“Unione Industriale” Congress Center

6th UHMWPE International Meeting

October 10-11 2013

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6th UHMWPE International Meeting

Dear Participant,

The purpose of the meeting is to bring together engineers, scientists, and clinicians from academia and industry and present leading edge research on advancements in medical grade UHMWPE technology and clinical applications. The focus of the 6th meeting is on retrieval studies of highly crosslinked UHMWPE, with a special emphasis on the performance of thin acetabular liners and knee arthroplasty; advances in Vitamin E and new antioxidant technologies for UHMWPE; structural composites and woven fiber applications of medical grade UHMWPE; as well as advances in biologic aspects of UHMWPE wear debris.

Abstracts were evaluated by the Scientific Committee for inclusion in the program, either as a podium presentation or a poster.

Scientific Committee:

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Clare Rimnac, Ph.D.

Ebru Oral, Ph.D.

Michael Beeman

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6th UHMWPE International Meeting – AGENDA: Thursday, October 10, 2013

7.00 a.m.	On-Site Registration Opens	
8:00 a.m.	Welcome, Opening Remark	*Pierangiola Bracco, Ph. D., and Steven Kurtz, Ph.D.*
Session I:	**Wear and Mechanical Behavior of HXLPE** Session Co-Moderators: *Anuj Bellare, Ph.D., and José Antonio Puertolas, Ph.D.*	
8:15 a.m.	**Invited Talk 1:** Understanding Crack Propagation from Clinically Relevant Notch Geometries in UHMWPE	*Clare Rimnac, Ph. D.*
8:35 a.m.	**Podium Talk 1:** Microhardness, microcreep and microplasticity of virgin, crosslinked and/or aged ultrahigh molecular weight polyethylenes	*M. Slouf, Ph.D.*
8:50 a.m.	**Podium Talk 2:** Using a surrogate contact pair to evaluate UHMWPE wear in knee condyle applications	*A. Sanders, Ph.D*
9:05 a.m.	**Podium Talk 3:** Failure Analysis of Crosslinked UHMWPE Implants with Stress Concentrations: Clinical Implications	*F. Ansari, Ph.D.*
9:20 a.m.	**Podium Talk 4:** Does cyclic stress play a role in HXLPE oxidation?	*J. Sanchez, Ph.D.*
9:35 a.m.	Round Table Q/A and Discussion of Session 1	
9:50 a.m.	Morning Coffee Break	
Session II:	**Anti-Oxidants in UHMWPE** Session Co-Moderators: *Luigi Costa, Ph.D., and Ebru Oral, Ph.D.*	
10:20 a.m.	**Invited Talk 2**: Mechanisms of Oxidation and Anti-Oxidant Stabilization	*Pierangiola Bracco, Ph.D.*
10:40 a.m.	**Invited Talk 3:** A Comparison of the Efficacy of Various Antioxidants on the Oxidative Stability of Irradiated Polyethylene	*Anuj Bellare, Ph.D.*
11:00 a.m.	**Podium Talk 5:** Natural Polyphenols as Alternatives for Stabilisation of Highly Crosslinked UHMWPE with High Strength and Low Wear**.**	*J. Fu, Ph.D.*
11:15 a.m.	**Podium Talk 6:** A Hindered Phenol Stabilized UHMWPE for Tibial Knee Inserts	*V. Narayan, Ph.D.*
11:30 a.m.	**Round Table Q/A and Discussion of Session 2 (I)**	
11:45 a.m.	**Invited Talk 4:** High Temperature Melting of UHMWPE for Improved Toughness	*Ebru Oral, Ph. D.*
12:00 p.m.	**Podium Talk 7:** Effects of antioxidative substrate and cartilage-inspired surface on the durability of acetabular liner	*Masayuki Kyomoto, Ph.D.*
12:15 p.m.	**Podium Talk 8:** Is Vitamin E a Plasticizer for UHMWPE?	*Nathalie Hope, Ph.D.*
12:30 p.m.	**Round Table Q/A and Discussion of Session 2(II)**	
12:45 p.m.	How to Write for CORR	*Clare Rimnac, Ph.D.*

12:50 p.m.	**Buffet Lunch and POSTER SESSION**	
Session III:	**Clinical Performance of HXLPEs in Hips vs. Knees** Session Co-Moderators: *Clare Rimnac, Ph.D., and Alessandro Bistolfi, M.D.*	
2:00 p.m.	**Invited Talk 5:** What Are the Current Gaps in the Literature for HXLPE in Hips and Knees?	*Stuart Goodman, M.D.*
2:20 p.m.	**Invited Talk 6:** Crosslinked Versus Conventional Polyethylene in Total Joint Arthroplasty: Risk of Aseptic Revision	*Liz Paxon*
2:40 p.m.	**Invited Talk 7:** OUS Registry Perspective for HXLPEs	*Henrik Malchau, Ph.D.*
3:00 p.m.	**Invited Talk 8:** 1st and 2nd Generation HXLPE Hip and Knee Implants: Lessons from Retrieval Analysis	*Steve Kurtz, Ph.D.*
3:20 p.m	**Round Table Q/A and Discussion of Session 3**	
3:35 p.m.	Afternoon Coffee Break	
Session IV:	**Retrieval Experience of HXLPEs** Session Co-Moderators: *Steven Kurtz, Ph.D. and Pierangiola Bracco, Ph.D.*	
4:10 p.m.	**Invited Talk 9:** Clinical and Retrieval Performance of E-Poly	*Orhun Muratoglu, Ph.D.*
4:30 p.m.	**Podium Talk 9:** MicroCT Analysis of Wear and Deformation for Remelted HXLPE in TKA	*Dan MacDonald, Ph.D.*
4:45 p.m.	**Podium Talk 10:** Acute fracture of XLPE patellar components are not associated with wear damage: A retrieval analysis	*Shannon Rowell*
5:00 p.m.	**Podium Talk 11:** High Wear Scar Symmetry on Tibial Polyethylene Inserts from Bilateral Total Knee Replacement Patients	*C. Knowlton, Ph.D.*
5:15 p.m.	**Podium Talk 12:** Bearing Surface Damage Analysis of Coupled Total Shoulder Replacement Retrievals	*L. Malito, Ph.D*
5:30 p.m.	**Round Table Q/A and Discussion of Session 4**	
5:45 p.m.	**Day 1 Meeting Adjourns**	
7:30 p.m.	**Reception and Dinner Begins at Palazzo Saluzzo di Paesana**	

6th UHMWPE International Meeting – AGENDA: FRIDAY, October 11, 2013

7:30 a.m.	**On Site Registration Opens**	
Session V:	**Wear Debris** Session Co-Moderators: *Joanne Tipper, Ph.D., and Amanda Marshall, M.D.*	
8:00 a.m.	**Invited Talk 10:** Biologic Response to Wear Debris Containing Antioxidants	*Joanne Tipper, Ph.D.*
8:20 a.m.	**Podium Talk 13:** Particles from vitamin-E-diffused highly cross-linked UHMWPE induce less osteolysis compared to virgin highly cross-linked UHMWPE in a murine calvarial bone	*David Bichara, M.D.*
8:35 a.m.	**Podium Talk 14:** Stem Cell Uptake of UHMWPE and its Effect on Osteoblastic and Adipocytic Differentiation: Dose- and Size-Dependency	*Amanda Marshall, M.D.*
8:50 a.m.	**Round Table Q/A and Discussion of Session 5(I)**	
9:05 a.m.	**Podium Talk 15:** Biological Response to Wear Debris in the Spine	*Sai Veruva*
9:20 a.m.	**Podium Talk 16:** In Vitro Investigation to Determine if Vitamin E-Blended UHMWPE has the Ability to Prevent Bacterial Attachment and Biofilm Formation	*Roy Bloebaum, Ph.D.*
9:35 a.m.	**Podium Talk 17:** Interplay between surface properties of standard, vitamin E blended and oxidized ultra UHMWPE for total joint arthroplasty	*A. Bistolfi, M.D.*
9:50 a.m.	**Podium Talk 18:** Biological activity and migration of wear particles in the knee joint – an in vivo comparison of six different polyethylene materials	*S. Utzschneider, Ph.D.*
10:05 a.m.	**Round Table Q/A and Discussion of Session 5(II)**	
10:15 a.m.	**Morning Coffee Break and POSTER SESSION**	
Session VI:	**New Frontiers in UHMWPE** Session Co-Moderators: *Orhun Muratoglu, Ph.D., and Luigi Costa, Ph.D.*	
10:45 a.m.	**Invited Talk 11:** The Future for UHMWPE	*Luigi Costa, Ph.D.*
11:05 a.m.	**Podium Talk 19:** Novel radiopaque UHMWPE sublaminar wires for application in a growth-guidance system for the treatment of early onset scoliosis: a large animal study	*A. Roth*
11:20 a.m.	**Podium Talk 20:** Shelf Stability of a Crosslinked and Mechanically Deformed UHMWPE	*Dave Schroeder*
11:35 a.m.	**Round Table Q/A and Discussion of Session 6(I)**	
11:50 a.m.	**Invited Talk 12:** New carbon reinforcements for UHMWPE-based composites. Are They A Real Alternative?	*José Antonio Puertolas, Ph.D.*

12:10 p.m.	**Podium Talk 21:** Wear of large diameter vitamin-E blended HXLPE hip bearings against uncoated and chromium nitride coated metal	*D. De Villiers, Ph.D.*
12:15 p.m.	**Podium Talk 22:** Processing UHMWPE materials to enhance tribological properties for orthopaedic applications	*J. Sague*
12:30 p.m.	**Round Table Q/A and Discussion of Session 6(II)**	
12:45 p.m.	**Closing Remarks**	*Pierangiola Bracco, Ph.D.*
12:50 p.m.	**Meeting Adjourn**	

6th UHMWPE International Meeting-Poster Presentations

002	In Vivo Oxidative Stability and Clinical Performance for 1st- and 2nd-Generation Highly Crosslinked Polyethylenes	*S. Kurtz*
003	Oxidation Induced by Compressive Cyclic Loading of Conventional UHMWPE	*Z.B. Konsin*
013	Confirmation of Increased Oxidation in Remelted Highly Cross-linked UHMWPE after Synovial Fluid Soaking, Accelerated Aging and Solvent Extraction	*K.P. Le*
014	In vivo oxidation in sequentially irradiated and annealed UHMWPE components	*S.L. Rowell*
015	He ion implantation as a barrier to squalene effects in UHMWPE	*M.J. Martínez-Morlanes*
019	Dielectric effects induced by gamma irradiation and vitamin E in ultra high molecular weight polyethylenes	*J.A. Puértolas*
025	Effect of Antioxidant on Polyethylene Particle Induced Inflammation and Cellular Activation	*L. Song*
026	Toughness Changes with Radiation Dose in an Antioxidant Stabilized UHMWPE	*V.S. Narayan*
027	Mediators of the inflammatory response to joint replacement devices	*N. Cobelli*
028	Characterization of High-Density Polyethylene Changes Induced by Gamma Irradiation	*M. Nevoralova*
030	Wear and deformation of novel anti-oxidant UHMWPE acetabular cups for total hip replacement under standard gait and adverse loading conditions	*S. Partridge*
031	Preparation and characterization of sodium alginate modified UHMWPE	*G. Zsoldos*
032	Radiation-induced graft polymerization of UHMWPE fiber and dying application	*S. Soeda*
033	Similar surface damage observed in XLPE acetabular liners across manufacturers	*M.P. Ast*
034	Impact resistance and fractography in highly crosslinked polyethylenes	*F.J. Pascual*
035	Wear Performance of MPC-grafted UHWMPE for Total Hip Replacement	*R. Siskey*
036	The relationship between graft polymerization to UHMWPE and the depth distribution of hydroperoxide	*I. Enomoto*
037	Effect of mechanical activation on UHMWPE-based composites perspective for cartilage defects replacement	*F.S. Senatov*
039	Fracture of highly cross-linked UHMWPE liners: An analysis of 75 reports of a single design to the FDA	*M.P. Ast*
042	The effectiveness of vitamin E for maintaining the low wear rates of hip replacement polyethylene liners after simulated aging.	*D.W. Schroeder*
043	Influence of radial mismatch and UHMWPE additivation on glenoid liner wear performance	*P. Dalla Pria*

6th UHMWPE International Meeting-Poster Presentations (cont.)

044	Regulation of radical reactions in electron-beam irradiated dl-□-Tocopherol blended Ultra High Molecular Weight Polyethylene	*S. Nogi*
045	The effect of sample preparation and measurement setup, on oxidation index and trans-vinylene index analysis of uhmwpe.	*S.J. Johnson, M.D. Allen*
046	Third Body Wear of Vitamin E Blended Highly Cross-linked Polyethylene in a Hip Simulator	*M. Hintner*
047	Correlation between mechanical and oxidative stability of various UHMWPE materials	*S. Sundaramurthy*
048	Can Pin on Disk Testing Be Used to Assess the Wear Performance of Retrieved UHMWPE Liners?	*D.W. MacDonald*
050	Is In Vivo Oxidation of HXLPE Greater in the Knee than in the Hip?	*S.M. Kurtz*
053	24 Weeks Accelerated Aging study for HALS and Vitamin E stabilized 100 kGy irradiated UHMWPE	*H. Smelt*
058	Wear, Wear particle Characterization and Biocompatibility of UHMWPE/Multiwalled Carbon Nanotubes Nanocomposites	*Tipper, Joanne*
059	Hip Simulator Wear and Lock Detail Performance of Crosslinked UHMWPE Blended with a Hindered Amine Light Stabilizer (HALS)	*Webb, Nathan*
060	In vitro wear simulation under prolonged ageing and third-body particle conditions of a vitamin E stabilised polyethylene for hip arthroplasty	*Grupp, Thomas*
061	Vitamin E Stabilized Polyethylene for Hip Endoprostheses– Mechanical Properties and Long-term Stability	*Streller, Rouven*

6th UHMWPE International Meeting

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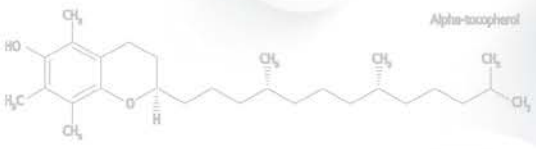

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Microhardness, microcreep and microplasticity of virgin, crosslinked and/or aged ultrahigh molecular weight polyethylenes

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Introduction: Modern total joint replacements (TJR) use ultrahigh molecular weight polyethylene (UHMWPE) components with various modifications. Almost each manufacturer uses its own combination of UHMWPE irradiation, thermal treatment, sterilization and/or vitamin E stabilization [1]. Consequently, the UHMWPE liners exhibit various crosslinking, oxidation resistance, and mechanical properties [2]. Measurement of mechanical properties of UHMWPE liners is problematic due to their small size and irregular shape: specimens for standard tensile testing (ASTM D638-03) are too big, which lead to introduction of small punch tests (SPT) for UHMWPE characterization (ASTM F2183-02). In this contribution, we show yet another method – Vickers microhardness – which uses even smaller specimens than SPT. We demonstrate that careful and precise measurements yield not only standard microhardness, but also microcreep and microplasticity of UHMWPE with various modifications.

Materials and methods: Modified UHMWPE samples (Table 1) were prepared by standard industrial procedures (MediTECH, Vreden, Germany; starting material Chirulen 1020; irradiation, annealing and/or remelting at low-oxygen atmosphere). Sample preparation details can be found in our previous work [3]; here we just used the samples for microhardness experiments.

Sample ID	IRR1 [kGy]	TT1 [type]	IRR2 [kGy]	TT2 [type]	IRR3 [kGy]	TT3 [type]
M0	x	x	x	x	x	x
M1	75	RM	x	x	x	x
M2	75	AN	x	x	x	x
M3	37.5	AN	37.5	AN	x	x
M4	25	AN	25	AN	25	AN
M5	25	AN	25	AN	25	RM

Table 1. List of modified UHMWPEs; IRR: irradiation, TT: annealing (AN; 110 °C) or remelting (RM; 150 °C).

The second set of samples (Table 2) were virgin (PE-0) and vitamin E blended UHMWPE (PE+E). The samples were aged according to our own protocol (unpublished). The protocol gives >60% shortening of aging time in comparison with previous studies [4] and no aldehyde peak in the IR spectrum.

Sample ID	Vitamin E [%]	Accelerated aging
PE-0	0	no aging / 105 days
PE+E	0.1	no aging / 105 days

Table 2. UHMWPE samples, which were subjected to accelerated aging; for each sample, the first part was kept in refrigerator and the second was aged for 105 d.

Microhardness, MH, was measured by means of a microhardness tester (VMHT AUTO man; UHL) using Vickers method (square pyramid of diamond with angles between non-adjacent faces 136° is forced against flat surface of the specimen). For each sample, at least 30 indents were made (3 smooth surfaces prepared by microtomy, 10 indents on each, load F = 200 gf; load time t = 6s), average diagonal length (d = average of the two diagonals of the indent) was measured with a light microscope and the final MH value was calculated [5]:

$$\mathrm{MH} = H[\mathrm{MPa}] = 1.854 \times F[\mathrm{N}]/d^2[\mathrm{mm}^2] \quad (1)$$

Microcreep, MC, was determined from the microhardness values (H, Eq. 1) measured at different load times (t). The H-t relationship is described by time law (Eq. 2a, [5]). In this work, we define microcreep, MC, as the creep constant from the above mentioned time law (Eq. 2b):

$$H = H_0 t^{-K} \quad (2a)$$
$$\mathrm{MC} = -K \quad (2b)$$

Microplasticity, MP, was calculated from the residual impression parameter h/a (Fig. 1; [5,6]). The half of the indenter diagonal length (a) and the depth of the indent (h) were determined from SEM micrographs of tilted indents [6], exactly after 3 days to eliminate time-dependent behavior. MP was defined as follows:

$$\mathrm{MP} = h/a \times 7/2 \times 100\% \quad (3)$$

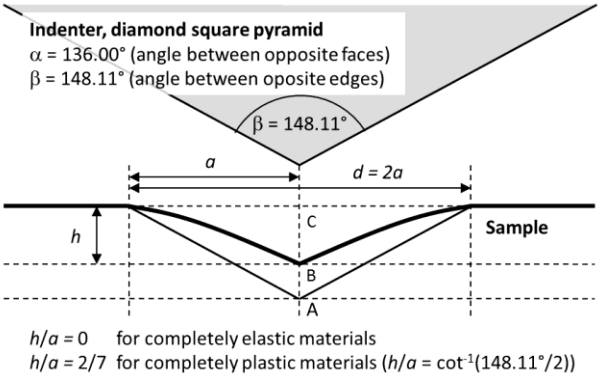

Figure 1. Contact geometry and residual impression parameter, h/a, from Vickers pyramid indenter. The loaded indenter penetrates into the sample up to point A. After unloading, ideally plastic material remains deformed (point A), real material, such as UHMWPE, exhibits (visco)elastic recovery (point B), and ideally elastic material is completely recovered (point C).

Supplementary experiments. Oxidation index (OI), trans-vinylene index (VI) and crystallinity index (CI) profiles were determined by IR according to Medel et al. [7]. Melting points (T_m) and crystallinities (CR) were determined from DSC as described elsewhere [3].

