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Improvements to UHMWPE

A Scientific Review

July 10, 2010

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Abstract

Ultra high molecular weight polyethylene (UHMWPE) is a material used in artificial implants for articular joint replacements. However, these implants have a limited lifespan in which the patient will be pain-free due to the wear of the UHMWPE components. Recently crosslinking, or exposing the material to radiation, has been used to extend the wear resistance of UHMWPE. Crosslinking introduces another set of drawbacks; mainly the reduction of the fracture toughness of UHMWPE and the generation of free radicals, which leave the polymer vulnerable to damage from oxidation. Currently, research is being conducted on other methods to increase the wear resistance of UHMWPE including the introduction of filler particles into the polymer and lubrication or other cushioning methods that could make the implant more like a natural joint. This project is a review of the current research.

Introduction

In the 1950's, Dr. John Charnley started work on total hip arthroplasties (THAs), as described by Kurtz [1]. He developed the design that is still used today. His first design was a polytetraflurorethylene (PTFE, or Teflon) ball that fit into a cup attached to the acetubulum. This design yielded unsatisfactory results and was modified to include a metallic head which articulated with a PTFE cup. The cup was fixed to the acetubulum using dental cement. As Figure 1 shows, Dr. Charnley only slightly modified his THA design, mainly changing the diameter of the metallic head with hope of reducing the amount of friction between the head and the PTFE cup. Dr. Charnley hoped that by reducing the friction, the wear of PTFE would be reduced [1].

Figure 1: Dr. Charney's THA designs and modifications [1]

Ultra high molecular weight polyethylene was first used for acetabular cups in November, 1962, when it replaced the PTFE's unacceptable wear rate. Joints with PTFE had failed due to aseptic loosening about two years after implantation. UHMWPE was chosen as an alternative PTFE because of its wear rate and strength properties. In fact, replacing PTFE with UHMWPE increased the life span of a THA to about ten years. In the 1990's it was discovered that crosslinking UHMWPE, or exposing it to radiation, would increase the life of the implant by decreasing the wear rate of the material. Crosslinked UHMWPE was first used in total joint arthroplasties (TJAs) in 1998, and its life expectancy in vivo, in the body, was about twice that of untreated, or neat, UWMWPE. Furthermore, more research on alternative treatments or materials is currently important due to the increasing number of people who need a TJA and the increasing length of time they will live with the implant. Figure 2 shows the projected increase in TJAs from the year 2000 to 2030. It is expected that the number of patients needing a TJA will double within the 30 year period [1].

About 90% of all TJAs that have been completed worldwide have either UHMWPE or crosslinked UHMWPE components. However, other options include metal on metal (MOM) or ceramic on ceramic (COC) designs, which do not use any UHMWPE components. MOM and COC designs release much less wear debris, but they are much more expensive to make and require more precision in implantation than their UHMWPE counterparts. Questions have arisen regarding the long term toxicity of MOM implants because their wear particles are small enough to be digested by the cells in the surrounding tissues, which could lead to other health issues such as cancer. This is not a problem with the COC implant, although fracture is. Ceramics are brittle materials and subjecting the TJA to excessive loading could cause it to fracture; this could cause catastrophic bone damage if it were to happen in vivo. As a result, both MOM and COC implants are available alternatives to traditional UHMWPE implants, and they have their own unique issues and will not replace the need for UHMWPE implants in the near future [1].

Crosslinked UHMWPE

Crosslinking is currently the most common method to reduce the wear of UHMWPE. The steps involved in crosslinking are shown by Kurtz [1] in Figure 3 below. The first step involves exposing UHMWPE to radiation, either gamma or electron beam radiation can be used for this step. The higher the radiation dose, the less the wear rate will be and the more the mechanical properties are decreased. The second step in the process, thermal treatment, is to reduce the amount of free radicals in the material. Free radicals are unpaired electrons trapped within the material. By heating the UHMWPE, the polymer molecule's mobility increases, allowing the free radicals to interact with adjacent polymer chains and create more crosslinks. Crosslinking increasesthe wear, but reduces other mechanical properties of UHMWPE. Therefore, crosslinking UHMWPE is not the ideal solution to the wear problems of UHMWPE [1].

