition, an analysis of variance shows that all oxidation indices increased by statistically significant amounts after storage in air ($p < 0.01$). For the UV irradiated samples, this oxidation was expected since the samples were not annealed following irradiation and they were shelf-aged in air. However, the increases in average OI for the unmodified (C-RE and C-CM) and the gamma-irradiated and annealed (G-RE) samples were surprising. Recent studies have shown increased variation in average OI measurements for materials with low levels of oxidation.^{132,133} This increased variation might explain the larger error bars (standard deviations) on these materials but would not necessarily explain the relatively large increases in OI after storage. While the average post-storage oxidation indices were relatively low, it would be expected that these values would continue to increase with further shelf-aging.

7. Conclusions

The UHMWPE materials tested include conventional, unmodified, ram extruded (C-RE); gamma-irradiated (7.5 Mrads), ram extruded (G-RE); UV irradiated (100 J/cm²), ram extruded (UV100-RE); UV irradiated (150 J/cm²), ram extruded (UV150-RE); conventional, unmodified, compression molded (C-CM); and UV irradiated (150 J/cm²), compression molded (UV150-RE). The UV irradiated material sets were exposed to UV radiation ($\lambda=248$ nm) at various doses to induce crosslinking within the polymer. The unmodified, conventional compression-molded polyethylene (C-CM) material set demonstrated the lowest average wear rate and modified wear factor under these test conditions. However, the only statistically significant differences in wear rates and modified wear factors were between the C-CM material and the UV150-CM material, the G-RE material, and the UV100-RE material. The large standard deviation in the wear data is primarily due to the relatively small amount of wear that occurs with polyethylene and the resultant difficulty in measuring this wear. Using profilometry as a means of wear quantification exacerbated this problem. With this method, the wear analysis was too dependent on the evaluator's judgment as to the location and width of the wear track. Despite the large standard deviations within the material sets, the UT pin-on-disk test apparatus appears to produce wear factors for polyethylene similar to those reported in the literature thereby validating the test apparatus.

The oxidation index, as determined by FTIR, appeared to decrease immediately following irradiation. Furthermore, the oxidation index increased in all material sets after a minimum of 1 year of shelf-storage. Finally, it is important to note that the range of wear factors calculated for the variety of materials tested on the UT pin-on-disk machine are within the range of wear factors reported in the literature.

8. Future Work

A large range of work remains to be investigated in this area of polyethylene modification. In the future, this evaluation might be greatly enhanced through the use of an alternative form of wear quantification or an improved profilometry technique. With the current methodology, the signal-to-noise ratio is too low and the differences between material groups are statistically insignificant. In addition to the resolution problems encountered using profilometry, there is also the difficulty in separating wear from the viscoelastic response (creep) of the polymer. If profilometry is used, the viscoelastic response of each material set should be characterized so that the amount of material removed through wear might be determined. Performing wear tests for greater lengths of time or altering other variables in order to produce a greater amount of wear might also greatly improve the signal-to-noise ratio and assist the evaluator in identifying the location and width of the wear track in the profiles. Finally, automation of the wear evaluation calculations through the use of software such as Matlab® would also simplify this evaluation process and should provide more accurate results.

Furthermore, the typical penetration depth of UV radiation needs to be determined both through analytical techniques as well as through calculation. The determination of penetration depth would provide more insight into the efficacy of UV irradiation of polyethylene. In future studies, it would be useful to anneal the UV irradiated samples as well as artificially age them in order to examine long-term oxidation. Finally, it is recommended that, if possible, all future FTIR spectra be collected in the transmission mode from microtomed samples as opposed to the attenuated total reflectance (ATR) mode from bulk samples. It is believed that this would greatly increase the signal-to-noise ratio of the spectra and provide more statistically significant information on both oxidation and crystallinity changes within the material sets.

LIST OF REFERENCES

1. Willert, H.G.; and Buchhorn, G.H. "Particle Disease Due to Wear of Ultrahigh Molecular Weight Polyethylene" in Biological, Material, and Mechanical Considerations of Joint Replacement. B.F. Morrey, Ed., New York: Raven Press, 1993. ISBN: 0-7817-0008-6
2. Amstutz, H.C.; Campbell, P.; Kossovsky, N.; and Clarke, I.C. "Mechanism and Clinical Significance of Wear Debris-Induced Osteolysis." Clinical Orthopaedics and Related Research 276:7-18; 1992.
3. Kurtz, S.M.; Muratoglu, O.K.; Evans, M.; Edidin, A.A. "Advances in the processing, sterilization, and crosslinking of ultra-high molecular weight polyethylene for total joint arthroplasty." *Biomaterials*, Sep 1999; 20(18):1659-1688. ISSN: 0142-9612
4. Lewis, G. "Polyethylene wear in total hip and knee arthroplasties." *J Biomed Mater Res*, Spring 1997; 38(1):55-75. ISSN: 0021-9304
5. Schmalzried, T.P.; Kwong, L.M.; Jasty, M.; et al. "The mechanism of loosening of cemented acetabular components in total hip arthroplasty." *Clin Orthop*, 1992; 274:60-78. ISSN: 0009-921X
6. Xenos, J.S.; Hopkinson, W.J.; Callaghan, J.J.; Heekin, R.D.; and Savory, C.G. "Osteolysis around an uncemented cobalt chrome total hip arthroplasty." *Clin Orthop*, 1995; 317:29-36. ISSN: 0009-921X
7. Livingston, B.J.; Chmell, M.J.; Spector, M.; and Poss, R. "Complications of total hip arthroplasty associated with the use of an acetabular component with a Hylamer liner." *J Bone Joint Surg*, Oct 1997; 79A(10):1529-1538.
8. Grobbelaar, C.J.; Du Plessis, T.A.; and Marais, F. "The radiation improvement of polyethylene prostheses." *J Bone Joint Surg*, Aug 1978; 60B(3):370-374. ISSN: 0301-620X
9. Hollis, B.K.T. "Analysis of the Wear Behavior of VUV Radiated Ultrahigh Molecular Weight Polyethylene." July, 1999. University of Tennessee, Knoxville, TN.
10. Ohan, F. "Investigation of the Effect of Vacuum Ultraviolet Irradiation on Surface Properties." August, 2000. University of Tennessee, Knoxville, TN.
11. Taber's Cyclopedic Medical Dictionary, Ed. C.L. Thomas, Philadelphia: F.A. Davis Company, 1997. ISBN: 0-8036-0194-8
12. "Future demand for orthopaedic skills to soar," The American Academy of Orthopaedic Surgeons Bulletin. Jun 1999; 47:3
13. "Arthritis," *Microsoft® Encarta® Encyclopedia 2000*. © 1993-1999 Microsoft Corporation.
14. Lichtenstein, L. Diseases of Bone and Joints. 2nd Ed., St. Louis: C.V. Mosby Company, 1975. ISBN: 0-8016-3007-X
15. "Osteoarthritis," *Microsoft® Encarta® Encyclopedia 2000*. © 1993-1999 Microsoft Corporation.
16. Li, S. "Polyethylene," in The Adult Hip, Vol. 1, J.J. Callaghan, A.G. Rosenberg, and H.E. Rubash, Eds., Philadelphia: Lippincott-Raven Publishers, 1998. ISBN: 0-397-51704-1
17. Waugh, W. John Charnley, the man and the hip. New York: Springer-Verlag, 1990.

18. Jasty, M.; Bragdon, C.; Lee, K.; Hanson, A.; and Harris, W.H. "Wear of Polyethylene in Total Joint Arthroplasty" in Biological, Material, and Mechanical Considerations of Joint Replacement. Ed. B.F. Morrey. New York: Raven Press, 1993. ISBN: 0-7817-0008-6
19. Huiskes, R.; and Verdonchot, N. "Biomechanics of Artificial Joints: The Hip" in Basic Orthopaedic Biomechanics, 2nd Ed., V.C. Mow and W.C. Hayes, Eds., Lippincott-Raven Publishers, Philadelphia, 1997.
20. Bisson, E.E., "Various Modes of Wear and Their Controlling Factors" in Evaluation of Wear Testing, ASTM STP 446, American Society for Testing and Materials, Union City, NJ, 1969.
21. Czichos, H. Tribology. Amsterdam: Elsevier Scientific Publishing Co., 1978. ISBN: 0-444-41676-5
22. Dowson, D., History of Tribology, 2nd Ed. London: Professional Engineering Publishing, 1998. ISBN: 1-86058-070X
23. Barwell, F.T., "Friction and Wear, Detection and Measurement" in Lubrication and Wear in Living and Artificial Human Joints, The Institution of Mechanical Engineers, Proceedings 1966-67, Vol. 181, Part 3J, Westminster, London, 1967.
24. Salomon, G. and Gee, A.W.J., "Wear Research in Europe" in Evaluation of Wear Testing, ASTM STP 446, American Society for Testing and Materials, Union City, NJ, 1969.
25. Kjeldsberg, C.R.; and Knight, J.A. Body Fluids, 3rd Ed. Chicago: American Society of Clinical Pathologists, 1993. ISBN: 0-89189-344-X
26. McKellop, H.A.; and Clarke, I.C. "Evolution and Evaluation of Materials-Screening Machines and Joint Simulators in predicting *In Vivo* Wear Phenomena" in Functional Behavior of Orthopedic Biomaterials, Vol. 2, Paul Ducheyne and Garth W. Hastings, Eds., CRC Press, Boca Raton, FL, 1984.
27. McKellop, H. "Wear of artificial joint materials II – Twelve-channel wear-screening device: Correlation of experimental and clinical results." *J Eng Med, Proc Inst Mech Eng [H]*, 1981; 10(3):123-136. ISSN: 0046-2039
28. ASTM G99-95a. Annual Book of ASTM Standards, American Society for Testing of Materials,
29. McKellop, H.A.; Shen, F.W.; Bin, L.; Campbell, P.; and Salovey, R. "Development of an extremely wear-resistant ultra high molecular weight polyethylene for total hip replacements." *J Orthop Res*, Mar 1999; 17(2):157-167.
30. Walker, P.S.; Blunn, G.W.; and Lilley, P.A. "Wear testing of materials and surfaces for total knee replacement." *J Biomed Mater Res*, Fall 1996; 33(3):159-175. ISSN: 0021-9304
31. Rose, R.M.; Crugnola, A.; Ries, M.; Cimino, W.R.; Paul, I.; and Radin, E.L. "On the origins of high in vivo wear rates in polyethylene components of total joint prostheses." *Clin Orthop*, Nov-Dec 1979; (145):277-286. ISSN: 0009-921X
32. Hailey, J.L.; Ingham, E.; Stone, M.; Wroblewski, B.M.; and Fisher, J. "Ultra-high molecular weight polyethylene wear debris generated in vivo and in laboratory tests; the influence of counterface roughness." *J Eng Med, Proc Inst Mech Eng [H]*, 1996; 210(H1):3-10. ISSN: 0954-4119

33. Wang, A.; Essner, A.; Stark, C.; and Dumbleton, J.H. "Comparison of the size and morphology of UHMWPE wear debris produced by a hip joint simulator under serum and water lubricated conditions." *Biomaterials*, 1995; 17(9):865-871. ISSN: 0142-9612
34. Rose, R.M.; Nusbaum, H.J.; Schneider, H.; Ries, M.; Paul, I.; Crugnola, A.; Simon, S.R.; and Radin, E.L. "On the true wear rate of ultra high-molecular-weight polyethylene in the total hip prosthesis." *J Bone Joint Surg*, June 1980; 62A(4):537-549.
35. Wang, A.; Sun, D.C.; Yau, S.S.; Edwards, B.; Sokol, M.; Essner, A.; Polineni, V.K.; Stark, C.; and Dumbleton, J.H. "Orientation softening in the deformation and wear of ultra-high molecular weight polyethylene." *Wear*, 1997; 203-204(2):230-241. ISSN: 0043-1648
36. Niedzwiecki, S.; Klapperich, C.; Short, J.; Jani, S.; Ries, M.; and Pruitt, L. "Comparison of three joint simulator wear debris isolation techniques: Acid digestion, base digestion, and enzyme cleavage." *J Biomed Mater Res*, 2001; 56(2):245-9.
37. Campbell, P.; Ma, S.; Yeom, B.; McKellop, H.; Schmalzried, T.P.; and Amstutz, H.C. "Isolation of predominantly submicron-sized UHMWPE wear particles from periprosthetic tissues." *J Biomed Mater Res*, Jan 1995; 29(1):127-131. ISSN:0021-9304
38. Campbell, P.; Doorn, P.; Dorey, F.; and Amstutz, H.C. "Wear and morphology of ultra-high molecular weight polyethylene wear particles from total hip replacements." *Proceedings of the Institution of Mechanical Engineers. Part H. J Eng Med* 1996, 210: 167-174.
39. Schmalzried, T.P.; Campbell, P.; Schmitt, A.; Brown, I.; and Amstutz, H. "Shapes and dimensional characteristics of polyethylene wear particles generated *in vivo* by total knee replacements compared to total hip replacements." *J Biomed Mater Res* 1997;36: 203-210.
40. Dumbleton, J.H. Tribology of Natural and Artificial Joints, Tribology Series, Vol. 3. Amsterdam: Elsevier Scientific Publishing Company, 1981. ISBN: 0-444-418989
41. Walker, P.S.; and Erkman, M.J. "Metal on metal lubrication in artificial human joints." *Wear*, 1972; 21:377-392
42. Walker, P.S. "A comparison of normal and artificial human joints." *Acta Orthop Belg*, 1973; 39(Suppl 1):43-54.
43. Wright, K.W.J. "Friction and wear of materials and joint replacement," in Biocompatibility of Orthopaedic Implants. Vol I, D. Williams, Ed., Boca Raton, FL: CRC Press, 1982; 141-195.
44. McKellop, H.A. "Wear Assessment," in The Adult Hip, Vol. 1, J.J. Callaghan, A.G. Rosenberg, and H.E. Rubash, Eds., Philadelphia: Lippincott-Raven Publishers, 1998. ISBN: 0-397-51704-1
45. Simon, S.R.; Paul, I.L.; Rose, R.M.; and Radin, E.L. "'Stiction-friction' of total hip prostheses and its relationship to loosening." *J Bone Joint Surg*, 1975; 57A(2):226-230. ISSN: 0021-9355

