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Friction and wear behavior of ultra-high molecular weight polyethylene as a function of crystallinity and in the presence of the phospholipid DPPC (dipalmitoyl phosphatidylcholine)

by

Angela Lynette Bruck

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
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Major: Mechanical Engineering

Program of Study Committee:
Sriram Sundararajan, Major Professor
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Iowa State University

Ames, Iowa

2007

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Chapter 1. Introduction and theory

1.1 Tribology

Tribology is a study of the interaction between adjacent, articulating surfaces, in relative motion. It encompasses both friction and wear science. Either may prove to be beneficial or detrimental, depending on the situation. For a very long time, friction and wear were studied only in a macroscopic sense. Recently, however, advances in micro and nanotechnology have pushed scientists and engineers to consider the effects of tribology on a smaller scale. In the race to produce smaller, more efficient, parts and machinery, new light has been shed on the impact friction and wear have at both micro and nanoscales. Behavior at the interface of mating surfaces has become crucial in the engineering of micro and nanoscale devices, as well as equipment that has implications at those scales.

Factors that contribute to surface interaction include chemical and morphological characteristics of the materials in contact [1], in addition to the physical processing of those materials. Variables such as surface roughness and wettability begin to be significant in a tribological sense. Theories and models have been developed to not only explain but predict the interfacial behavior of interacting materials based on their local environmental conditions and bulk mechanical properties, such as elasticity and hardness, among others. For example, the strength of a material can be defined by its yield stress, the critical limit of pressure that will induce plastic deformation. In tribology, yielding of a material occurs close to the surface rather than in the bulk, therefore surface mechanics must be applied in order to calculate loads and pressures that the system can withstand. Von Mises yield criterion utilizes Hertzian contact theory to derive the limit of elastic deformation of a surface. Assuming axisymmetric loading, a sphere on sphere contact will have circular area with a radius, a , defined by

$$a = \left(\frac{3WR}{4E^*} \right)^{\frac{1}{3}} \quad (0.1)$$

where R is the composite radius of the two spheres, given by $\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2}$, W is the load, and E^*

is the composite elastic modulus of the two materials calculated from $\frac{1}{E^*} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2}$. The

maximum contact pressure that the surface will experience is at the center and can be calculated using

$$p_0 = \frac{3W}{2\pi a^2} \quad (0.2)$$

Substituting equation 1.1 into 1.2 from above gives

$$p_0 = \left(\frac{6WE^{*2}}{\pi^3 R^2} \right)^{\frac{1}{3}} \quad (0.3)$$

the maximum contact pressure. In Herzian contact, however, yielding begins beneath the surface of the softer material. Von Mises yield criterion states that for two contacting spheres of $\nu = 0.3$, the contact pressure that will initiate yield in the material is greater than Y by

$$(p_0)_y = 1.60Y = 2.8k \quad (0.4)$$

Therefore, setting equation 1.4 equal to equation 1.3 and solving for W , will derive the load that will initiate yield,

$$W_y = 21.17R^2Y \left(\frac{Y}{E^*} \right)^2 \quad (0.5)$$

Knowing how mechanical properties of a material influence its performance while in contact with other surfaces, one can predict the durability and lifespan of a surface under specified

conditions. Having that knowledge allows manufacturers to effectively choose materials that are suitable and economical for the desired application.

It has been documented that wear of a material is directly related to its hardness relative to the hardness of the mating material [2]. Adhesive wear occurs when fragments of a material are removed from its surface and stuck to the opposing surface, resulting from the shearing force of the interface overcoming the shear, cohesive force that holds the softer material together. Abrasive wear occurs when chunks of a surface are removed and become third-body particles at the interface, or with ploughing from a sharper contact. The nature of contact between the materials determines the shape and distribution of the removed material, though some materials, like polymers, are generally more prone to wear.

1.2 Polymers

Polymers are considered viscoelastic materials, exhibiting both mechanical and rheological behavior. The extent to which a polymer displays either of these characteristics depends upon the morphology of its molecules; specifically, the ratio of amorphous to crystalline regions [3]. It has been shown that mechanical properties, such as elastic modulus, tend to increase with increases in crystalline structure within the bulk material [4, 5]. It can be argued that the strength of a polymer is dependant on its degree of crystallinity. In an effort to strengthen a polymer, one may want to maximize the presence of crystalline regions within its volume.

As with any crystalline solid, melting temperature marks a transition from solid to liquid. Polymers are unique in that their high molecular weight prevents them from flowing like a liquid. Their long-chain, backbone structure causes entanglements between molecules that

inhibit free-flow motion [6]. Polymers tend towards an ordered, crystalline structure by retracting their long molecules into folded, or lamellar, formations which results in a lower energy state [3].

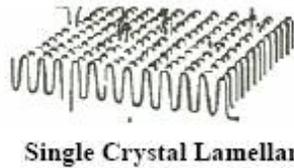


Figure 1. Example of a lamellar-folded single crystal [3].

Heating a polymer above its critical melting temperature adds energy and disorders the polymer into a spaghetti-like, amorphous phase which typically allows the polymer to become malleable. An increase in the presence of crystalline structure raises the temperature at which the material will melt, and the longer the process of disordering will take.

Recrystallization of a polymer may occur at a temperature 10-20 degrees lower than it takes to melt it because of the extra energy required to align chain segments [3]. The rate and volume in which a polymer will recrystallize is dependant on several things: the molecular weight of the polymer, its chemical make-up and microstructure, and the holding temperature. For example, a linear polymer will fold into lamellar structure with greater ease than a polymer with branching side groups that would hinder close, uniform folds [6]. Crystallization is also a function of how well the lamellar folds stack upon one-another, which can also be affected by the aforementioned. A particular temperature exists for a given polymer that maximizes rate and efficiency of crystallization based on polymer characteristics. Annealing a polymer at this temperature proves to be an effective method of recrystallization. This knowledge allows one the ability to alter crystallinity of a polymer sample in order to study the direct effects

crystallinity has on its mechanical properties. Using this as a means to strengthen a polymer can be valuable for manufacturers who are limited to only a specific polymer.

1.3 Total Joint Replacement (TJR)

Engineering of biomaterials is an example of an industry that is restricted to a narrow range of compatible materials. A common application of biomaterials is in Total Joint Replacements (TJR), such as the knee or hip. Tribology plays a very crucial role in the success of these mechanisms within the body. Unfortunately, the extremely low friction and wear characteristics of natural human joints have yet to be duplicated. In an effort to emulate nature's perfection, experimentation with TJR parts have tested ceramics (alumina), metals (stainless steel, cobalt chrome), and polymers (Teflon, polyethylene, and ultra-high molecular weight polyethylene). Low friction and wear of articulating ceramic surfaces have encouraged its use, but the risk of catastrophic failure as a result of its brittleness has pushed doctors away from using it. Presently, the most common combination of materials is a cobalt chrome femoral head articulating on polymer-lined acetabular metal cup [7], as seen in Figure 2 below.

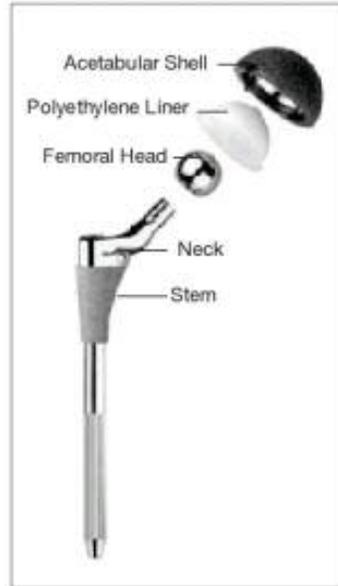


Figure 2. Image of a Total Hip Replacement (THR) implant.

1.3.1 Ultra-High Molecular Weight Polyethylene

For the past forty years, Ultra-high molecular weight polyethylene (UHMWPE) has been the primary material used for the articulating cup of artificial hip joints [4, 7-14]. Its viscoelasticity and low friction resemble properties of cartilage lining natural human joints more than any other biocompatible material. However, it has been found that polymeric wear particles from the UHMWPE in Total Hip Replacements (THR) have been the major factor limiting the life of an implant, causing osteolysis and loosening of the joint [5, 15], requiring revision surgery. Much attention has been on the tribological behavior of UHMWPE in an effort to reduce its wear. Many studies conducted have focused on altering the physical and chemical properties of UHMWPE to increase wear resistance, such as gamma-irradiated cross-linking [16] and orientating crystalline [17] structure, which have correlated with decreases in wear. Others have focused on the environment of the joint interface *in vivo*.

1.3.2 Synovial Fluid

Human joints are examples of natural ball-bearing mechanisms. Just like oils used in machinery, the body provides a lubricating fluid for its joints. Synovial fluid (SF), as it is called, is a complex plasma solution mostly of proteins, hyaluronic acid, and lipids and is sealed by the joint capsule, comprising of a membrane-lined fibrous layer of connective tissue [18]. Healthy, human joints lubricated by synovial fluid achieve remarkably low friction behavior, with coefficients as small as 0.002-0.006 [19]. Though UHMWPE in TJR, in a sense, imitates human cartilage, its synthetic origin can hardly compete with those friction values. One reason is because it does not interact with synovial fluid the same as a natural joint lining would. Research has been done on UHMWPE to establish which constituent of the synovial fluid is responsible for the highest lubricating contribution. Sawae et al. compared friction of UHMWPE in the presence of albumin (major protein component of synovia) versus hyaluronic acid (HA, a polysaccharide) and found albumin cause higher friction than HA [11]. Gispert et al. also compared friction between albumin and HA, as well as a solution of albumin and HA. There was not a consistent, reproducible result of whether or not albumin showed higher friction, but it was clear that the combination of albumin and HA as a lubricating solution caused the lowest friction response and wear rate [20]. These inconsistencies have lead researchers to believe that another component of synovial fluid dominates the lubrication system.

1.3.3 The role of phospholipids

Surface active phospholipids (SAPL) have been reported to act as a boundary lubricant in human joints [19, 21, 22]. A boundary lubricant, SAPL, by definition, are adsorbed to the surface and become a monolayer such that penetration of the counter face asperities is reduced.

Adsorption occurs when the polar phosphate head group of the SAPL attaches to the hydrophilic surface, leaving the non-polar fatty acid tails to create a hydrophobic monolayer as the new surface [19].

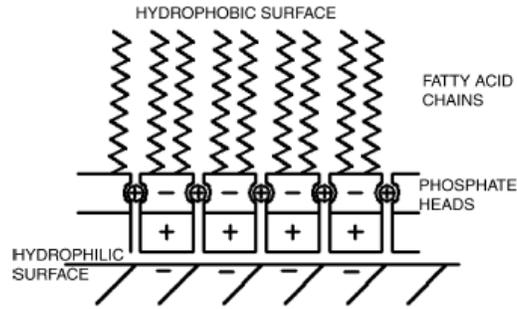


Figure 3. Image of phospholipids attaching to a hydrophilic surface [23].

Higher adsorption of phospholipids lends a more hydrophobic surface, allowing liquid to slip smoothly at the interface. It has been demonstrated that without SF between interacting surfaces of adsorbed SAPL, the surfaces will adhere and increase friction. Inversely, only when this hydrophobic SAPL monolayer is incorporated do HA and other synovia constituents lubricate. When articulating surfaces were rinsed with a lipid solvent, friction drastically increased. It has been shown that in osteoarthritic (OA) joints, the synovial fluid does not lubricate as well [24, 25] and there is often a deficiency of SAPL [23]. This supports the theory that phospholipids play a crucial role in the lubrication of joints and are a key factor in reducing friction.