Figure 3: The crosslinking process [1]

UHMWPE and Wear

Failure of a TJA can be directly attributed to the wear of the implant, which is why developing a material with improved wear characteristics is so vital. UHMWPE wear is caused by the metal femoral head rubbing against the UHMWPE acetabular cup during joint movement. Over time wear debris is released into the tissue surrounding the implant, and the body responds to the foreign particles by sending macrophages to attack these particles. This immune response can lead to osteolysis, or the degeneration of bone tissue. The loss of bone tissue around the implant leads to aseptic loosening of the implant and ultimately results in implant failure. Improving the biocompatibility of UHMWPE will lessen the body's negative response to the wear particles, thus lengthening the life of TJAs.

Figure 4: Radiograph of aseptic loosening caused by osteolysis [1]

It was shown by Davey et. al. [2] that the gait of a person has an effect on the wear rate of the implant. Seven patients who underwent implant revision surgery were chosen to participate in this study. The day before their implants were replaced, the patients' gaits were analyzed using a six camera VICON 370 motion analysis system with VICON Plug-In-Gait software. An aspect ratio, or the length divided by the width (L/B), of the walking path was measured, as seen in Figure 5. The next day, during their surgery, their prosthetic joints were retrieved for study [2].

Figure 5: Illustration of aspect ratio calculation [2]

As shown in Table 1, the average wear rate for the patients involved in the study was 0.11mm/yr. It was realized that the aspect ratio was inversely related to the wear rate. Therefore, the more multi-directional the motion of the hip joint, the greater the wear rate was, as shown in Figure 6. A larger aspect ratio's decreased wear can be attributed to work hardening of the UHMWPE. The more straight line motion involved in the patient's gait, the

more molecular orientation occurs in the lamella, as seen in Figure 7. This causes the surface of UHMWPE to become harder, decreasing the wear [2].

Table 1: Aspect ratios and wear rates taken from pre-revision surgery patients [2]

Patient	Sex	Age (yr)	BMP	Time in vivo (yt)	Average aspect ratio.	Linear penetration (mm)	linear wear rate (mm/yr)	Volumetric wear (mm ⁻)	Vol. wear rate (mn'/vr)
		65	34.11	7.0	4.46	0.82	0.12	506.86	72.46
в		83	27.82	23.9	2.08	2.92	0.12	1796.03	75.12
	M	73	26.67	7.6	2.37	0.99	0.13	610.68	80.85
Ð	M	47	28.73	8.4	2.92	0.85	0.10	523.39	62.00
		69	34.45	9.0	2.74	1.12	0.12	687.18	76.35
	м	71	28.85	11.0	3.40	1.25	0.11	771.99	70.18
G	F	83	26.84	6.0	5.36	0.38	0.06	236.45	39.41
Ave.		70.	29.6	10.4	3.33	.19	0.11	733.23	68.06

"BMI, Body mass index = Mass (kg) (Height (m))².

Figure 6: Linear wear rate versus inverse of aspect ratio [2]

Figure 7: Electron micrograph taken showing orientation of polymer lamellae (a) from hip socket of patient G (b) from hip socket of patient C [2]

Wear Tests

As stated by Plumtree and Schwartz [3], the dual axis wear simulator (DAWS) was developed specifically to be used as a screening device for materials to be used as THA bearing surfaces. As the name suggests, there are two degrees of freedom in the test. The samples are loaded into computer operated carriages that are capable of moving the samples in complicated multidirectional patterns. The samples slide against a rotating shaft, which allows for a second degree of freedom, which makes the test more realistic. To more accurately predict in vivo wear, the tests are conducted in a heated environment with a protein enriched lubricant, similar to synovial fluid found in joints, as seen in Figures 8 and 9 [3].