46. Simon, S.R.; and Radin, E.L. "Lubrication and wear of the Charnley, Charnley-Muller, and McKee-Farrar prostheses with special regard to their clinical behavior," in The Hip, St. Louis: C.V. Mosby Co., 1973;33-45. ISBN: 0-8016-0019-7
47. McKellop, H.A.; Clarke, I.; Markolf, K.; and Amstutz, H. "Wear characteristics of UHMW polyethylene: A method for accurately measuring extremely low wear rates." *J Biomed Mater Res*, 1978; 12:895-927. ISSN: 0021-9304
48. Cooper, J.R.; Dowson, D.; and Fisher, J. "The effect of transfer film and surface roughness on the wear of lubricated ultra-high molecular weight polyethylene." *Clin Mater*, 1993; 14:295-302. ISSN: 0267-6605
49. Wang, A.; Essner, A.; Stark, C.; and Dumbleton, J.H. "Comparison of the size and morphology of UHMWPE wear debris produced by a hip joint simulator under serum and water lubricated conditions." *Biomaterials*, 1995; 17(9):865-871. ISSN: 0142-9612
50. Saikko, V.; Ahlroos, T. "Wear simulation of UHMWPE for total hip replacement with a multidirectional motion pin-on-disk device: Effects of counterface material, contact area, and lubricant." *J Biomed Mater Res*, Feb 2000; 49(2):147-154. ISSN: 0021-9304
51. Saikko, V.; Ahlroos, T. "Type of motion and lubricant in wear simulation of polyethylene acetabular cup." *Proc Inst Mech Eng [H]*, 1999; 213(4):301-310.
52. Wang, A.; Essner, A.; Stark, C.; and Dumbleton, J.H. "Comparison of the size and morphology of UHMWPE wear debris produced by a hip joint simulator under serum and water lubricated conditions." *Biomaterials*, 1995; 17(9):865-871. ISSN: 0142-9612
53. McKellop, H.A.; Clarke, I.C.; Markolf, K.L.; and Amstutz, H.C. "Polyethylene wear in prosthetic joints," in Evaluation of Artificial Joints, V. Wright and D. Dowson, Eds. London: F.S. Moore Ltd., 1977. ISBN: 0-904716-06-6
54. Besong, A.A.; Tipper, J.L.; Mathews, B.J.; Stone, M.H.; and Fisher, J. "The influence of lubricant on the morphology of ultra-high molecular weight polyethylene wear debris generated in laboratory tests." *J Eng Med, Proc Inst Mech Eng [H]*, 1999; 213(2):155-158. ISSN: 0954-4119
55. Liao, Y.S.; Benya, P.D.; Lu, B.; and McKellop, H. "Stability of serum as a lubricant in wear simulator tests of prosthetic joints," in *Transactions of the Fifth World Biomaterials Congress*, Vol. 1, May 29-June 2, 1996; Toronto, Canada, p. 871.
56. Walker, P.S.; and Erkman, M.J. "Metal on metal lubrication in artificial human joints." *Wear*, 1972; 21:377-392. ISSN: 0043-1648
57. Weightman, B.; Simon, S.; Paul, I.; Rose, R.; and Radin, E. "Lubrication mechanism of hip joint replacement prostheses," in *Trans ASME, J Lub Tech*, 1972; 94:131-135.
58. McKellop, H.A.; Campbell, P.; Park, S.H.; "The origin of submicron polyethylene wear debris in total hip arthroplasty." *Clin Orthop*, 1995; 311:3-20. ISSN: 0009-921X
59. Wang, A.; Polineni, V.K.; Essner, A.; Stark, C.; and Dumbleton, J.H. "The impact of lubricant protein concentration on the outcome of hip joint simulator wear testing," in *Transactions of the 25th Annual Meeting of Soc. For Biomaterials*, April 28-May 2, 1999; Providence, RI, p. 178.

60. Saari, H. *J Rheum*, 1993; 20(1):87.
61. Weightman, B.; and Light, D. "The effect of surface finish of alumina and stainless steel on the wear rate of UHMW polyethylene." *Biomaterials*, Jan 1986; 7:20-24. ISSN: 0142-9612
62. Fisher, J; Dowson, D.; Hamdzah, H.; and Lee, H.L. "The effect of sliding velocity on the friction and wear of UHMWPE for use in total artificial joints." *Wear*, 1994; 175(1):219-225. ISSN: 0043-1648
63. Lancaster, J.G.; Dowson, D.; and Fisher, J. "The influence of femoral material, manufacturing technique and surface topography on the wear of UHMWPE in total joint replacement," in *Transactions of the Fifth World Biomaterials Congress*, Vol. 1, May 29-June 2, 1996; Toronto, Canada, p. 581.
64. Que, L.; and Topoleski, L.D.T. "Effect of CoCrMo surface roughness on the wear of UHMWPE/alloy bearing couple," in *Transactions of the 24th Annual Meeting of Soc. For Biomaterials*, April 22-26, 1998; San Diego, CA, p. 446.
65. Dowson, D.; Diab, M.M.; Gillis, B.J.; and Atkinson, J.R. "Influence of counterface topography on the wear of UHMWPE under wet and dry conditions." *Polym Prepr Am Chem Soc Div Polym Chem*, 1985; 287:171.
66. Dowson, D.; Taheri, S.; and Wallbridge, N.C. "The role of counterface imperfections in the wear of polyethylene." *Wear*, 1987; 119:277-293. ISSN: 0043-1648
67. Essner, A.; Polineni, V.K.; Wang, A.; Stark, C.; and Dumbleton, J.H. "Effect of femoral head surface roughness and crosslinking on the wear of UHMWPE acetabular inserts," in *Transactions of the 24th Annual Meeting of Soc. For Biomaterials*, April 22-26, 1998; San Diego, CA, p. 4.
68. Wang, A.; Polineni, V.K.; Stark, C.; and Dumbleton, J.H. "Effect of femoral head surface roughness on the wear of ultrahigh molecular weight polyethylene acetabular cups." *J Arthroplasty*, Sep 1998; 13(6):615-620. ISSN: 0883-5403
69. Dumbleton, J.H. Tribology of Natural and Artificial Joints, Tribology Series, Vol. 3. Amsterdam: Elsevier Scientific Publishing Company, 1981. ISBN: 0-444-418989
70. Muratoglu, O.K.; Bragdon, C.R.; O'Connor, D.O.; Jasty, M.; Harris, W.H.; Gul, R.; and McGarry, F. "Unified wear model for highly crosslinked ultra-high molecular weight polyethylenes (UHMWPE)." *Biomaterials*, 1999; 20(16):1463-1470. ISSN: 0142-9612
71. Rose, R.M.; Nusbaum, H.J.; Schneider, H.; Ries, M.; Paul, I.; Crugnola, A.; Simon, S.R.; and Radin, E.L. "On the true wear rate of ultra high-molecular-weight polyethylene in the total hip prosthesis." *J Bone Joint Surg*, June 1980; 62A(4):537-549.
72. Wang, A.; Sun, D.C.; Stark, C.; and Dumbleton, J.H. "Effects of sterilization methods on the wear of ultra-high molecular weight polyethylene acetabular cups," in *Transactions of the Fifth World Biomaterials Congress*, Vol. 2, May 29-June 2, 1996; Toronto, Canada, p. 198.
73. Nusbaum, H.J.; and Rose, R.M. "The effects of radiation sterilization on the properties of ultrahigh molecular weight polyethylene." *J Biomed Mater Res*, Jul 1979; 13(4):557-576. ISSN:0021-9304

74. Costa, L.; Luda, M.P.; Trossarelli, L.; Brach del Prever, E.M.; Crova, M.; and Gallinaro, P. "Oxidation in orthopaedic UHMWPE sterilized by gamma-radiation and ethylene oxide." *Biomaterials*, 1998, 19:659-668. ISSN: 0142-9612
75. McGinniss, V.D. "Cross-linking with radiation," in Encyclopedia of Polymer Science and Engineering, Vol. 4, New York, NY: John Wiley and Sons, Inc., 1986; 418-449.
76. Gsell, R.A.; Lee, K.; Chu, C.; and Lin, S. "Minimizing oxidative degradation on gamma sterilization," in *Transactions of the Fifth World Biomaterials Congress*, Vol. 2, May 29-June 2, 1996; Toronto, Canada, p. 191.
77. Flynn, M.A.; Greer, K.W.; Hamilton, J.V.; and Treacy, D.J. "Correlation between oxidation, crystallinity and density of shelf-aged UHMWPE implants," in *Transactions of the Fifth World Biomaterials Congress*, Vol. 2, May 29-June 2, 1996; Toronto, Canada, p. 187.
78. Trieu, H.H.; Haggard, W.O.; Conta, R.L.; and Parr, J.E. "Investigation of free radicals in shelf-aged polyethylene tibial components," in *Transactions of the Fifth World Biomaterials Congress*, Vol. 2, May 29-June 2, 1996; Toronto, Canada, p. 298.
79. Streicher, R.M. "Ionizing irradiation for sterilization and modification of high molecular weight polyethylenes." *Plast Rub Process Appl*, 1988; 10:221-229. ISSN: 0144-6045
80. Streicher, R.M. "Sterilization and long-term aging of medical-grade UHMWPE." *Radiat Phys Chem*, 1995; 46(4-6):893-896. ISSN: 0969-806X
81. Premnath, V.; Harris, W.H.; Jasty, M.; and Merrill, E.W. "Gamma sterilization of UHMWPE articular implants: an analysis of the oxidation problem." *Biomaterials*, Sep 1996; 17(18):1741-1753. ISSN: 0142-9612
82. Boehm, G.G.A. "Diffusion theory of the post-irradiation oxidation of polyethylene." *J Poly Sci*, 1960; 5(A2):639-652.
83. Roe, R.J.; Grood, E.S.; Shastri, R.; Gosselin, C.A.; and Noyes, F.R. "Effect of radiation sterilization and aging on UHMWPE." *J Biomed Mater Res*, 1981; 13():209-230. ISSN:0021-9304
84. Goldman, M.; Lee, M.; Gronsky, R.; and Pruitt, L. "Oxidation of ultrahigh molecular weight polyethylene characterized by fourier transform infrared spectrometry." *J Biomed Mater Res*, Oct 1997; 37(1):43-50. ISSN: 0021-9304
85. Muratoglu, O.K.; Bragdon, C.R.; Elder, J.R.; Jasty, M.; and Harris, W.H. "In vivo advancement of oxidation front in ultra-high-molecular-weight-polyethylene components," in *Transactions of the Fifth World Biomaterials Congress*, Vol. 2, May 29-June 2, 1996; Toronto, Canada, p. 519.
86. Muratoglu, O.K.; Bragdon, C.R.; Jasty, M.; and Harris, W.H. "An oxidation mechanism in γ -sterilized ultra-high-molecular-weight-polyethylene components," in *Transactions of the Fifth World Biomaterials Congress*, Vol. 2, May 29-June 2, 1996; Toronto, Canada, p. 192.
87. Goldman, M.; Lee, M.; Pruitt, L.; and Gronsky, R. "A comparison of sterilization techniques on the structure and morphology of medical grade UHMWPE," in *Transactions of the Fifth World Biomaterials Congress*, Vol. 2, May 29-June 2, 1996; Toronto, Canada, p. 189.