Investigations on the tribological influence of phospholipids on UHMWPE have correlated decreasing friction and wear in the presence of phospholipids [26]. The most common phospholipid studied on UHMWPE is DPPC (dipalmitoyl phosphatidylcholine), presumably because it has been reported as the most abundant lipid in synovial fluid at 45 % [22]. In the cases where DPPC was dissolved in propylene glycol and tested on sheep joints, it was shown

that DPPC gave a lower friction response on UHMWPE than propylene glycol alone, though wear behavior was inconclusive [21]. The same friction trend showed up when ethanol-dissolved DPPC on UHMWPE was compared to regular saline as lubricants [19]. Mazzucco et al. reported a lubricant of DPPC in phosphate buffered solution (PBS) to have the lowest coefficient of friction between polyethylene and cobalt chrome surfaces, when compared to HA and protein dissolved in PBS [26]. As stated, it has been established that phospholipids, specifically DPPC, tend to reduce friction between surfaces. Similarly, it is hypothesized that the presence of phospholipids between articulating surfaces would also reduce wear by reducing interfacial contact, though further studies are need to confirm this theory. Furthermore, it seems reasonable that making UHMPWE more prone to the adsorption of surface-active phospholipids would best imitate natural joints, creating a more desirable implant material.

1.3.4 Adsorption, wettability, and contact angle

SAPL have an affinity for hydrophilic surfaces due to their ionic phosphate heads [19]. UHMWPE is considered a hydrophobic polymer, which has low wettability and the potential to resist adsorption of the lipid. Wetting of a substance is determined by the chemical and physical characteristics of the outermost layer of its surface, and is directly related to surface tension [27]. On way to quantify the wettability of a material is by its contact angle, in other words, “the angle that is formed at the junction of three phases” [28] and can be measure by the tangent of a droplet of water makes with the surface. High surface energies typically result low contact angle and the surface will wet, vice versa with low surface energies having high contact angles resistance to wetting [28]. Modifying surface properties will affect the contact angle. Wetting agents consisting of polar or non-polar molecules may be used to chemically induce wetting [1].

Physical modifications like surface roughness may also influence contact angle; it is generally noted that a higher roughness gives a higher contact angle.

With UHMWPE, Karuppiah et al. showed that a smooth, melted sample had a contact angle approximately 30 degrees lower than a rough, milled sample and that those same samples after protein adsorption showed a difference in contact angle [29]. Gispert et al. also showed a marked change in contact angle and surface tension of UHMWPE after exposure to HA and bovine serum, respectively [20]. The effect of crystalline morphology at the surface on the contact angle of polypropylene was examined by Yui et al. and found to correlate well: higher crystallinity at the surface gave lower contact angles, confirming that crystalline regions of polypropylene contain more surface energy than amorphous regions [30]. Molecular simulations have shown similar trend in polyethylene [31]. One potential for increasing adsorption of SAPL onto UHMWPE is to increase the crystallinity of the material.

1.4 Present work

In the present studies, friction and wear behavior of UHMWPE as a function of crystallinity are being investigated. Two UHMWPE samples with different crystallinities were made using specific thermal treatment. Both samples were used for dry and lubricated tribology studies. All friction and wear test were done in ball-on-flat format with a custom-built microtribometer. The current objectives are to show a variance in friction response and wear resistance comparing high versus low crystallinities in UHMWPE, under dry conditions and lubricated with a phospholipids solution. Dry sliding friction and scratch response of medical grade UHMWPE as a function of crystallinity were tested at both the microscale and nanoscale, using a custom-made microtribometer and atomic force microscope (AFM), respectively.

Lubricated friction and wear tests were completed with the microtribometer. All other processing methods are carefully controlled so that conclusions drawn can be directly correlated with the difference in degree of crystallinity between the samples.

1.5 Thesis organization

Chapters 2 and 3 correspond with research objective of the present work, friction and wear behavior of UHMWPE as a function of crystallinity and when in the presence of the phospholipid DPPC, respectively. Overall thesis conclusions are summarized in Chapter 4.

Chapter 2. Friction and wear behavior of ultra-high molecular weight polyethylene as a function of polymer crystallinity

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Abstract

In this study the friction, wear, and surface mechanical behavior of medical grade ultra-high molecular weight polyethylene (UHMWPE) (GUR 1050 resin) were evaluated as a function of polymer crystallinity. Crystallinity was controlled by heating UHMWPE samples to a temperature above its melting point and varying the hold time and cooling rates. Degree of crystallinity of the samples was evaluated using differential scanning calorimetry (DSC). A higher degree of crystallinity in the UHMWPE resulted in lower friction force and an increase in scratch resistance at the micro and nano-scales. Reciprocating wear tests performed using a micro-tribometer showed that an increase in crystallinity also resulted in lower wear depth and width. Nanoindentation experiments also showed an increase in values with an increase in sample crystallinity.

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2.1 Introduction

Total joint replacement (TJR) is a procedure in which osteoarthritic joints, such as the knee or hip, are surgically replaced with an artificial device (prosthesis). Researchers have estimated that the demand for TJR is expected to increase dramatically in the next 25 years [32-34]. Though these procedures are common and generally successful, the life-span of a hip TJR with UHMWPE is often limited in patients, typically only 15-20 years. After awhile, the joints can become unstable and fail from material wear [35]. In a hip prosthesis, a metallic femoral head component articulates with a polymer lined acetabular cup that is embedded into the former hip socket. Ultra-high molecular weight polyethylene (UHMWPE) paired with a metal (cobalt chrome or Titanium alloys) or ceramic (alumina or zirconia) are the most common combination of materials used in Total Hip Replacements (THR) [4, 7, 8, 13, 14]. Low friction and resistance to cracking make the polymer especially advantageous for enduring stresses occurring in the hip joint. However, the polymeric nature of UHMWPE makes it susceptible to wear [8], releasing tiny particles into the joint capsule, causing osteolysis which leads to aseptic loosening and eventual failure of the implant [5, 15].

Tribological properties of the articulating metal on UHMWPE surfaces in TJRs have been recognized as critical factors affecting their durability and reliability [4, 7, 8, 14, 29, 36, 37]. Specifically, the characteristics of the softer, polymeric material have become an important area of study to reduce the problem of material wear in hip replacements, without compromising its low-friction and high impact strength advantage. It has been documented that adhesive, abrasive, and fatigue are the primary mechanisms of wear in polymers [2]. Studies have shown that a polymer's resistance to wear is

directly related to its mechanical properties, which have been linked to the polymer's physical morphology, such as crystallinity [3]. Energy caused by viscoelastic deformation is adsorbed by shear yielding in the crystalline regions of polymers, where the lamellar structure unfolds and allows the energy to dissipate more efficiently than the amorphous regions where chain motion is restricted by entanglements. Hence, a higher degree of crystallinity should give higher elastic modulus, toughness, and elongation to break. Researchers have shown increase in yield strength and elastic modulus of cross-linked UHMWPE with an increase in crystallinity [7, 13]. Kang et al [8] showed that a higher degree of crystallinity in cross-linked UHMWPE resulted in higher tensile strength with lower creep deflection, but also higher wear rate. Increases in elastic modulus, yield strength, as well as microhardness and fracture toughness have also been established through increasing crystallinity in UHMWPE independent of cross-linking [5]. Studies compared mechanical properties of virgin, rod-stock UHMWPE to a pressure-induced high crystallinity UHMWPE, called Hylamer™, without the effects of cross-linking and confirmed higher mechanical properties such as yield stress and elastic modulus corresponded to higher crystallinity; however, this material did not show significantly higher wear resistance [8]. The relationships between friction, wear, and crystallinity remain unclear. Thermal processing affects the morphology, crystallinity and mechanical properties of a polymer, all of which can affect its tribological performance [38, 39]. Understanding how morphology and crystallinity affect friction and wear behavior is imperative in the pursuit of developing a superior joint material.

The objective of this study is to measure the tribological and properties of medical grade UHMWPE as a function of crystallinity at both the microscale and nanoscale.

Adjusting thermal treatment between two similar polymer samples gives the variance in crystallinity that is needed for the study. All other processing methods are carefully controlled so that conclusions drawn can be directly correlated with the difference in degree of crystallinity between the samples.

2.2 Experimental details

2.2.1 Materials

Commercially available, ram extruded GUR 1050, rod-stock; medical grade UHMWPE (Poly Hi Solidur, Fort Wayne, Indiana) was cut into two 30 mm square pieces, 2 mm thick. Samples were soaked in methanol and held in an ultra-sonic bath for over an hour to remove any residue. They were then air-dried with nitrogen. Differential Scanning Calorimetry (DSC) gave a peak melt transition temperature of 140 °C for rod-stock UHMWPE. Samples were separately heated in a vacuum oven to 200 °C and held at this temperature for 3 hours to ensure thorough melting of each sample. After melting the first sample, the oven temperature was reduced to 110 °C, the recrystallization temperature, where the sample remained for 48 hours in order to allow time for lamellar folding into a crystalline state. After melting, the second sample was rapidly cooled by a liquid nitrogen quench to minimize recrystallization. Both samples were clamped with low pressure against a clean quartz plate while heating to impart low, consistent surface roughness. Prior to all friction and wear tests, UHMWPE samples were rinsed with methanol and air-dried with nitrogen.

2.2.2 Differential Scanning Calorimetry (DSC)

A Perkin-Elmer DSC (Pyris 1) was used to characterize the melting point and percentage crystallinity of the polymer samples after thermal treatment. 10 mg of the sample was used for all DSC runs. The samples underwent a heating cycle from room temperature to 200 °C at a rate of 10 °C/min and also a cooling cycle from 200 °C to room temperature at a rate of 10 °C/min. The melting point was calculated from the crossover point of the tangents drawn to the horizontal and vertical portion of the melting peak. The percentage of crystallinity was calculated from the ratio of the area under the melting peak to the enthalpy of melting of a 100 % crystalline sample—291 J/g [40].

2.2.3 Nanoindentation

Nanoindentation was performed on the polymer samples with a Berkovich indenter using a Hysitron Triboscope (Hysitron Inc., Minneapolis, Minnesota, USA) in conjunction with an Atomic Force Microscope (NanoScope Dimension™ 3100, Digital Instruments, Veeco Metrology Group). Two different loading profiles were used for the test. One was a trapezoidal loading profile with a peak indentation force of 25 µN (loading time 2.5 seconds, holding time 1 second, and unloading time 0.5 second, respectively). The other was a partial loading and unloading profile with an equal loading and unloading rate of 10 µN/s and ten different peak indentation loads ranging from 5 to 50 µN. During indentation tests, the sample was held firmly by the vacuum chuck of the AFM. The mechanical properties, namely hardness and elastic modulus, were analyzed using the Oliver and Pharr method [41]. A common Poisson's ratio 0.36 of polymer was used for all of the elastic modulus calculations.

2.2.4 Microtribometer

Microscale friction was obtained using a custom-built reciprocating microtribometer. Four ball-on-flat tests were conducted on each sample using a smooth, spherical Si_3N_4 probe (radius ~ 1.2 mm) (Figure 1) over a single stroke (length 20 mm) at a rate of 1 mm per second with a linear increase in the normal load (0 – 200 mN).