Figure 8: DAWS machine (left) and close-up of sample holders and shaft (right) [3]

Joint simulators also use a biaxial rocking motion, as explained by Wang et. al. [4] in combination with loading that varies, to mimic the human walking motion and the forces applied to the joint during the motion. Other important characteristics of the MTS hip joint simulator test are that it is completed in the anatomical position, a lubricant similar to in vivo conditions is used, materials are in a heated environment, and a physiological and kinetically accurate load is applied [4].

However, other hip simulators can also be used. These other simulators are very similar to the MTS model, in that similar loading conditions are used, according to Ge, Wang, and Huang [5]. But, the main difference between the apparatuses is that the acetabular cups are not tested in anatomical position, or the natural body positioning. The simulator in Figure 10 is an example of a hip simulator loaded in non-anatomical position. In this case, the acetabular cup is underneath the femoral head, making this configuration equivalent to an upside down hip joint [5].

Figure 10: Schematic of a hip joint simulator [5]

Another wear method, as disscussed by Liu, Wang and Ge [6] is a ball-on-disc tester, as shown in Figure 11. A ball-on-disc wear tester uses a 4mm diameter ceramic ball that is fixed to a load arm. The material being tested is fixed to a platform which rotates in a circular path. A fixed load is applied to the test material through the ceramic ball. This test can also be used to determine the friction coefficient of the material. The steady state coefficient of friction is determined by finding the average friction during the second half of the test [6].

Figure 11: Schematic diagram of the ball-on-disc tester [6]

Another technique used to test the wear of materials is the ball-on-prism test, as described by Xue et. al. [7]. This test involves placing two test samples on either side of the prism, a counterpart ball is placed on top of the samples, and a load is applied using dead weights. During the test, the ball rotates uniformly around its veritcal axis, which causes the ball to slide over the two samples. Figures 12 and 13 show the ball-on-prism test setup. The wear results are separated from the creep by statically loading the counterface ball until the ball has reached a penetration depth where the contact area is increased to a point where the creep became nonexistent, at this time the wear test is started [7].

Figure 12: Schematic of ball-on-prism tribometer [7]

Figure 13: Prism loaded with two specimens and counterpart ball [7]

Data

Researchers are focusing on two ways to improve the wear characteristics of UHMWPE, lubrication, and composites. Lubrication can improve wear rates by decreasing the friction between the articulating surfaces and therefore reducing UHMWPE's wear. Creating a composite material by adding a filler material will improve the wear of UHMWPE by increasing its strength.

UHMWPE and Hyaluronan

Hyaluronan (HA) is a natural lubricant found in synovial fluid, or the fluid within human joints. Therefore, it was thought that adding HA to UHMWPE's surface would cause it to behave more like a natural joint and increase lubrication, as hypothesized by Zhang et. al. [8]. UHMWPE/HA composites were manufactured by using two different methods. The first method involved soaking the preforms in a 25mg/mL silyl HA-CTA solution followed by crosslinking with a 5% Desmodular solution. This was repeated using both 50 and 75mg/mL solutions. Finally a 1% HA solution was used to coat the samples before being crosslinked the Desmodular solution a final time and hydrolysis was performed in solution of 0.2M NaCl of water and ethanol. The second method employed to create the composites was to soak the preforms in a 50mg/mL silyl HA-CTA solution and then crosslink using a 2% Desmodular solution. Next hydrolysis was performed using a 0.2M NaCl solution of water and ethanol, only the solution was changed every ten hours. These samples were then coated with a 1% HA solution twice before being crosslinked again with the 2% Desmodular solution. The preforms made from these two methods were then molded to UHMWPE samples and tested. The table below describes the final product the composites made [8].

Table 2: The micro composite data [8]

Nomenclature: T, tensile (diak diameter 10.2 cm); W, wear (disk diameter 3.8 cm); H, half microcomposite; Q, quarter
microcomposite; T2-40-H represents that the microcomposite was treated with Method 2, the porosity of its % HA content based on weight gain of sample.

Wear testing was done with the pin-on-plate method using a CoCrMo (cobalt-chromiummolybdenum) alloy asthe counter face material, with a square waveform path with each side measuring 15mm. The test was done at room temperature, using bovine serum as lubricant, and each pin was tested for one million cycles. The results are shown Figures 14 and 15 [8].