88. McKellop, H.; Shen, F.W.; Ye, E.; and Lu, B. "Comparison of long-term oxidation of conventional and hylamer UHMWPE," in *Transactions of the 24th Annual Meeting of Soc. For Biomaterials*, April 22-26, 1998; San Diego, CA, p. 127.
89. Sun, D.C.; Yau, S.S.; Stark, C.; and Dumbleton, J.H. "The location of the oxidation maximum in relation to the post-radiation history of UHMWPE implants," in *Transactions of the Fifth World Biomaterials Congress*, Vol. 1, May 29-June 2, 1996; Toronto, Canada, p. 297.
90. Sun, D.C.; Yau, S.S.; Wada, M.; Stark, C.; and Dumbleton, J.H. "Analysis of double white bands observed in a clinically retrieved UHMWPE implant," in *Transactions of the 25th Annual Meeting of Soc. For Biomaterials*, April 28-May 2, 1999; Providence, RI, p. 518.
91. Farber, K.B.; and Collier, J.P. "Oil red O staining: Determining oxidation of ultra high molecular weight polyethylene," in *Transactions of the Fifth World Biomaterials Congress*, Vol. 1, May 29-June 2, 1996; Toronto, Canada, p. 294.
92. Jahan, M.S.; Stovall, J.C.; Thomas, D.E.; and Buncick, M.C. "White band and free radicals in gamma-sterilized UHMWPE," in *Transactions of the 24th Annual Meeting of Soc. For Biomaterials*, April 22-26, 1998; San Diego, CA, p. 156.
93. Jahan, M.S.; and McKinny, K.S. "Radiation-sterilization and subsequent oxidation of medical grade polyethylene: an ESR study." *Nuclear Instruments and Methods in Physics Res*, 1999; B 151:207-212. ISSN: 0168-583X
94. Fisher, J.; Chan, K.L.; Hailey, J.L.; Shaw, D.; and Stone, M. "Preliminary study of the effect of aging following irradiation on the wear of ultrahigh-molecular-weight polyethylene." *J Arthroplasty*, Oct 1995; 10(5):689-692.
95. Gsell, R.; and Lin, S. "Improved resistance to oxidation degradation of 1900H net-shape compression molded components," in *Transactions of the 24th Annual Meeting of Soc. For Biomaterials*, April 22-26, 1998; San Diego, CA, p. 123.
96. Afflitto, R.M.; Poggie, R.A.; Cohen, R.C.; and Averill, R.G. "Comparison of the resistance to oxidation of three types of polyethylene," in *Transactions of the 24th Annual Meeting of Soc. For Biomaterials*, April 22-26, 1998; San Diego, CA, p. 157.
97. Bell, C.J.; Walker, P.S.; Abeysundera, M.R.; Simmons, J.M.; King, P.M.; and Blunn, G.W. "Effect of oxidation on delamination of ultrahigh-molecular-weight polyethylene tibial components." *J Arthroplasty*, Apr 1998; 13(3):280-290. ISSN: 0883-5403
98. Shen, F.W.; McKellop, H.; and Salovey, R. "Improving the resistance to wear and oxidation of acetabular cups of UHMWPE by gamma radiation crosslinking and remelting," in *Transactions of the 24th Annual Meeting of Soc. For Biomaterials*, April 22-26, 1998; San Diego, CA, p. 3.
99. Bragdon, C.R.; O'Connor, D.O.; Muratoglu, O.K.; Jasty, M.; Ramamurti, B.; Merrill, E.; and Harris, W. "A new polyethylene with undetectable wear at 12 million cycles," in *Transactions of the 24th Annual Meeting of Soc. For Biomaterials*, April 22-26, 1998; San Diego, CA, p. 2.
100. Charnley, J.; and Halley, D.K. "Rate of wear in total hip replacement." *Clin Orthop*, 1975; 112:170-179. ISSN: 0009-921X

101. Wroblewski, B.M.; Siney, P.D.; Dowson, D.; and Collins, S.N. "Prospective clinical and joint simulator studies of a new total hip arthroplasty using alumina ceramic heads and cross-linked polyethylene cups." *J Bone Joint Surg*, 1996; 78B:280-285. ISSN: 0301-620X
102. Hernandez, J.R.; Keating, E.M.; Faris, P.M.; Meding, J.B.; and Ritter, M.A. "Polyethylene wear in uncemented acetabular components." *J Bone Joint Surg*, Mar 1994; 76B(2):263-266. ISSN: 0301-620X
103. Cates, H.E.; Faris, P.M.; Keating, E.M.; and Ritter, M.A. "Polyethylene wear in cemented metal-backed acetabular cups." *J Bone Joint Surg*, Mar 1993; 75B(2):249-253. ISSN: 0301-620X
104. Griffith, M.; Seidenstein, M.; Williams, D.; and Charnley, J. "Eight-year results of Charnley arthroplasties of the hip with special reference to the behavior of cement." *Clin Orthop*, 1978; (137):24-36. ISSN: 0009-921X
105. McKellop, H.A.; Clarke, I.; Markolf, K.; and Amstutz, H. "Friction and wear properties of polymer, metal, and ceramic prosthetic joint materials evaluated on a multichannel screening device." *J Biomed Mater Res*, 1981; 15:619-653. ISSN: 0021-9304
106. Isaac, G.H.; Wroblewski, B.M.; Atkinson, J.R.; and Dowson, D. "A tribological study of retrieved hip prostheses." *Clin Orthop*, 1992; 276:115. ISSN: 0009-921X
107. Dowling, J.M. "Wear analysis of retrieved prostheses," in Biocompatible Polymers, Metals, and Composites, M. Szycher Ed., Lancaster, PA: Technomic Publishing Co., 1983. ISBN: 87762-323-6
108. James, S.P.; Lee, K.R.; Beauregard, G.P.; Rentfrow, E.D.; and McLaughlin, J.R. "Clinical wear of 63 ultrahigh molecular weight polyethylene acetabular components: Effect of starting resin and forming method." *J Biomed Mater Res*, 1999; 48(3):374-384. ISSN: 0021-9304
109. Atkinson, J.R.; Dowson, D.; Isaac, G.H.; and Wroblewski, B.M. "Laboratory wear tests and clinical observations of the penetration of femoral heads into acetabular cups in total replacement hip joints III: The measurement of internal volume changes in explanted Charnley sockets after 2-16 years *in vivo* and the determination of wear factors." *Wear*, 1985; 104(3):225-244. ISSN: 0043-1648
110. Campbell, P.; Dorey, F.; and Amstutz, H.C. "Wear and morphology of ultra-high molecular weight polyethylene wear particles from total hip replacements." *J Eng Med, Proc Inst Mech Eng [H]*, 1996; 210(H3):167-174. ISSN: 0954-4119
111. Maloney, W.J.; Smith, R.L.; Schmalzried, T.P.; Chiba, J.; Huene, D.; and Rubash, H. "Isolation and characterization of wear particles generated in patients who have had failure of a hip arthroplasty without cement." *J Bone Joint Surg*, Sep 1995; 77A(9):1301-1310. ISSN: 0021-9355
112. Margevicius, K.J.; Bauer, T.W.; McMahon, J.T.; Brown, S.A.; and Merritt, K. "Isolation and characterization of debris in membranes around total joint prostheses." *J Bone Joint Surg*, Nov 1994; 76A(11):1664-1675. ISSN: 0021-9355
113. Hirakawa, K.; Bauer, T.W.; Stulberg, B.N.; Wilde, A.H.; and Secic, M. "Characterization and comparison of wear debris from failed total hip implants of different types." *J Bone Joint Surg*, Aug 1996; 78A(8):1235-1243. ISSN: 0021-9355

114. Shanbhag, A.S.; Jacobs, J.J.; Glant, T.T.; Gilbert, J.L.; Black, J.; and Galante, J.O. "Composition and morphology of wear debris in failed uncemented total hip replacement." *J Bone Joint Surg*, Jan 1994; 76B(1):60-67. ISSN: 0301-620X
115. Shanbhag, A.S.; Bailey, H.O.; Hwang, D.S.; Cha, C.W.; Eror, N.G.; and Rubash, H.E. "Quantitative analysis of ultrahigh molecular weight polyethylene (UHMWPE) wear debris associated with total knee replacements." *J Biomed Mater Res*, 2000; 53(1):100-110. ISSN: 0021-9304
116. Hirakawa, K.; Bauer, T.W.; Stulberg, B.N.; Wilde, A.H.; and Secic, M. "Characterization and comparison of wear debris from failed total hip implants of different types." *J Bone Joint Surg*, Aug 1996; 78A(8):1235-1243. ISSN: 0021-9355
117. Besong, A.A.; Hailey, J.L.; Ingham, E.; Stone, M.; Wroblewski, B.M.; and Fisher, J. "A study of the combined effects of shelf ageing following irradiation in air and counterface roughness on the wear of UHMWPE." *Biomed Mat Eng*, 1997; 7(1):59-65.
118. McKellop, H.A.; Shen, F.W.; Campbell, P.; and Ota, T. "Effect of molecular weight, calcium stearate, and sterilization methods on the wear of ultra high molecular weight polyethylene acetabular cups in a hip joint simulator." *J Orthop Res*, May 1999; 17(3):329-339.
119. Edidin, A.A.; Pruitt, L.; and Jewett, C.W.; Crane, D.J.; Roberts, D.; and Kurtz, S.M. "Plasticity-induced damage layer is a precursor to wear in radiation-cross-linked UHMWPE acetabular components for total hip replacement." *J Arthroplasty*, 1999; 14(5):616-627. ISSN: 0883-5403
120. Edidin, A.A.; Jewett, C.W.; Foulds, J.R.; and Kurtz, S.M. "Direct correlation of abrasive wear resistance of irradiation-crosslinked UHMWPE cups with large-deformation mechanical behavior determined at the articulating surface," in *Transactions of the 24th Annual Meeting of Soc. For Biomaterials*, April 22-26, 1998; San Diego, CA, p. 220.
121. Choudhury, M.; and Hutchings, I.M. "The effects of irradiation and ageing on the abrasive wear resistance of ultra high molecular weight polyethylene." *Wear*, 1997; 203-204:335-340. ISSN: 0043-1648
122. Burroughs, B.R.; and Blanchet, T.A. "Enhanced wear of irradiation sterilized UHMWPE via post-irradiation storage," in *Transactions of the 25th Annual Meeting of Soc. For Biomaterials*, April 28-May 2, 1999; Providence, RI, p. 521.
123. Mosleh, M.; Eisenberg, J.; and Suh, N.P. "Influence of sterilization technique on wear of polyethylene," in *Transactions of the Fifth World Biomaterials Congress*, Vol. 2, May 29-June 2, 1996; Toronto, Canada, p. 185.
124. Fisher, J.; Reeves, E.A.; Isaac, G.H.; Saum, K.A.; and Sanford, W.M. "Comparison of the wear of aged and non-aged ultrahigh molecular weight polyethylene sterilised by gamma irradiation and by gas plasma," in *Transactions of the Fifth World Biomaterials Congress*, Vol. 1, May 29-June 2, 1996; Toronto, Canada, p. 971.
125. Brossa, F.; Chiesa, R.; Cigada, A.; Galli, A.; Paracchini, L.; and Tanzi, M.C. "Degradation of UHMWPE due to compression molding and γ -sterilization," in *Transactions of the Fifth World Biomaterials Congress*, Vol. 2, May 29-June 2, 1996; Toronto, Canada, p. 197.

126. McKellop, H., Lu, B.; and Benya, P. "Friction, lubrication and wear of cobalt-chromium, alumina and zirconia hip prostheses compared on a joint simulator," in *Trans Orthop Res Soc*, 1992;402
127. Clarke, I.C. "Wear of artificial joint materials I, Friction and wear studies: Validity of wear-screening protocols." *Engr Med*, 1981; 10(3):115-122. ISSN: 0046-2039
128. Skoog, D.A.; and Leary, J.J. Principles of Instrumental Analysis. Fort Worth: Saunders College Publishing, 1992.
129. Fox, M.A.; and Whitesell, J.K. Organic Chemistry. Boston: Jones and Bartlett Publishers, 1994.
130. Solti, A.; Hummel, D.O.; and Sirmac, P. "Computer supported infrared spectroscopy of polyethylene, ethylene copolymers, and amorphous poly(alkyl)ethylenes." *Makromol Chem, Macromol Symp*, 1986; 5:105-133.
131. Triola, M.F. Elementary Statistics, 7th Ed., Reading, MA: Addison-Wesley, 1998. ISBN: 0-201-859203
132. Kurtz, S.M.; Muratoglu, O.K.; Buchanan, F.; Currier, B.; Gsell, R.; Greer, K.; Gualtieri, G.; Johnson, R.; Schaffner, S.; Sevo, K.; Spiegelberg, S.; Shen F.W.; and Yau, S.S. "Interlaboratory reproducibility of standard accelerated aging methods for oxidation of UHMWPE." *Biomaterials*, 2001; 22:1731-1737.
133. Kurtz, S.M.; Muratoglu, O.K.; Gsell, R.; Greer, K.; Shen, F.W.; Cooper, C.; Buchanan, F.J.; Spiegelberg, S.; Yau, S.S.; and Edidin, A.A. "Interlaboratory validation of oxidation index measurement methods for UHMWPE after long-term shelf aging." From http://www.uhmwpe.org/features/white_papers/validate_oxi_ind_std.html
134. Dowson, D. "Lubrication in human joints," in Lubrication and Wear in Joints. V. Wright, Ed.; Philadelphia: J.B. Lippincott Co., 1969.
135. Bechtol, C.O.; Ferguson, A.B., Jr.; and Laing, P.G. Metals in Engineering in Bone and Joint Surgery. Lippincott, Williams & Wilkins, 1959.