Results: The modified UHMWPE samples (Table 1) were all irradiated with the same dose of 75 kGy. They differed by the irradiation procedure (one-step vs. sequential process) and by thermal treatment (AN vs. RM). Fig. 1 shows that the AN-samples (M2, M3, M4; the last thermal treatment step was AN) exhibited higher microhardness than the non-modified sample (M0) and RM-samples (M1, M5; the last thermal treatment step was RM). This behavior was connected with crystallinity and lamellar thickness, as evidenced by DSC and IR (data not shown) and discussed below (Eq. 4).

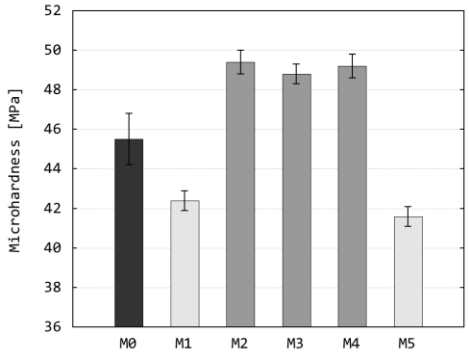

Figure. 2. Microhardness (MH, Eq. 1) of one-step and sequentially irradiated UHMWPE samples (Table 1).

As for the microcreep (MC = -*K*; Eq. 2a,b), the modified UHMWPE samples (Table 1) were split into three groups as well: all AN-samples had lower MC, all RM-samples showed higher MC, and non-modifed sample (M0) was in between (Fig. 3). The differences among *K* values were small, but the results were in agreement with literature [8] and the grouping of samples was evident (Fig. 3).

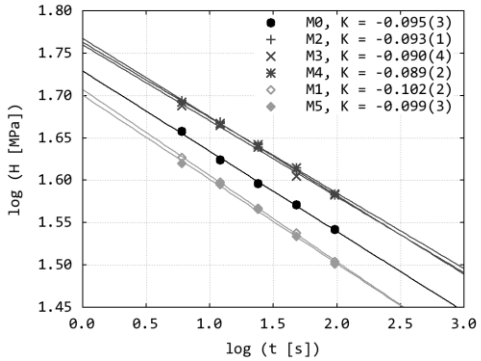

Figure 3. Microcreep (MC, Eq. 2a,b) of one-step and sequentially irradiated UHMWPE samples (Table 1).

Microplasticity (MP; Eq. 3) was determined just for one RM-sample (Table 1, M1; MP = 24.7%) and one AN-sample (Table 1, M2; MP = 29.7%). The results were at the edge of statistical significance (two-sample t-test, P-value = 0.0448). Nevertheless, the measurable difference between AN-samples and RM-samples was confirmed.

In the last experiment, we verified the sensitivity of MH measurements towards oxidative degradation. We tested samples subjected to aging *in vitro* (Table 2). The oxidation index, crystallinity index and microhardness profiles (OI, CI, and MH as functions of the distance from the surface) showed very similar trends; this was in agreement with the previous study of Medel et al. [7].

Discussion and conclusion: Microhardness, *H*, of polyethylene is closely connected with its morphology, namely with its overall crystallinity (w_c) and thickness of crystalline lamellae (l_c), as shown by Eq. 4:

$$H = w_c \frac{H_c^0}{1 + b/l_c} \qquad (4)$$

where H_c^0 is the microhardness of infinitely thick crystal and b is a parameter connected with surface and deformation energy of the crystals [5]. Therefore, the increase in w_c and l_c of UHMWPE samples resulted in higher microhardness, MH (in accord with Eq. 4), lower microcreep, MC (crystalline phase is more resistant to creep), and higher microplasticity, MP (crystalline phase is harder, but more plastic).

We have already suggested [3] that the structure and properties of the one-step and sequentially irradiated samples were determined rather by the last thermal treatment step than by the number of irradiation cycles. In this contribution, we focused on micromechanical properties (Eq. 1–3) of sequentially irradiated samples (Table 1) and the above-mentioned results [3] were confirmed: the AN-samples (M2, M3, M4; the last thermal treatment was AN) showed the highest w_c and l_c regardless of the number of irradiated cycles. As a result, all AN-samples exhibited higher MH, lower MC, and higher MP in comparison with all RM-samples.

We conclude that microhardness is a sensitive tool for characterization of UHMWPE samples with various modifications (Table 1) or oxidative degradations (Table 2).

Acknowledgement:
IGA MZ CR NT12229-4/2011 and TACR TA01011406.

References:

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[3] Slouf M. *J Biomed Mater Res B* 2013;101B:414-422.
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Failure Analysis of Crosslinked UHMWPE Implants with Stress Concentrations: Clinical Implications

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Introduction: Over the past two decades, gamma irradiated (crosslinked) ultra-high molecular weight polyethylene (UHMWPE) has become a popular bearing material of choice in total hip replacements (THR) due to its superior wear resistance [1]. Its success has driven orthopedic device manufacturers to consider incorporation in total knee replacements (TKR) and total shoulder replacements (TSR), which experience significantly higher contact stresses *in vivo* [2,3]. However, laboratory testing has demonstrated tradeoffs in UHMWPE mechanical properties – including reduced resistance to fatigue crack propagation and oxidation-induced embrittlement – with increasing crosslinking dosage [4,5]. In combination with higher stresses, the use of crosslinked UHMWPE in TKR and TSR thus has a greater potential for premature failure, as evidenced by retrievals analyses of highly crosslinked implants that demonstrated crack initiation at high stress concentrations [6-9]. This work examines several crosslinked UHMWPE retrievals from both THR and TKR that fractured *in vivo*.

Methods and Materials: Four fractured modular total hip and knee components were retrieved and evaluated:

Two Zimmer Legacy Posterior-Stabilized (LPS) NexGen moderately crosslinked, gamma inert sterilized, tibial plateaus were retrieved from two male patients (58 and 68 years old) at eight years postoperatively due to fractured tibial posts (**Figure 1(a-b)**). Both fractured implants were found to be otherwise well-fixed and aligned at time of retrieval.

A Zimmer Longevity highly crosslinked melt annealed acetabular liner was retrieved three years postoperatively from a 60 year old female patient due to an irreducible hip dislocation (**Figure 1(c)**). The retrieved liner revealed a fractured locking rim that had deformed inward, preventing reduction of the femoral head.

A Depuy Marathon highly crosslinked melt annealed acetabular liner was retrieved from a 65 year old male patient after dissociation and displacement of the liner from the acetabular shell after eight years *in vivo* (**Figure 1(d)**). Damage to the extracted retrieval included deformation of the upper rim and fracture of five of the six liner locking tabs.

Optical and scanning electron microscopy (SEM) were used to examine fracture surfaces on all four retrievals. Finite element analysis (ABAQUS v6.9) was also performed on the Marathon acetabular liner locking mechanism to model boundary displacements of the rim during impingement using a bilinear elasto-plastic model. Oxidative analysis was performed on the two LPS NexGen tibial posts using Fourier Transform Infra-Red (FTIR) spectroscopy.

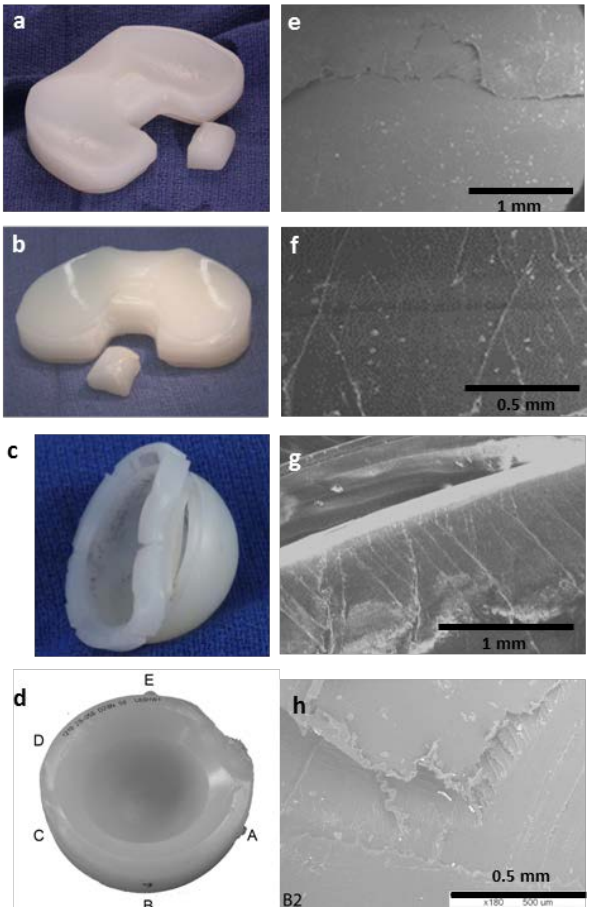

Figure 1 | Two LPS tibial post fractures (a-b), the Longevity acetabular liner (c) and the Marathon acetabular liner (d) are shown. SEM images (e)-(h) reveal reduced ductility and/or classic features from crack propagation on the fracture surfaces of each retrieval.

Results: Analysis of the fracture surfaces using SEM revealed features indicative of reduced ductility in all four cases (**Figure 1(e-h)**) [4]. One tibial post fracture site presented little ductile tearing but instead a predominantly flat, brittle surface (**Figure 1(e)**). Fractography of the second tibial post (**Figure 1(f)**) revealed classic criss-cross patterns indicative of fatigue crack propagation in UHMWPE [4]. These same features were detected on the fracture rim of the highly crosslinked Longevity liner (**Figure 1(f)**). The five fractured tabs on the highly crosslinked Marathon acetabular liner also displayed limited ductile tearing and flat surface texture associated with brittle fracture processes (**Figure 1(h)**).

Optical analysis of one of the tibial post fracture sites (**Figure 2a**) revealed white banding along the perimeter characteristic of oxidative degradation. FTIR analysis

confirmed elevated oxidative levels with an oxidation index of 1.5 – above the 1.25 threshold indicating susceptibility to oxidative embrittlement [10]. Optical micrographs of the other post exposed deformation and striations that initiated from both anterior-medial and posterior-lateral corners. Oxidation levels were normal.

Finite element analysis of the Marathon liner during impingement shows peak tensile stresses in the locking ring of 19 MPa, and as high as 80 MPa in linear tabs upon dissociation of the liner from the metal shell – sufficient to initiate failure of crosslinked UHMWPE, which has a yield stress around 20 MPa [11].

Discussion: The four retrievals from THR and TKR demonstrated similar fracture surface features indicative of failure mechanisms associated with crosslinking. SEM and optical micrographs revealed criss-cross patterns and flat surfaces consistent with crosslinked UHMWPE fracture surfaces from laboratory studies [4,5]. All four implants included stress concentrations in their design – the tibial post for TKRs and liner locking mechanisms for THR liners – from which cracks initiated and propagated due to either an overload event or fatigue.

Finite element analysis of the Marathon Liner confirmed that peak stresses in the liner tabs were four times the yield stress of UHMWPE during an impingement event [8]. Furthermore, FTIR analysis of one of the tibial inserts shows a reduction in oxidative resistance as a result of ionizing radiation, leading to mechanical embrittlement and premature failure at one of the tibial posts.

The analysis presented in this work substantiates previously published clinical evidence that crosslinked devices are susceptible to reduced mechanical integrity and oxidative degradation *in vivo* [6-9]. This is particularly damaging in the presence of stress concentrations that served as crack initiation sites, such as the TKR's tibial posts and THR's liner locking mechanisms [7,9]. While crosslinked UHMWPE exhibits superior wear resistance in comparison to the conventional polymer, radiation crosslinking can compromise UHMWPE's resistance to fatigue crack propagation and oxidative resistance [4,5], ultimately limiting the life of a device. While both TKR implants were moderately crosslinked, the two failures explored in this study provide clinical evidence that even a slight reduction in radiation dose is still accompanied by a tradeoff in mechanical properties that needs to be considered in implant design. This becomes particularly concerning as device manufacturers trends toward increase use of crosslinked UHMWPE in less conforming TKRs and TSRs, which experience high contact stresses.

This work provides evidence that premature clinical fracture of crosslinked UHMWPE can occur *in vivo*, especially in the presence of high stress concentrations in the TKR and THR. Ionizing radiation of UHMWPE to increase wear resistance thus comes with a compromise in resistance to fatigue, risk of fracture, and potential for oxidative degredation that should be considered for implant designs that incorporate stress concentrations or experience high contact stresses.

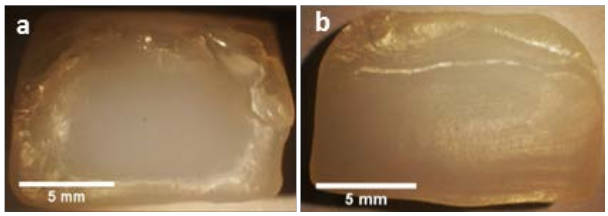

Figure 2 | Optical microscopy images of both tibial post fracture sites: (a) one with white banding due to oxidative embrittlement and (b) the other with clamshell markings due to a fatigue-related fracture.

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Does cyclic stress play a role in HXLPE oxidation?

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Introduction: The orthopedic community has devoted innumerable efforts to minimize the impact of oxidation of ultra-high molecular weight polyethylene (UHMWPE) components used in total joint arthroplasty [1]. Among the strategies to reduce oxidation in first-generation highly crosslinked polyethylenes (HXLPE), post-irradiation remelting has been considered to virtually provide complete oxidative stability. However, recent studies have documented measurable oxidation [2-3], and even *ex vivo* stability loss of remelted polyethylene retrievals [4]. Biological pro-oxidants, such as squalene [5], and physiological loading have been proposed as potential mechanisms. Our objective was to assess the impact of cyclic stress, if any, in the oxidative stability of HXLPE.

Methods and Materials: Prismatic GUR 1050 UHMWPE pre-forms underwent electron beam irradiation in air (dose~50 kGy). Upon irradiation, UHWMPE prisms were subjected to either annealing (130 °C; 2 hours; vacuum) or remelting (150 °C; 2 hours; vacuum) thermal treatments. Afterwards, they were machined to a final size of 50x50x12 mm. Ready-to-test samples were run in a custom-built ball-on-flat wear simulator. The two degrees of freedom simulator operated at a frequency of 1 Hz and under a 200N load (nominal contact pressure 37 MPa), so the stainless steel ball bore against the prismatic samples for $5x10^5$ cycles. In some cases, wear-tested UHMWPE prisms were artificially aged in air (120 °C; 36 hours), and then tested once again for other $5x10^5$ cycles. Wear tracks were characterized by means of a confocal microscope (Sensofar Plμ 2300; Optical Imaging Profiler) to assess volume changes. Finally, FTIR spectroscopy was performed on 200 microns-thin slices taken from cross-sections of UHMWPE prisms. Spectra of both loaded and unloaded regions were recorded at 100 microns increments starting from the surface. Oxidation indices were calculated as the area ratio of the 1650-1850 cm^{-1} and 1330-1396 cm^{-1} absorption bands (ASTM F2102). Additionally, crystallinity indices were calculated as the area ratio of the band centered at 1890 cm^{-1}, and the reference band.

Results: Annealed HXLPE (B50A) was observed to delaminate after the consecutive application of cyclic stress, a severe oxidative challenge, and cyclic stress steps. Coherently, its topographic map revealed the deepest wear track (peak-to-valley: 184.2 μm) among the tested samples (Figure 1). On the contrary, remelted HXLPE samples showed no evidence of significant wear, except for a thin transfer film layer onto the metallic ball. Regarding oxidation, annealed HXLPE subjected to cyclic stress both before and after the severe oxidative challenge exhibited the highest oxidation indices (>3 in near surface areas). As-aged annealed HXLPE (unloaded) showed slightly lower oxidation. As expected, remelted HXLPE (B50R) had inferior oxidation indices (OI≤1) when was subjected either to cyclic stress or aging alone. However, oxidation indices doubled (OI~2) in near-surface regions when B50R materials were subjected to cyclic stress and aging conditions. Moreover, oxidation proceeded further when loaded and aged remelted specimens were cyclically loaded once again. Finally, the influence of cyclic stress on crystallinity was confirmed as surface regions exhibited elevated indices in both unaged and aged B50R samples.

Discussion: Our findings suggest that cyclic stress may exacerbate the progression of oxidation even in the case of remelted HXLPE. Also, it appears that its effects might be accumulative. Potential long-term oxidation-related complications in active patients implanted with remelted HXLPE implants should not be discarded, and warrant more research.

Acknowledgements: Research funded by MAT2010-16175 and CONSOLIDER-INGENIO CDS 2008-0023.

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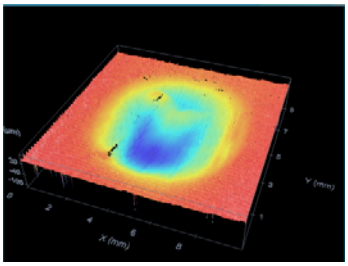

Figure 1. Wear track corresponding to B50A HXLPE (0.5 Mc+Aging+0.5Mc)

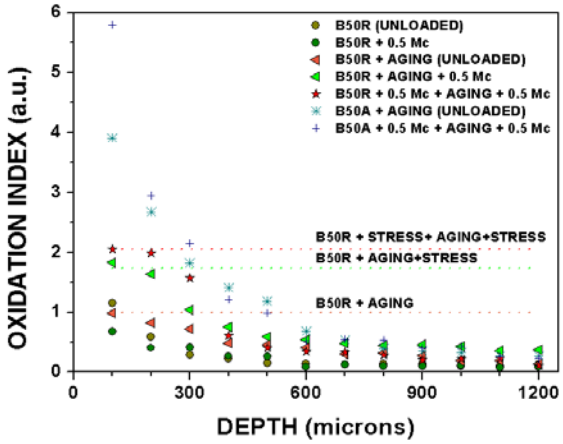

Figure 2. Oxidation indices vs depth for HXLPE

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Natural Polyphenols as Alternatives for Stabilisation of Highly Crosslinked UHMWPE with High Strength and Low Wear

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Introduction: Highly crosslinked ultra high molecular weight polyethylenes (XL-PEs) with low wear have been widely used for joint implants[1]. Mid-term clinical outcome appears encouraging [2]. Usually, XL-PEs are produced by radiation crosslinking and post-irradiation remelting or annealing to eliminate or reduce the free radical levels in order to stabilize the crosslinked polymer [3], which decrease the strength, toughness, and fatigue resistance of the materials and the components[4].

Vitamin E (VE) is effective in protecting irradiated UHMWPE from oxidation [5]. VE can be either blended with UHMWPE powders before consolidation and irradiation[6] or diffused into irradiated UHMWPE blocks [7]. Irradiation of consolidated VE/UHMWPE blends can depress the activity of the antioxidant at low content (< 0.05wt%)[8]. On the other hand, high content (> 0.3wt%) VE hinders crosslinking[6]. Diffusion of vitamin E into irradiated UHMWPE does not hinder crosslinking or change the chemical structures of vitamin E, yielding high crosslink density (and thus low wear) and oxidation stability, as well as improved strength and toughness.