Figure 14: The wear results of the UHMWPE/HA tests [8]

Figure 15: The wear rates of the UHMWPE/HA tests [8]

Figures 14 and 15 clearly show that the composites with a HA content of 1.1% by weight (samples W2-40-1 and W2-40-2), had a wear rate less than that of the UHMWPE (control sample), up through one million cycles, but it was significantly higher than the wear rate of the crosslinked sample tested (sample XLPE). At the one million cycle mark, the wear rate of this composite was about 25 times greater than that of the crosslinked sample. Also, the strength properties of all of the UHMWPE/HA compositestested were approximately 40% of neat UHMWPE [8].

The mechanical properties of these composites, shown in Table 3, were also tested, and it was found that the composites' results were less than neat UHMWPE's on every test. This made the HA treated UHMWPE an unsuitable alternative for use in TJAs [8].

Table 3: The results of mechanical testing of UHMWPE and HA [8]

Soluble Proteins as Lubricants

Another method of lubrication that has been researched was the effects of soluble proteins as boundary lubricants in TJAs. These tests were done using a hip simulator machine and each test lasted one million cycles, as described by Wang et. al. [4]. Neat UHMWPE was used in all of the tests, and a CoCrMo ball was used as a counter face surface and the lubricant was varied from water to protein enriched bovine serum [4].

Unfortunately, as seen in Figure 16, solutions with a protein concentration similar to that of synovial fluid, were the most ineffective lubricants of all of the solutions tested. Thus, natural joint fluids are ineffective as boundary lubricants in TJAs. However, more realistic results for any UHMWPE wear research will be found if the lubricants used mimic natural joint fluids. To this point lubricants have been ineffective in reducing the wear of UHMWPE [4].

UHMWPE and Bovine Bone Hydroxyapatite

Bovine bone hydroxyapatite (BHA) is a good filler material because it is biocompatible, according to Liu, Wang and Ge [6]. The Idea is that if a material adds to the biocompatibility of UHMWPE then the body's negative immune response will be lessened, resulting in a decrease of osteolysis and aseptic loosening, ultimately increasing the life of the TJA. BHA was acquired for this study from fresh bovine femoral bones. After removing the marrow, the bones were thoroughly dried, and then reduced into a powder. Next the BHA powder was disinfected and sintered at 80 degrees Celsius before a coupling agent was coated on the BHA. The powder was dried again, before being added to the UHMWPE in a rotary ball mill where the mixture was milled with ethanol. Next, it was dried before finally being hot pressed into discs [6].

Wear tests were done using the ball-on-plate method. The test was conducted using a $Si₃N₄$ ceramic ball with human plasma lubrication at room temperature. This test can also be used to determine the friction coefficient of the test material. The friction and wear rates are closely related, as can be seen in Figures 17 and 18 below [6].

Both the friction and the wear results show that the BHA content affects the results; the best results can be seen in for the 20% BHA concentration. Although all of the UHMWPE/BHA composites tested showed improvements over neat UHMWPE, the UHMWPE/20% BHA composite's wear was roughly half of the neat sample. Also, the average friction coefficient of the 20% sample was clearly reduced [6].

UHMWPE/Coral Composites

Another extremely biocompatible additive, with good results, was coral. The coral used in this study was harvested from a reef off of the coast of eastern China, as described by Ge, Wang, and Huang [5]. The coral was treated, cleaned, and then crushed into powder. The powder was treated with a silane coupling agent to increase its bonding to UHMWPE. Next, the desired amount of coral powder was mixed with UHMWPE powder in a ball milling machine. The samples were solidified by a thermal compression process [5].

The wear tests were conducted using a joint simulator machine. The joint simulator used was set using a CoCrMo counter face ball, and also required non-anatomical position mounting of the UHMWPE composite material. The tests were conducted at a temperature of 37 ± 10 , bovine serum was used as a lubricant, and the test lasted for one million cycles [5].