APPENDICES

APPENDIX A

Tables

Table 1. Relative advantages of screening devices as compared to joint simulators.

(Reprinted from McKellop, H. "Wear of artificial joint materials II – Twelve-channel wear-screening device: Correlation of experimental and clinical results." *Eng in Med*, Copyright 1981, with permission from the Council of the Institution of Mechanical Engineers.)

Screening Devices	Joint Simulators
1. Simple, inexpensive sample fabrication.	1. Material variables exactly duplicate those of implanted prostheses (grain structure, hardness, surface finish, molecular weight, crystallinity, etc.)
2. Simple sample geometry permits accurate weight and dimensional measurements.	2. Load pattern, contact area and stress distribution are more representative of <i>in vivo</i> conditions.
3. Multi-sample capacity for rapid evaluation of numerous parameters (material, processing, lubricant, surface finish, etc.)	3. Tests evaluate the design of the components concurrently with the properties of the materials used.

Table 2. Comparison of the composition of synovial fluid and serum. (Adapted from Walker, P.S. "A comparison of normal and artificial human joints." *Acta Orthop Belg*, Copyright 1973, with permission from Acta Orthopaedica Belgica)

Synovial Fluid Source	Hyaluronic Acid Content (mg/mL)	Total Protein Concentration (mg/mL)
Normal Joint	3.5	17.2
Bovine Serum (as-received)	--	60-85
Bovine Serum (40% H ₂ O)	--	24-34
Hip, McKee-Farrar Implant (2 years)	0.56	32
Hip, McKee-Farrar Implant (1 year) Rheumatoid Arthritis	0.34	--
Hip, Cup Arthroplasty Implant (4 years)	0.28	58
Knee, Arthritis	3.5	30
Knee, Medial Meniscus Tear	1.4	35
Knee, Moderate Osteoarthritis	0.81	46

APPENDIX B

Figures

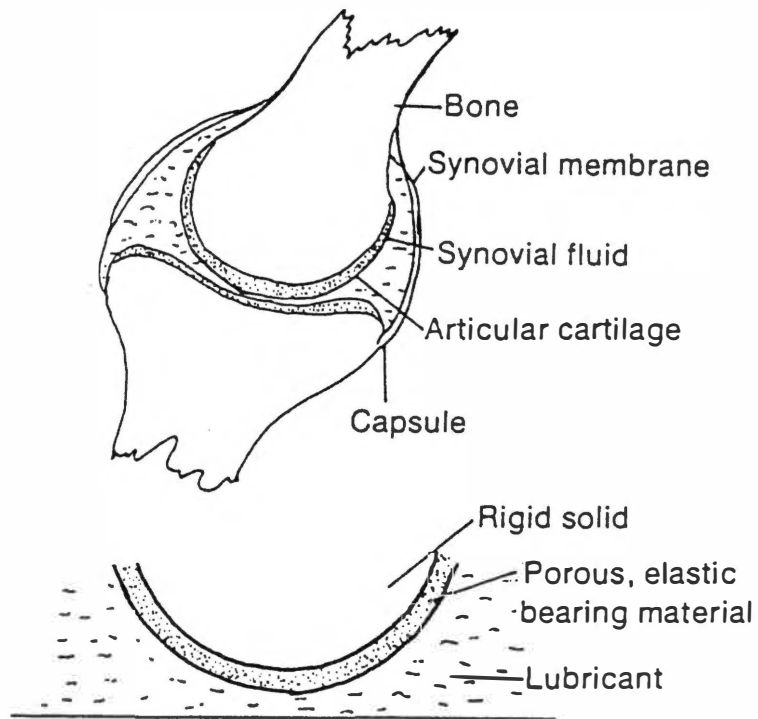


Figure 1. A schematic diagram of a synovial joint.¹³⁴ (Reprinted from Dowson, D. "Lubrication in Human Joints," in Lubrication and Wear in Joints, V. Wright, Ed.; Copyright 1969, with permission from Lippincott, Williams & Wilkins)

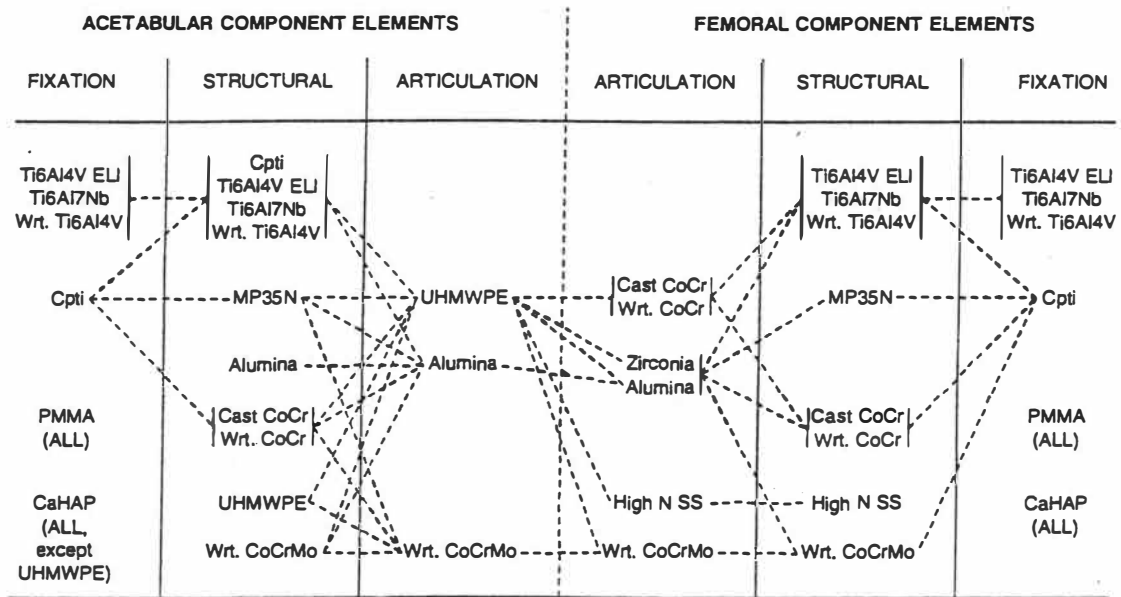


Figure 2. Combinations and uses of biomaterials that have been utilized in total hip arthroplasty.¹⁶ (Reprinted from Li, S. "Polyethylene," in *The Adult Hip*, Vol. 1, J.J. Callaghan, A.G. Rosenberg, and H.E. Rubash, Eds., Copyright 1998, with permission from Lippincott, Williams & Wilkins.)



Figure 3. Common total hip arthroplasty components.

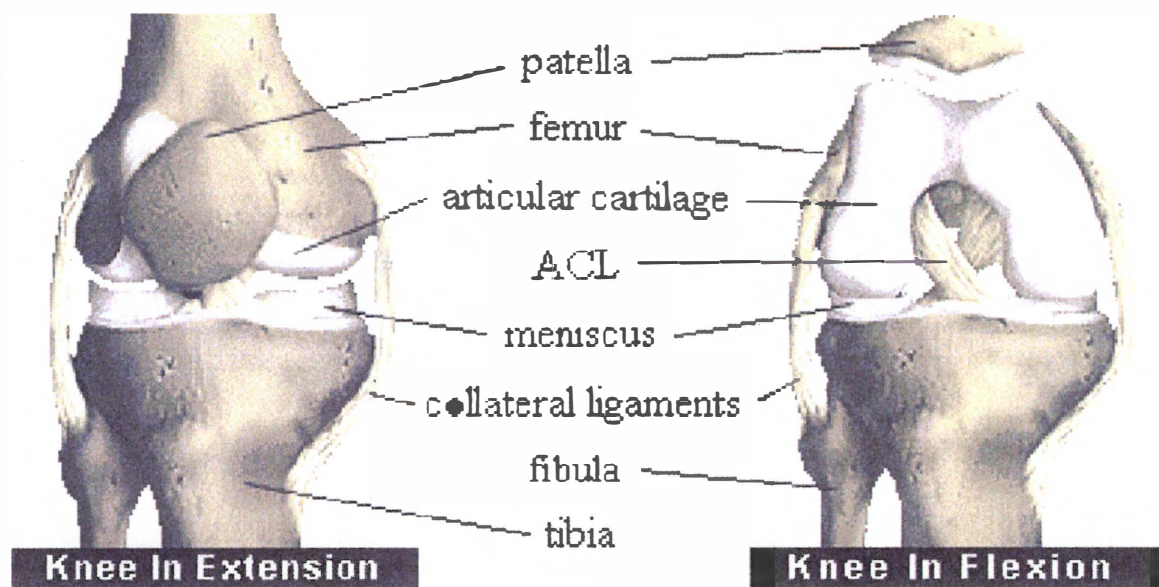


Figure 4. A schematic diagram of the knee joint.

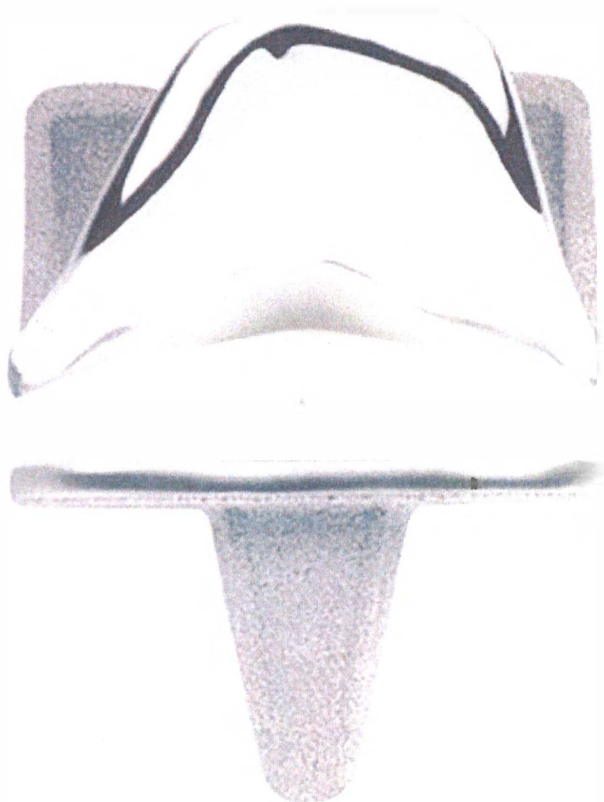


Figure 5. Common total knee arthroplasty components.

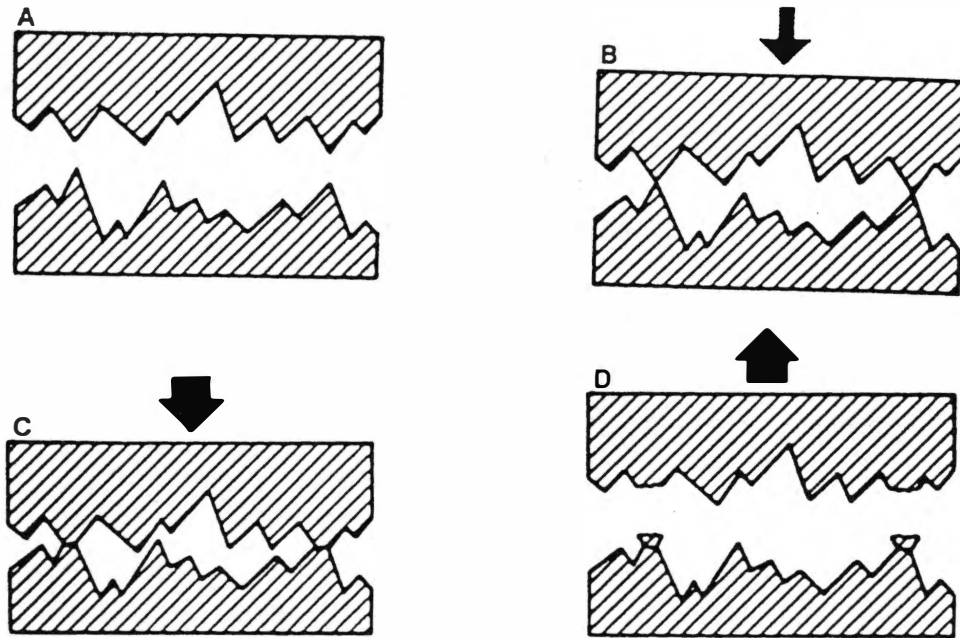


Figure 6. Schematic diagram of adhesive wear or "cold welding." In B, contact is made between asperities. In C, asperities in contact are deformed due to applied normal force and "cold welding" occurs. In D, the surfaces are separated and fracture occurs within one material instead of at the interface resulting in material transfer.¹³⁵ (Reprinted from Bechtol, C.O.; Ferguson, A.B., Jr.; and Laing, P.G. Metals in Engineering in Bone and Joint Surgery. Copyright 1959, with permission from Lippincott, Williams & Wilkins.)