New stabilisers are needed to offer excellent oxidation resistance while helping mantaining excellent properties in comparison to VE. Natural polyphenols are used in food and pharmaceutics as potent antioxidants. We hyposthesized that not all the phenolic groups, as blended with polyethylene, are consumed upon irradiation. The residual phenolic groups can further donate their protons to terminate the alkyl free radicals. Thus, we anticipate improved oxidation stability in comparison to the VE counterparts. Two natural origin polyphenols, i.e., gallic acid (GA) and dodecyl gallate (DG), are used as alternative antioxidants for UHMWPE to achieve improved oxidative stability, mechanicals, crosslink density and wear resistance after radiation crosslinking

Methods and Materials: GUR 1050 powders were blended with vitamin E (VE), gallic acid (GA), and dodecyl gallate (DG) at 0.05wt% and 0.1wt% (weight percent), consolidated and e-beam irradiated with doses of 50, 100, and 150 kGy. The crosslinked UHMWPEs were subjected to uni-axial tensile tests, double notched Izod impact test, and accelerated ageing at 120°C in air. The wear rates were determined by using a custom-built pin-on-disc (POD) tester at constant load. FT-IR spectroscopy was used to track the oxidation kinetics and the changes in the structures of the polymers and the antioxidants.

Results: The oxidation resistance of irradiated VE/UHMWPE, GA/UHMWPE, and DG/UHMWPE at 70°C in 5atm O_2 showed no significant differences. Adverse oxidative challenging of these irradiated UHMWPEs was conduced at 120°C. The presence of antioxidants at 0.05wt% and 0.1wt% significantly retarded the oxidation initation time (t_{OXI}). With higher irradiation dose, the t_{OXI} values decreased. For all the doses and antioxidant concentrations, the t_{OXI} values for the GA/UHMWPE and DG/UHMWPE were larger than those of the VE/UHMWPE (Figure 1).

Despite of the strong antioxidation potency, the presence of GA and DG did not hinder the crosslinking of the polymer as vitamin E did (Figure 2). At antioxidant concentrations from 0.05wt% to 0.3wt%, the irradiated GA/UHMWPE and DG/UHMWPE showed higher crosslink densities than those of irradiated VE/UHMWPE at 50, 100, and 150kGy.

Irradiation decreased the tensile strength and impact toughness of these stabilized polymers. The addition of antioxidants improved the impact toughness of the irradiated UHMWPE. These mechanical properties did not change after ageing at 70°C in O_2 for two weeks, while the 100kGy irradiated UHMWPE became very brittle after ageing. The impact strength values of the irradiated GA/UHMWPE and DG/UHMWPE were higher than those of the irradiated UHMWPE.

POD tests demonstrated low wear of these irradiated AO/UHMWPE materials (Figure 3). For example, the 100kGy irradiated 0.05wt% GA/UHMWPE showed a wear rate of 1.65 mg/MC, in comparison to 2.05 mg/MC for the 0.05wt% VE/UHMWPE and 2.29mg/MC for the 0.05wt% DG/ UHMWPE receiving the same dose. These wear rate are very close to the 100kGy irradiated and remelted UHMWPE (1.68mg/MC)[9].

In vitro culture with osteoblasts in PBS on the slices of irradiated AO/UHMWPE showed slightly improved cell adhesion and growth in comparison to that on virgin UHMWPE, based on both fluorescent imaging and quantitative characterisation, indicating excellet cell compatibility of these new materials.

Discussion: Polyphenols used in this study exhibited superior antioxidation activity to vitamin E after irradiation. Such potency may originate from that fact that irradiation did not change the chemical structures, especially the phenolic C-OH groups of the pholyphenols , as evidenty by the FTIR data, which is in contrast to the phenol loss of vitamin E upon high dose irradiation. Moreover, these polyphenols upon irradiation showed limited interferences on the crosslinking of UHMWPE so that the crosslink densities were close to those of the irradiated virgin polyethylene. It is likely that these polyphenols did not react with free radical during irradiation and thus remain their antioxidation potency when subjected to oxidative challenging. The mechanism is not clear and under investigation.

The oxidation stability of the irradiated polyphenol/ UHMWPE blends results in less change in the mechanical properties after accelerated ageing. The mechanical properties are much better than the first generation irradiated and remelted polyethylenes.

The results show that a low concentration (0.05wt%) of polyphenol after irradiation appears potent to protect improved resistance to adverse oxidative challenging, in comparison to the 0.05wt% vitamin E. Therefore, a lower safe antioxidant concentration should be expected for these polyphenols.

Radiation sterilisation has been abandonned by most manufacturers for the first generation highly crosslinked implants to avoid introduction of additional free radicals. With the presence of high efficent antioxidants, radiation sterilisation at 25-40kGy may become popular since the antioxidant activity after sterilisation will minimize the oxidation levels in the long term.

Acknowledgement: J. F. is grateful to the support by the Hundred Talents Program of the Chinese Academy of Science and the K. C. Wong Education Foundation, Hong Kong.

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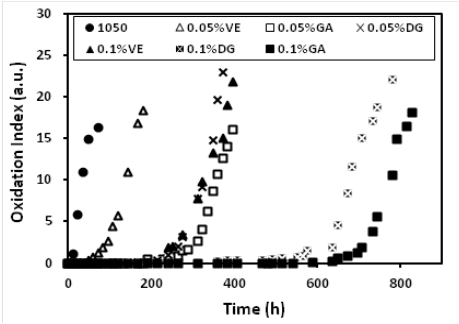

Figure 1. The oxidation level evolution with the ageing time at 120°C of 100kGy irradiated UHMWPEs.

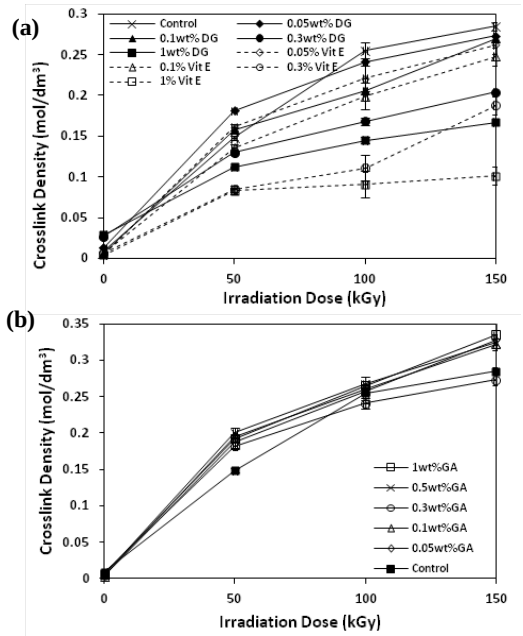

Figure 2. The crosslink densities of irradiated UHMWPE with (a) vitamin E and dodecyl gallate, and (b) gallic acid at different doses.

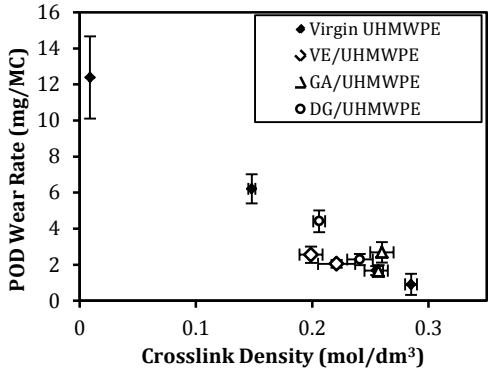

Figure 3. The dependence of POD wear rate on the crosslink density of irradiated and remelted polyethylene, along with the irradiated polyethylene with vitamin E, gallic acid, and dodecyl gallate.

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A Hindered Phenol Stabilized UHMWPE for Tibial Knee Inserts

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Introduction: Antioxidant-stabilized ultra high molecular weight polyethylene (**UHMWPE**) materials build upon the learning from the evolution in polyethylene materials so far. Previous UHMWPE materials, which have incorporated a high degree of crosslinking using high energy ionizing radiation such as gamma or e-beam, have been stabilized by thermal means with varying success. The incorporation and characterization of a hindered phenol antioxidant, tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate], **PBHP**, into GUR 1020 UHMWPE that was compression molded and irradiated, to yield an antioxidant-stabilized UHMWPE, **AOX™**, is described here.

Methods and Materials: GUR 1020 (Ticona, US) UHMWPE material stabilized with 0.075% (w/w) PBHP was consolidated by compression molding (MediTECH, IN). Samples were machined, washed, vacuum foil packaged and crosslinked and sterilized using a gamma radiation dose of 80 KGy. Characterization includes mechanical properties such as tensile, fatigue crack resistance toughness, oxidative stability, wear resistance relative to a predicate device, biocompatibility and a toxicological risk assessment based on chemical identification of by-products generated by gamma irradiation. Additionally, the uniformity of distribution of PBHP within GUR 1020, both in powder form as well as upon consolidated has been reported[1].

Results: Physical and performance characteristics for the stabilized polymer irradiated to 75 KGy have previously been compared against a stabilized polyethylene that is irradiated to a nominal dose of 50 KGy and remelted[2], **XLK™**. In the current study, it has been noted that the tensile strength values for AOX, owing to the avoidance of remelting which results in some loss in crystallinity, is approximately 15% higher than that for XLK. For similar reasons, the fatigue crack propagation resistance, measured as ΔK_{incep}, is approximately 20% higher. The higher crystallinity in AOX relative to XLK (approximately 20%) also provides creep reduction of about 20%. Due to a combination of material and design changes, the current fixed bearing knee, **Attune™**, shows measurably lower wear than **Sigma™** on the knee wear simulator[3]. However, based on an evaluation of the materials alone, AOX shows comparable pin-on-disk wear as XLK. The uniformity in the distribution of PBHP has been validated in a large scale (1000lb) manufacturing process and has been verified to be consistently with a 3σ variance of within 100 ppm about the nominal concentration of 750 ppm.
Comprehensive biocompatibility studies based on ISO 10993 test standards were conducted on AOX which demonstrates comparable biocompatibility as an HDPE control in the long-term animal implantation studies[4].
Employing state-of-the-art extraction techniques such as Dynamic Head Space Extraction (DHSE) and Stir Bar Sorptive Extraction (SBSE) techniques, coupled with analysis by GC-MS/MS and LC-MS/MS, identification and quantification of the γ-radiation byproducts of PBHP has been verified to have a leachable and extractable potential well below safety concern threshold levels of 150 ng/day[5]. Osteolytic potential characterization has been effected using a Mouse Calvaria model to demonstrate equivalent osteolytic activity when compared with a host of UHMWPE materials with substantial clinical history[6].

Discussion/Conclusion: A hindered phenol antioxidant stabilized GUR 1020 has been generated and comprehensively characterized prior to use in a tibial knee component as AOX which exhibits an optimal balance of physical and mechanical properties coupled with good wear characteristics and outstanding oxidative stability. The stabilized polyethylene has been further shown to demonstrate good biocompatibility and an extremely high safety profile from a toxicological risk standpoint.

Table 1
Comparative Physical and Mechanical Characteristics of AOX & XLK

Property	XLK	AOX
ΔK_{Incep}, MPa(m)$^{1/2}$	1.27	1.5
Yield Strength	20.7 ± 0.2	24.1 ± 0.4
Ultimate Tensile Strength, MPa	41.6 ± 4.3	46.7 ± 0.8
% Elongation to failure	313 ± 22	300 ± 6
9 MPa Creep Strain (%)	6.76 ± 0.29	5.39 ± 0.36
% Crystallinity	51.7 ± 2.8	63.1 ± 0.6

* Statistically not significant ($p > 0.05$)

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Effects of antioxidative substrate and cartilage-inspired surface on the durability of acetabular liner

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Introduction: Over the last half century, total hip arthroplasty (THA) has been one of the most successful joint surgeries. Most patients have experienced dramatic pain relief and improvement in their quality of life after THA. However, aseptic loosening resulting from periprosthetic osteolysis caused by wear particles of polyethylene (PE) and its inflammatory response in the THA is a serious issue. Previous studies have revealed that PE wear particles play a major etiological role in periprosthetic osteolysis. To reduce wear, we have recently developed a novel articular cartilage-inspired technology for surface modification (Aquala® technology) with poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) grafting for a life-long acetabular liner in an artificial hip replacement [1]. A nanometer-scale layer of PMPC was formed on a cross-linked PE (CLPE) surface to better reproduce the ideal hydrophilicity and lubricity of the physiological joint surface [2]. However, lubrication is only one of several important indicators of the clinical performance of acetabular liners. Oxidation degradation of the first generation CLPE with gamma-ray sterilization has been concerned. Hence, other important indicators include oxidation and simultaneously preserve the mechanical properties of CLPE. The incorporation of the antioxidant vitamin E has been proposed recently as an alternative to post melting treatment after gamma-ray irradiation to avoid oxidation.
The purpose of this study was to investigate the effects of antioxidative substrate and cartilage-inspired surface on the oxidative stability and wear resistance of liners for artificial hip joints.

Methods and Materials: Compression-molded bar stock of 0.1 mass% of vitamin E-blended polyethylene (GUR1020E resin; Orthoplastics Ltd.) was irradiated with a high dose of gamma-rays (100–150 kGy) and annealed at 120°C for 12 hours for cross-linking (HD–CLPE(VE)). HD–CLPE(VE) liners were machined from this bar stock. Liners coated with benzophenone were immersed in a 0.5 mol/L aqueous MPC solution. The photo-induced graft polymerization on the HD-CLPE(VE) surface was carried out under ultraviolet irradiation of 5 mW/cm^2 at 60°C for 90 min. Untreated and PMPC-grafted CLPE liners treated with gamma-ray irradiation of 50 kGy were used as controls. All liners were then sterilized by with a 25-kGy dose of gamma-rays under N_2 gas. Surface properties of the liners were examined by Fourier-transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and static water-contact angle measurement. A cross-section of the PMPC-grafted layers on the CLPE surface was observed under a transmission electron microscope (TEM). The oxidative stability (oxidation induction time) of liners was evaluated by differential scanning calorimetry according to the ASTM D3895. The oxidative degradation of accelerative aged liners (ASTM F2003) was evaluated by FT-IR according to the ASTM F2102. Mechanical properties of the substrate were evaluated according to the ASTM F648. Multidirectional wear test were performed using a pin-on-disk testing machine (Ortho POD; AMTI) according to the ASTM F732. Surface morphology of disk was observed with a non-contact three-dimensional (3D) profiler system (Talysurf CCI Lite; AMETEK Taylor Hobson). The 5.0 × 10^6 cycles wear test was performed using a 12-station hip joint simulator (MTS System Corp.) according to the ISO14242-3. A 26-mm Co-Cr-Mo alloy femoral head component was used for the tests.

Results: After PMPC grafting, the peaks ascribed to the MPC unit were clearly observed in both FT-IR and XPS spectra. The static water-contact angle of both PMPC-grafted CLPE and HD–CLPE(VE) was approximately 15°. Oxidative resistance (oxidation-induction times and indices) of PMPC-grafted HD–CLPE(VE) was significantly higher compared with non-additive CLPE regardless of PMPC-grafting (Fig.1).

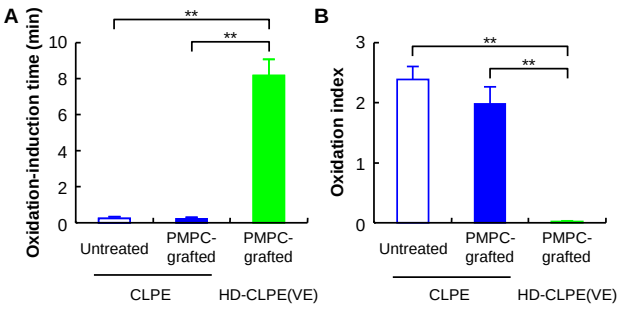

Fig. 1. (A) Oxidation-induction times and (B) indices of untreated CLPE and PMPC-grafted CLPE with/without vitamin E. Bar; SDs, ** $p < 0.01$.

Mechanical properties of the CLPE substrate were hardly changed regardless of vitamin E-blending and PMPC grafting (Table 1).

Table 1 Mechanical properties of untreated CLPE and PMPC-grafted CLPE with/without vitamin E

Sample	Ultimate tensile strength (MPa)	Elongation (%)	Creep deformation (%)	Hardness (shore D)
CLPE	54.4 (±3.8)	346.0 (±18.1)	0.75 (±0.08)	66.8 (±0.4)
PMPC-grafted CLPE	52.8 (±2.1)	351.6 (±35.6)	0.75 (±0.07)	66.8 (±0.3)
PMPC-grafted HD-CLPE(VE)	55.3 (±3.9)	317.0 (±16.2)	0.71 (±0.03)	66.6 (±0.8)

After the pin-on-disk test, both PMPC-grafted CLPE and HD–CLPE(VE) were found to show extremely low (Fig.

2A). The surface deformation of PMPC-grafted disk was smaller than that of untreated disk (Fig. 2B).

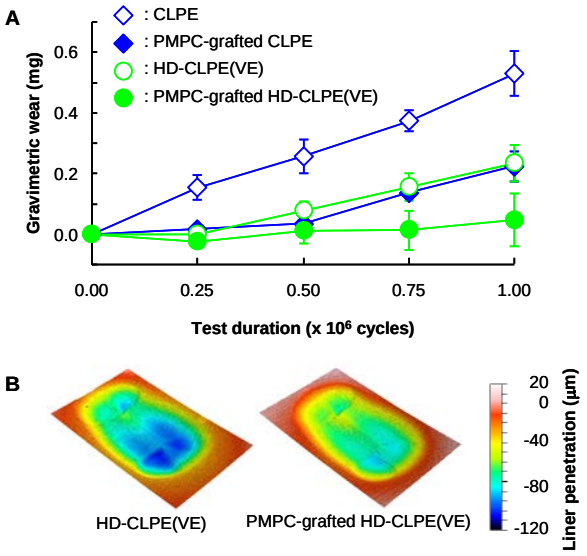

Fig. 2. Wear resistances of untreated CLPE and PMPC-grafted CLPE with/without vitamin E disks in the multi-directional pin-on-disk test. (A) Gravimetric wear, bar; SDs, and (B) 3D-surface deformation of disks.

After 5.0 × 10^6 cycles of the simulator test, both PMPC-grafted CLPE and HD–CLPE(VE) were found to show extremely low and stable wear (Fig. 3A). The 3D-coordinate measurements of PMPC-grafted liners revealed little or no detectable volumetric wear, whereas substantial volumetric wear was detected in untreated CLPE liners (Fig. 3B). The 3D-coordinate measurement images supported the gravimetric wear results. The wear particles isolated from lubricants were predominantly submicrometer-sized granules (Fig. 3C). Substantially fewer wear particles were found for both PMPC-grafted liners than for untreated CLPE liners.

Discussion: In this study, we investigated the effects of vitamin E-blending and PMPC-grafting, on the oxidative and tribological stabilities of CLPE liner and to examine the possibility of controlling the longevity of artificial hip joints by utilizing this material.