Reciprocating wear tests were completed on each sample using the microtribometer and a smooth, spherical Si_3N_4 probe of radius ~ 1.2 mm (Figure 1) in controlled low humidity (<15 % RH). A 125 mN constant normal load was applied to the samples for one thousand cycles of 20 mm stroke lengths at a speed of 5 mm per second. A dry scratch test was performed using a conical diamond probe (radius ~ 100 μm) over a single stroke (length 20 mm) at 1 mm per second with a linear increase in normal load (0 – 750 mN). A profilometer was used to measure depth and width of the tracks from all wear tests.

2.2.5 Atomic Force Microscopy (AFM)

Experiments in contact mode were carried out with a Dimension™ 3100 AFM (Nanoscope IV, Veeco Instruments, Santa Barbara, CA) in controlled low humidity (6 ± 2 % RH) conditions to minimize effects of adsorbed water vapor. Standard V-shaped silicon nitride probes from Veeco with a quoted normal spring constant of 0.58 N/m and tip radius of 10-40 nm were used. The normal spring constant of the cantilever used was calibrated to have an actual value of 0.35 N/m using the reference lever method [42].

Friction force data presented are averages of five measurements at multiple sample locations. The friction force was calibrated using Ruan and Bhushan's method

[43]. The radius of the tip was characterized before and after the experiments using a commercially available tip characterizer sample TGT01 (Mikromasch). The images were analyzed using SPIP software (Image Metrology) to calculate the tip radius. The tip profiles were generated using a MATLAB code.

2.2.6 Scanning Electron Microscopy (SEM)

A JEOL JSM-606LV scanning electron microscope was used to image the microtribometer wear tracks from both the cyclic wear and the scratch tests. The sample chamber was low-vacuum and accelerating voltages of 1-2 kV at ranges of 10-200x magnification were used. These images were used to measure wear widths and scratch lengths. SEM was also used to image the Si₃N₄ probes to confirm a spherical shape (Figure 1) and to check for polymer film transfer after reciprocating wear tests. A conductive, gold layer (~ 200 Å thick) was sputter-coated onto the probes before imaging. Low accelerating voltage, 1-2 kV, was used.

2.2.7 Optical Microscopy

An Olympus BX51WI (Leeds Precision Instruments, Inc.) Twin Epi-Flourescence Optical Pathway (Prairie Technologies) microscope was used to image the wear tracks from the diamond probe scratch test.

2.3 Results

The sample held at 110 °C for 48 hrs showed a degree of crystallinity of 52.5 % and a melting temperature of 140 °C. The sample which was immediately quenched in

liquid nitrogen had 45.6 % crystallinity and a melting temperature of 135 °C. This evidence shows that the first sample resulted in a higher degree of crystallinity. Topography images of both samples were taken using the AFM and are shown in Figure 2. The surface of the higher crystallinity (HC-PE) sample displayed a lamellar type of structure that is indicative of crystalline regions in semicrystalline polymers [4]. The lower crystallinity (LC-PE) sample did not display any distinct lamellar structure at this scale. The final surface roughness (RMS) of the HC-PE and LC-PE samples were 4.58 ± 0.18 nm and 3.18 ± 0.18 nm ($1 \mu\text{m} \times 1 \mu\text{m}$ scan) respectively, as measured using the AFM. The difference in roughness levels between the two samples is small and, hence, can be considered to have negligible impact on the observed difference in the tribological behavior at either scale. Physical parameters of UHMWPE as a function of crystallinity are shown in Table 1.

Figure 3 (a) shows the typical load penetration depth curves of nanoindentation tests on two polymer samples using the same trapezoidal loading profile. Indentation on the HC-PE has a higher peak load while shallower penetration depth compared with the LC-PE sample. The average elastic modulus and hardness of five indentations for the two samples are shown in Table 1. The results show that the HC-PE has a higher elastic modulus and hardness than LC-PE. Figure 3 (b) shows the typical load penetration depth curves of nanoindentation tests with partial loading and unloading profile. The elastic modulus and hardness are determined from the partial unloading curves at different peak loads. The variations of average elastic modulus and hardness with the average indentation contact depth of five indentations for the two samples are plotted in Figure 4. Both elastic modulus and hardness for all the polymers decrease with the increase of

contact depth. When contact depth is less than 80 nm, partial loading and unloading tests show similar trends that elastic modulus and hardness of HC-PE are higher than LC-PE. For contact depth larger than 80 nm, both samples give almost the same elastic modulus and hardness.

The friction responses of the UHMWPE at the microscale and nanoscale are shown in Figure 5. For both of the samples across scales the friction force increased with an increase in normal load. The data indicates that HC-PE results in a lower friction response than LC-PE at both the micro and nanoscale.

Optical microscopy showed that the friction experiments completed with the Si_3N_4 probe on the tribometer had no visible wear prior to 75 mN on either sample. Friction coefficients for each sample at the microscale were calculated for two regions, before and after the observed onset of damage, as shown in Figure 5a. Linear fits in region 1 showed friction coefficients for HC-PE and LC-PE to be 0.31 and 0.42, respectively. Fits from region 2 gave a coefficient of 0.17 for HC-PE and 0.23 for LC-PE. For the AFM friction experiments, no discernable wear was observed up to loads of 60 nN. Measured friction coefficients at the nanoscale were 0.035 for HC-PE and 0.063 for LC-PE. The friction coefficients were one order of magnitude different from the nano to microscale. In both cases, LC-PE gave a higher friction coefficient.

Microscale ramped-load scratch tests using the diamond probe caused damage in the early stages of the tests for both samples. For both samples, the rate of friction response to normal load was non-linear, corresponding to deeper probe penetration into the sample at higher loads. Using an optical microscope and SEM the damage onset for the LC-PE sample occurred at lower normal load (between 50-70 mN) than for the HC-

PE sample (between 90-100 mN). LC-PE exhibited higher scratch depth at all applied normal loads, as was measured with a profilometer. The scratch depth width at the maximum load of 750 mN (Figure 7) was measured on both samples and is reported in Table 2 below. The LC-PE sample exhibited a scratch depth that was 100 nm larger than that of the HC-PE sample. In the case of AFM scratch tests, LC-PE exhibited higher scratch depth than HC-PE at all applied normal loads at certain locations and comparable scratch depths in other locations. This is likely a result of variance in lamellar structure at the surface.

The dry-sliding, reciprocating wear test performed using the microtribometer and a spherical Si_3N_4 probe showed the LC-PE friction response to level-off at around 27 mN compared to the lower friction response of HC-PE, which leveled-off at about 15 mN (Figure 8). The profilometer revealed wear depth measurements of $0.205 \pm .016 \mu\text{m}$ and $0.117 \pm .030 \mu\text{m}$, respectively. These are consistent with the LC-PE exhibiting more damage than the HC-PE. SEM images of the probes taken after wear tests revealed no polymer film transfer. The results of the tribological tests are summarized in Table 2. The data shows that the wear resistance of UHMWPE increases with an increase in crystallinity, resulting in higher hardness and elastic modulus [44], hence, enhanced resistance to surface damage.

2.4 Discussion

After completing DSC, the thermal treatment performed proved to be effective in controlling differences in crystallinity. Turell et al observed that at the nanoscale, lamellar structure of semicrystalline UHMWPE can be identified [4]. In a comparison

between images of the slowly cooled and nitrogen quenched samples, the lamellar morphology is much more apparent in the former sample. Turell pointed out that the size of lamellae is increased with slow cooling and annealing, and decreased by quenching, which accounts for the differences in detail of the crystalline structures. In the present study, AFM images confirm that the UHMWPE samples indeed display different crystalline morphology, and that the slowly cooled (and predicted higher crystallinity) sample demonstrated a more evident presence of lamellae. As anticipated, the slowly cooled sample resulted in a higher degree of crystalline volume and the quenched sample came out with a significantly lower crystalline volume. Rod-stock control UHMWPE and methods of high compression moulding [39] and annealing [7] of the polymer below its melting temperature have proven to prepare samples with crystallinities as high as 60-75%. However, in order to control the surface roughness parameter, it was necessary in the current study to melt the UHMWPE samples to eliminate variations from milling effects.

Mechanical properties of semicrystalline polymers depend on many variables, including the degree of crystallinity and operating temperature [3]. Results of nanoindentation show a 41.5 % higher elastic modulus and a 78.6 % higher hardness value for HC-PE over LC-PE. The lower wear of HC-PE in cyclic and abrasive scratch tests can be linked to higher mechanical properties, hence increased wear resistance.

HC-PE showed a slightly lower coefficient of friction than LC-PE. Ho et al. observed similar correlation on UHMWPE and suggested that the increase in coefficient of friction with decreased crystallinity could be due to the decreased storage modulus caused by the decreased crystallinity [39]. Friction responses of the diamond scratch test

performed by the microtribometer indicate that as wear depth increases, coefficient of friction will increase as well. LC-PE experienced a higher friction response than HC-PE, corresponding with deeper wear tracks. Wear profiles of diamond scratching on each sample revealed ploughed grooves and lipped edges characteristic of deformation from abrasive wear. SEM images confirm the occurrence of abrasive wear ribboning on the low crystallinity sample (Figure 8).

Another explanation for the observed tribological differences between the high and low crystallinity samples takes a closer look at the probe-sample interface. Friction under high pressures can elevate the asperity-contact temperature, sometimes reaching hundreds of degrees above the bulk temperature [2]. These “flash temperatures” can cause localized melting at an interface, altering their mechanical properties and making them more susceptible to plastic deformation in those regions. The melting transition of a polymer is influenced by its degree of crystallinity and size of crystalline structure [3, 6]. Enlarging crystals and crystalline volume will increase temperature required for complete melting, while the opposite is true for lower crystallinity volume, which was supported by the DSC data from this study. Therefore, it is likely that under the high pressures of the diamond probe, the LC-PE sample could experience the effects of localized melting sooner than the HC-PE sample, making it more vulnerable to deformation.

During reciprocating wear after the initial static friction response, friction dropped dramatically for both samples as shown in Figure 5. In the case of the LC-PE sample, the friction response increased until the sliding distance reached about 10 m, at which point the friction response appeared to level-off at around 27 mN. It can be expected that the

probe continued to groove the sample until it reached a maximum level of deformation at that load, causing friction to become nearly steady. Friction response of HC-PE only showed a decreasing trend, even with the occurrence of plastic deformation. Though the plot seems to level-off at around 15 mN, a slight downward slope remains, even after 1000 cycles.

Wear depths showed that LC-PE had deeper tracks than HC-PE, indicating that that higher crystallinity is more resistance to wear from fatigue mechanisms. Kang et al [8] also showed lower microscale wear of a slowly cooled, higher crystalline sample of cross-linked UHMWPE compared to a quenched sample, attributed to the formation of larger lamellae and mechanical reinforcement. Comparing the effects of cyclic stress on the experimental samples, it is reasonable to conclude that long term stress on a higher crystallinity UHMWPE cup lining would lead to less friction *in vivo* than that of a lower crystallinity lining.

2.5 Conclusions

The results indicate that increasing the surface crystallinity of UHMWPE decreases the friction response of the polymer at both the microscale and nanoscale. Increased crystallinity also resulted in an increase in scratch and wear resistance which is attributed to increase in hardness and elastic modulus.