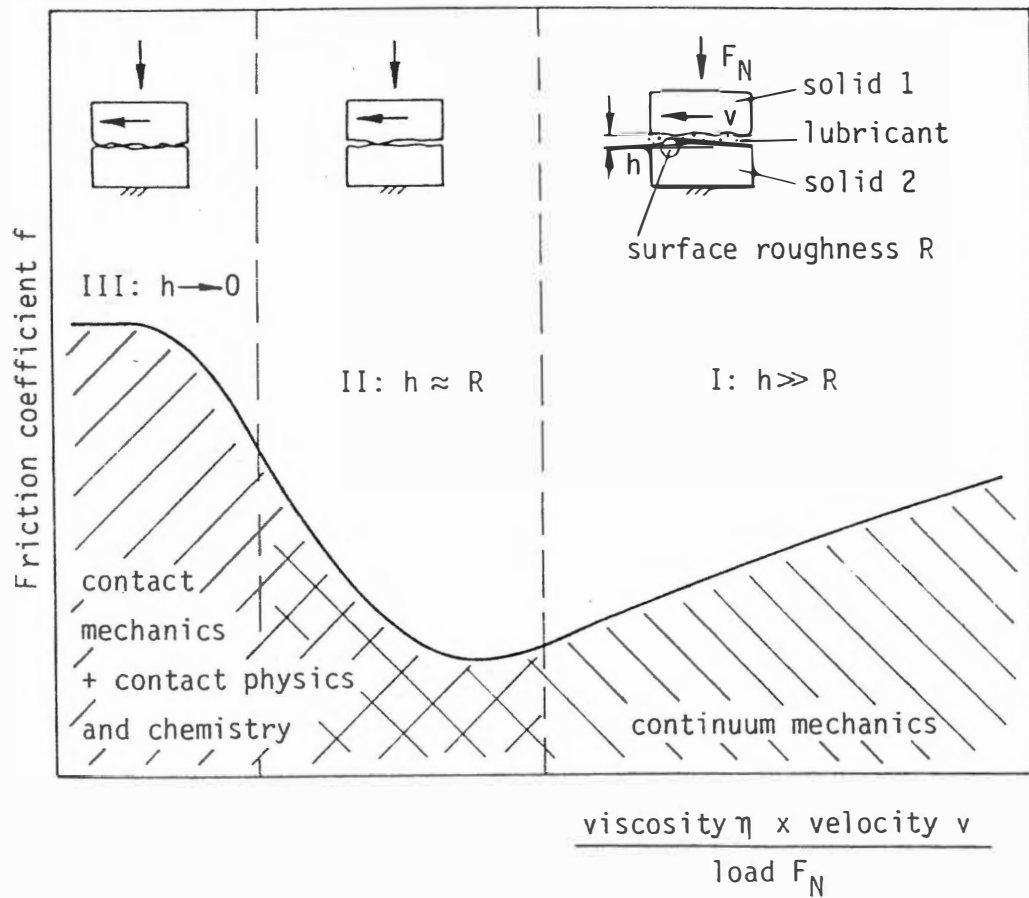


Figure 7. The Stribeck curve.²¹ (Reprinted from Czichos, H. *Tribology*, pg. 131, Copyright 1978, with permission from Elsevier Science.)

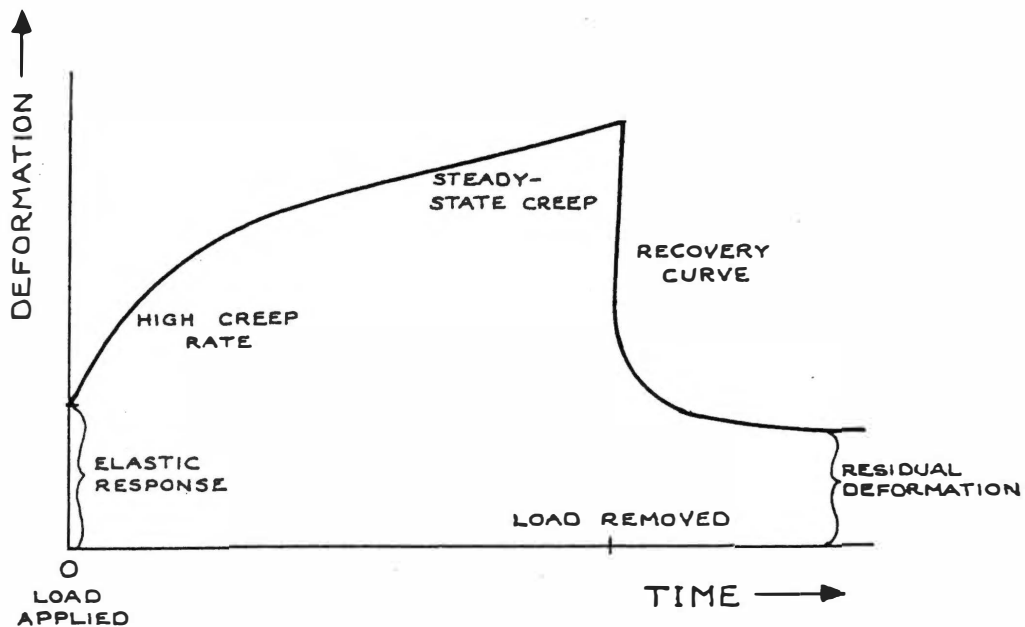


Figure 8. Characteristic creep response and stress relaxation of a viscoelastic polymer.⁴⁰
 (Reprinted from Dumbleton, J.H. Tribology of Natural and Artificial Joints, Tribology Series, Vol. 3. Copyright 1981, with permission from Elsevier Science.)

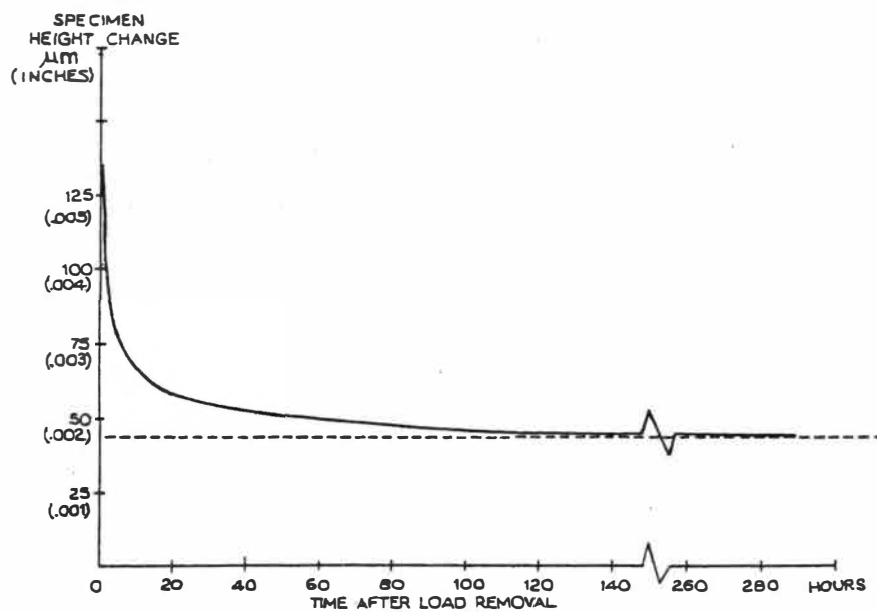


Figure 9. Stress relaxation curve for UHMWPE after one week loading at 6.9 MPa (1000 psi).⁴⁰ (Reprinted from Dumbleton, J.H. Tribology of Natural and Artificial Joints. Copyright 1981, with permission from Elsevier Science.)

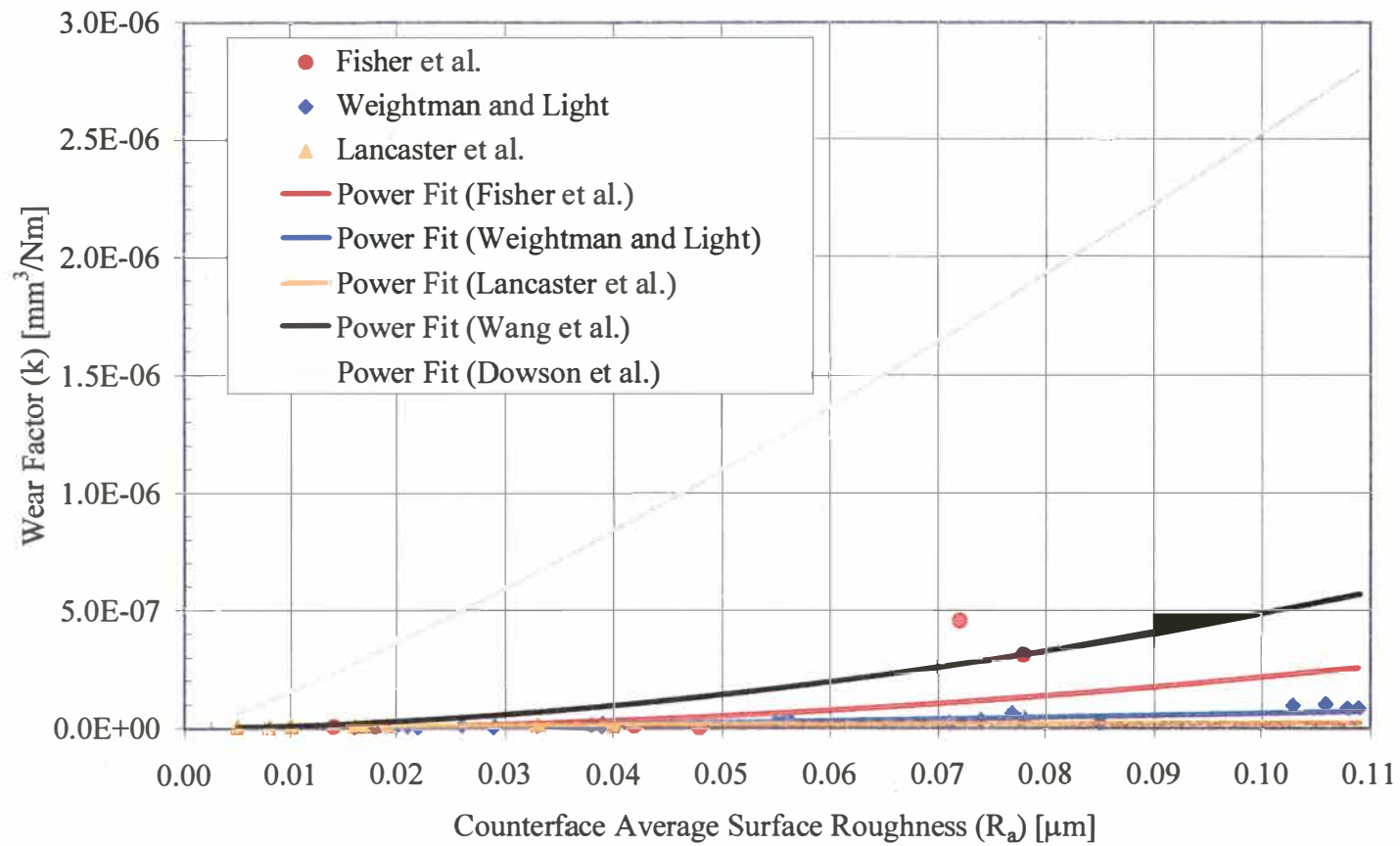


Figure 10. Plot demonstrating derived relationships of UHMWPE wear factors (k) as a function of average counterface surface roughness (R_a).