The PMPC-grafted HD–CLPE(VE) provided high oxidative stability and wear resistance. The PMPC-grafted layer leads to a significant reduction in the sliding friction between the surfaces because PMPC grafting causes formation of water thin films that can act as extremely efficient lubricants. Furthermore, and in spite of high-dose gamma-ray irradiation for cross-linking, the substrate modified by vitamin E blending maintains high oxidation resistance. Indeed, vitamin E is an extremely efficient radical scavenger. The results clearly show that the mechanical properties of the substrate were minimally

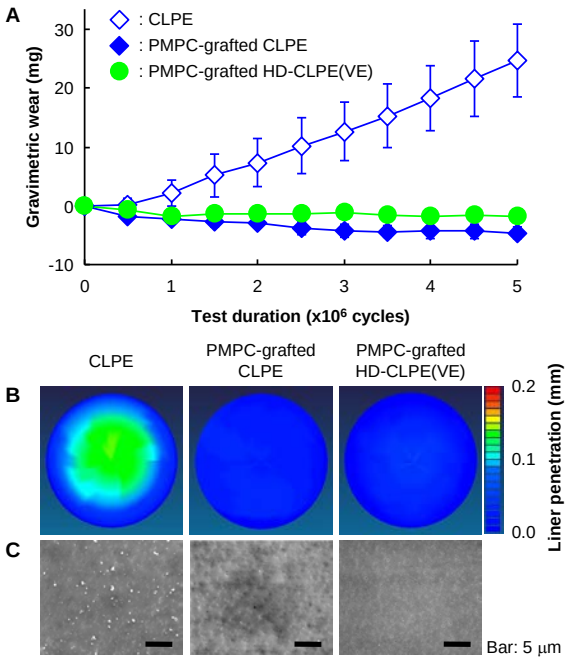

Fig. 3. Wear resistances of several types of CLPE liners in the hip joint simulation test. (A) Gravimetric wear, bar; SDs, (B) 3D coordinate measurements of liners, and (C) SEM images of wear particles isolated from lubricants.

changed, if at all, even after vitamin E-blending and/or PMPC grafting. Retaining the properties of the substrate unchanged is very important in clinical use, because the acetabular cup acts not only as a bearing material but also as a structural material in the artificial hip joint system. Generally, increased cross-linking in the CLPE degrades its mechanical properties, producing a trade-off between wear-resistance and mechanical properties. It is desirable to reduce wear while maintaining the mechanical properties necessary for proper *in vivo* function. The advantage of PMPC-grafting comes from the fact that the PMPC layer gave a high lubricity only on the surface, and had no effect on the bulk properties of the substrate.

In conclusion, antioxidative substrate and cartilage-inspired surface of the PMPC-grafted HD–CLPE(VE) provides not only high wear resistance but also high oxidative stability.

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Is Vitamin E A Plasticizer for UHMWPE?

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Introduction: Ultra high molecular weight polyethylene (PE) is subjected to ionizing radiation to a dose of 50 – 100 kGy to produce highly crosslinked polyethylene (HXLPE). Both laboratory [1, 2] and clinical [3] studies of total joint replacement prostheses have shown that HXLPEs have a greater resistance to wear in these orthopedic implants. The first generation HXLPEs were subjected to post-radiation remelting or annealing at elevated temperatures to quench the free radicals and thereby to induce resistance to oxidative degradation associated with the presence of free radicals trapped in the lamellar regions of HXLPEs. However, studies showed that irradiation as well as post-radiation thermal treatment results in a decrease in several mechanical properties [4, 5]. While radiation is needed for crosslinking, which is known to induce high resistance to the generation of particulate wear in joint replacements, the thermal treatment step can be avoided by addition of a biocompatible antioxidant or stabilizer, such as Vitamin E (or α-tocopherol) [6] (see Figure 1) and it is now FDA approved for clinical use in total joint replacement prostheses. In this study, we studied the effect of varying content of Vitamin El in PE to determine whether PE acts as either a solvent or a plasticizer for PE in addition to being a radical scavenging antioxidant. Our hypothesis was that Vitamin E would act as a plasticizer at high concentrations, exceeding 1 weight %, which is the concentration required for most plasticizers to have a plasticization effect, but Vitamin E would not act as a plasticizer at the lower concentrations required to induce sufficient oxidation resistance in PE. A combination of morphological and mechanical properties measurements was employed to verify our hypothesis.

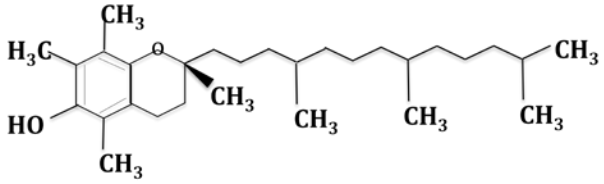

Figure 1. Chemical structure of α-tocpherol.

Methods and Materials: Medical grade GUR 1020 resin (Ticona GmbH, Oberhausen, Germany) was soaked in solutions of DL-α-tocopherol (Acros Organics) in ethanol and dried to provide PE with the following weight % of Vitamin E: 0 (control-PE), 0.1, 0.25, 0.5, 1.0, 1.5, 3 and 4. A Carver hydraulic press was used to mold each powder into approximately 2 mm thick sheets at 180°C and 10 MPa applied pressure, and then quenched using recirculating cold water. One set of sheets was further subjected to remelting and isothermal crystallization for 24 hours at 126±0.5 °C and then slow cooled. One half of the quenched (Q) and isothermally crystallized (IC) PE sheets were subjected to 10 Mrad dose of electron beam radiation. Differential scanning calorimeter (DSC) (Q2000 series, TA Instruments) was used to determine crystallinity of all samples prior to irradiation [n = 3]. Crystallinity was calculated using a heat of fusion of 100% UHMWPE equal to 288 J/g. ASTM 638-Type V tensile specimens were sectioned from the sheets and subjected to tensile tests [n=6] using an Admet tensile tester operating at a crosshead speed of 10 mm/min. Selected pre-weighed, control unirradiated PE tensile specimens were immersed in a Vitamin E bath with a 100:1 (w/w) ratio of Vitamin E to PE and maintained at 200°C for 24 hours in order to determine whether excessive amount of Vitamin E dissolves non-crosslinked PE. After 24 hours the bath was immersed in cold water to quench the melted PE and the samples were weighed.

Results: Maintaining 1 weight % non-crosslinked control PE samples in a Vitamin E bath at 200°C did not dissolve PE but swelled the PE almost 7-fold while retaining its shape, as shown in Figure 2.

Figure 2: A tensile specimen of control PE (left) and Vitamin E infused PE (right)

There was a significant increase ($p<0.05$, ANOVA) in the crystallinity of isothermally crystallized PEs, which ranged from 49.6 ± 1.9 to 55.8 ± 1.4 compared to the quenched PE which ranged from 42.8 ± 0.5 to 45.7 ± 1.1, but there was no trend in crystallinity ($p>0.05$, ANOVA) with respect to Vitamin E content, as shown in Figure 3.

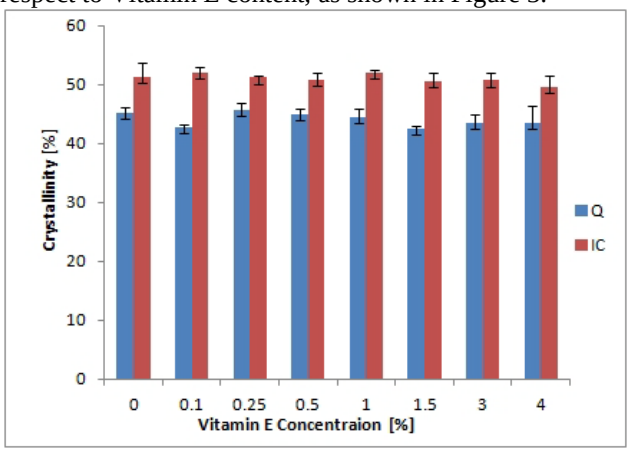

Figure 3: Crystallinity [%] for quenched PEs (Q) and isothermally crystallized PEs (IC) with respect to Vitamin E concentration.

Tensile tests of PE showed that modulus of both unirradiated PE-Q and PE-IC gradually decreased with increase in Vitamin E content, as shown in Figure 3. This trend persisted for PE-Q after irradiation but there was not much of a trend observed with Vitamin E content in the tensile modulus of PE-IC after irradiation.

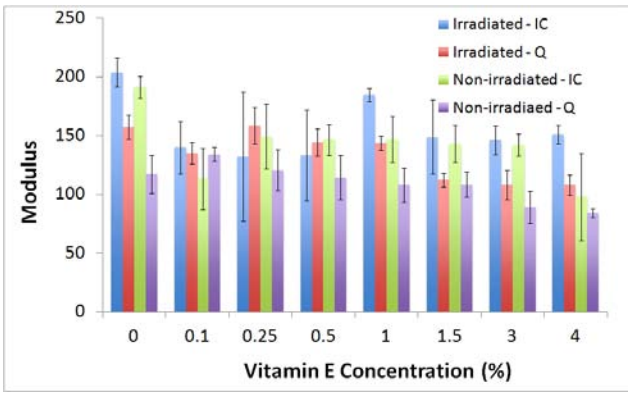

Figure 4. Tensile Modulus of Non-irradiated and Irradiated PE that was quenched (Q) or Isothermally crystallized (IC) prior to irradiation.

The maximum strain of non-irradiated PE-Q and PE-IC containing Vitamin E did not show any trend with Vitamin E content, as shown in Figure 4. However, PE-IC both irradiated and non-irradiated failed at very low maximum strain when there was no Vitamin E incorporated in it. After radiation, there was a strong monotonic increase in maximum strain in both PE-Q and PE-IC with Vitamin E content, beginning with a low value of maximum strain and approaching the maximum strain of non-irradiated PE-Q and PE-IC at the highest concentration of Vitamin E.

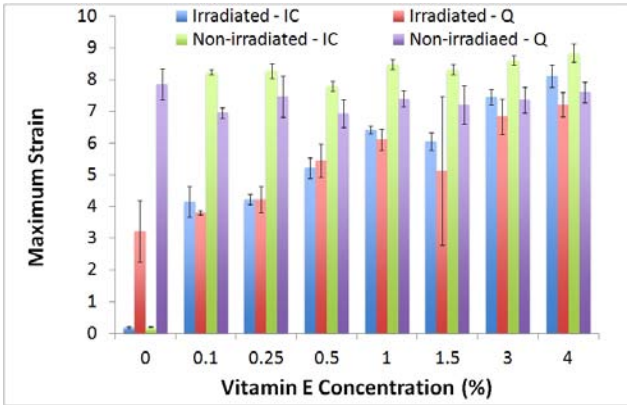

Figure 4. Maximum of Non-irradiated and Irradiated PE that was quenched (Q) or Isothermally crystallized (IC) prior to irradiation.

The yield stress and ultimate tensile stress did not vary significantly among the PE groups and is not discussed.

Discussion: Swelling of non-irradiated PE in Vitamin E in a 1:100 (w/w) ratio for 24 hours at 200°C showed that Vitamin E is not a solvent for PE, at least at this concentration of PE and higher, unlike xylene which dissolves and completely changes the shape of PE at most concentrations. It is however possible that the lower molecular weight fractions of PE dissolved in Vitamin E since the Vitamin E in the bath became more viscous after the experiment was completed.

The DSC experiments showed no trend in crystallinity with increase in Vitamin E content, indicating that if Vitamin E is a plasticizer for PE, it must be a weak one since it did not significantly alter the degree of crystallinity of PE over a range of 0-4 weight % Vitamin E. Effective plasticization of the melt would have rendered greater chain mobility to PE, resulting in more disentanglement during crystallization and thereby a higher crystallinity with increasing Vitamin E content. However, this was not observed and the crystallinity remained relatively constant over this range of Vitamin E content.

Tensile tests however showed that the modulus of PE, quenched or isothermally crystallized, generally decreased with Vitamin E content, especially at the higher concentrations indicating that Vitamin E acts as a diluent in the amorphous regions of PE, thereby decreasing the overall tensile modulus with increasing content. It is also very likely that at the highest concentrations, PE would have been saturated by Vitamin E and the Vitamin E may have segregated into segregated Vitamin-E rich domains. This however must be verified morphologically. The maxim strain of non-irradiated quenched PE did not increase with Vitamin E content, however there was a small but statistically significant increase in maximum strain in the non-irradiated isothermally crystallized PE at the highest concentrations of 3 and 4% Vitamin E. Increasing in maximum strain of this group may perhaps reflect the additional hours in the melt state after molding along with 24 hours at an elevated temperature, thereby allowing Vitamin E to diffuse into and "heal" grain boundaries. However, this effect was still relatively small. The large decrease in maximum strain with radiation for the low concentrations of Vitamin E reflects increase in crosslinking, which is known to decrease tensile strain. The well known crosslinking suppression with increasing Vitamin E content [6] likely resulted in the maximum strain approaching that of unirradiated PE at high Vitamin E content. However, all of these effects are negligible at the low concentration of 0.1% Vitamin E that is deemed necessary to induce sufficient oxidative resistance in clinically relevant radiation doses in crosslinked PE.

In summary, Vitamin E does not dissolve PE at low concentrations of 1% PE in Vitamin E, is a weak plasticizer which does not affect crystallinity at up to 4% concentration, is a diluent which steadily lowers modulus of PE, up to 4% concentration and can increase maximum strain of unirradiated PE to a small extent when allowed sufficient time at high temperature and at high concentrations. However, none of these effects are discernible at the 0.1% concentration of Vitamin E that is deemed necessary to induce oxidation resistance in irradiated PE for total joint replacement prostheses

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Acute fracture of XLPE patellar components are not associated with wear damage: A retrieval analysis

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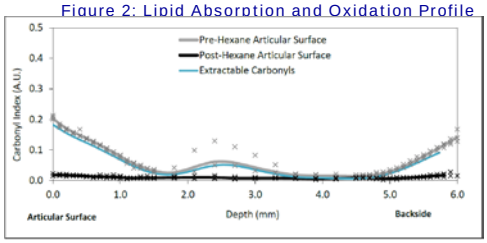
Introduction: The incidence of shear failure of all polyethylene patellar components in total knee arthroplasty has been estimated to be 0.4%. Cross-linking has been introduced into polyethylene components due to its favorable wear properties in vitro. It has been shown that these failures in highly cross-linked all polyethylene patellar components are caused by cyclic compression and shear loading., however limited information exists to determine whether wear damage plays a role in this mechanism of component failure. The purpose of this study was to examine the wear related damage of retrieved, irradiated and melted, highly cross-linked, UHMWPE (XLPE) patellar components to determine whether wear plays a role in this mechanism of patellar component failure. We hypothesize that failed components will show limited wear, thereby confirming that these shear failures are caused by acute fracture due to the decreased mechanical properties associated with cross-linking

Methods and Materials: One sample was examined and discarded with no appreciable gross evidence of wear. Our next sample underwent photography, optical imaging and micro-ct imaging. Then, detailed materials testing, including infrared microscopy, gravimetric swelling analysis, and differential scanning calorimetry was performed.

Results: Minor wear/creep, consistent with typical in vivo service, was identified at the dome of the articular surface. No material properties were determined to have changed as a result of in vivo service. Without any oxidation or material changes, neither oxidative embrittlement nor any concomitant mechanical changes were at cause for the fracture line along the backside of the patellar button, and thus, wear should not be considered the cause of these types of fractures.

Figure 2: Lipid Absorption and Oxidation Profile



Absorbed lipids, identified as "extractable carbonyls", reached a depth of approximate 1.1mm below the articular surface of the patellar component. After extraction of the lipids through boiling in hexanes, no detectable carbonyls, indicative of oxidation, were measurable (CI < 0.1).

Discussion: This analysis demonstrates that the crack failure noted in this highly cross-linked UHMWPE component was in fact caused by acute fracture and not a result of wear induced damage. Cross-linking of UHMWPE has been associated with a decrease in fatigue crack resistance in acetabular liners but has not previously been shown in patellar components of total knee replacement. The previous reports on this subject, including our own, have theorized that these cracks are not wear induced, and this analysis now verifies those assumptions.

These finding should be taken into consideration as the use of highly cross-linked UHMWPE continues to rise in total knee replacement surgery due to its improved wear profile and potential for longer lifespan. Care should be taken to balance the potential benefit of decreased wear of the patellar component with the increased risk of failure due to fracture.

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High Wear Scar Symmetry on Tibial Polyethylene Inserts from Bilateral Total Knee Replacement Patients

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Introduction: The significance of factors leading to wear of the ultrahigh molecular weight polyethylene (UHMWPE) tibial component of a total knee replacement (TKR) are poorly understood. Particularly, recent studies have scrutinized the importance of subject-specific gait [1] in light of the fact that current international standards for *in vitro* wear testing use a single representative input pattern for testing of *in vivo* wear. In order to better understand the dependence of wear on patient variability, this study compares bilateral UHMWPE tibial component retrievals using high-resolution quantitative volumetric analysis. It was hypothesized that the symmetry between paired medial sides and paired lateral sides of contralateral wear scars from different patients would be lower than the symmetry of contralateral wear scars from the same patient.

Methods and Materials: Bilateral TKR patients with available right and left Miller-Galante II UHMWPE components (Zimmer, Warsaw, IN) were included in this study Articular surfaces were scanned at 100x100µm using a low-incidence laser coordinate measuring machine (SmartScope, OGP Inc., Rochester, NY). Autonomous mathematical reconstruction of the original surface was used to calculate volume loss, center of volume loss and linear penetration maps of the medial and lateral tibial plateaus [2]. Wear scars were defined as regions that exceeded 75 µm penetration, from which binary black-and-white scar images were created, like those in Fig. 1a. All scars were normalized to medium-sized right side knees and overlaid in pairs, as in Fig. 1b. Medial and lateral sides of paired contralateral knees from the same patient were analyzed for symmetry by calculating the distances between centers of volume loss and percentages of overlapping scar areas:

$$Overlap\ \% = \frac{2 * Area_1 \cap Area_2}{Area_1 + Area_2}$$

The overlap was calculated such that non-intersecting scars resulted in 0% overlap, while scars of identical size and location resulted in 100% overlap, indicating low and high symmetry, respectively. Medial and lateral sides of paired contralateral knees from different patients were used to demonstrate the expected inter-patient variability. Two-tailed Student's t-tests were used to compare groups.

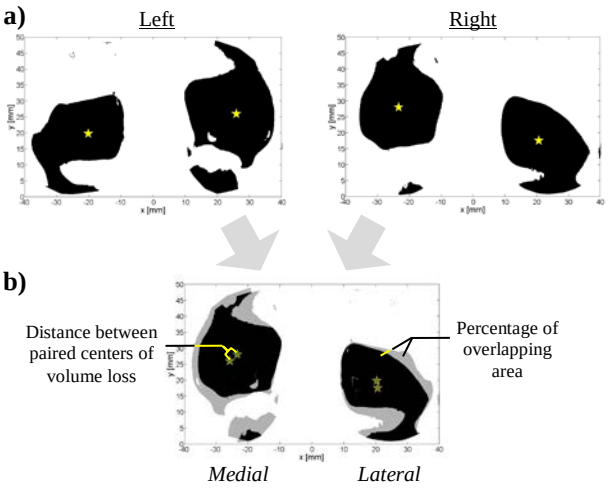

Figure 1: a) Wear scars were self-selected using a penetration threshold of 75µm with centers of volume loss marked by yellow stars. b) Normalized scars were overlaid to calculate distance between volume centers and percentage of overlapping area for both medial and lateral sides.