Acknowledgments

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Table 1. Summary of physical parameters of UHMWPE as a function crystallinity

Sample	Crystallinity (%)	RMS surface roughness (nm)	Elastic Modulus (GPa)	Hardness (GPa)
HC-PE	52.5	4.58 ± 0.18	2.42 ± 0.014	0.25 ± 0.03
LC-PE	45.6	3.18 ± 0.18	1.71 ± 0.03	0.14 ± 0.004

Table 2. Summary of friction coefficients and wear measurements as a function of UHMWPE crystallinity

Sample	Microscale Coefficient of friction (Tribo)	Nanoscale Coefficient of friction (AFM)	Wear depth ^a (μm)	Wear width ^a (μm)	Scratch depth ^b (μm)	Scratch width ^b (μm)	Scratch depth ^c (nm)
HC-PE	0.15 ± 0.02	0.035	0.117 ± .030	85.0 ± 5.9	0.46 ± .01	85.2 ± .01	3.98 ± .99
LC-PE	0.22 ± 0.01	0.063	0.205 ± .016	113.5 ± 9.3	0.52 ± .01	102.3 ± .01	6.55 ± .37

^aMeasured using a Si₃N₄ probe on the microtribometer for 1000 reciprocating, 20 mm cycles at an applied load of 125 mN.

^bAbrasive wear using a diamond probe on the tribometer for a 0-750 mN ramped-load scratch test. Depth measurements shown represent those at maximum load, 750 mN.

^cMeasured using AFM at a normal load of 80 nN and 40 cycles.

Figure captions

Figure 1. SEM image of spherical, Si_3N_4 probe (radius ~ 1.2 mm) **(a)** and AFM surface roughness **(b)** used on microtribometer.

Figure 2. Topography maps of high crystallinity and low crystallinity samples **(a)** $5 \mu\text{m} \times 5 \mu\text{m}$ and **(b)** $1 \mu\text{m} \times 1 \mu\text{m}$ scan sizes obtained using an atomic force microscope (AFM).

Figure 3. Load-penetration (P-h) curves from nanoindentation tests on both low crystallinity and high crystallinity samples with standard loading profile **(a)** and partial loading and unloading profile **(b)**.

Figure 4. Elastic modulus (E) **(a)** and **(b)** hardness (H) as a function of indentation contact depth (h_c).

Figure 5. Microscale (tribometer) **(a)** and nanoscale (AFM) **(b)** friction response as a function of normal load for both the high crystallinity and low crystallinity samples. Friction response is higher for the low crystallinity sample in both cases.

Figure 6. Microscale (tribometer) friction response of UHMWPE using a diamond probe as a function of normal load for both the high crystallinity and low crystallinity samples. Friction response is higher for the low crystallinity sample.

Figure 7. Optical images of dry scratch tests with diamond probe performed with the microtribometer on high crystallinity **(a)** and low crystallinity **(b)**.

Figure 8. Microscale (tribometer) friction response of Si_3N_4 probe (radius ~ 1.2 mm) on high crystallinity and low crystallinity samples and a function of sliding distance in a dry, reciprocating wear test with a constant load of 125 mN

Figure 9. SEM images of tracks from reciprocating wear tests with Si_3N_4 probe (radius ~ 1.2 mm) performed using the microtribometer on high crystallinity **(a)** and low crystallinity **(b)**.

Figure 10. SEM image of wear ribboning occurring on the low crystallinity sample at the initial onset of deformation during scratch test with diamond probe.

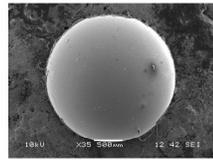
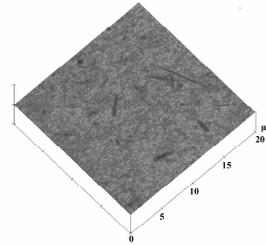
Figure 1.**(a)****(b)**

Figure 2.

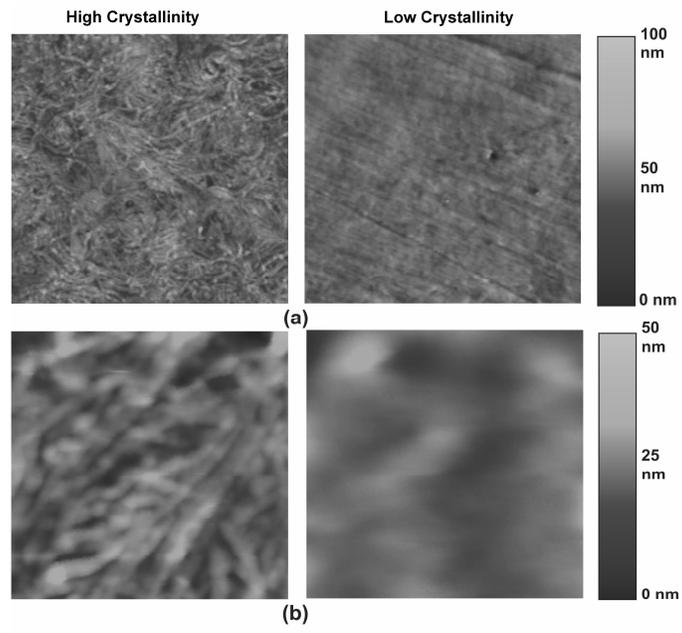


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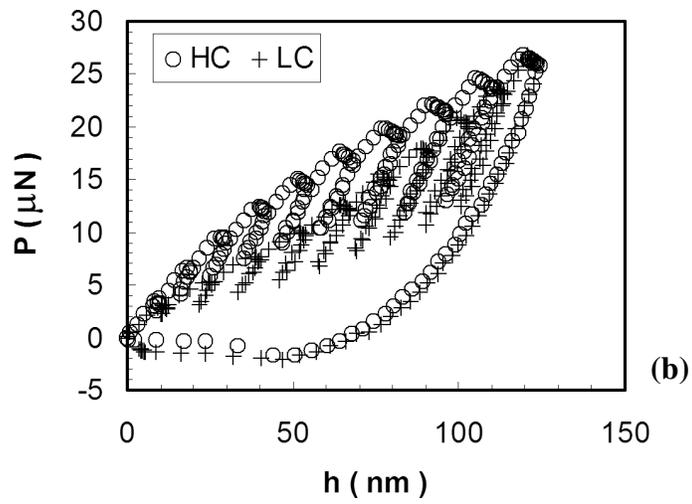
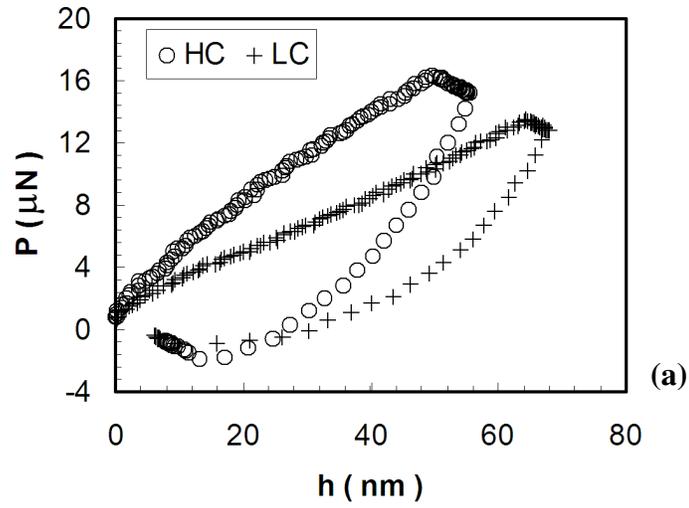


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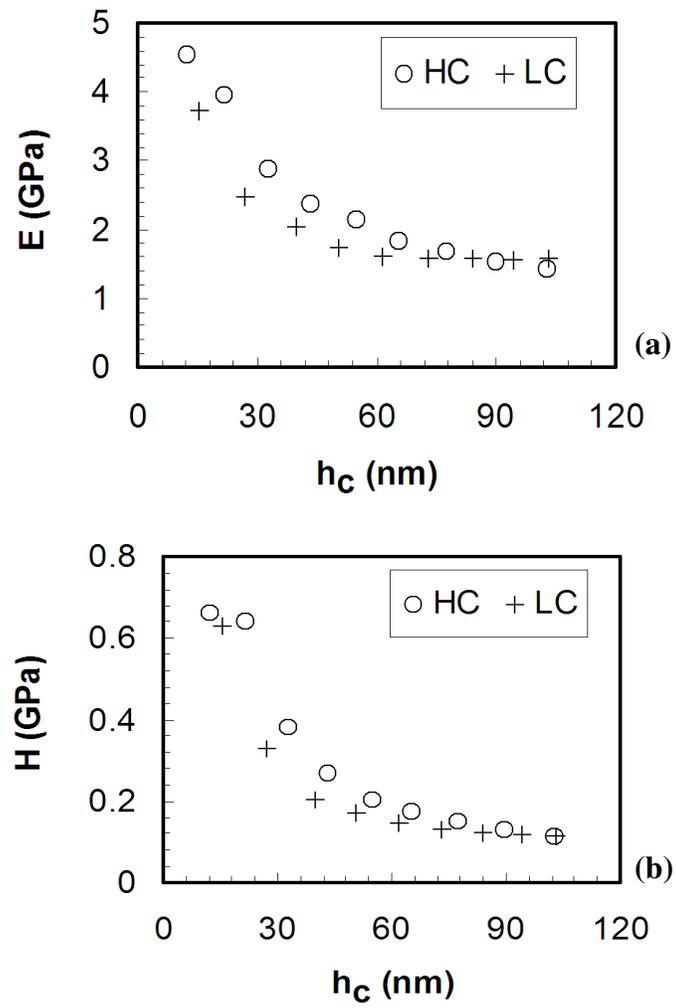


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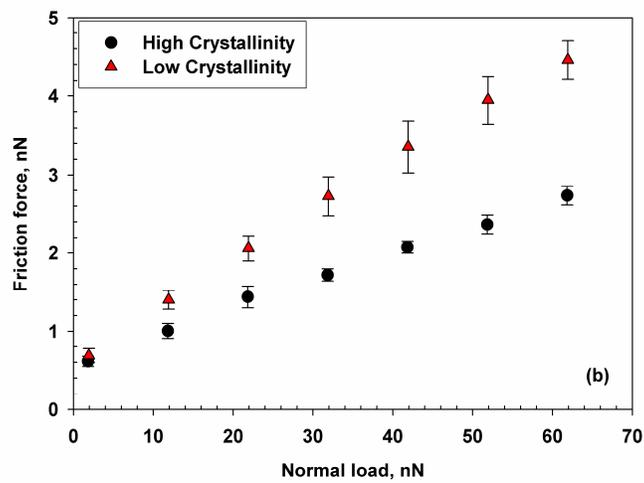
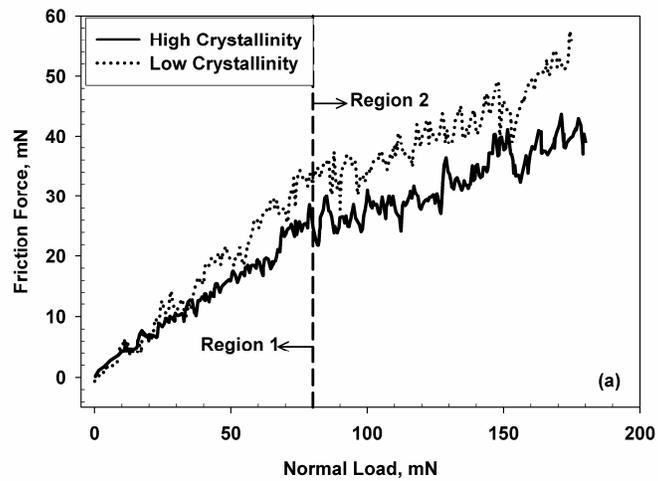