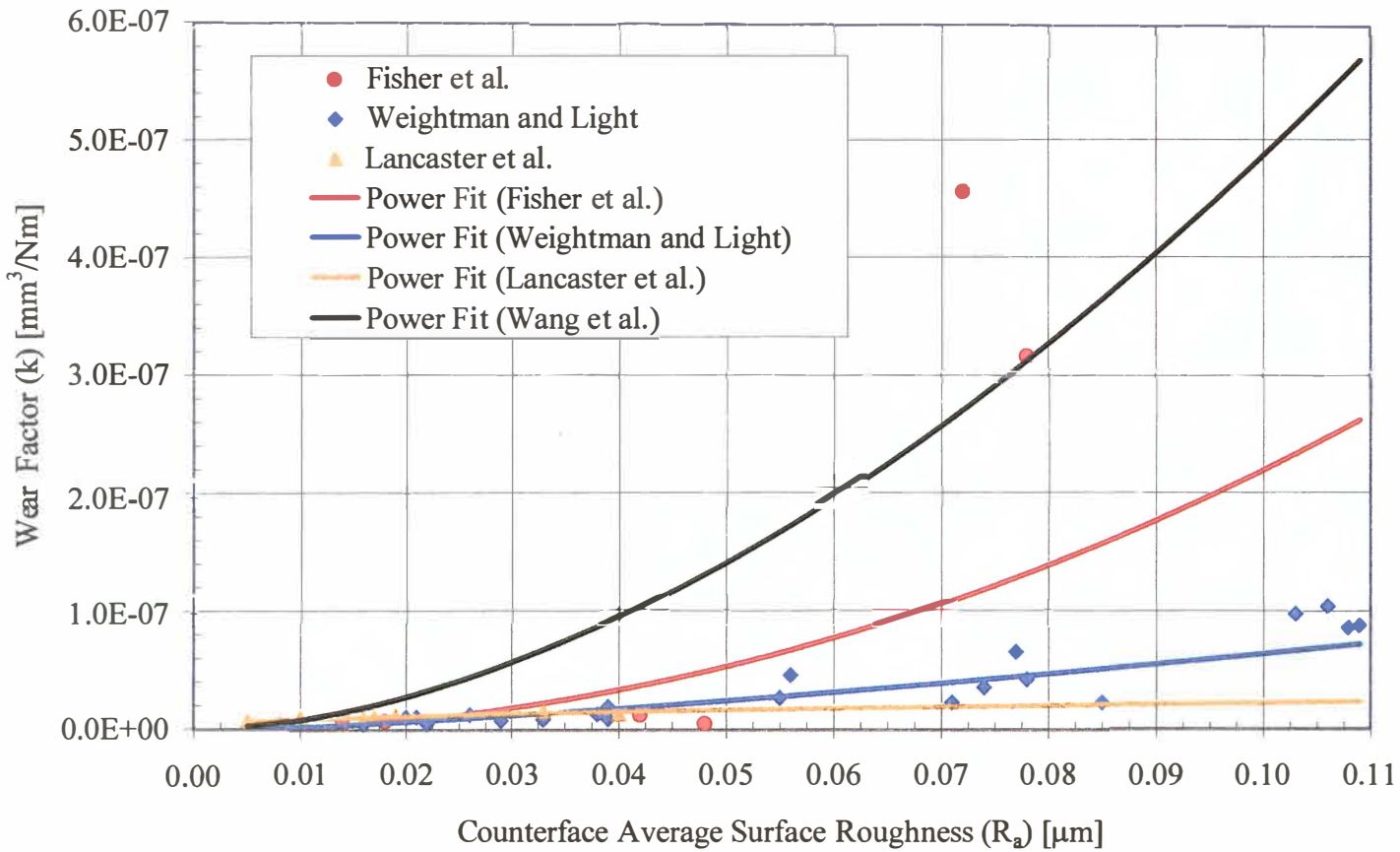


Figure 11. Plot demonstrating derived relationships of UHMWPE wear factors (k) as a function of average counterface surface roughness (R_a) with the Dowson model removed.

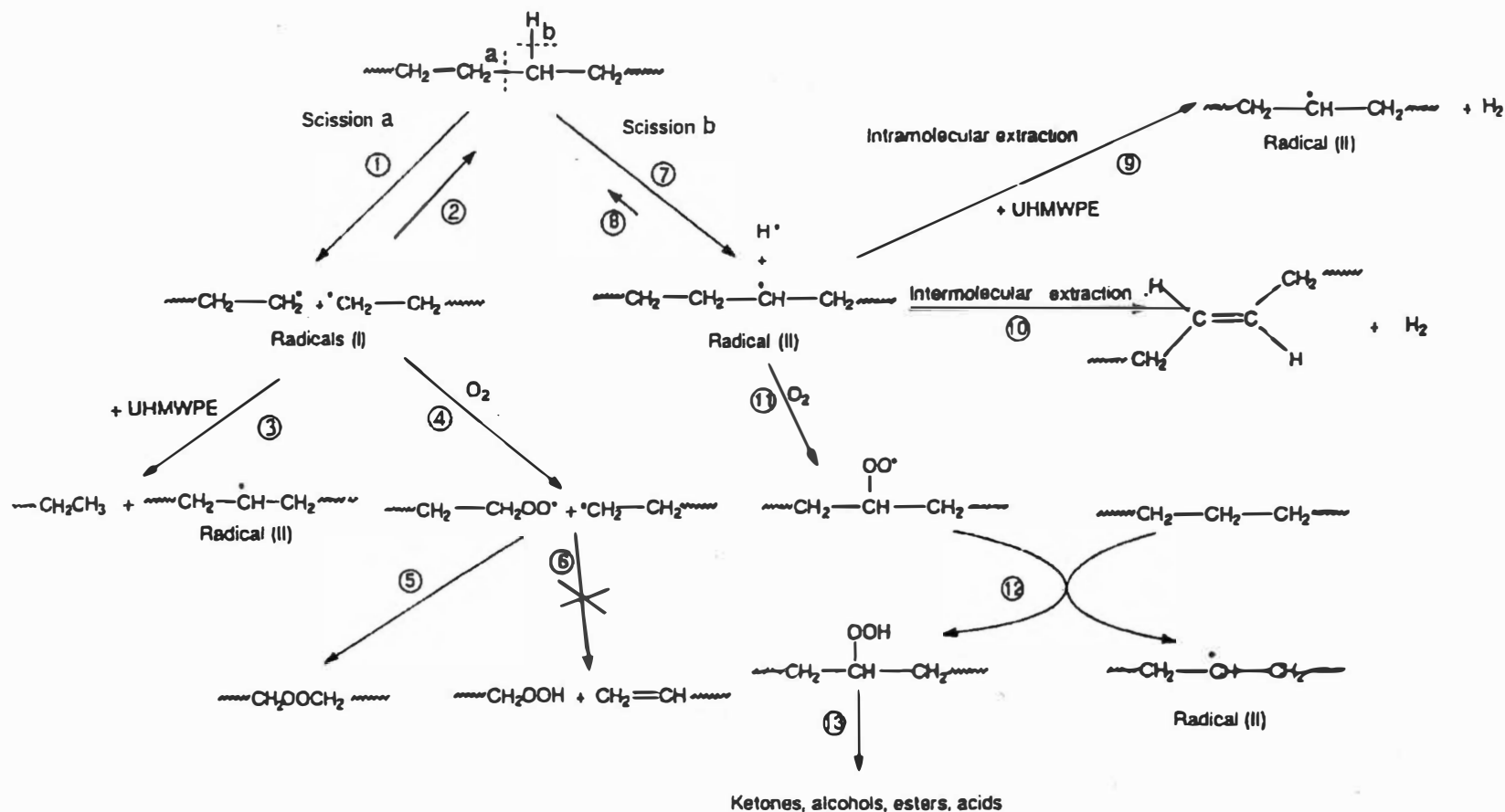


Figure 12. Schematic diagram demonstrating possible pathways of structure modification upon irradiation of UHMWPE.⁷⁴
 (Reprinted from Costa et al. "Oxidation in orthopaedic UHMWPE sterilized by gamma-radiation and ethylene oxide." *Biomaterials*, Copyright 1998, with permission from Elsevier Science)

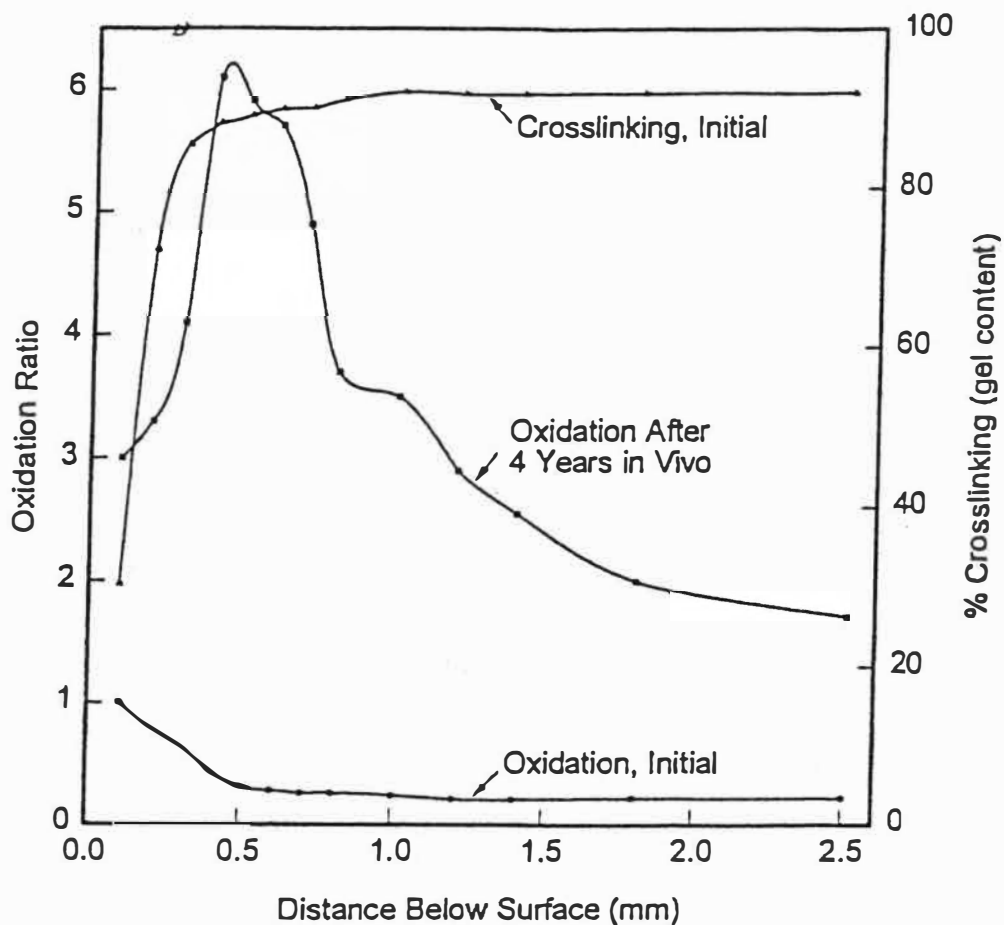


Figure 13. Oxidation and crosslinking profile across the wall thickness of UHMWPE acetabular cups.¹⁶ (Reprinted from Li, S. "Polyethylene," in *The Adult Hip*, Vol. 1, J.J. Callaghan, A.G. Rosenberg, and H.E. Rubash, Eds., pg. 242, Copyright 1998, with permission from Lippincott, Williams & Wilkins.)

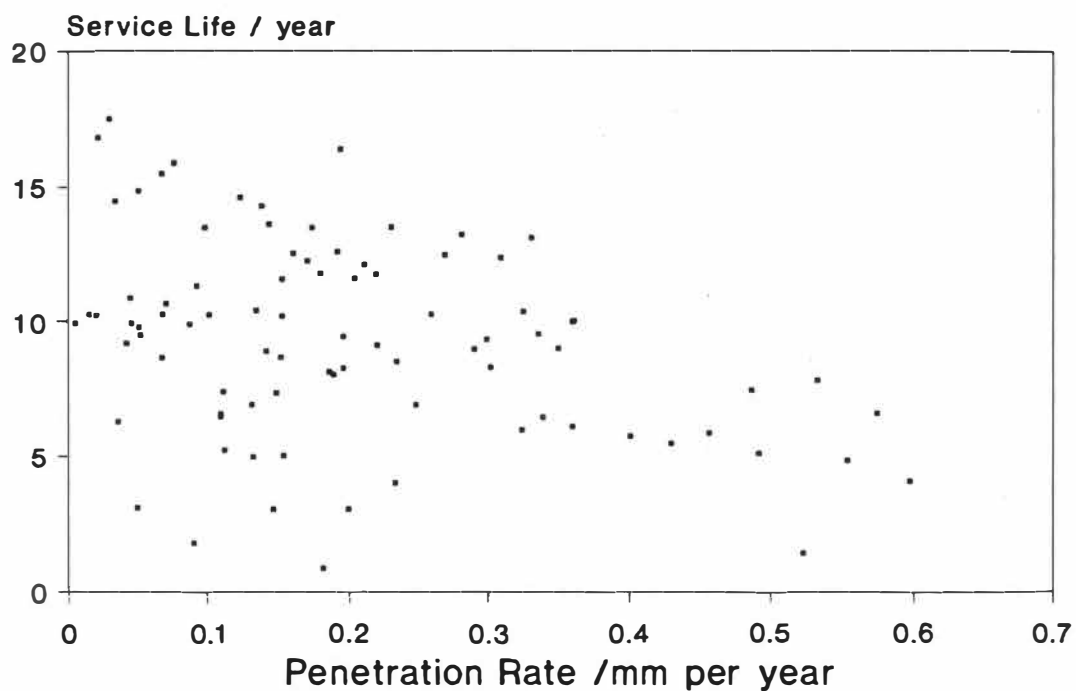


Figure 14. UHMWPE acetabular cup service life as a function of penetration rate.¹⁰⁶
 (Reprinted from Isaac, G.H.; Wroblewski, B.M.; Atkinson, J.R.; and Dowson, D. "A tribological study of retrieved hip prostheses." *Clin Orthop*, Copyright 1992, with permission from Lippincott, Williams & Wilkins)