Results: Nine patients with available bilateral TKR inserts were identified from an IRB approved retrieval repository. For this study, pilot data of four patients ((3 postmortem / 1 revision, 2M/2F, 64.5±9.0 years old at implantation, 97.7±30.9 months *in situ*) are reported. The distances between centers of volume loss for medial and lateral sides tended to be shorter for contralateral knees from the same patient (mean±SD: 2.46±1.58mm and 2.02±0.37mm, respectively) than for contralateral knees across patients (5.29±2.86mm and 8.66±3.85mm, p=0.08 and p<0.001, respectively) (Fig. 2a). Similarly, the overlap between contralateral same-patient scars on the medial sides (77.4±15.1%) and lateral sides (79.5±5.6%) were significantly greater than the corresponding overlapping areas across patients (61.4±12.1% and 49.2±24.7%, p=0.049 and p=0.002, respectively) (Fig. 2b).

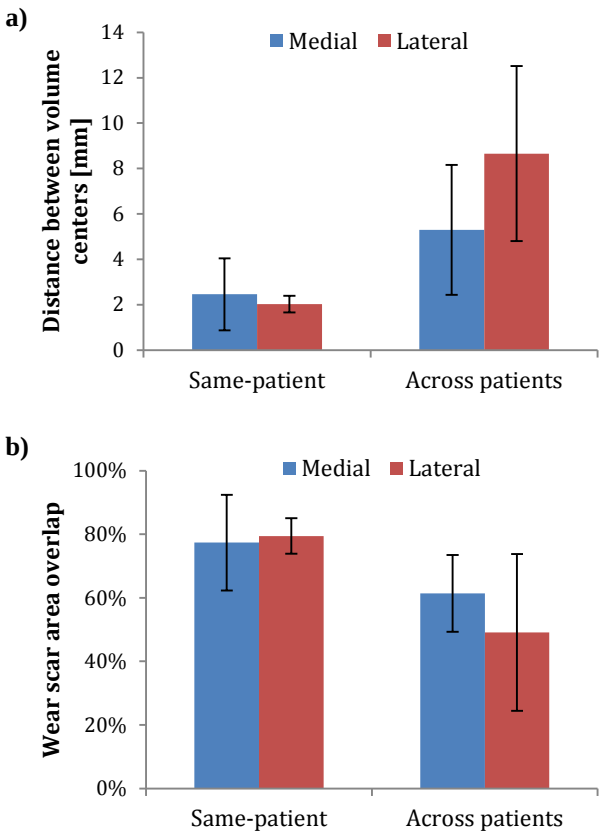

Figure 2: Symmetry of wear in terms of (a) distance between the centers of volume loss and (b) percentage overlap of wear scar areas for contralateral same-patient and contralateral different-patient paired components.

Discussion: The results of this pilot study support our hypothesis; namely, the medial and lateral articular surfaces of tibial components retrieved from bilateral TKR patients exhibit higher wear symmetry contralaterally within a patient than across patients. This finding supports previous studies that suggest that TKR wear depends on patient-specific factors. Wear scars are not only a representation of gait pattern [1,3] but also a reflection of the activity profile of the patient [4]. These patient specific factors may explain the high variability in wear scarring between patients despite identical prosthesis design. Although there were differences in implantation times and surgical placement between left and right knees, strong interlimb symmetry was found, which supports gait studies of knee replacement patients that have found that patients tend to use both legs symmetrically [5,6]. The focus on one design and small sample size limit the scope and implications of this study. However, five sets of bilateral TKR postmortem retrievals of various designs have recently become available for analysis, of which four patients have gait testing data. Future studies should incorporate multiple prosthetic designs to investigate the importance of design over gait pattern, which will help elucidate the relationship between patient-specific activity and wear of total knee replacements.

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Bearing Surface Damage Analysis of Coupled Total Shoulder Replacement Retrievals

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Introduction: *In vivo* surface damage of total joint replacements can have significant clinical consequences as ultrahigh molecular weight polyethylene (UHMWPE) wear debris can initiate osteolysis and implant loosening [1]. Damage to metallic counterbearing surfaces can significantly increase UHMWPE wear [2]. The majority of retrieval studies have focused on polymer bearing damage in total hip replacements (THR) and total knee replacements (TKR)[3,4]. These analyses have been essential for our understanding of how crosslinked UHMWPE behaves *in vivo*. However, little attention has been given to total shoulder replacements (TSR), which experience modes of loading spanned by THR and TKR [5]. Few retrievals studies have examined trends in surface damage for mated metal and polymer bearings. Our work presents a methodology that classifies the mode, geometric extent, and severity of surface damage in TSR retrievals. We quantify trends in UHMWPE glenoid damage with that of mated cobalt chrome (CoCr) humeral head components in an effort to provide insight on the origin, evolution and consequences of bearing damage *in vivo*.

Methods and Materials: Detailed protocols were developed to assess bearing surface damage on humeral head and glenoid components [6,7]. Twenty-five retrieved humeral head components (65 ± 12 months *in vivo*) were gridded with each surface divided into 40 regions of equal area (**Fig. 1a**). Within each region, at least two observers noted the occurrence, geometric extent and severity of damage. Six modes of damage were used for CoCr components (**Fig. 2**). Average scores were combined into a total damage score for each sample by summing regional scores for each damage mode (product of the severity and geometric extent scores) across all 40 regions, for a maximum score of 3000.

Six retrieved glenoid components (66 ± 46 months *in vivo*) were analyzed, all of which mated with one of the earlier mentioned humeral heads. Each component was gridded and divided into 17 sections of equal area for monitoring location, geometric extent, and severity (**Fig. 1b**). Each region was photographed using a Nikon 1 J1 camera (Tokyo, Japan) and Infinivar Video Microscope lens (Infinity Photo-Optical Company, Boulder, CO) at 249 dpi under an AmScope (iScope Corporation, Irvine, CA) LED ring light. A minimum of 2 observers recorded the presence, geometric extent, and severity per glenoid region selecting from 13 UHMWPE damage modes: scratching, striations, pitting, abrasion, adhesion, fracture, burnishing, wear through, surface deformation, rim erosion, delamination, subsurface cracking, and embedded debris (**Fig. 3**) [7]. Damage scores were calculated for each mode in all of the 17 regions and damage index (DI) was calculated by summing the scores for all 17 areas finally dividing by a maximum score of 2856. In addition inter-observer agreement was calculated by averaging the agreement on damage between observers for each glenoid region and then averaging agreement across all samples. For the 6 mated components, the total geometric extent of each severity level for all damage modes were correlated between glenoids and humeral heads using a non-parametric Spearman's rank correlation coefficient (ρ) in Matlab.

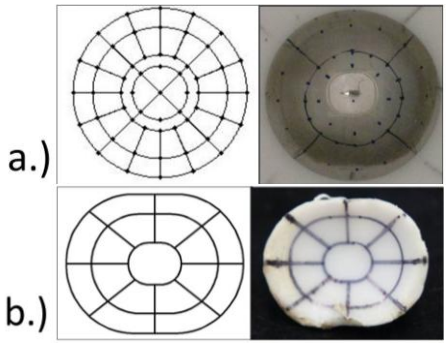

Fig. 1. Grids for (a) humeral head and (b) glenoid.

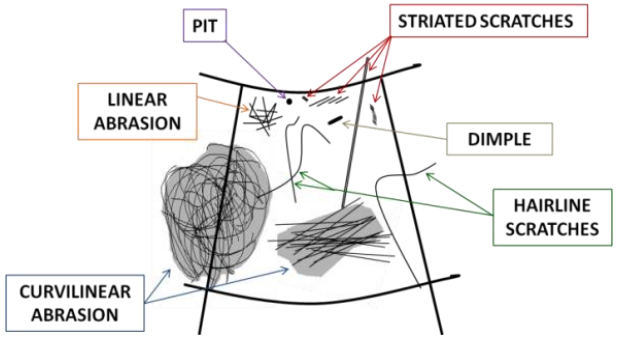

Fig. 2. Gridding scheme and damage modes for CoCr humeral heads.

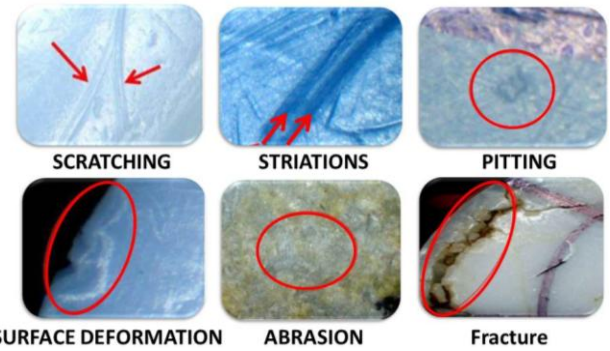

Fig. 3. Primary damage modes observed on UHMWPE glenoids.

Results: All analyzed implants showed at least one instance of damage. Trends in damage were assessed as a basis for clinically relevant questions. Hairline scratching, striated scratching and curvilinear abrasion were present on over 90% of the humeral head samples, while less than 70% of the samples exhibited linear abrasion, pitting and dimpling. All damage modes on the humeral head tended to occur at the center of the head. Finally, curvilinear abrasion and striated scratching, when present, occurred in 50% of the regions.

Damage Modes		Spearman Rank Coefficent (rho), $p < 0.05$
CoCr Humeral Head	UHMWPE Glenoid	
Curvilinear Abrasion	Scratching 1	-0.89
Pitting	Scratching 1	0.77
Striated Scratching	Surface Deformation 1	0.78
Linear Abrasion	Delamination 1	-0.85
	Delamination 3	-0.85

Table 1: Humeral head and glenoid damage mode correlations.

Trends in glenoid damage are shown in **Fig. 4**. Glenoids demonstrated instances of scratching, striations, pits and surface deformation in at least 75% of the regions. Striations and pitting had a slight tendency to occur in the central 9 regions; a single instance of embedded debris was also present in the center. Abrasion, delamination, fracture and surface deformation preferentially occurred in the outer 8 regions.

Statistical correlations demonstrate that certain trends may be able to reveal mechanisms of damage accumulation (**Table 1**). For example, a positive correlation between CoCr pitting and UHMWPE mild scratching suggests that pitting may be a primary culprit for generating scratching damage on glenoid surfaces. Establishing trends in location of damage on both the humeral head and mating glenoid may elucidate the effects of conformity in implant design.

Our method for scoring the CoCr humeral heads demonstrated a minimum average agreement of 89% between observers on damage modes present. In addition the glenoid scoring method demonstrated a minimum average agreement of 84%.

Conclusions: To our knowledge, this is one of the few studies that assesses both bearing surfaces of TSRs, and directly compares damage modes on CoCr humeral heads with mated UHMWPE glenoid devices. UHMWPE glenoids exhibit damage modes and occurrence frequencies that are similar to those observed in THR and TKR with longer implantation times [3,4,6-9]. In addition there are additional damage modes seen in TSR but not in THR and TKR [8].Thus, damage in TSR is not only distributed over a smaller area, but also accumulates at a faster rate than in THR and TKR. This greater severity in UHMWPE damage suggests that increased metal bearing damage plays an important role in TSR wear *in vivo*. Trends in glenoid damage location are also revealing of damage mechanisms: delamination and fracture occurred in the outer 8 gridded regions of the glenoid, consistent with higher contact stresses that may be due to edge loading. As a result, further investigation should concentrate on how changing the conformity of a glenoid might affect the predominant locations of damage on CoCr heads to quantify the severity and degree of potential edge-loading. Furthermore, the degree and extent of damage seen in shoulders with conventional UHMWPE raises concern with regard to the recent introduction of cross-linked UHMWPE in knees, which experience higher contact stresses due to reduced conformity [10]. Ongoing assessment of humeral head and glenoid pairs will provide additional insight as to trends in type, severity and coverage, correlations between mated surfaces and potential damage mechanisms.

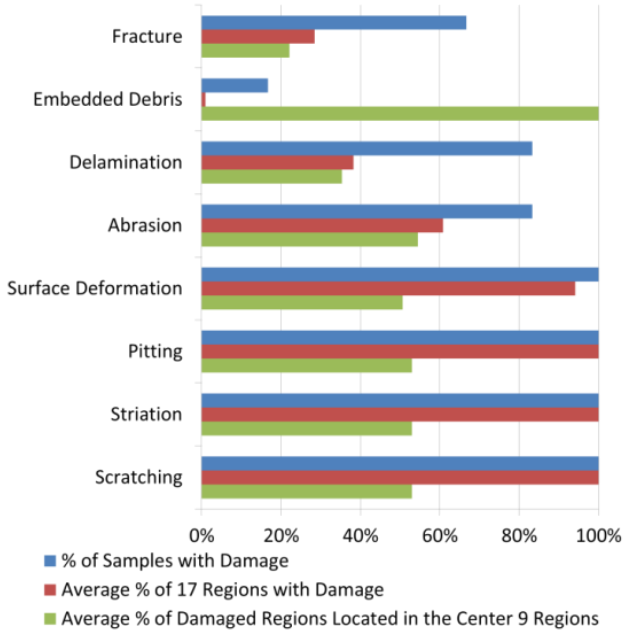

Fig. 4. Summary of coverage data for each damage mode. Burnishing, wear through and subsurface cracking were analyzed for trends but were not listed in the figure.

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Particles from vitamin-E-diffused highly cross-linked UHMWPE induce less osteolysis compared to virgin highly cross-linked UHMWPE in a murine calvarial bone model

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Introduction: Ultra high-molecular weight polyethylene (UHMWPE) particle-induced osteolysis is one of the major causes of arthroplasty revisions. The lack of particle clearance from the joint inevitably leads to the upregulation of the inflammatory cascade, resulting in bone resorption and implant loosening. Recent *in vitro* findings (Bladed C. L. et al, JBMR B 2012 and 2013) have suggested that UHMWPE wear particles containing vitamin-E (VE) may have reduced functional biologic activity and decreased potential to cause osteolysis. This is of significant importance since VE-stabilized cross-linked UHMWPEs were recently introduced for clinical use, and there is no *in vivo* data determining the effects of wear debris from this new generation of implants. In this study we hypothesized that particles from VE-stabilized, radiation cross-linked UHMWPE (VE-UHMWPE) would cause reduced levels of osteolysis in a murine calvarial bone model when compared to virgin gamma irradiated cross-linked UHMWPE.

Methods and Materials: Study groups included were (i) radiation cross-linked VE-UHMWPE, approximately 0.8% by weight, diffused after 100 kGy; (ii) radiation cross-linked virgin UHMWPE (virgin UHMWPE); (iii) sham controls. Particles were generated for each group by Bioengineering Solutions (Oak Park, IL). After IACUC approval, C57BL/6 mice (n=12 for each group) received equal amount of particulate debris (3mg) overlying the calvarium and were euthanized after 10 days. High resolution micro-CT scans were performed using an X-Tek HMX ST 225 with a set voltage of 70 kV and current of 70 µA. Each calvarial bone (interparietal, right and left parietal, right and left frontal) was blindly scored using the following scale: 0=No osteolysis, defined as intact bone; 1=Minimal osteolysis, affecting 1/3 or less of the bone area; 2=Moderate osteolysis, affecting at least 2/3 of the bone area; 3=Severe osteolysis, defined as completely osteolytic bone. H&E and TRAP staining was performed on tissue to confirm the micro-CT findings and to quantify osteoclasts. Inter-rater analysis was performed using Cohen's kappa analysis. An inter-rater coefficient >0.65 was considered as high inter-rater agreement. Comparison between groups was made using one-way ANOVA with post hoc Bonferroni correction for multiple comparisons. Correlations are reported as Spearman's rho. A p-value<0.05 was considered statistically significant.

Results: More than 83% of the VE-UHMWPE and more than 85% of the virgin UHMWPE particles measured less than 1 µm in mean particle size (Fig. 1). The mean particle size for VE-UHMWPE was 1.12 µm (range 0.28 to 79.08 µm), while virgin UHMWPE particles measured 1.22 µm (range 0.28 to 82.04 µm). There was a statistically significant greater level of osteolysis visualized on the topographical grading scale in calvaria implanted with virgin UHMWPE wear particles. The micro-CT findings were confirmed histologically (Fig. 2). A greater amount of inflammatory tissue overlaying the calvaria was observed in the virgin UHMWPE group when compared to both shams and VE-UHMWPE groups. Post hoc analysis revealed significant difference between VE-UHMWPE and virgin UHMWPE for the topographical osteolysis grading score (p=0.002) but no difference in osteoclast count (p=0.293).

Discussion: This is the first *in vivo* study reporting the effects of clinically-relevant UHMWPE particles generated from a VE-UHMWPE implant that is in current clinical use. These results suggest that VE-UHMWPE particles have reduced osteolysis potential *in vivo* when compared to virgin, highly cross-linked UHMWPE in a murine calvarial bone model. Arthroplasty procedures using VE-UHMWPE might be less susceptible to peri-prosthetic loosening caused by wear debris.

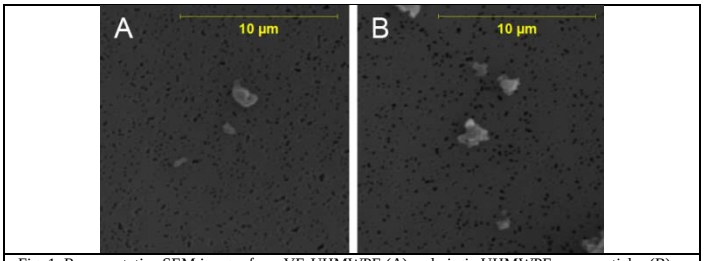

Fig. 1. Representative SEM images from VE-UHMWPE (A) and virgin UHMWPE wear particles (B).

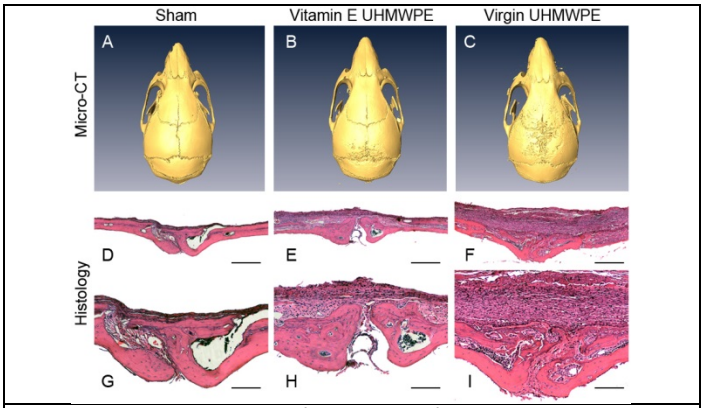

Fig. 2. Representative 3D images obtained after micro-CT scans from sham (A), VE-UHMWPE (B) and virgin UHMWPE (C) groups. There was a statistically significant greater level of osteolysis visualized on the topographical grading scale in calvaria implanted with virgin UHMWPE wear particles. The micro-CT findings were confirmed histologically. A greater amount of inflammatory tissue overlaying the calvaria was observed in the virgin UHMWPE group (F) when compared to both shams (D) and VE-UHMWPE (E) groups. Scale bar: D-F, 500µm; G-I, 100 µm.