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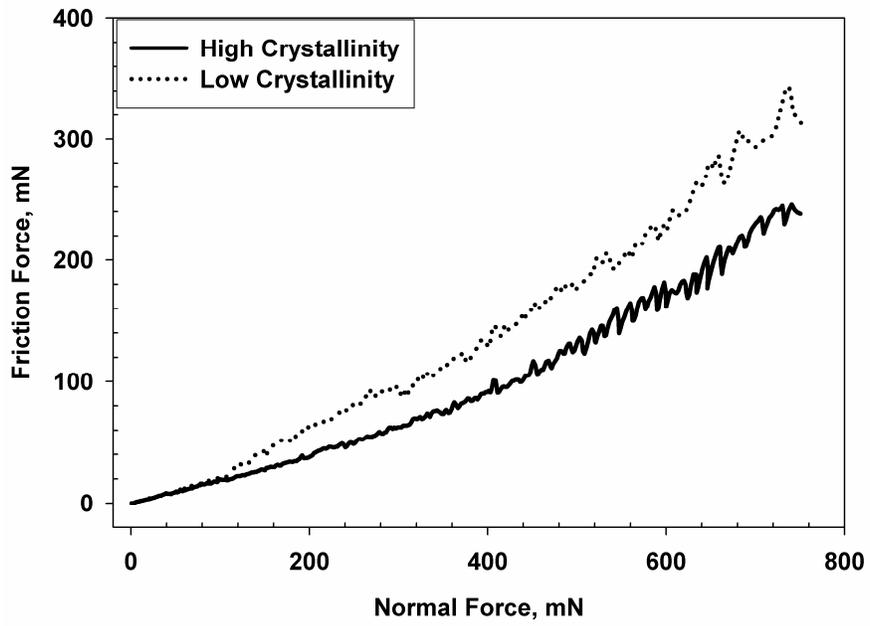


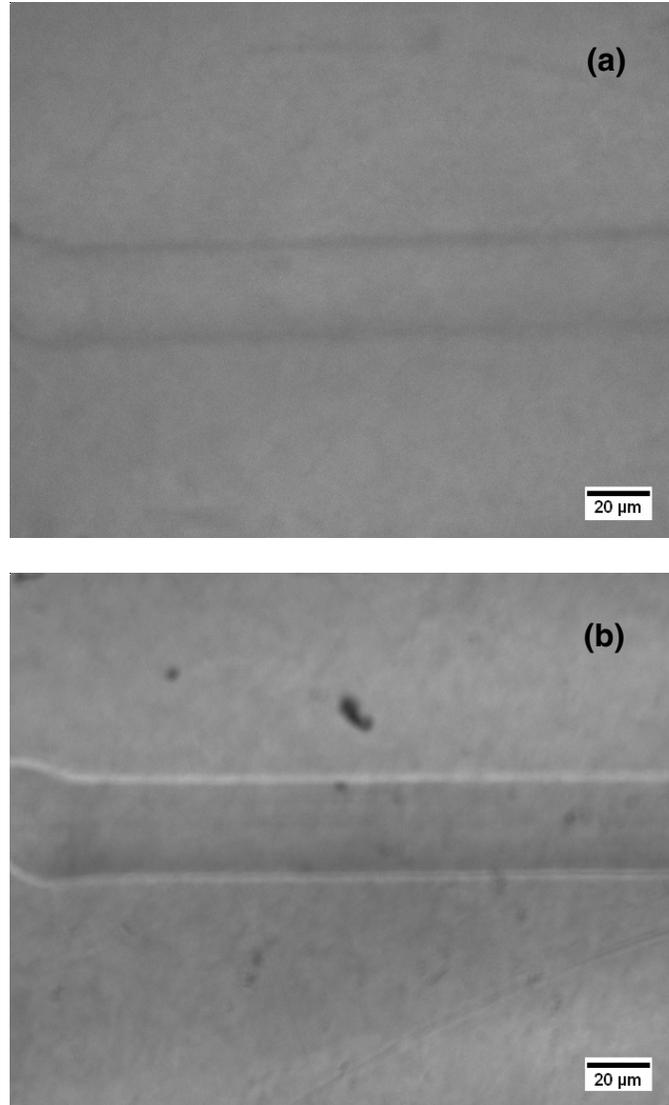
Figure 7.

Figure 8.

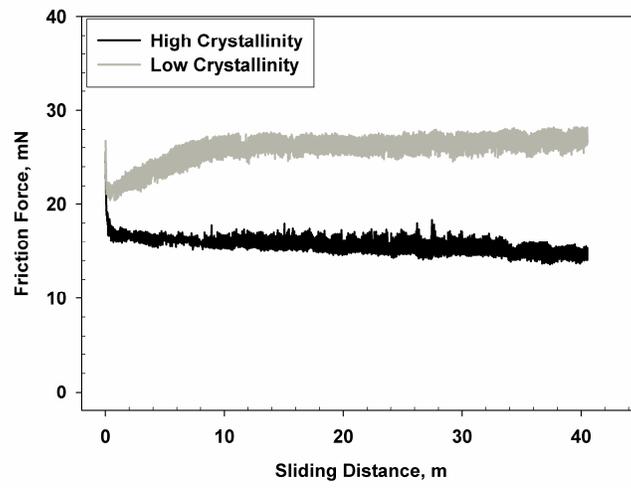


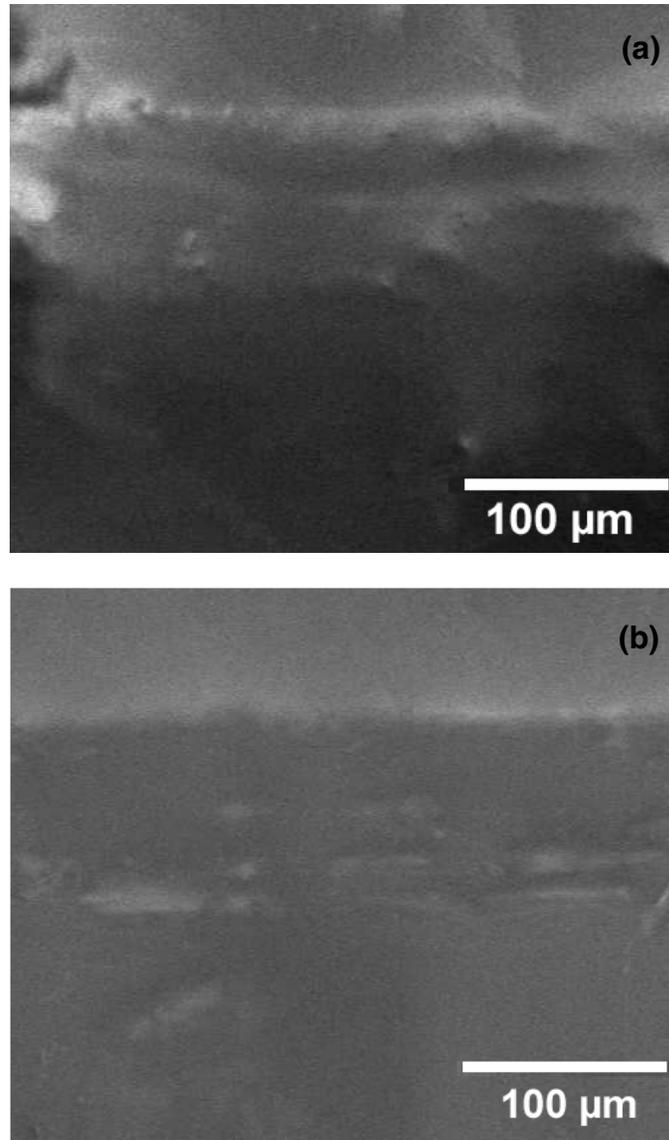
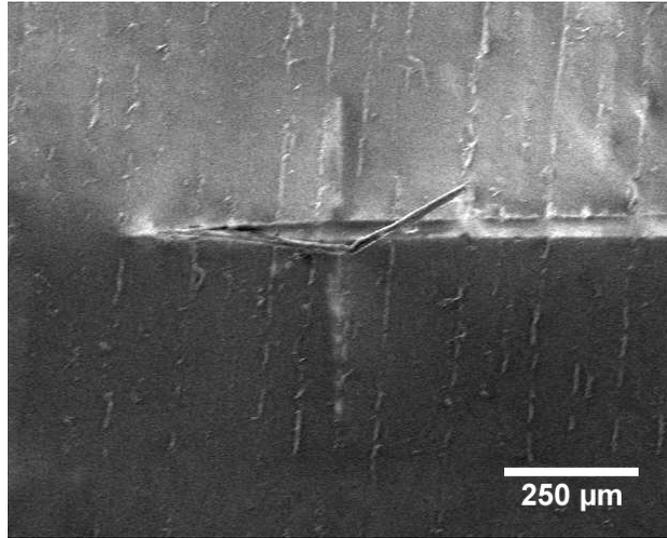
Figure 9.

Figure 10.

Chapter 3. Friction and wear behavior of ultra-high molecular weight polyethylene as a function of crystallinity in the presence of the phospholipid DPPC (dipalmitoyl phosphatidylcholine)

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Abstract

In this study the friction and wear behavior of ultra-high molecular weight polyethylene (UHMWPE) were evaluated as a function of polymer crystallinity in the presence of the phospholipid DPPC (dipalmitoyl phosphatidylcholine) dissolved in ethanol. Samples of UHMWPE were separately heat-treated to get high and low crystallinity samples. Degree of crystallinity was evaluated using differential scanning calorimetry (DSC). Quantitative friction and wear experiments were conducted using a custom-made microtribometer with commercially available spherical Si₃N₄ probes in controlled and phospholipid-dissolved lubricants. The higher crystallinity sample exhibited slightly lower friction than the lower crystallinity in the control, and decreased significantly when phospholipids were present. The higher crystallinity sample showed a higher wear resistance than the lower crystallinity sample during all reciprocating wear tests. DPPC acting as a lubricant had a marginal effect on increasing the wear resistance of high crystallinity UHMWPE, whereas the low crystallinity sample became more prone to wear. AFM topography images and contact angle measurements of both samples before and after phospholipid exposure indicate that the higher crystallinity sample absorbed a greater density of DPPC. Increasing crystallinity is a way of escalating adsorption of SAPL onto UHMWPE, in order to make a more wear-resistant load bearing material for Total Joint Replacement.

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3.1 Introduction

For the past forty years, ultra-high molecular weight polyethylene (UHMWPE) has been the primary material used for the articulating cup of artificial hip joints [4, 7-14]. Its viscoelasticity, low friction, and low wear resemble properties of cartilage lining natural human joints more than any other biocompatible material. However, it has been found that polymeric wear particles from the UHMWPE in artificial hip joints have been the major factor limiting the life of an implant, causing osteolysis and loosening of the joint [5, 12], requiring revision surgery. Much attention has been on the tribological behavior of UHMWPE in an effort to reduce its wear. Many studies conducted have focused on altering the physical and chemical properties of UHMWPE to increase wear resistance, such as gamma-irradiated cross-linking [16] and orientating crystalline [17] structure, which have correlated with decreases in wear. Others have focused on the environment of the joint interface *in vivo*.