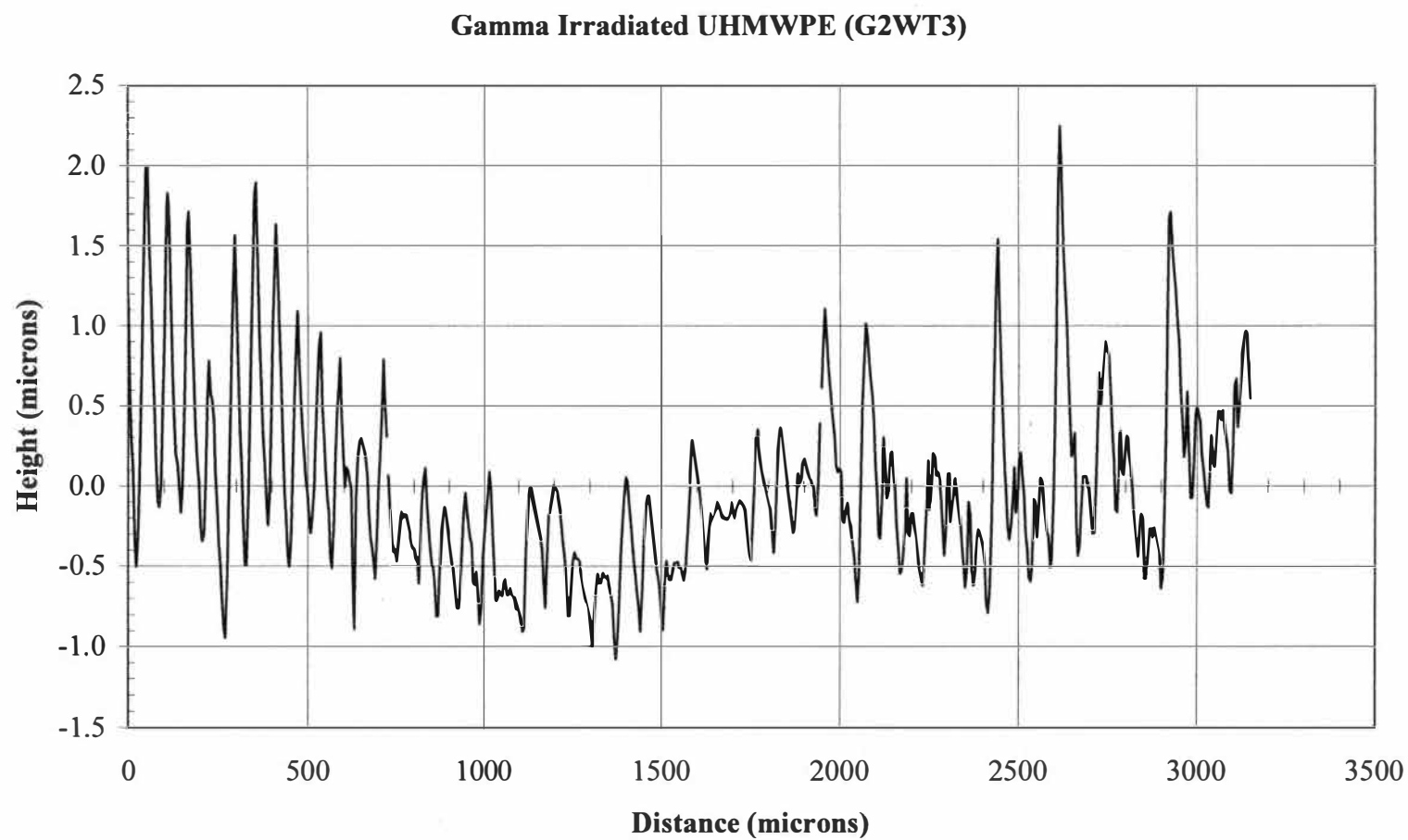


Figure 15. Example of a wear track profile before analysis.

Gamma Irradiated UHMWPE (G2WT3)

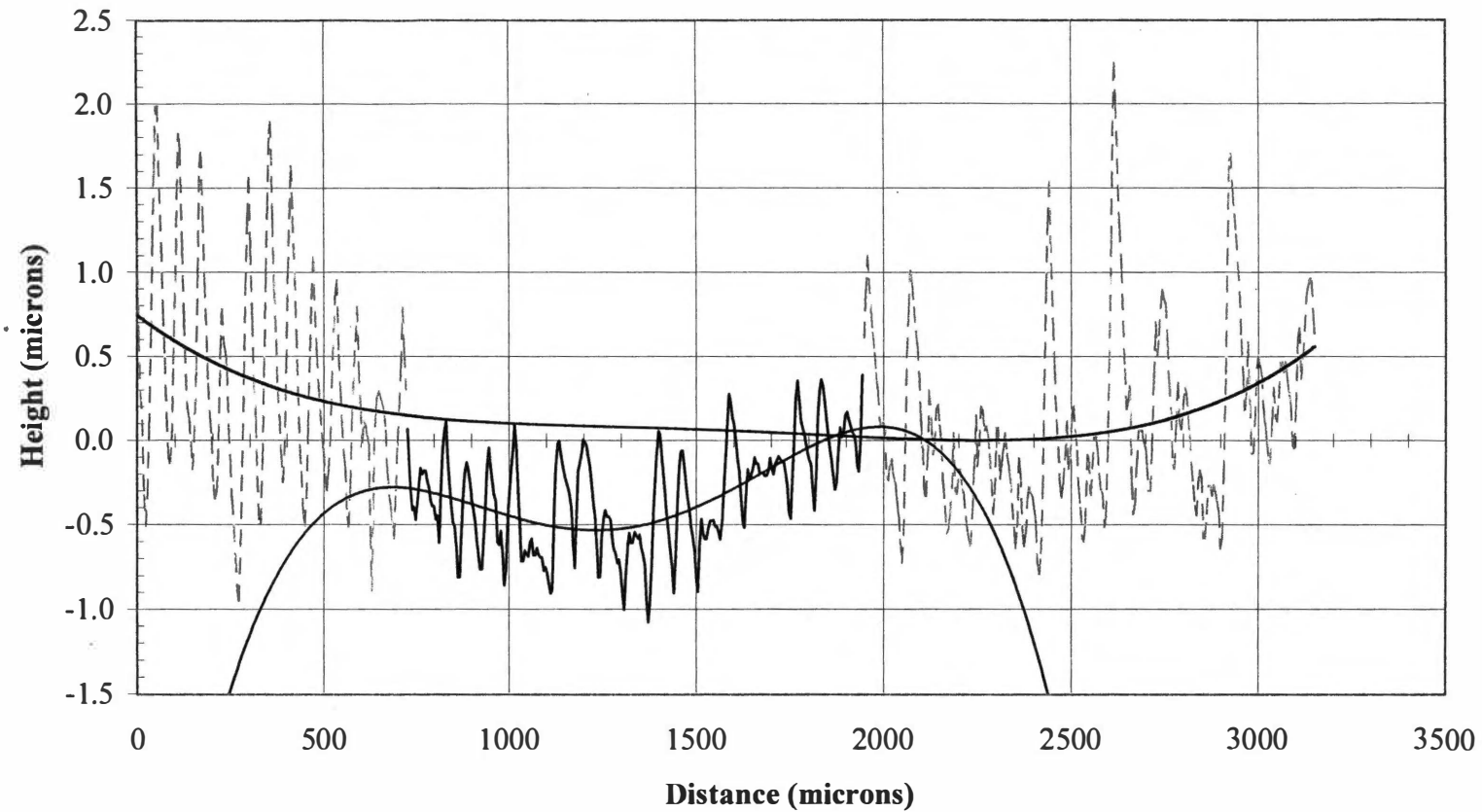


Figure 16. Example of a wear track profile after fitting polynomials to the wear track (solid line) and unworn surface (broken line).

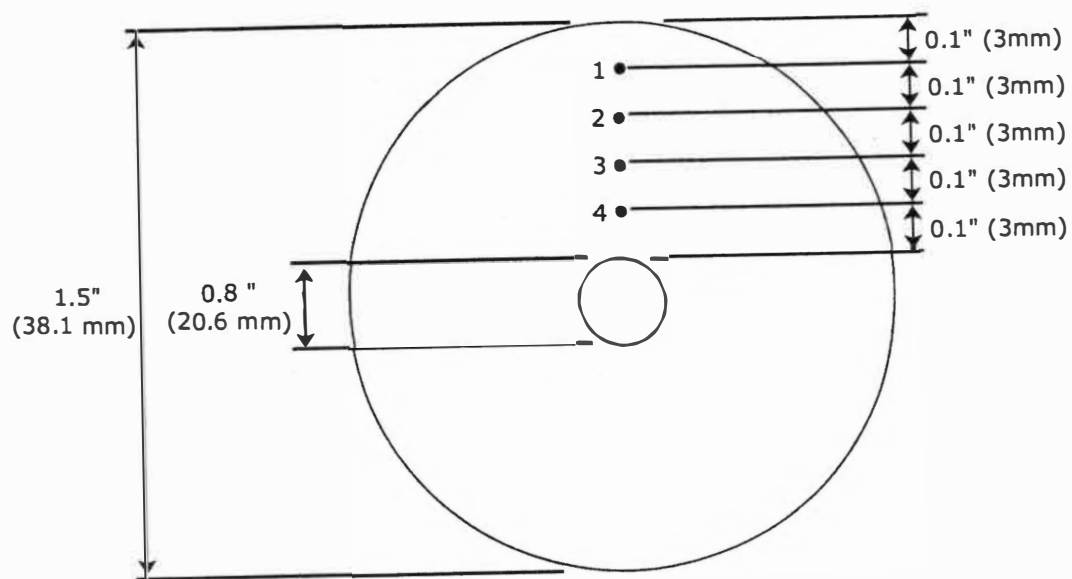


Figure 17. Schematic diagram of four locations along the wear surface of the UHMWPE samples where FTIR spectra were collected.

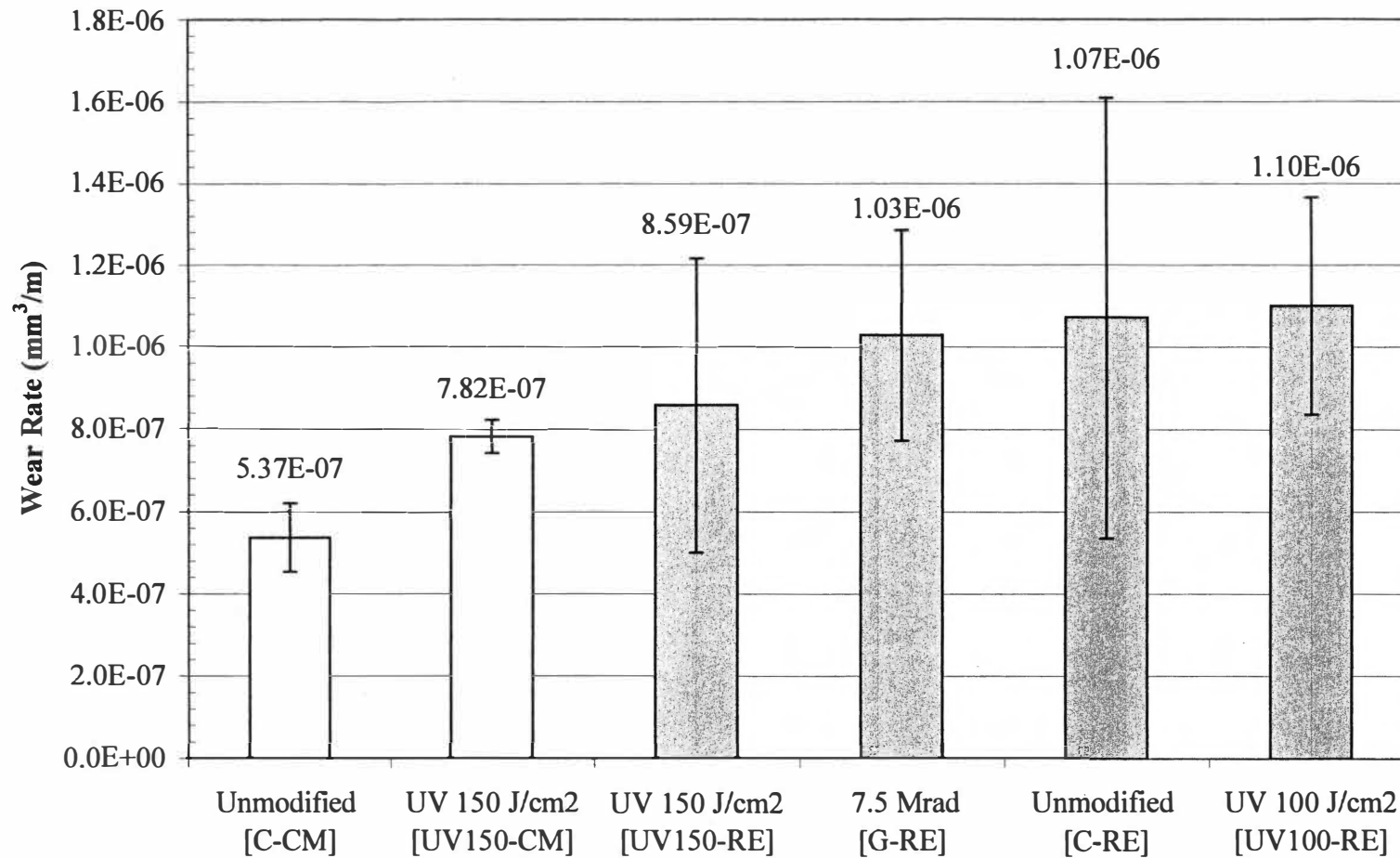


Figure 18. Chart of average calculated wear rates for all pin-on-disk wear tests, with each test corresponding to a simulated 6 years of *in vivo* use.