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Stem Cell Uptake of UHMWPE and its Effect on Osteoblastic and Adipocytic Differentiation: Dose- and Size-Dependency

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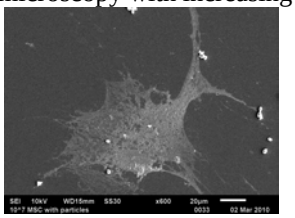
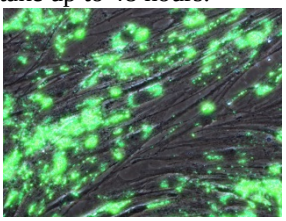
Introduction: Ultra high molecular weight polyethylene (UHMWPE) remains the most widely used bearing surface in the world for arthroplasties. Overall, it provides excellent long term outcomes, but unfortunately its consequences of osteolysis and ultimately aseptic loosening account for the majority of revisions. The osteolytic process involves an interaction of several cell types including the osteoblast and its precursor, the mesenchymal stem cell. The goal of this study is to investigate the direct effect of UHMWPE wear debris on the stem cell's ability to differentiate into an osteoblast. In addition, the variables of dose and size of the particulate debris were studied.

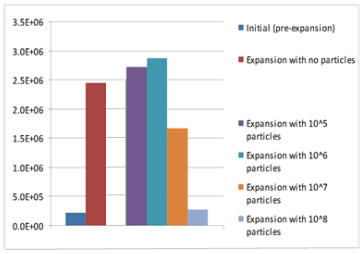
Methods and Materials: GUR1050 UHMWPE particles suspended, characterized, and serial diluted to 4 treatment doses($1x10^5$,10^6,10^7,10^8particles/mL). Young adult MSC's treated with increasing doses of particles (mean 0.4µm{range,16nm-7µm}). SEM analysis to verify cellular uptake. Time dependent uptake visualized with confocal microscopy utilizing UHMWPE auto-fluorescence over 6 time periods (1,6,12, 24,48,72 hrs). Total cell counts obtained and apoptosis determined via flow cytometry Annexin V assay. Fluospheres (polystyrene) of three sizes (20nm, 100nm, and 1 micron) prepared for size dependency studies at two doses ($1x10^7$,10^8particles/mL). The MSC self-renewal capacity determined by CFU-F assay. Osteoblastic differentiation potential determined by CFU-OB assay and vonKossa staining for calcified matrix. Differentiation into adipocytes determined by CFU-AD assay stained with Oil Red O. Experiments performed with two different seeding densities in triplicate for three MSC donors. FACS analysis to characterize MSC's phenotype profile. Statistical analysis with ANOVA and student's t-test.

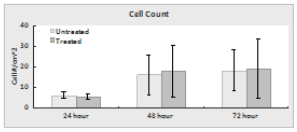
Results: SEM analysis revealed intracellular particle uptake. A time dependent uptake was seen via confocal microscopy with increasing uptake up to 48 hours.

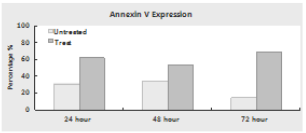




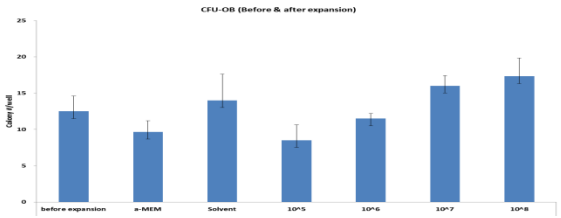
A dose-dependent response of MSC replication to UHMWPE particles observed. Control MSCs not subjected to particles demonstrated $2.4x10^6$ CFU-Fs. Addition of low doses of particles caused a mild elevation ($p>0.5$) in CFU-Fs to $2.8x10^6$. However, particle concentrations of $1x10^7$particles/mL revealed a cytotoxic effect on the MSCs lowering the CFU-Fs to $1.8x10^6$($p<0.05$). Further increasing the dose of particles ($1x10^8$ particles/mL) inhibited replication to $3x10^5$ CFUs($p<0.05$).Overall, this represents an 8-fold decrease in self-renewal capacity for the highest particle load.







Cell counts were equivalent at 48 and 72 hours , however the Annexin V expression demonstrated apoptosis in the UHMWPE treated cells increased over time. Enhanced osteogenic differentiation potential (CFU-OB) seen with increasing UHMWPE dose. Low-dose particle burden with higher adipocytic potential (CFU-AD).



Cell surface antigen testing indicates retained pluripotent nature of these treated cells. The size dependent studies reveal larger particles (1 micron) to decrease overall cell number and replication potential (CFU-F). The osteoblastic potential (CFU-OB) greatest with the nanoparticle subgroup compared to the larger micron particles.

Discussion: This study is the first investigation of UHMWPE's effect on MSC replication and differentiation and programmed cell death. UHMWPE has a dose-dependent effect on MSC replication and differentiation. At $1x10^7$particles/ml, this debris negatively impacts the MSC's replication potential. However, these cells have greater osteoblastic potential at higher particle doses. The higher doses more negatively influence the adipogenic potential. Also, this is the first size-dependent effect study on MSCs. The MSC response is opposite that of the osteoblast—the nanoparticle subpopulation is more deleterious to the osteoblast but the stem cell number, replication, and osteoblastic potential is more negatively affected by the larger micron size particle. This information will prove helpful in developing treatment strategies to improve the longevity of existing implants.

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In Vitro Investigation to Determine if Vitamin E-Blended UHMWPE has the Ability to Prevent Bacterial Attachment and Biofilm Formation

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Introduction: Periprosthetic infections that accompany the use of total joint replacement devices cause unwanted and catastrophic outcomes for patients and clinicians. These infections become particularly problematic in the event that bacterial biofilms form on an implant surface. When antibiotics become ineffective and patient morbidity becomes chronic, costly revision surgery is the most viable option to allow for debridement, implant replacement and healing to occur. In an effort to prevent biofilm-related periprosthetic infections, implant materials can be modified in a variety of ways. For example, previous reports have suggested that the addition of Vitamin E to ultra-high-molecular-weight polyethylene (UHMWPE) may prevent the adhesion of bacteria to its surface and thus reduce the risk of biofilm formation and subsequent infection.[1-3] In this study, Vitamin E was blended with two types of UHMWPE material. It was hypothesized that the Vitamin E blended UHMWPE would resist the adhesion and formation of clinically relevant methicillin-resistant *Staphylococcus aureus* (MRSA) biofilms.

Methods and Materials: Five sample types were manufactured, machined and sterilized (Table 1). Each sample had dimensions of 2 cm x 2 cm by 1 cm. To determine if the growth of MRSA biofilms would be reduced or prevented on the surface of the Vitamin E (VE) loaded samples (HXL VE 150kGy and HXL VE 75kGy) in comparison to the other three clinically relevant material types, each material type was tested for biofilm formation using a flow cell system developed by the Bone and Joint Research Lab.[4] The flow cell consisted of six chambers, each having a dimension of 4 cm x 4 cm x 2 cm.

Table 1: The five different material types used in this study.

Sample
HXL (Highly cross-linked UHMWPE)
CM (Compression molded UHMWPE)
HXL VE 75kGy
HXL VE 150kGy
PEEK (polyetheretherketone)

Direct Bacterial Quantification--An n=7 samples of each material type were placed individually into a chamber of the flow cell. A solution of 10% modified brain heart infusion (BHI) broth containing 10^5 MRSA cells/mL was flowed through each chamber at a rate that simulated the flow of body fluids. The BHI broth with bacteria was kept on ice outside of the incubator in which the flow cell had been placed. Using previously established protocols,[4-7] after 48 hours of growth, each sample was removed, rinsed 3x in phosphate buffered saline (PBS), placed into 20 mL of PBS, vortexed for 1 minute, and sonicated for 10 minutes. A 10-fold dilution series was used to quantify the number of colony forming units (CFU) that were attached to/formed into biofilms on the surface. Data were compared using the ANOVA statistical approach.

SEM Imaging--Using the same protocol as above, after the 48-hour incubation period, an n=7 of each material type were fixed in 2.5% glutaraldehyde, dehydrated in ascending concentrations of ethanol (70%, 95%, 100%), coated with carbon and imaged using scanning electron microscopy (SEM).

Results: Results indicated that the Vitamin E blended materials did not resist the attachment/formation of MRSA biofilms to any greater degree than the other three material types. All materials had greater than 10^7 CFU/cm^2 (Figure 1). The only statistically significant difference in the number of bacteria was between the HXL and PEEK materials (p=0.014). All other materials had statistical differences that were greater than p=0.05.

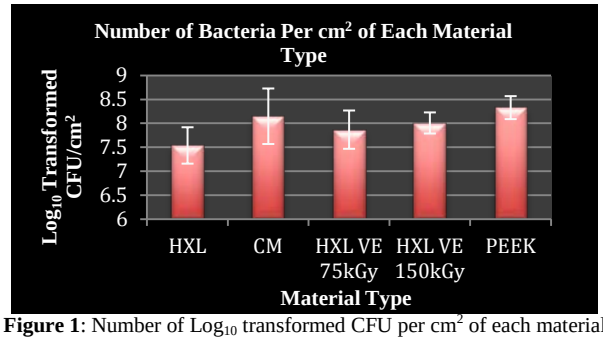

Figure 1: Number of Log_{10} transformed CFU per cm^2 of each material type.

The SEM images corroborated with the quantification data showing areas of significant biofilm formation on each of the five material types (Figure 2).

Discussion: The data collected from this study indicated that the Vitamin E blended UHMWPE did not have the ability to prevent or reduce the attachment/formation of bacterial biofilms on their surface. The HXL material had the fewest number of bacteria that adhered to its surface. In contrast to previously published results, these data indicated that Vitamin E blended UHMWPE may not

have the ability to prevent biofilm formation of a clinical MRSA isolate from occurring.

Previous reports in the literature have indicated that the opposite may be true. For example, Molina-Manso *et al.*[3] and Gomez-Barrena *et al.*[2] performed a study with a rapid adherence test wherein materials were exposed to bacterial suspensions containing 10^8 bacteria for 90 minutes. Since bacteria require roughly 24 hours to form a mature biofilm, this would not have been enough time to determine biofilm formation on the surface of their material. Their results also indicated that clinical isolates of *S. aureus* showed no difference in the amount that adhered to their control or Vitamin E samples. In contrast, their collection strains of *S. aureus* had less adherence.

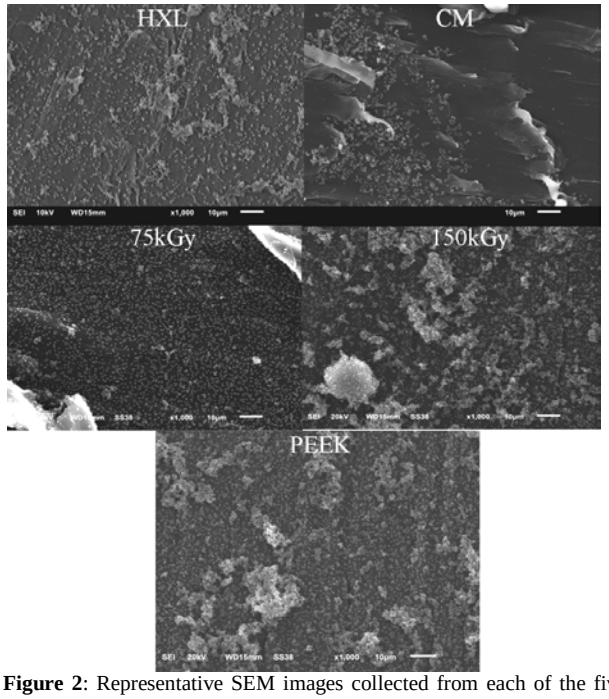

Figure 2: Representative SEM images collected from each of the five material types following 48 hours of incubation. Each material type had areas wherein bacteria attached to the surface as well as biofilms that formed.

In a separate study by Banche *et al.*,[1] three material types were exposed to an initial inoculum of 10^7 bacteria for various times including 24 hours and 48 hours. These tests were not performed under flow conditions. There was a statistically significant difference in the amount of *S. epidermidis* that adhered to Vitamin E loaded materials and polyethylene only samples. More specifically, there were greater than 10^7 bacteria on the Vitamin E loaded material compared to 10^8 on the polyethylene only samples. However, though statistically significant, this difference may not be clinically significant as a biofilm with 10^7 or 10^8 bacteria may have significant potential to cause infection.

Taken together, these data indicated that Vitamin E blended UHMWPE may not be effective in preventing the growth/formation of biofilms of a clinically relevant strain of MRSA. Though further data may need to be collected, this study demonstrated the ability of a clinically relevant isolate of MRSA to adhere to and/or form biofilms on the surface of Vitamin E blended UHMWPE as well as other material types that are used clinically. The hypothesis that the Vitamin E blended UHMWPE would resist biofilm formation was not supported.

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Interplay between surface properties of standard, vitamin E blended and oxidized ultra UHMWPE for total joint arthroplasty and adhesion of *Staphylococcus epidermidis, S. aureus* and *Escherichia coli*.

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Introduction

The increasing number of total joint replacement (TJR) in orthopaedic surgery, led to the development of new diseases related to the biomaterials themselves: biomaterial associate infection (BAI). BAI is initiated by the adhesion and subsequent growth of microorganisms to the implant surface. Staphylococci are the most common microorganisms causing BAI, followed by streptococci and Gram-negative bacilli. It is widely known that the initial adherence of microorganisms to biomaterials is a process related to a series of physico-chemical interactions between substratum and microorganisms. The physical properties of the biomaterial surface, such as roughness, hydrophobicity, surface energy, electrostatic charge, and coating also influence the feasibility and kinetics of microbial adhesion. A complex strategy is required to efficaciously deal with the BAI. The best aseptic techniques cannot totally remove contamination risk and peri-operative antibiotic prophylaxis is not sufficient. Reducing microbial adhesion to the biomaterial could be an attractive mean to reduce BAI. Starting almost 50 years ago, Ultra High Molecular Weight Polyethylene (UHMWPE) has a long successful clinical record as bearing material in TJR. However, this long clinical history has revealed weak points of this polymer: in particular, it has been demonstrated that oxidation due to sterilization by gamma rays, resulting in a severe decreased in molecular mass, has been the main cause of many dramatic implant failures over the 1980s and 1990s. As a consequence, many efforts have been made to improve the quality and the performance of UHMWPE *in vivo*, for example through reducing or eliminating the oxidation: the newest frontier is the addition of antioxidants, such as the alphatocopherol (vitamin E).

Aims

The purpose of this interdisciplinary study was to assess the different adhesive strength of some of the most common bacteria associated with periprosthetic infection on various types of UHMWPE components, assuming that a different chemical composition of the surface corresponds to a different bacterial adhesion.

Methods

We examined the adhesion of ATCC biofilm producing strains of *Staphylococcus epidermidis*, *Staphylococcus aureus* and *Escherichia coli* on standard GUR 1020 UHMWPE, vitamin E blended polyethylene (VE-PE) and oxidized polyethylene on purpose (OX-PE) at different incubation times (3, 7, 24 and 48 hours). Quantitative *in vitro* analysis of bacterial adhesion was performed by using a sonication protocol to dislodge adherent microorganisms. The biomaterials were physico-chemically characterized by means of scanning electron microscopy (SEM), water contact angle (CA) measurements and attenuated total reflectance (ATR)-Fourier transform infrared (FTIR) spectroscopy, before and after adhesion assays. The experiments were assayed in triplicate and repeated a minimum of three times. A statistical analysis on results (T-Student test) was conducted.

Results

No significant difference of the surface roughness and CA was found among the different samples, while a lower CA was observed for OX-PE, if compared to the other two groups. Again, with ATR-FTIR spectroscopy, the only significant difference was observed in the spectrum of the aged group, OX-PE, indicating adsorption of protein-like substances on the polymer surface. This different protein adsorption has been shown to influence bacterial adhesion. In fact, adhesion assays, performed on the three polyethylenes by using the ATCC biofilm producing *S. epidermidis*, *S. aureus* and *E. coli* strains evidenced a significant ($p<0.05$) decrease in the number of adhered bacteria on VE-PE and a considerable enhancement of adhered bacteria on OX-PE, compared to standard UHMWPE after 24 and 48 hours of incubation. [Figure 1-2] A similar trend of adhesion was observed testing both biofilm not producing ATCC bacterial strains and clinical biofilm producing strains.

Conclusions

Since it is widely known that BAI in TJR causes a decrease in the success rate of the implant with consequent enormous burden on the patients and high costs to the healthcare system, the results obtained in this interdisciplinary study may have important clinical implications concerning one aspect of the multifactorial septic loosening. We highlight that initial adhesion on inert surfaces is strain-dependent and it is

strictly influenced by biomaterial surface chemistry: VE-PE reduces *S. epidermidis*, *S. aureus* and *E. coli* adhesive ability and its antioxidant properties, due to vitamin E addition, may be one of the key points.

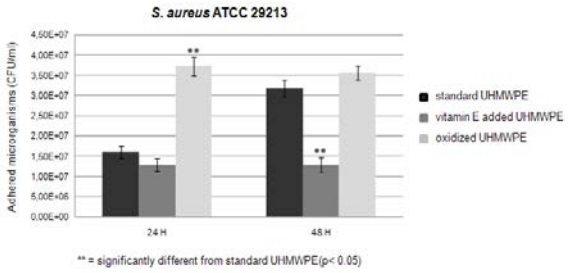

Figure 1 - Differences in adhered bacteria *S. aureus* ATCC 29213 (CFU/mL) to the different assayed biomaterials at 24 and 48h.

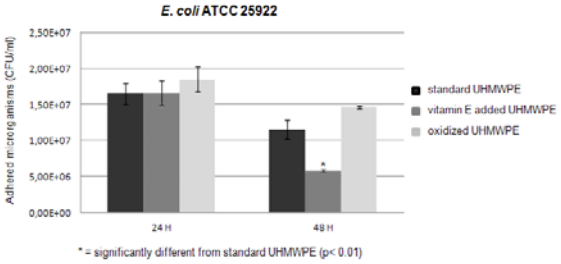

Figure 2 - Differences in adhered bacteria *E. coli* ATCC 25922 (CFU/mL) to the different assayed biomaterials at 24 and 48h.