Healthy, human joints are lubricated by synovial fluid and can achieve remarkably low friction behavior, with coefficients as small as 0.002-0.006 [19, 23]. Synovial fluid is a complex plasma solution mostly of proteins, hyaluronic acid, and lipids and is sealed by the joint capsule, comprising of a membrane-lined fibrous layer of connective tissue [18]. With the growing industry for total joint replacements, research has been done on UHMWPE to establish which constituent of the synovial fluid is responsible for the highest lubricating contribution. Sawae et al. compared friction of UHMWPE in the presence of albumin (major protein component of synovia) versus hyaluronic (HA) and found albumin caused higher friction than HA [11]. Gispert et al. also compared friction between albumin and HA, as well as a solution of albumin and HA combined. There

were no consistent results as to the individual contributions to friction and lubrication, but it was clear that the combination of albumin and HA in a lubricating solution caused the lowest friction response and wear rate [20].

Surface active phospholipids (SAPL) have been reported to act as a boundary lubricant in human joints [19, 21, 22] by adsorbing phosphate head groups onto the surface of the joint, and leaving fatty-acid tails to create a hydrophobic monolayer [19]. It has been shown that in osteoarthritic joints, the synovial fluid does not lubricate as well as in healthy joints [24, 25] and this is often attributed to a deficiency of SAPL [23]. Investigations on the tribological influence of phospholipids on UHMWPE have correlated decreasing friction and wear in the presence of phospholipids [26]. The most abundant lipid in synovial fluid is DPPC (dipalmitoyl phosphatidylcholine), making up 45 % of the total volume weight of lipids [22], and is one of the most common phospholipids studied on UHMWPE. DPPC dissolved in propylene glycol and ethanol on UHMWPE have shown lower friction values when compared to control lubricant without DPPC [19]. Mazzucco et al. reported a lubricant of DPPC in phosphate buffered solution (PBS) to have the lowest coefficient of friction between polyethylene and cobalt chrome surfaces, when compared to HA and protein dissolved in PBS [26]. It is hypothesized that the presence of phospholipids between articulating surfaces would also reduce wear by reducing interfacial contact, though further studies are needed to confirm this theory.

SAPL have an affinity for hydrophilic surfaces due to their ionic phosphate heads [19]. UHMWPE is considered a hydrophobic polymer (contact angle ~80-100 degrees), which has low wettability and the potential to resist adsorption of the lipid. Gispert et al.

showed a marked change in contact angle and surface tension on UHMWPE using separate solutions of saline with HA and bovine serum albumin (BSA) compared to saline alone. The presence of HA in saline increased the contact angle whereas BSA decreased the angle [20]. The effect of crystalline morphology at the surface on the contact angle of polypropylene was examined by Yui et al. and found to correlate well: higher crystallinity at the surface gave lower contact angles, confirming that crystalline regions of polypropylene contain more surface energy than amorphous regions [30]. Molecular simulations have shown similar trend in polyethylene [31]. One potential for increasing adsorption of SAPL onto UHMWPE is to increase the crystallinity of the material.

In the present study, friction and wear behavior of UHMWPE as a function of crystallinity in the presence of a DPPC-ethanol lubricant was investigated. Two UHMWPE samples with different crystallinities were made using specific thermal treatments. Friction and wear tests were done with a custom-built ball-on-flat microtribometer under separate lubricant of a pure ethanol control and a solution of DPPC phospholipids dissolved in ethanol.

3.2 Experimental details

3.2.1 Materials

Commercially available, ram extruded GUR 1050, rod-stock; medical grade UHMWPE (Poly Hi Solidur, Fort Wayne, Indiana) was cut into two 30 mm square pieces, 2 mm thick. Samples were soaked in methanol and held in an ultra-sonic bath for over an hour to remove any residue. They were then air-dried with nitrogen. Differential

Scanning Calorimetry (DSC) gave a peak melt transition temperature of 140 °C for rod-stock UHMWPE. Two samples with significant difference in crystallinity were desired. Separately, samples were heated in a vacuum oven to 200 °C. To create a high crystallinity polymer, the first sample was held at this temperature for 3 hours to ensure thorough melting; the oven temperature was then reduced to 110 °C, the recrystallization temperature, where the sample remained for 60 hours in order to allow time for lamellar folding into a crystalline state. The second sample was held for 5 hours at 200 °C, to give sufficient time for thorough melting and disordering of the chains. After holding the second sample for 5 hours, it was rapidly cooled by a liquid nitrogen quench to freeze amorphous entanglements and minimize recrystallization. Both samples were clamped with low pressure against a clean quartz plate while heating to impart low, consistent surface roughness. All UHMWPE samples were rinsed with methanol and air-dried with nitrogen before further treatment or testing.

3.2.2 Differential Scanning Calorimetry (DSC)

A Perkin-Elmer DSC (Pyris 1) was used to characterize the melting point and percentage crystallinity of the polymer samples after thermal treatment. 10 mg of the sample was used for all DSC runs. The samples underwent a heating cycle from 25 °C to 200 °C at a rate of 10 °C/min and also a cooling cycle from 200 °C to 25 °C at a rate of 10 °C/min. The melting point was calculated from the crossover point of the tangents drawn to the horizontal and vertical portion of the melting peak. The percentage of crystallinity was calculated from the ratio of the area under the melting peak to the enthalpy of melting of a 100 % crystalline sample (291 J/g) [40].

3.2.3 Phospholipids

The phospholipids used in this study were synthetic, 99% pure L- α -Phosphatidylcholine, dipalmitoyl (DPPC), P0763 by Sigma-Aldrich Chemical Company. The DPPC was dissolved into ethyl alcohol at a concentration of 0.5 mg/mL, corresponding to the approximate concentration of DPPC found in human synovial fluid [26]. Sodium azide (~ 0.01%) was added to prevent microbial growth. The liquid was then vortex mixed for 3-4 minutes and ultrasonicated for 30 minutes at a temperature of 43 °C to create a homogeneous solution. The DPPC-ethanol solution was used as a lubricant in friction and wear tests of the polymer samples; prior to lubricated tests, samples were covered and soaked in the solution for ~ 3 hours before testing. Throughout testing, surfaces were submerged in the solution.

3.2.4 Microtribometer

Microscale friction was obtained using a custom-built reciprocating microtribometer. Four ball-on-flat tests were conducted on each sample using a smooth, spherical Si₃N₄ probe (radius ~ 1.2 mm) over a single stroke (length 15 mm) at a rate of 1 mm per second with a linear increase in the normal load (0 – 200 mN). Reciprocating wear tests were completed on each sample using the microtribometer and a smooth, spherical Si₃N₄ probe (radius ~ 1.2 mm). A 140 mN constant normal load was applied to the samples for one thousand cycles of 15 mm stroke lengths at a speed of 5 mm per second. Dry-sliding friction and wear tests were complete in dry conditions, (<15 %

humidity). Lubricated friction and wear tests were done in ambient conditions. A profilometer was used to measure depth and width of the tracks from all wear tests.

3.2.5 Atomic Force Microscopy (AFM)

An AFM was used to measure surface roughness and wear track profiles of the two polymer samples. Experiments in contact mode were carried out with a DimensionTM 3100 AFM (Nanoscope IV, Veeco Instruments, Santa Barbara, CA) in controlled low humidity (6 ± 2 % RH) conditions to minimize effects of adsorbed water vapor. Standard V-shaped silicon nitride probes from Veeco with a quoted normal spring constant of 0.58 N/m and tip radius of 10-40 nm were used. The normal spring constant of the cantilever used was calibrated to have an actual value of 0.35 N/m.

3.2.6 Scanning Electron Microscopy (SEM)

A JEOL JSM-606LV scanning electron microscope was used to image the microtribometer wear tracks from both the cyclic wear and the scratch tests. The sample chamber was low-vacuum and accelerating voltages of 1-2 kV at ranges of 10-200x magnification were used. These images were used to measure wear widths and scratch lengths. SEM was also used to image the Si₃N₄ probes to confirm a spherical shape (Figure 1) and to check for polymer film transfer after reciprocating wear tests. A conductive, gold layer (~ 200 Å thick) was sputter-coated onto the probes before imaging. Low accelerating voltage, 1-2 kV, was used.

3.2.7 Optical Microscopy

An Olympus BX51WI (Leeds Precision Instruments, Inc.) with Twin Epi-Fluorescence Optical Pathway (Prairie Technologies) microscope used to image the wear tracks and probes.

3.2.8 Contact angle measurements

Hydrophobicity of the UHMWPE before and after exposure to DPPC was measured using contact angle measurements. Contact angles were measured using analysis of high magnification digital images from a CCD camera of 10 μ l water droplets on each sample before and after soaking in the phospholipids solution.

3.3 Results and discussion

Differential scanning calorimetry (DSC) revealed that the two heat treated samples of UHMWPE had different crystallinities. Melting temperatures peaked at 134.5 °C for the nitrogen quenched sample and 139.5 °C for the slowly cooled sample. The peak melt transition temperature generally defines the point at which the largest lamellae of a polymer completely melt, and is characteristic of the degree of crystallinity in the bulk polymer [3]. The crystallinity percentages of the samples were calculated from the heat of enthalpy measured over that of a 100% crystalline sample, 291 J/g [40]. Heat of enthalpy for the quenched sample was 129.7 J/g and 162.5 J/g for the slowly cooled sample, giving crystallinities of 44.6 % and 55.8 %, respectively.

Topography maps of the two polymer samples taken by the AFM after heat treatment showed comparable surface roughness on both samples. HC-PE gave an RMS

roughness of 7.27 ± 0.96 nm and LC-PE gave an RMS roughness of 5.70 ± 0.93 nm for $5 \mu\text{m} \times 5 \mu\text{m}$ scans. The sample with higher crystallinity (HC-PE) displayed lamellar structure when examined with AFM (Figure 1), which is typical of recrystallization [4]. Lamellae were not as evident in the lower crystallinity (LC-PE) sample, and it is unlikely that spherulites were formed while quenching the sample. Roughness values after the polymer samples were exposed to the lipid solution were measured at 11.03 ± 3.33 nm and 5.81 ± 0.76 nm for the HC-PE and LC-PE samples respectively. Roughness increased 50 % more for the HC-PE sample when compared to the LC-PE.

AFM topography images after exposure to lipids revealed the presence of particles on both samples (Figure 1). The HC-PE sample had a considerably higher density of particles on the surface. Since both samples had been rinsed and nitrogen dried after being submerged in the DPPC-ethanol solution for friction and wear testing, it can be expected that the particles were adsorbed onto the surface. Rahamim et al. [45] identified phospholipids on the surface of a temporomandibular joint using electron microscopy. They found the phospholipids to be spherical, granular bodies ranging from 170-280 nm in diameter, and homogeneously distributed on the surface [45]. Our AFM topography images showed that particles on the surfaces were similar in size and shape to that of Rahamim's group. Given that the samples were only exposed to the phospholipid solution, rinsed and nitrogen-dried, it can be reasonably assumed that the particles represent DPPC adsorption to UHMWPE. The images illustrate a strong presence of globules scattered throughout the HC-PE sample, but are barely noticeable on the LC-PE sample. This indicates that the HC-PE sample adsorbed significantly more DPPC than the LC-PE sample.