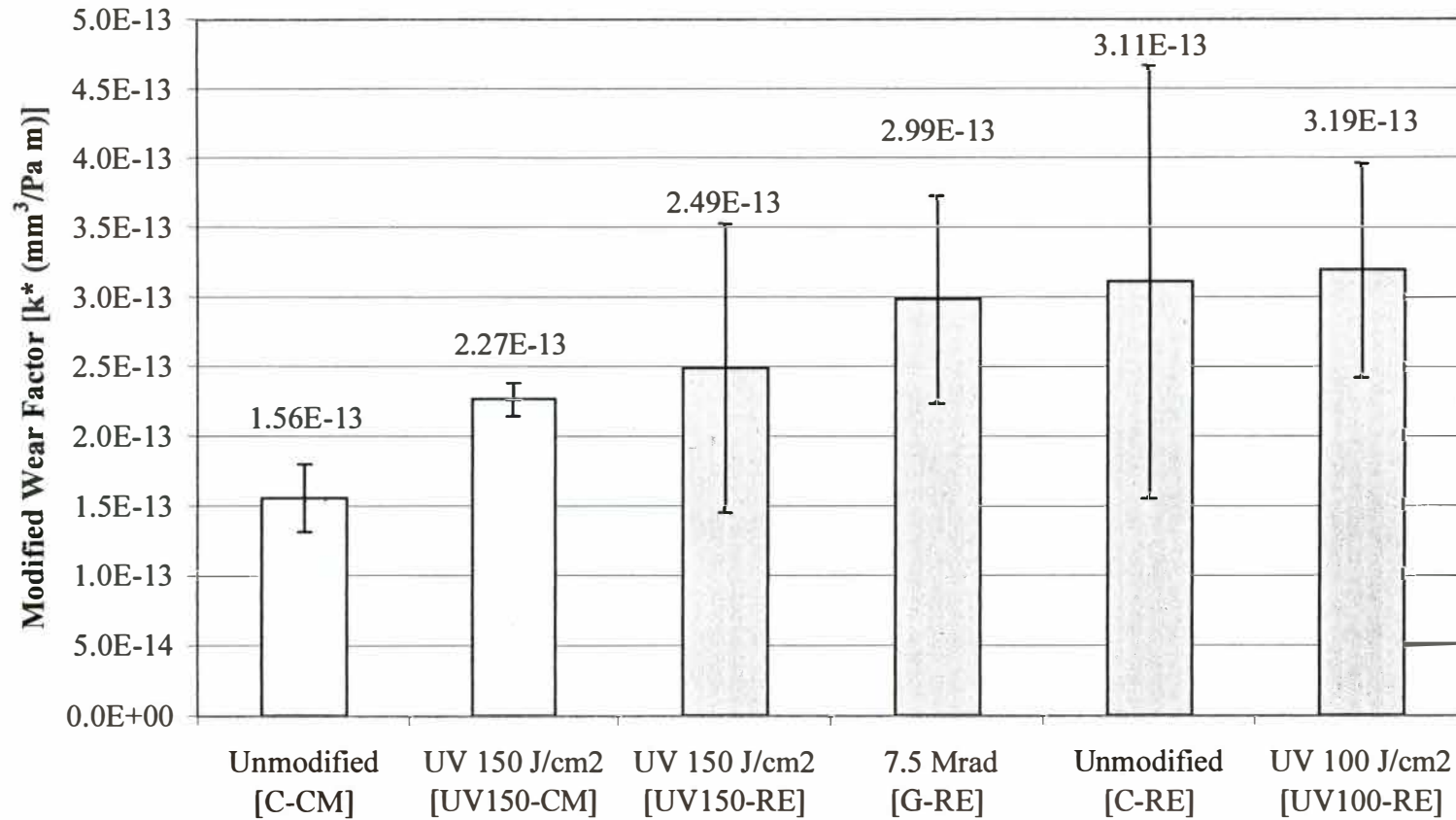


Figure 19. Chart of average modified wear factors for all pin-on-disk wear tests, with each test corresponding to a simulated 6 years of *in vivo* use.

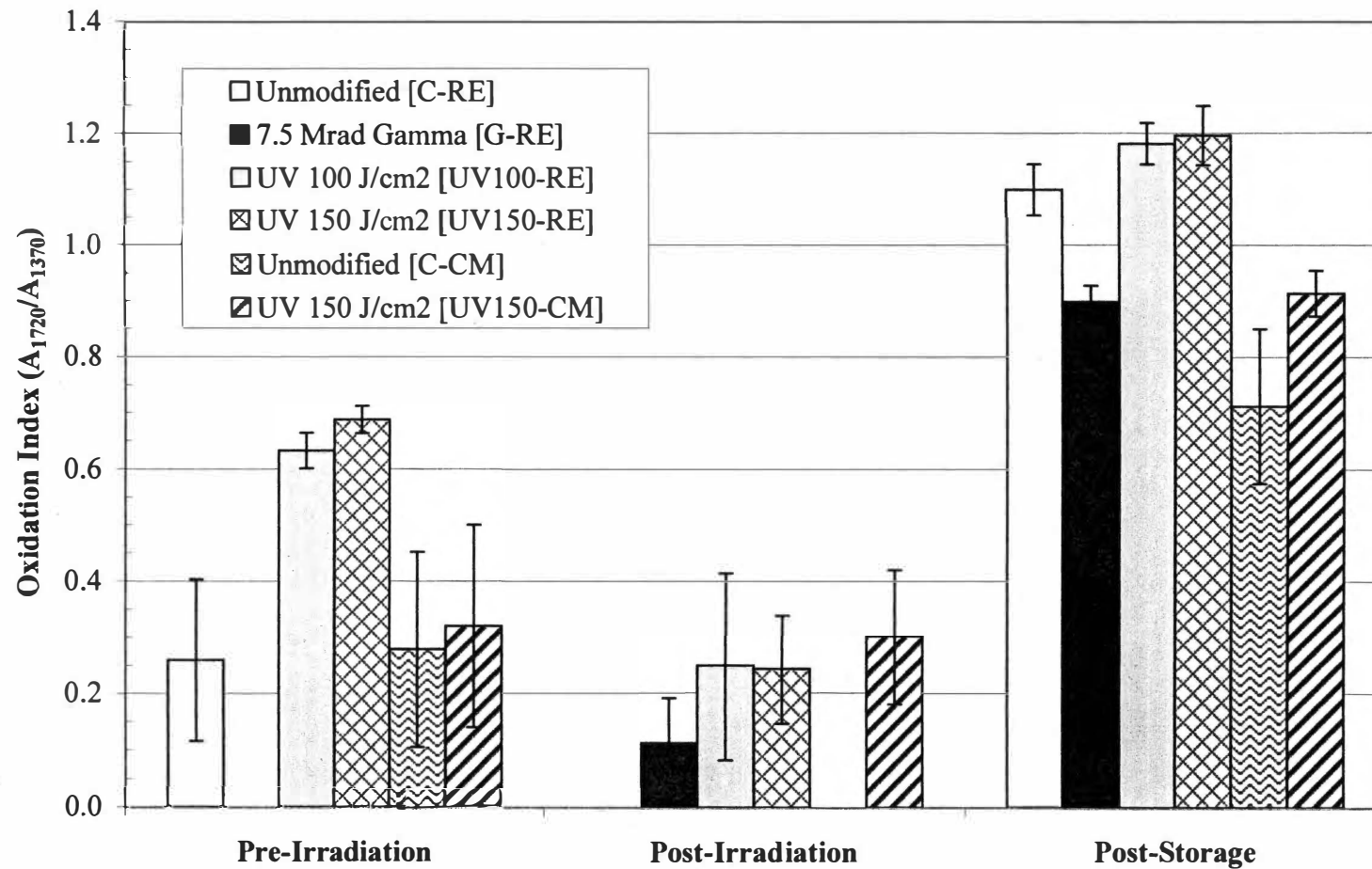


Figure 20. Chart of average oxidation indices (OI) for all material sets before irradiation, after irradiation and after storage (RE = Ram extruded, CM = Compression molded).

APPENDIX C

Sample Cleaning Protocols

Method for Cleaning of Polymer Specimens Before Testing

1. Rinse with distilled water to remove bulk contaminants.
2. Wash in an ultrasonic cleaner in a solution of 1% detergent for 15 minutes.
3. Rinse in a stream of distilled water.
4. Rinse in an ultrasonic cleaner in distilled water for 5 minutes.
5. Rinse in a stream of distilled water.
6. Dry with lint-free tissue.
7. Immerse in methyl alcohol for 3 minutes.
8. Dry with lint-free tissue.
9. Air-dry in a dust-free environment at room temperature for 30 minutes.

Method for Cleaning of Polymer Specimens After Testing

1. Rinse with distilled water to remove bulk contaminants.
2. Rinse in an ultrasonic cleaner in distilled water for 15 minutes.
3. Rinse in a stream of distilled water.
4. Dry with lint-free tissue.
5. Store in a dust-free environment at room temperature.

APPENDIX D

Experimental Data

Sample	Wear Track Area (μm^2)								Average Wear Track Area (μm^2)
	1	2	3	4	5	6	7	8	
C-RE1	1181.44	133.80	3099.93	2592.17	0.00	530.55	1670.01	0.00	1150.99
C-RE2	1397.20	355.62	315.51	1053.32	986.92	2485.86	157.48	488.86	905.10
C-RE3	644.25	0.00	1248.13	264.28	0.00	0.00	572.36	0.00	341.13
C-RE4	587.01	344.36	199.92	236.02	212.44	703.70	999.81	926.11	526.17
G-RE1	624.77	1009.65	445.16	678.36	884.12	481.62	739.61	526.88	673.77
G-RE2	0.00	1984.36	594.02	1064.25	0.00	2307.48	0.00	1158.22	888.54
G-RE3	407.95	716.54	427.40	478.61	580.82	848.37	484.77	395.02	542.44
UV100-RE1	1700.85	1147.95	420.49	496.33	1577.11	78.93	894.07	430.30	843.25
UV100-RE2	1802.55	0.00	86.29	1653.08	1982.71	0.00	150.68	1246.97	865.29
UV100-RE3	1161.02	1060.69	0.00	416.94	401.33	811.71	0.00	486.98	542.33
UV150-RE1	613.17	704.92	1352.10	786.70	715.81	1065.18	921.05	735.78	861.84
UV150-RE2	309.20	644.98	138.37	791.02	307.26	187.55	549.50	296.84	403.09
UV150-RE3	733.01	469.80	404.99	688.75	460.29	543.08	204.42	419.97	490.54
C-CM1	422.17	207.44	582.80	127.16	470.00	292.40	416.43	430.33	368.59
C-CM2	244.63	187.39	364.70	432.94	303.52	278.59	86.54	562.44	307.59
C-CM3	52.19	248.82	958.56	341.62	626.32	626.30	471.94	43.25	421.13
UV150-CM1	588.30	457.72	591.08	876.49	405.13	452.10	458.99	278.17	513.50
UV150-CM2	0.00	845.14	737.85	405.65	753.59	462.38	753.64	462.15	552.55

Materials	C-RE	G-RE	UV100-RE	UV150-RE	C-CM	UV150-CM
Average Wear Track Area (μm^2)	730.85	701.58	750.29	585.16	365.77	533.02
Standard Deviation	365	175	180	244	57	28
Simulated Test Time (Years)	6	6	6	6	6	6
Sliding Distance (km)	64.2	64.2	64.2	64.2	64.2	64.2
Total Average Wear Volume (μm^3)	0.0689	0.0661	0.0707	0.0552	0.0345	0.0502
Wear Rate (mm^3/m)	1.07E-06	1.03E-06	1.10E-06	8.59E-07	5.37E-07	7.82E-07
Standard Deviation	5.36E-07	2.56E-07	2.65E-07	3.58E-07	8.34E-08	4.05E-08
k ($\text{mm}^3/\text{N m}$)	1.57E-07	1.51E-07	1.61E-07	1.26E-07	7.86E-08	1.15E-07
Standard Deviation	7.86E-08	3.76E-08	3.88E-08	5.24E-08	1.22E-08	5.94E-09
k* ($\text{mm}^3/\text{Pa m}$)	3.11E-13	2.99E-13	3.19E-13	2.49E-13	1.56E-13	2.27E-13
Standard Deviation	1.56E-13	7.43E-14	7.68E-14	1.04E-13	2.42E-14	1.18E-14

VITA

Mark L. Morrison was born in Memphis, Tennessee, on February 14, 1976. He was raised in Memphis and graduated from Briarcrest High School in 1994. Mark began his college education in 1994 at The University of Tennessee at Knoxville and graduated in May, 1999, with a B.S. degree in materials science and engineering. After living in Ireland for the summer and traveling around Europe, he returned to Knoxville and began work on a graduate degree in January, 2000. Mark is currently pursuing his doctorate in materials science and engineering at The University of Tennessee at Knoxville and The Institute for Materials Research at Tohoku University, Sendai, Japan.

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