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Biological activity and migration of wear particles in the knee joint – an *in vivo* comparison of six different polyethylene materials

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Introduction:
Crosslinked polyethylenes (XPEs) are used to reduce wear in total knee replacement. While a lot is known about the role of conventional polyethylene wear particles in the process of periprosthetic osteolysis [1], less is known about crosslinked materials [2]. Moreover, the inflammatory response of polyethylene wear with articular cartilage is mostly unknown [3]. But that the latter is of interest in unicondylar knee replacement. Considering that these bearing materials are not only used for bicondylar but also for unicondylar knee prostheses, the biological effect of these polyethylenes on these tissues should be investigated.
The hypothesis of this study was that conventional ultra-high-molecular-weight-polyethylene (PE) and XPE wear particles, lead to similar biological effects in the knee joint: The synovial layer, the adjacent bone and the articular cartilage had been taken into account. The second hypothesis was that the PE as well as the XPE particles show a similar migration behaviour in the tissues around the joint.

Methods and Materials:
Particle generation, characterization and preparation: Using a knee-joint-simulator (Stallforth-Ungethuem), four different XPE and two PE inserts were tested over 5 x 10^6 cycles (ISO 14243; 25% (v/v) newborn calf serum with 0.1% (m/v) sodium azide solution in sterile water) in three repetitions [4]. The lubricant was changed every six days and inserts were weighed every 0.5 million cycles [4]. The particles were separated (20 nm-nucleopore-filter; acid digestion method [5]) and analyzed in size and morphology by SEM and image analyzer (Leica QWin). After removing of endotoxin [6], the particles were suspended in Phosphate Buffered Saline (PBS) Solution with a particle concentration of 1 mg/ml.
In vivo analysis: 56 female Balb/c mice were randomly assigned to one of seven treatment groups with particles from four XPEs, two PEs and control (PBS). 50 µl of a particle suspension were injected into the left murine knee joint under sterile conditions. As established before, the leukocyte–endothelial cell interactions and the synovial microcirculation were performed by intravital fluorescence microscopy one week after particle injection to assess the inflammatory reaction against the particles in the mouse knee joint [7].
Histology and Immunohistochemistry: After these measurements the mice were sacrificed, the left knee joints were embedded in paraffin (6 µm thin sections) and stained with hematoxylin and eosin (HE) as well as with antibodies against IL-1β and TNF-α as inflammatory markers. The tissues of the samples were evaluated semiquantitatively using light microscopy, the localization of the particles in and around the knee joints was detected using a polarization filter.
For statistical analysis the Kruskal-Wallis test was applied, followed by an all pairwise multiple comparison procedure, for the immunhistochemical data with a Bonferroni correction. The level of significance was set at $p < 0.05$, respectively $p = 0.0024$ including the Bonferroni correction.

Results:
Wear particles of all polyethylene varieties were predominantly smooth, granular and irregular with few fibrillar particles and showed similar size distributions. More than 85% of all particles were submicron. Concerning the intravital microscopic measurements, the fraction of rolling leukocytes, the number of adherent cells and the FCD showed a difference in all groups compared with the control group ($p<0.05$) without any statistically significant difference between the test groups ($p>0.05$). Furthermore, all particle-stimulated groups presented a thickened synovial layer with an enhanced cellular infiltration in the histological evaluation.
Whereas the biological effects on the synovial tissue and the adjacent bone marrow of femur and tibia were similar for all tested polyethylenes, even within the immunohisto-chemical analysis two highly irradiated XPE materials showed an elevated expression of TNF-α in the articular cartilage ($p\leq0.001$).
Furthermore, the distribution of particles in and around the joint was dependent on the injected polyethylene material. Those XPE particles, which remained mainly in the joint space, showed an increased expression of TNF-alpha in articular cartilage.

Discussion:
The first hypothesis has been partially confirmed. Wear particles of XPE and PE showed similar biological activity in the synovial tissue and adjacent bone, however, differences were observed with articular cartilage challenging the use of crosslinked polyethylenes for unicondylar knee prosthesis. The second hypothesis has to be rejected. Different particle distributions around the joint were detected, clearly dependent on the material that was used. The impact of these aspects must be clarified in further studies.

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Novel radiopaque UHMWPE sublaminar wires for application in a growth-guidance system for the treatment of early onset scoliosis: a large animal study

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Introduction: Growth-guidance or self-lengthening rod systems are an alternative to subcutaneous growing rods and the vertical expandable prosthetic titanium rib for the treatment of early onset scoliosis. Their main perceived advantage over growing rods is the marked decrease in subsequent operative procedures. The Shilla growth-guidance system and a modern Luque trolley are examples of such systems; both depend on gliding pedicle screws and/or sliding titanium sublaminar wires. However, the unknown consequences of metal-on-metal wear debris are reason for concern especially in young patients. In this study, instrumentation stability, residual growth in the operated segment after surgery and biocompatibility of the novel radiopaque UHMWPE cables as an alternative to gliding pedicles screws or titanium sublaminar wires were assessed in an immature sheep model.

Materials and Methods: Twelve immature sheep were treated with segmental sublaminar spinal instrumentation: dual CoCr rods were held in place by pedicle screws at the most caudal instrumented level (L5) and novel radiopaque UHMWPE (Bi_2O_3 additive) woven cables were placed at 5 thoracolumbar levels. Lateral radiographs were taken at 4-week intervals to evaluate growth of the instrumented segment. Four age-matched, unoperated animals served as radiographic control. After 24 weeks follow-up, the animals were sacrificed and the spines were harvested for histological evaluation and CT analysis.

Results: No neurological deficits and no complications occurred during the initial postoperative period. One animal died during follow-up due to unknown cause. At sacrifice, none of the cables had loosened and the instrumentation remained stable. Substantial growth occurred in the instrumented segment (L5-T13) in the intervention group. No significant difference in growth of the operated segment was found between the intervention and control groups. Histological analysis showed fibrous encapsulation of the novel radiopaque UHMWPE sublaminar cable in the epidural space, with no evidence of chronic inflammation.

Discussion: Novel radiopaque UHMWPE cables may be a promising alternative to gliding pedicle screws or titanium sublaminar cables within a growth-guidance system. UHMWPE cables may improve growth results due to the smooth surface properties of the UHMWPE cable and address concerns regarding the consequences of metal-on-metal wear debris.

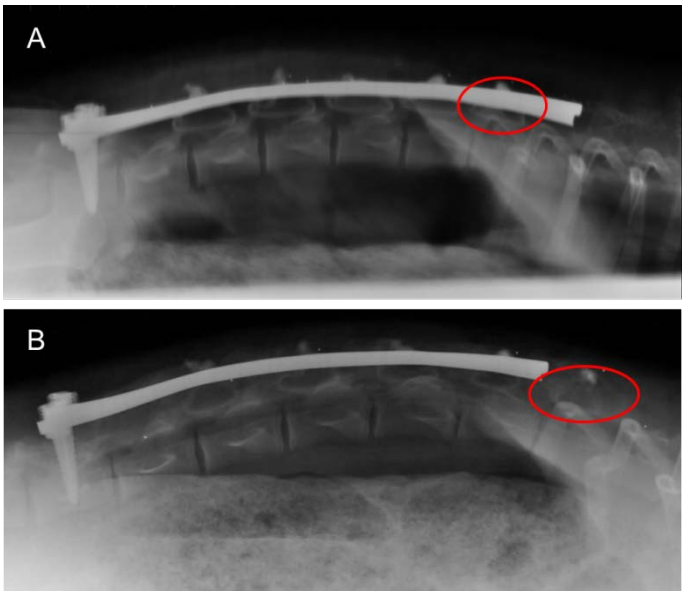

Figure 1: (A) Direct postoperative and (B) 24-weeks postoperative lateral X-ray of the instrumented sheep spine. Marked growth of the instrumented segment has occurred as illustrated by sliding of the most cranial UHMWPE sublaminar wire (circled). Novel radiopaque UHMWPE sublaminar wires are clearly visible on X-ray.

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Shelf Stability of a Crosslinked and Mechanically Deformed UHMWPE

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Introduction: With the introduction of barrier film packaging for gamma sterilized ultra-high molecular weight polyethylene (UHMWPE), the risk of oxidation due to shelf aging was reduced[1]. With the introduction of thermally stabilized highly crosslinked polyethylenes that quench or reduce the number of residual free radicals, the products were non-energetically sterilized and packaged in air. The re-melted materials have shown no evidence of oxidation on the shelf[2] because melting allows for all residual free radicals to be quenched. In contrast, annealing or below-melt heating, leaves free radicals in the material[3]. Shelf aged annealed materials have been shown to have significant levels of oxidation after shelf aging up to 5 years[4]. Another below-melt process combines below melt heating with mechanical deformation to stabilize free radicals. The mechanical deformation removes more free radicals than annealing alone, however it has been reported that this material does have detectable levels of residual free radicals[5]. The purpose of this study is to evaluate the oxidation levels and mechanical properties of shelf aged crosslinked and mechanically deformed liners.

Methods and Materials: Twenty-three ArComXL liners of varying geometries, with an average shelf storage time of 81.3 ± 0.5 months, were used for this study. All liners were past their expiration date of 60 months. The liners were packaged in gas permeable packaging and stored in typical warehouse conditions. Three ArComXL liners were manufactured, sterilized and tested within 2 weeks of sterilization to use as non-shelf aged controls.

The control liners and eight of the shelf-aged liners were sectioned for small punch testing. For each liner, a thin section was taken from Regions 1 and 4 (Figure 1) as the most likely places to have a reduction in mechanical properties due to oxidation. The thin sections were small punch tested per ASTM F2183. Load at yield, ultimate load, work to failure, and ultimate displacement were recorded. The results of the two groups were compared using simple t-test.

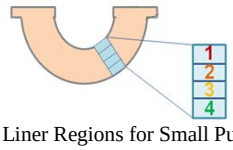

Figure 1: Liner Regions for Small Punch Testing

The remaining 15 shelf-aged liners were sectioned in half. 200 micron thin sections were cut using a microtome. FTIR spectroscopy was used to measure the oxidation index across the thickness of the liners per ASTM F2102.

Results: Figure 2 shows the small punch load versus extension curves for Region 4 of the control and shelf-aged liners. There were no significant differences in the small punch properties between region 4 and 1 of the aged and un-aged liners. Therefore, the data from both regions were combined for statistical comparison. The average small punch properties are shown in Table 1. The P values from the statistical comparison of the two groups are also included in Table 1.

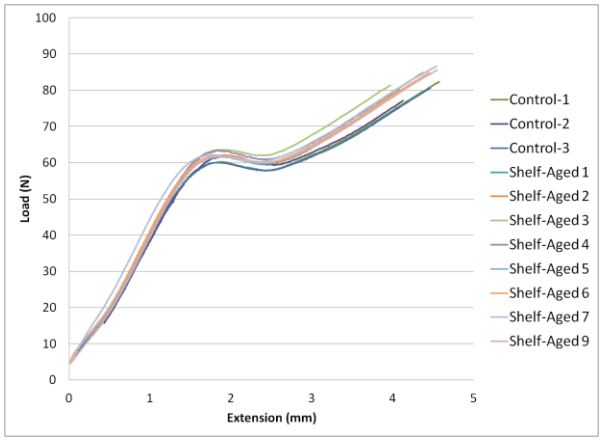

Figure 2: Representative Small Punch Load vs. Extension Curves for Region 4 of Shelf-Aged and Un-aged Liners

	Un-Aged	Shelf-Aged	P Value
Load at Yield (N)	60.5 (1.1)	62.1 (0.85)	0.002
Ultimate Load (N)	81.5 (3.5)	83.1 (2.4)	0.224
Work to Failure (mJ)	240.6 (17.6)	235.0 (16.9)	0.495
Ultimate Displacement (mm)	4.4 (0.2)	4.2 (0.2)	0.054

Table 1: Average Small Punch Properties and P-Values (Standard Deviation in Parentheses)

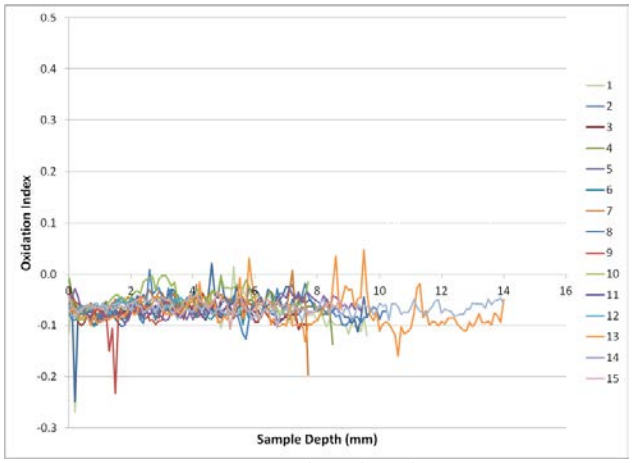

Figure 3: Oxidation Profiles of Shelf-Aged Liners

Oxidation profiles from the 15 shelf-aged liners are shown in Figure 3. There was no measurable oxidation at the surface of the bearings. There were a handful of

oxidation indices that measured above 0, however these appeared in the bulk of the material and appear to be due to measurement error and not oxidation. Since almost all of the oxidation indices are less than 0, the surface, bulk and maximum oxidation indices are not reported.

Discussion: With a p value less than 0.05, the only statistically significant difference for small punch testing was in load at yield. Although the difference was statistically significant, the aged group had higher yield and ultimate strengths than the un-aged group and is therefore not associated with property degradation. After more than 80 months on the shelf in air, the crosslinked and mechanically deformed liners showed no evidence of oxidation and showed no detectable degradation of material properties compared to non-aged control samples. This is in contrast to 30kGy gamma sterilized and air-aged components that show a significant loss in mechanical properties[1] and shelf-aged annealed liners that can show evidence of oxidation after shelf aging[4]. The combination of below-melt heat and mechanical deformation stabilizes the gamma irradiated polyethylene to a point where the material is oxidatively stable after more than 6 years of shelf-aging.

Conclusion: After more than 80 months of shelf aging, crosslinked and mechanically deformed UHMWPE liners showed no evidence of oxidation and retained their mechanical properties.

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Wear of large diameter vitamin-E blended HXLPE hip bearings against uncoated and chromium nitride coated metal

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Introduction: Polyethylene has been extensively developed since its initial use as a bearing surface in hip replacements in the 1960s, most noticeably in the use of irradiation to produce crosslinks in ultra high molecular weight polyethylene (UHMWPE). However the degradation of the material over time due to oxidation has been widely reported [1] with an early solution to irradiate in inert environments [2]. The introduction of an antioxidant such as vitamin-E has recently been proposed as a method to reduce the formation of free radicals, which are responsible for the oxidation observed, thus providing long term oxidative stability [3].

The occurrence of wear and the resultant wear particles have often been reported to be a limiting factor in the use of metal-on-polyethylene bearings; thus smaller diameter bearings have been used which reduce the sliding distance experienced by a bearing and therefore reduce the wear generated [4]. However, the improved wear resistance of highly-crosslinked polyethylene (HXLPE) incorporating vitamin-E may allow for larger diameter bearings to be used, increasing the range of motion possible for a patient, reducing the risk of impingement and dislocation [5].

Wear reduction of polyethylene liners has also been possible by the adoption of a ceramic head instead of a metallic head [6]. However, the brittle nature of bulk ceramics and the difficulty to manufacture without flaws have up to now limited the use of large head sizes. An alternative is to utilize a ceramic coating on the surface of the metallic head, providing the bulk properties of metal with the improved surface finish and increased abrasion resistance of a ceramic [7].

Simulator testing of large diameter HXLPE has been reported to produce identical wear rates of 31 mm^3/mc with ceramic and metallic heads under standard conditions therefore requiring adverse testing to distinguish between different head materials [8].

The current study considers the wear of large diameter vitamin-E blended HXLPE bearings paired with uncoated and chromium nitride (CrN) coated metal heads under standard and adverse conditions in a hip simulator. It is proposed that polyethylene wear can be reduced with the adoption of a CrN coated metal head.

Methods and Materials: Eight large (52 mm) diameter non-commercially available polyethylene liners were manufactured for testing purposes (GUR 1020 blended with 0.1 wt% vitamin-E, highly crosslinked at an irradiation dose of 120 kGy and mechanically annealed) (Corin, UK). All liners were presoaked in pure deionized water until their water uptake was stable. Three of the liners were paired with CoCrMo heads (MoP) while four were paired with CoCrMo heads coated with CrN using Electron Beam Physical Vapour Deposition (EBPVD) (CrNoP), (Tecvac, UK). One liner remained as an unloaded soak control.

The bearings were tested in an orbital hip simulator (MTS Systems, USA) for 5 million cycles (mc) under conditions described in ISO 14242-3. Aggressive, non-clinically relevant, third body testing was then conducted for 1 mc to look at the effect of severe head damage. Alumina particles (mean size 2.4 μm at a concentration of 0.15 mg/mL) in the test fluid were used [9]. Subsequently 1 mc of clean testing was conducted before 3 jogging intervals of 14,400 cycles at 1, 1.5, 1.75 Hz (slow, medium and fast respectively) were performed [10]. Wear was measured gravimetrically for both liners and heads throughout testing. Wear debris from fluid samples were analyzed using the protocol described by Billi et al. [11].

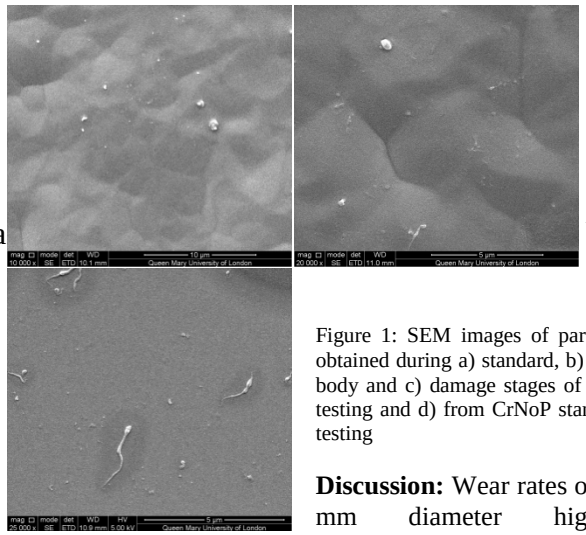
Results: Wear of the polyethylene liners paired with coated or uncoated heads under standard conditions showed no significant difference with wear rates of 9.2 ± 1.2 and 10.3 ± 1.6 mm^3/mc (mean ± s.d.) respectively (Table 1). Wear of all of the liners increased significantly with the introduction of alumina third body particles and wear of the MoP bearings was approximately ten times higher than CrNoP bearings. The metal heads showed directional grooves caused by the alumina particles while the CrN heads developed no such grooves.

Table 1: Gravimetric wear of highly crosslinked polyethylene liners incorporating vitamin E mm^3/mc (mean ± s.d.)

		MoP	CrNoP
Standard		9.2 ± 1.2	10.3 ± 1.6
3rd body		175.3 ± 145.2	18.3 ± 3.1
Damaged surfaces		469.3 ± 466.1	12.6 ± 3.6
Jogging	**Slow**	330.5 ± 312.6	17.9 ± 16.8
	Medium	475.5 ± 412.2	16.3 ± 14.9
	Fast	512.2 ± 415.8	19.1 ± 15.2

After the removal of the 3rd body alumina particles the wear of the CrNoP bearings recovered to wear rates similar to the initial phase of testing. The MoP bearings continued to wear at a higher rate than the CrNoP bearings, due to the damage observed on the heads. Wear of the liners did not significantly increase with the introduction of simulated jogging in either MoP or CrNoP.