As mentioned earlier, surface tension is one factor that determines wettability of a surface, and can correlate with adsorption onto a surface [1, 46, 47]. Yui et al. showed that higher crystalline structure correlates with increased surface energy of a polymer using a method of comparing contact angle measurements on crystalline versus amorphous regions of polypropylene [30]. In our case, contact angle measurements were taken from magnified digital images of droplets on the surfaces. Before exposure to phospholipids, LC-PE gave a contact angle of 88.2° and HC-PE was 59.4° . After being soaked in the DPPC solution, the contact angle of LC-PE decreased considerably to 45.4° and HC-PE increased to 76.8° . The digital images used to analyze contact angle are shown in Figure 5. Contact angle measurements on dry UHMWPE samples before lipid testing indicated that HC-PE had higher surface energy and would be more likely to adsorb the DPPC. Hills et al. showed that on healthy, bovine cartilage saline beads up, but on osteoarthritic cartilage deficient in SAPL, it will wet the surface [23]. His argument was that as the polar phosphate heads adsorbed to a hydrophilic surface, its fatty acid-chained tails create a hydrophobic monolayer surface [48]. The hydrophobicity of the new layer is dictated by the degree of adsorption onto the adsorbate, or its surface coverage [47, 48]. Contact angle measurements of the samples taken after exposure to the DPPC solution indicated that HC-PE became more hydrophobic, whereas LC-PE became more hydrophilic, agreeing with early statements of higher phospholipids adsorption onto the HC-PE sample.

Representative ramped-load friction responses of Si_3N_4 on UHMWPE are shown in Figure 2. The friction response of Si_3N_4 on LC-PE in both control and DPPC lubricated conditions was slightly higher than that of HC-PE. The presence of DPPC

corresponded with a 17 % reduction in friction coefficient of HC-PE and a 10 % increase in friction coefficient of LC-PE for ramped-load friction experiments. Friction response of reciprocating wear tests after 1000 cycles (a sliding distance of 30 m) in DPPC dissolved in ethanol showed a 17 % reduction in friction for HC-PE and a 22 % increase for LC-PE when compared to control tests.

Wear volume was also affected by the addition of DPPC into the tribological environment. Optical images of wear tracks in just ethanol are more visible than those after the addition of phospholipids, and profilometer measurements support that the HC-PE sample, DPPC in the lubricant increased wear resistance, and decreased wear resistance of LC-PE. After wear tests were completed, optical images and probes were analyzed to check for film transfer. It was anticipated that the DPPC solution would reduce, and even prevent adhesive wear. Based on images of the HC-PE probes, the opposite was true. Film transfer appeared in the case of HC-PE lubricated with DPPC in ethanol, indicating adhesive wear. Film transfer did not occur for HC-PE in the ethanol control. Optical images of the probe used in LC-PE tests on ethanol showed evidence of particles in the contact vicinity, and this material was interpreted as film transfer. SEM images of the probe used in phospholipid lubricant tests on LC-PE showed a slight presence of material on the surface of the probe which could not be seen with the optical microscope, therefore, it can be said that film transfer was miniscule. Based on profilometer depth measurements, the HC-PE sample showed higher wear resistance than LC-PE in both reciprocating tests. The presence of DPPC in the lubricant corresponded with decrease in wear depth only for the higher crystallinity sample.

The trends of microscale friction and wear tests on high versus low crystallinity UHMWPE in this study compared well with trends demonstrated by Karuppiah et al. on similar samples of low and high crystallinity. The present study supports their findings that higher crystallinity UHMWPE shows lower friction response and lower wear depth than lower crystallinity UHMWPE.

Friction results correspond well with trends found in literature that show SAPL such as DPPC to reduce friction behavior [19, 21, 26, 49-51]. Ozturk et al. showed a greater reduction in friction coefficient with an increase in DPPC concentration, and suggested that mixed or elastohydrodynamic lubrication occurred [21]. In contradiction to the mechanical theory that like materials in contact tend to adhere and fuse, friction tests show that articulating surfaces containing the phospholipid DPPC act as a releasing agent, much like Teflon® [23]. Hills and Thomas further explain that the nature of surfactants cause non-polar moieties to point outward, imparting hydrophobic surfaces less conducive to adhesion [49]. DPPC also acts as an effective boundary lubricant because of its ideal structure for monolayer cohesion [49]; a boundary lubricant is most successful when there is a strong cohesion within the bilayer, preventing asperity penetration from the counterface [19]. Bell et al. speculated that a bilayer created from SAPL acted as a boundary lubricant, illustrating that reduction of wear increased with SAPL concentration [52]. Saikko et al. also showed that DPPC as a boundary lubricant was highly effective in reducing wear volume [53]. The current study had results consistent with earlier findings that wear volume is reduced in the presence of phospholipids, particularly for the HC-PE sample. Based on the DPPC adsorption coverage seen on the sample, it's lowered friction and increased wear resistance, it is

possible that DPPC operated as a boundary lubricant for the higher crystallinity sample. The same cannot necessarily be concluded for the low crystallinity sample which showed only a small reduction in friction and no increase in wear resistance, incidentally a result of the poor adsorption pictured in Figure 1. Saikko et al. went on to note that the phospholipids did not prevent film transfer, which can be characteristic of adhesive wear, and they concluded that phospholipids are effective in reducing wear particle generation, but not transfer of the polymer [53]. Our study displayed similar phenomenon.

3.4 Conclusions

Contact angles measurements and topography maps of the two UHMWPE samples confirmed that higher crystallinity UHMWPE is more likely to adsorb SAPL than low crystallinity UHMWPE. Friction response analyses support that friction decreases in the presence of a lubricated film of the phospholipid DPPC. Wear resistance appeared to increase as a function of lipid adsorption, which corresponded with increased degree of crystallinity of the polymer. Therefore, increasing crystallization is a mode of escalating adsorption of SAPL to UHMWPE, lending a more wear-resistant load bearing material for Total Joint Replacement.

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Table 1. Physical and surface properties of UHMWPE samples as a function of crystallinity and exposure to DPPC.

Sample	Degree of crystallinity (%) ^a	RMS surface roughness (nm) ^b	Contact angle (degrees) ^c
Dry HC-PE	55.8	7.27 ± 0.96	59.4
Dry LC-PE	44.5	5.70 ± 0.93	88.2
HC-PE with DPPC	--	11.03 ± 3.3	76.8
LC-PE with DPPC	--	5.81 ± 0.76	45.4

^aCrystallinity percentage was calculated from enthalpy values taken from DSC over 100% crystalline sample.

^bSurface roughness measurements were taken on a 5 µm x 5 µm scan using AFM.

^cContact angle were measured using magnified digital images in Adobe Photoshop.

Table 2. Summary of friction coefficients and wear measurements as a function of UHMWPE crystallinity and exposure to DPPC.

Sample	Coefficient of friction ^a	Wear depth (nm) ^b	Film transfer
HC-PE with control	0.4348±.0012	165.9 ± 31.2	none
LC-PE with control	0.497±.0063	174.7 ± 13.8	yes
HC-PE with DPPC	0.3624±.012	100.6 ± 32.1	yes
LC-PE with DPPC	0.5478±.059	193.0 ± 38.7	traces

^aCalculated from the friction response of a Si₃N₄ probe on the microtribometer for ramped load friction tests of 0-200 mN.

^bMeasured using a profilometer on wear tracks from a Si₃N₄ probe on the microtribometer for 1000 reciprocating, 20 mm cycles at an applied load of 125 mN.

Figure 1. Topography maps of high crystallinity and low crystallinity samples from a 5 μm X 5 μm scan obtained using an atomic force microscope (AFM) **(a)** before and **(b)** after lipids.

Figure 2. Magnified digital images of water droplets on surfaces of high and low crystallinity samples of UHMWPE **(a)** before and **(b)** after exposure to phospholipid solution. Contact angles were measured from images.

Figure 3. Friction response of ramped-load friction tests performed by microtribometer of Si_3N_4 on high and low crystallinity UHMWPE in the ethanol control **(a)** and DPPC-ethanol solution **(b)**.

Figure 4. Friction response of reciprocating wear tests performed by microtribometer of Si_3N_4 on high and low crystallinity UHMWPE in the ethanol control **(a)** and DPPC-ethanol solution **(b)**.

Figure 5. Optical microscopy from reciprocating wear tracks of high and low crystallinity UHMWPE, in the ethanol control **(a)** and DPPC-ethanol solution **(b)**.

Figure 6. Optical images of the polymer contact regions on probes after reciprocating wear tests on high and low crystallinity UHMWPE in the ethanol control **(a)** and DPPC-ethanol solution **(b)**.

Figure 7. SEM images of the polymer contact regions on probes after reciprocating wear tests on high and low crystallinity UHMWPE in the ethanol control **(a)** and DPPC-ethanol solution **(b)**.

Figure 1.

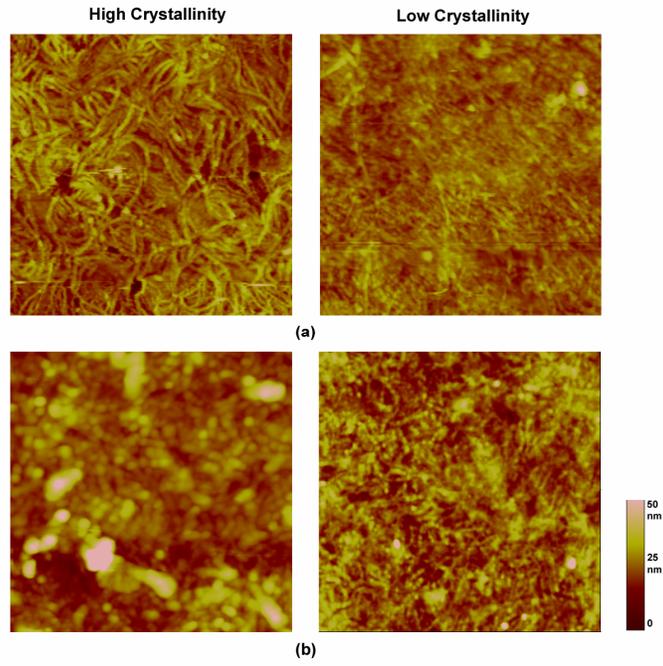


Figure 2.

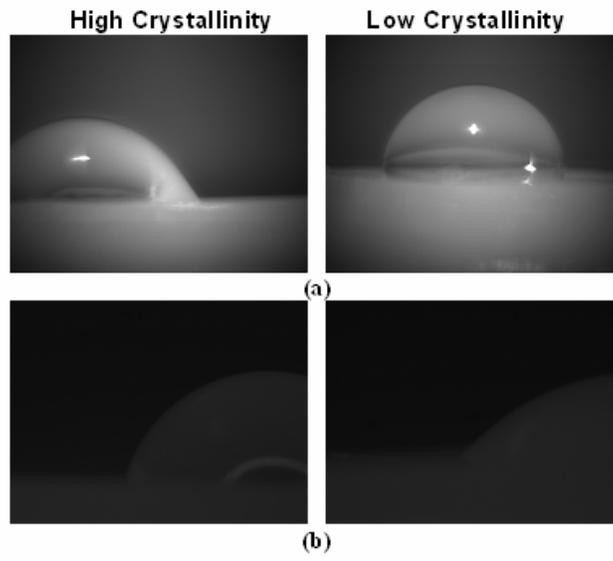


Figure 3.