Figure 19: UHMWPE/Coral wear rates (a) wear vs. cycles and (b) wear vs. coral content [5]

As seen in Figure 19, the coral filler was responsible for increasing the hardness of the material, while also reducing the wear rates as the amount of coral in the UHMWPE increased. UHMPWE, with a coral content of 30% by weight, yielded the best results. Neat UHMWPE total accumulated wear after one million cycles in a joint simulator was approximately 267% of the coral composite [5].

UHMWPE and Quasicrystals

Platinum and zirconium quasicrystals (QCs) were very effective fillers as well, as illustrated by Schwartz, Bahadur, and Mallapragada [9]. QCs metal alloys are created by rapidly cooling molten metal so that the complete crystalline structure does not have time to form. This technique allows QCs to possess characteristics like high hardness and low coefficients of friction. These properties make QCs very promising filler materials for UHMWPE. A Pt-Zr alloy was chosen in this case because both metals have shown to be fairly biocompatible on their own [9].

The composites were made by compression molding the UHMWPE and QC mixture into blocks. The neat UHMWPE samples were made by compression molding as well. The compression molding process involved heating the materials to 200C, with an applied pressure of 250MPa. Half of the samples were then crosslinked by dosing them with 50kGy of electron beam radiation and then thermal treating them in an air-circulating oven at 120C for ten hours [9].

The wear of UHMWPE/QC composite was tested in a DAWS machine at 37C, bovine serum was used as a lubricant, and the samples were tested through 250,000 cycles. The results of this test can be seen in Figure 20, which shows that the composite's wear was about half of the wear of neat UHMWPE. An improvement of about 25% was also noted when the composite was compared to crosslinked UHMWPE. The QC's also improved upon crosslinked impact

toughness by about 20%, but compared to UHMWPE the composite showed about a 15% decrease [9].

Figure 20: The wear rates of UHMWPE with Pt-Zr QCs, crosslinking, or both, after 250,000 cycles in a DAWS machine [9].

Multi-wall Carbon Nanotubes

Carbon nanotubes are very stiff and strong, which makesthen ideal reinforcement materials for polymers, as explained by Xue et. al. [7]. The samples prepared for these tests were 80% UHMWPE and 20% high density polyethylene (HDPE), a polymer with better creep resistance but a worse wear rate than UHMWPE. The samples were reinforced with multi-wall carbon nanotubes (MWCNTs). The composite UHMWPE/HDPE samples were manufactured by mixing 80% UHMWPE and 20% HDPE, by weight, powders in a kneader at a temperature of 210C, then the blend was compression-moulded into plates and cooled. The neat UHMWPE samples were made by simply pouring UHMWPE powder into the compression-moulder. UHMWPE/HDPE/MWCNT composites were also kneaded, then compression-moulded into

plates, and cooled. Two different treatments were used for the MWCNTs, they were either pretreated, or untreated. The pretreated MWCNTs were treated in an HNO₃ solution before being added to the kneader [7].

A ball-on-prism tribometer was used to determine the wear of these composites. The tests were conducted using balls with a diameter 12.7mm, with a normal load of 21.2N, and the test lasted 120 hours, 60 for creep and 60 for wear. Two different counterpart materials were used, an unalloyed martensitic bearing steel (100Cr6) and a low carbon steel (X5CrNi8-10) were used as counterpart balls. The results of this test can be seen in Figure 21. Also, depending upon the counterpart material, the wear rates of the MWCNT composites were less than that of neat UHMWPE. The UHMWPE/HDPE composite without the MWCNTs had the fastest wear rates [7].

Figure 21: Wear rate of UHMWPE/HDPE/MWCNT composites with two different counterpart materials[7]

Mechanical properties were also measured and the results are shown in Table 4. The MWCNT composites showed improvements of UHMWPE in all of the tested categories.