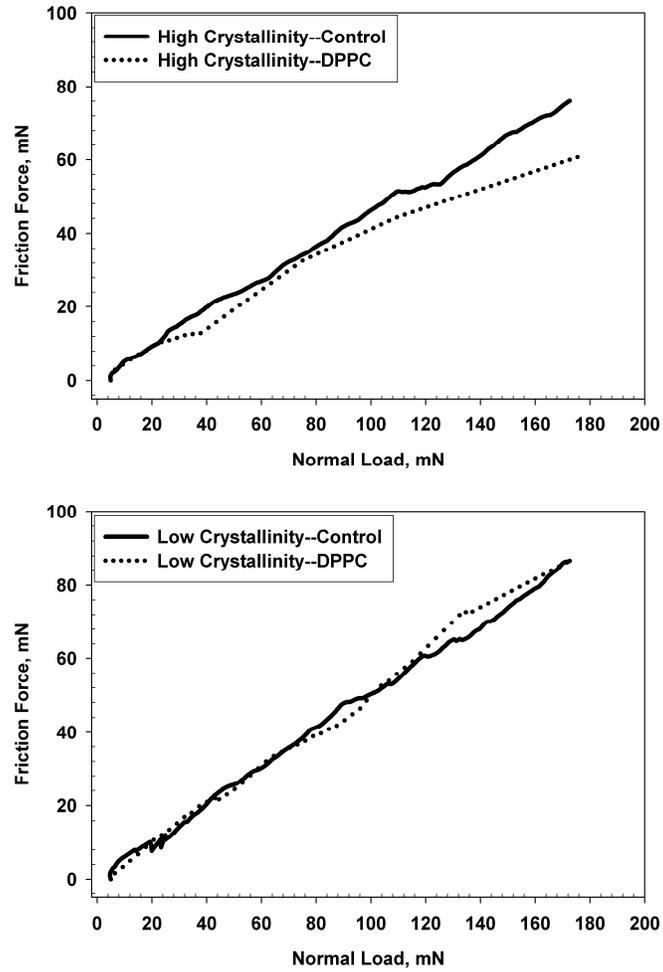


Figure 4. (a)

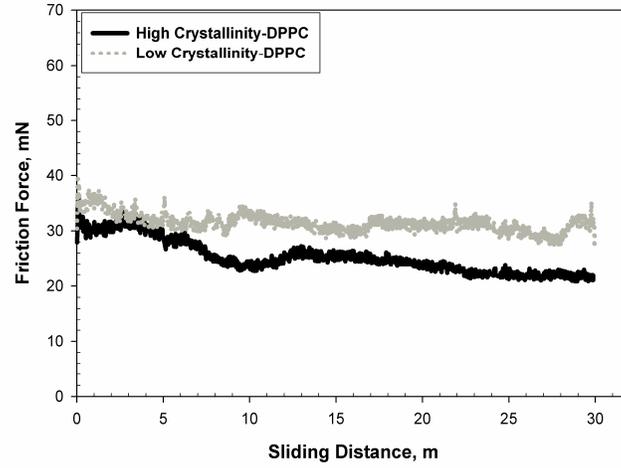
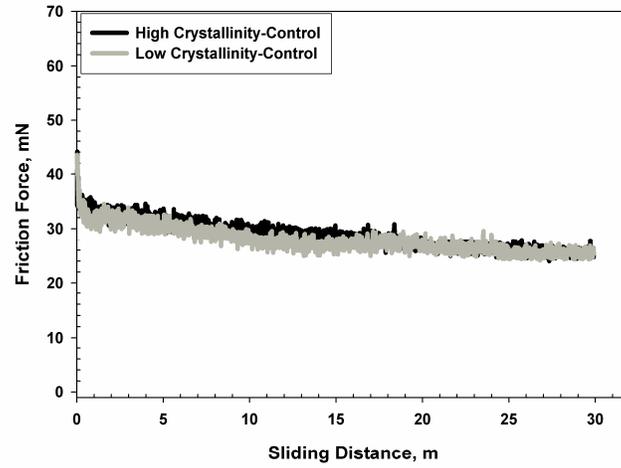


Figure 4. (b)

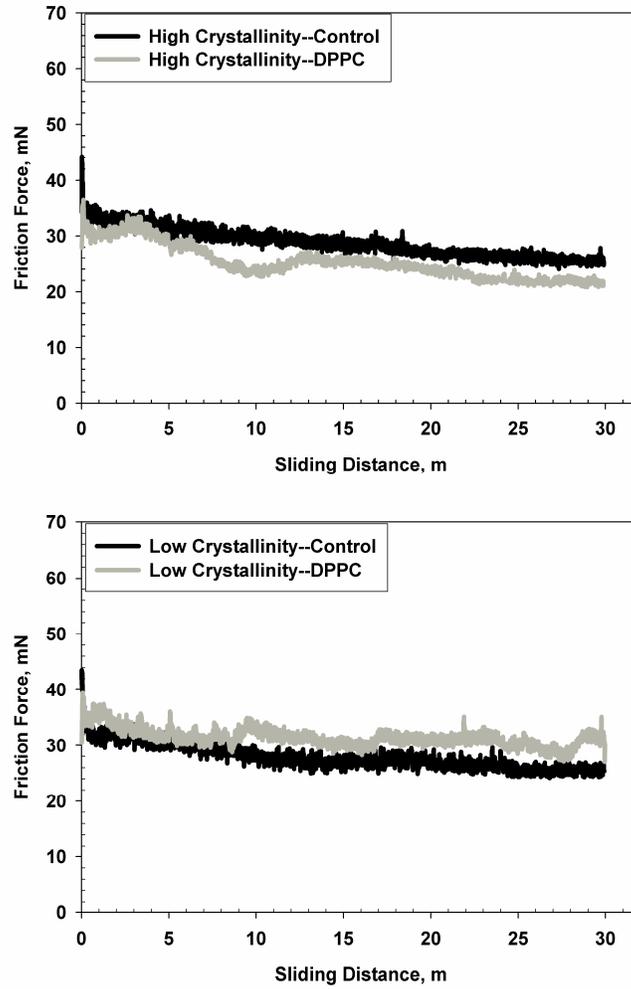


Figure 5.

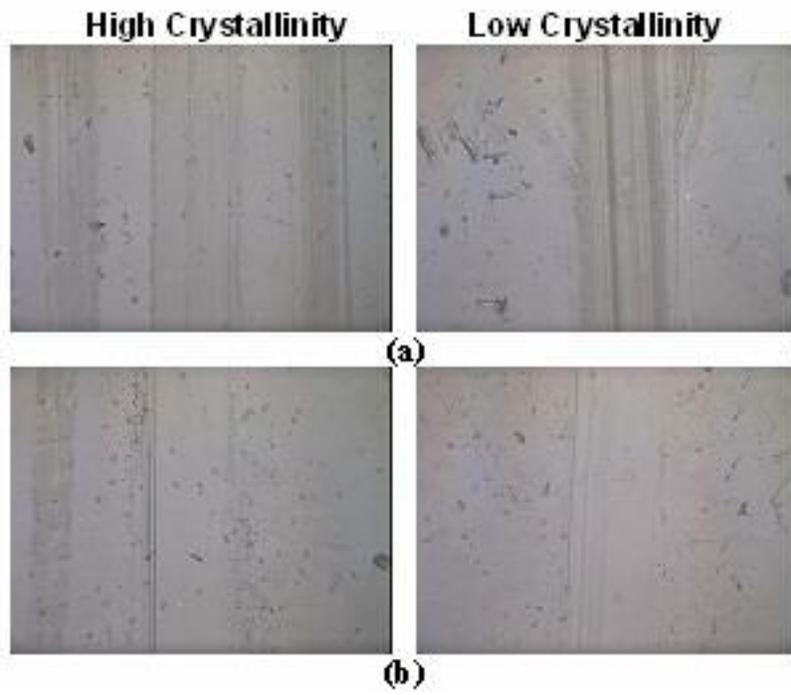


Figure 6.

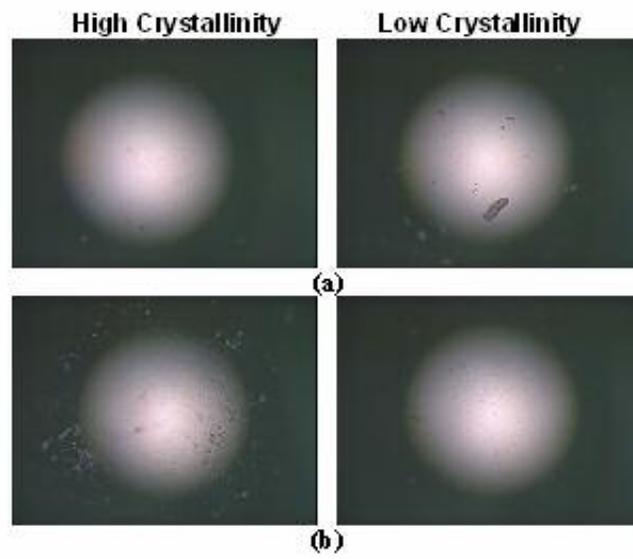
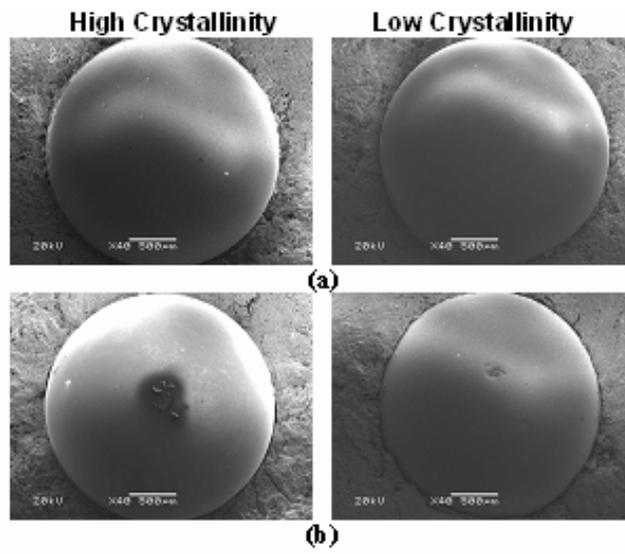


Figure 7.



Chapter 4. General conclusions

The tribological and material properties of UHMWPE were investigated as a function of percentage crystallinity. Tribological and surface properties were further studied as a function of crystallinity lubricated with a well-known surface-active phospholipid, DPPC. Microtribometer ball-on-disk ramped friction and reciprocating wear tests, as well as Atomic Force Microscope friction and scratch tests, were the primary methods employed in this study. Differential Scanning Calorimetry, nanoindentation, Scanning Electron and Optical Microscopy, contact angle measurement, and profile analysis aided in the procedure of characterizing the properties of UHMWPE.

Overall, the heightened crystallinity of UHMWPE resulted in higher wear resistance and lower friction. Comparison of contact angles and topography maps after surfaces were exposed to phospholipids portrayed higher crystallinity surfaces to have a greater ability to adsorb DPPC. Subsequent tribological testing showed a larger reduction in both friction and wear on higher crystallinity UHMWPE compared to lower crystallinity UHMWPE as a function of DPPC. Therefore, increasing the degree of crystallinity in UHMWPE has positively contributed to the properties associated with making superior articulating surfaces for Total Joint Replacements.

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