Designation	Composition	Yield stress [MPa]	Tensile strength MPal	Strain at break 19月	Young's modulus [MPa]
UHMWPE	100% GUR 2122	25.0	24.7	109	1187
Cop	80% UHMWPE +20% HDPE	28.4	27.8	26	1493
$Cop + 0.24p$	Cop+0.2% MWCNT (pre-treated)	29.6	29.7	34	1578
$Cop + 0.5%p$	Cop+0.5% MWCNT (pre-treated)	27.6	26.2	31	1610
$Cop + 1.0%p.$	Cop+1.0% MWCNT (pre-treated)	28.8	25.5	32	1603
$Cop + 2.0%p$	Cop+2.0% MWCNT (pre-treated)	30.8	28.7	29	1613
$Cop + 0.2%u$	Cop+0.2% MWCNT (untreated)	27.3	27.9	31	1508
$Cop + 0.5%u$	Cop+0.5% MWCNT (untreated)	26.2	24.7	30	1576
$Cop + 1.0%u$	Cop+1.0% MWCNT (untreated)	29.9	29.0	28	1594
$Cop + 2.0%u$	Cop+2.0% MWCNT (untreated)	29.9	28.0	30	1495

Table 4: The mechanical properties of UHMWPE/HDPE/MWCNT composites [7]

Vitamin E and Crosslinked UHMWPE

Another wear issue associated with UHMWPE, especially crosslinked UHMWPE, is oxidation. Vitamin E's stabilization effect on crosslinked UHMWPE was studied as a potential method to decrease the oxidation of UHMWPE, as shown by Costa, Carpentieri, and Bracco [10]. Vitamin E was a good candidate to reduce oxidation because it is an antioxidant, therefore it can be used to prevent oxidation, a process whose products are responsible for weakening the crosslinked material. The samples used in this experiment were made by blending pharmaceutical grade vitamin E with UHMWPE powder, the mixtures were then compression molded into blocks [10].

The effectiveness of the addition of vitamin E is measured by determining the concentrations of the products that are formed as oxidation occurs. The two main products of oxidation are ketones and hydroperoxide. Oxidation is detrimental to UHMWPE because the formation of these acids can lead to scission of the polymeric chain ultimately reducing the mechanical properties of the material. Therefore, the more effective the treatment, the lower the concentrations of ketones and hydroperoxide will be, and Figure 22 shows that vitamin E is an

effective stabilizing agent. For example, in the experiment, a 0.5% dose of vitamin E reduced the hydroperoxide and ketone concentrations in a sample of UHMWPE crosslinked with 90kGy of gamma radiation by about 0.015mol/L and 0.022mol/L, respectively. Although vitamin E reduces the amount of oxidation, thus maintaining the mechanical properties of crosslinked UHMWPE, vitamin E also reduces the efficiency of the crosslinking process. Vitamin E reduces the crosslinking efficiency by interacting with the free radicals within the polymer in such a way that the amount of crosslinking that takes place is reduced [10].

Figure 22: Vitamin E concentration versus oxidation products as a function of radiation dose (a) ketone concentration and (b) hydroperoxide concentrations [10].

Discussion

Recently, a significant amount of research has concentrated on possible filler materials for UHMWPE. Many metals and organic substances have been analyzed and tested as possible solutions, with progress towards an alternative composite material being made. The most important factors to consider for filler materials are biocompatibility and ease of dispersion. Also, there are no viable options for joint lubrication in vivo. Therefore, more research is needed on possible joint lubricant methods or techniques.

Additionally, standard conditions should be adopted for wear testing of UHMWPE. The results would be much easier to compare if all wear tests were done under the same conditions. The results of tests that use similar equipment, like joint simulators, are even difficult to compare because some machines operate in anatomical position, while others do not. Also, many different lubricants are used in current experiments, which add to the variables that must be considered when comparing wear results.

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Biographies

Brooke McKelvogue

I am from West Des Moines, IA, and I graduated from Valley High School in 2005. In May of 2010 I graduated from Minnesota State University, Mankato with a BSME (bachelor's degree in mechanical engineering). Next fall I will start graduate school at the University of Iowa where I hope to get my masters degree in biomedical engineering. My main interests in that field of engineering are prosthetics and biomaterials.