Polyethylene particles isolated from all stages of the testing showed a greater percentage of small particles (less than 0.1 μm) present in MoP bearings during severe tests. The shape of these particles were mainly round in standard conditions but during third body and damage tests, elongated and flake particles became more prevalent, Figure 1. The particles from CrNoP bearings showed little difference in size between test conditions with a mode size between 0.1 and 0.2 μm.



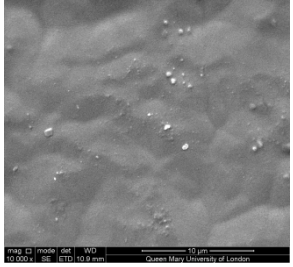
a b c d

Figure 1: SEM images of particles obtained during a) standard, b) third body and c) damage stages of MoP testing and d) from CrNoP standard testing

Discussion: Wear rates of 52 mm diameter highly-crosslinked vitamin-E blended polyethylene under standard conditions with uncoated or CrN coated CoCrMo heads were comparable to wear rates of 36 mm diameter polyethylene crosslinked at 95 kGy paired with uncoated metal heads [12].

A significant increase in wear rates was observed in both bearing couples during the highly aggressive third body test conditions. The wear rates of the MoP bearings increased 17-fold and were comparable to 28 mm non-crosslinked polyethylene under similar conditions [9]. The introduction of the alumina particles in the test serum represented an extreme, non-clinically relevant test designed to damage the head and severely challenge the bearings. The damage of the head increased wear after the particles were removed but was variable between MoP bearings. The wear rate under these conditions remained higher than tests with moderately or low levels of crosslinked polyethylene against metallic heads similarly damaged [13]. Under severe activity, polyethylene liners (Ø28 mm), crosslinked at 50 kGy have previously been shown to produce wear rates as high as 3000 mm^3/mc under fast jogging conditions [10], therefore the results presented here indicate the potential for highly-crosslinked vitamin-E polyethylene to be used for highly active patients.

The introduction of a CrN coating on the metallic head surface increased the abrasion resistance of the surface preventing runaway wear during adverse tests and maintaining consistently low wear rates. A significant increase in wear rate was established during 3rd body testing compared to standard conditions but a return to the standard rate was observed when the particles were removed. The CrN heads remained smooth with an average surface roughness, Ra, of 0.007 ± 0.003 µm, smoother than many pristine surface coatings [7, 14]. The wear rates of the CrNoP bearings were comparable or lower than metal on non-crosslinked polyethylene bearings under standard conditions and lower than 28 mm diameter CrN coated metal on polyethylene crosslinked at 40 kGy [7].



Vitamin-E crosslinked polyethylene materials have the potential for use as large diameter bearings although the choice of articulating component needs to be carefully considered. Polyethylene wear is dependent on the head roughness [10] and thus will increase with surface damage. Retrievals have documented scratching on metallic heads [15] indicating that this is an issue which needs to be addressed. In this study, a robust CrN coating on a CoCrMo substrate has been shown to be resistant to scratching thereby retaining a low polyethylene wear rate. This resistance, even at large diameters, makes a CrN coating promising as a bearing material given problems in fracture and sensitivity reactions reported in large diameter CoC and MoM bearing.

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In Vivo Oxidative Stability and Clinical Performance for 1st- and 2nd-Generation Highly Crosslinked Polyethylenes

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Introduction: Highly crosslinked polyethylenes (HXLPEs) have been in use in total hip replacement for more than a decade [1]. There is consensus in the literature that these materials show improved wear in vivo and significantly reduce osteolysis [2]. However, questions remain regarding the long-term oxidative stability of HXLPEs and the influence of mechanical behavior on THA clinical performance. Starting in 2005, 2nd generation HXLPEs were developed to improve the clinical performance of HXLPE. Examples of 2nd generation HXLPEs include sequentially annealed [3] and vitamin E diffused HXLPEs [4].

The purpose of this report was to update our previous study that was presented at this meeting in 2011 [7] that assessed the oxidative stability, mechanical behavior, wear and reasons for revision of 2nd generation HXLPEs and compare them to our ongoing retrieval collection of 1st generation annealed and remelted HXLPEs [5, 6]. We hypothesized the sequentially annealed components would exhibit wear rates similar to 1st generation HXLPEs. We also hypothesized that 2nd generation HXLPEs would be more oxidatively stable than 1st generation HXLPEs.

Methods: 475 hip liners were consecutively retrieved during revision surgeries at 11 surgical centers and continuously analyzed over the past 12 years in a prospective, multicenter study of THA revision outcomes and retrieval analysis. 26 liners were sterilized using non-ionizing methods (Gas Sterilized; Implanted 9.1±3.8 years), 43 liners were sterilized in an inert environment (Gamma Inert; Implanted 6.2±4.1 years), 217 were highly crosslinked and remelted (A-Class, AltrX, Durasul, Longevity, Marathon, XLPE: Remelted; Implanted 2.0±2.4 years), 82 were highly crosslinked and annealed (Crossfire: Annealed 1; Implanted 3.7±2.9 years), 102 were highly crosslinked and annealed in 3 sequential steps (X3: Annealed 2; Implanted 1.1±1.1 years), and 5 were Vitamin E diffused and highly crosslinked (E1: Vit E; Implanted 0.8±0.8 years).

The analytical methods have been described previously [5, 6], but are summarized below. Oxidation was characterized in accordance with ASTM 2102 using transmission FTIR performed on thin sections (~200µm) from the superior/inferior axis. Lipids were extracted from the HXLPEs prior to analysis by 6 hours in boiling hexane. Sections were then exposed to NO for 16 hours and rescanned using an FTIR spectrometer to assess hydroperoxide content, a metric of oxidation potential.

Mechanical behavior was assessed via the small punch test (ASTM 2183). Small cylindrical samples were taken from the superior and inferior regions of the inserts both at the surface and below the surface. Liner penetration was assessed directly using a calibrated micrometer.

Results: The predominant reasons for revision were loosening, instability, and infection for all cohorts (Fig. 1).

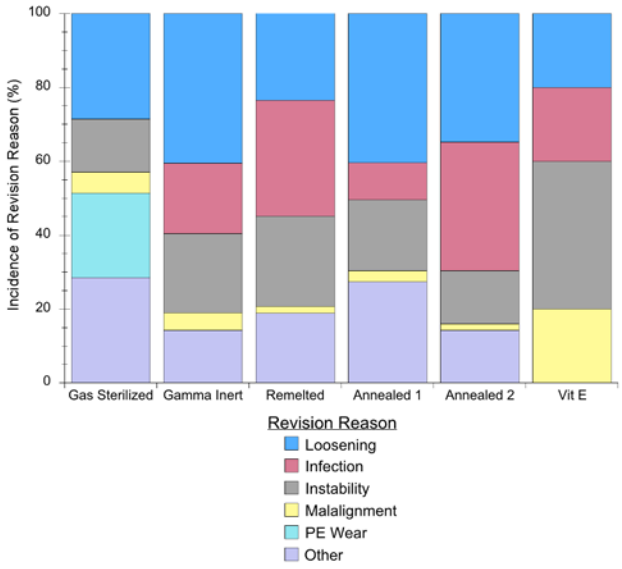

Figure 1: *Revision Reasons for the 475 acetabular liners.*

Oxidation and oxidation potential were higher in the Gamma Inert and both annealed groups than the Remelted and Gas Sterilization groups ($p<0.001$; Kruskal-Wallis Test), particularly at the rim (Figs. 3-4). This pattern was also observed when excluding implants over 3 years (the longest implanted Annealed 2 liner) (Figs. 3B&4B). Oxidation significantly correlated with implantation time at the rim of the Annealed and Sequentially Annealed liners (Rho=0.70; $p<0.0001$ and Rho=0.27; $p<0.007$, respectively) and the bearing surface of the Remelted (Rho=0.25; $p=0.0002$) and Annealed 2 liners (Rho=0.45; $p<0.0001$).

At the superior bearing surface, the ultimate load negatively correlated with implantation time in the Annealed and Sequentially Annealed liners (Rho<-0.26; $p<0.02$), but not with any other cohort ($p>0.05$). The Annealed groups had the highest ultimate load at the bearing surface (Kruskal-Wallis Test; $p<0.001$). The Gas Sterilized liners had the lowest superior surface ultimate load ($p<0.020$).

Gas Sterilized and Gamma Inert liners had significantly higher wear rates than all of the HXLPE cohorts ($p \leq 0.01$). No differences were detected in wear rates among the HXLPE liners ($p > 0.11$).

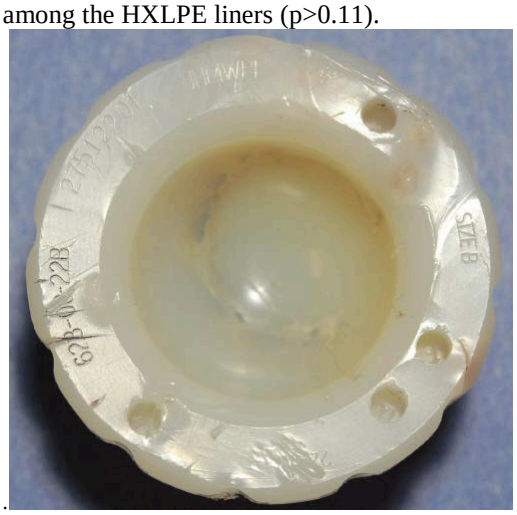

Fig. 2: Sequentially Annealed retrieved liner revised after 5y with notable evidence of rim impingement.

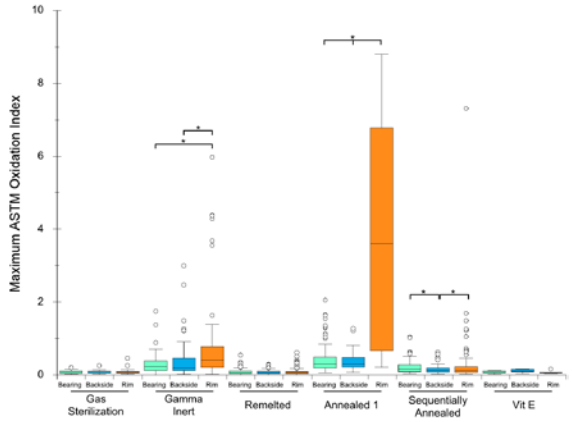

Figure 3: Regional oxidation of all the liners.

Conclusions: This ongoing study continues to evaluate the polyethylene properties and reasons for revision among clinically relevant HXLPEs used in total hip replacement, including 2nd generation HXLPEs. All of the HXLPEs materials in this study have thus far proven effective at reducing wear rates compared to the Gamma Inert and Gas Sterilized controls. The oxidative stability and mechanical behavior of these materials, however, is formulation dependent. With respect to oxidation, it is clear that sequential annealing reduced oxidation when compared with first-generation annealing. Additional Vitamin E retrievals are needed to compare with the existing collection of thermally stabilized HXLPEs that have been characterized thus far.

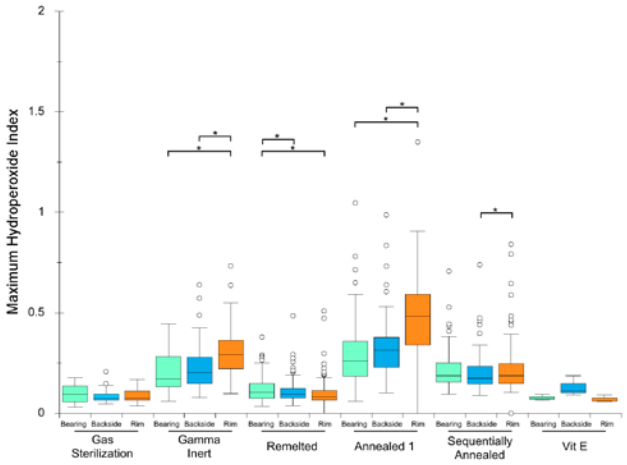

Figure 4: Regional hydroperoxide content of all the measured.

Acknowledgements: This study was supported by NIH R01 AR47904. Institutional support has been received from Stryker Orthopedics, Zimmer Inc., and Stelkast. Support was also provided by the Wilbert J. Austin Chair (CMR).

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Oxidation Induced by Compressive Cyclic Loading of Conventional UHMWPE

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Introduction: Oxidation of ultra high molecular weight polyethylene (UHMWPE) can lead to failure of implants used in total joints. A previous study showed that UHMWPE oxidized more rapidly under cyclic load at an elevated temperature than at an elevated temperature alone [1]. However, that study used a sinusoidal reciprocating force; in vivo cyclic loading is predominantly compressive without an external restoring force. The objective of this study was to determine if a more clinically relevant accelerated aging test, which incorporated only compressive cyclic loading, affected the oxidation of UHMWPE.

Methods and Materials: All samples were machined from GUR1050 UHMWPE that was gamma sterilized in inert gas. Each test sample was secured against a platen inside an environmental chamber with circulating 80°C air. Compressive cyclic loading was administered by a 12.5 mm diameter stainless steel load applicator affixed to a hydraulic testing system. In every trial, the test sample was exposed to load and heat with three heated controls that were not subjected to load.

Cyclic compressive stress was applied between 0.4 MPa and a target maximum stress at a frequency of 5 Hz. To investigate the effect of increasing cycle count on oxidation, samples were cyclically loaded to a maximum stress of 10 MPa for 3×10^6 load cycles, 9×10^6 load cycles, and 15×10^6 load cycles. To investigate the effect of increasing stress levels on oxidation, samples were cyclically loaded for 15×10^6 load cycles to a maximum stress of 10 MPa, 20 MPa, and 30 MPa.

Microtomed thin films from all samples were analyzed via FTIR to quantify oxidation per ASTM F2102. Oxidation was measured through the depth of the test sample at targeted distances away from the applied load, ranging from directly underneath the center of the load applicator to 20 mm away (Fig 1). FTIR analysis was also performed on the heated controls.

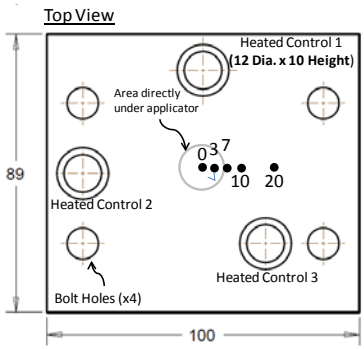

Fig 1: Thin films were taken at 0, 3, 7, 10, and 20 mm away from the center of the area directly underneath the load applicator. The gray ring outlines the area (12.5 mm in diameter) directly impacted by the load applicator.

Results: After 3×10^6 cycles of 10 MPa stress, there was no significant difference between the oxidation of the loaded test sample and the heated controls. There was significantly greater oxidation in the loaded test samples after 9×10^6 and 15×10^6 cycles of 10 MPa stress, indicating that more stress cycles can lead to more oxidation, as shown in Fig 2. Increasing the maximum stress level from 10 MPa to 20 MPa significantly increased the oxidation after 15×10^6 stress cycles across the entire test sample, from directly under the load applicator to 20 mm away (Fig 3). Samples tested under 30 MPa of cyclic stress oxidized so much that the material disintegrated during microtoming; therefore, the oxidation levels for this sample could not be measured directly under the load applicator.

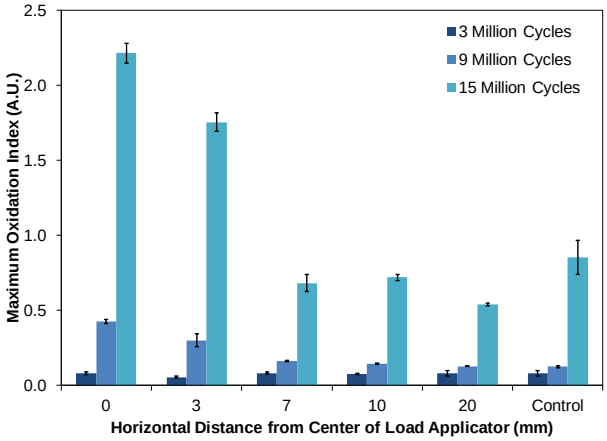

Fig 2: A bar graph summary of the maximum oxidation index measured in samples after 3, 9, and 15 million load cycles of 10 MPa stress.

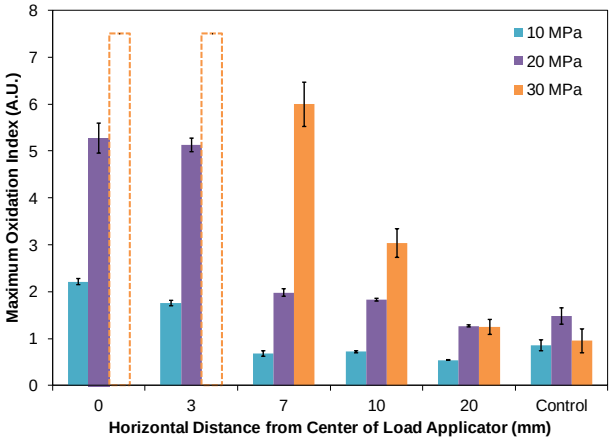

Fig 3: A bar graph summary of the maximum oxidation index measured in samples 15 million load cycles of 10 MPa, 20 MPa, and 30 MPa maximum stress.

Discussion: In nearly all tests, areas directly under the load applicator showed significantly greater oxidation than non-loaded samples, emphasizing the influence of compressive cyclic load on oxidation. The long-term performance of UHMWPE formulations with improved wear resistance could be compromised if this oxidation mechanism alters the chemical structure of the polymer and makes it more prone to fatigue cracking initiation and propagation. Therefore, oxidation resistance of UHMWPE formulations should be maximized.

Compressive cyclic loading of UHMWPE led to oxidation of the material. Since in vivo components also experience compressive cyclic loading, their longevity may be affected.

Reference: [1] Konsin Z, et al. 5th annual UHMWPE Meeting Philadelphia, 2012.

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Confirmation of Increased Oxidation in Remelted Highly Cross-linked UHMWPE after Synovial Fluid Soaking, Accelerated Aging and Solvent Extraction

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Introduction:
A previous experiment indicated that heptane or hexane extraction conducted on UHMWPE with bovine synovial fluid (BSF) uptake induced artifact in oxidation index (OI) measurement[1]. The present study seeks to confirm such a finding using legacy Gamma-in-Air sterilized (GammaAirPE) and remelted highly cross-linked (RM-HXLPE) materials.

Materials and Methods:
Two material groups (Table 1) were assessed on their response to soaking, accelerated aging and extraction.

Group ID	Stock	Irradiation/Thermal Treatment
GammaAirPE	GUR4150	30kGy in Air
RM-HXLPE	GUR1050	100 kGy in Air; Remelted (147 ^{o}C, 5hr)

Table 1: *Material groups*

ASTM F2003 accelerated aging and BSF soaking[1] were conducted to simulate shelf and in-vivo aging, respectively.

Concave discs approximately 19 mm in diameter and 3 mm in dome thickness were machined from stock materials prior to ASTM F2003 accelerated aging (Table 2). Pre- and post-F2003 sample groups were soaked in BSF under dynamic loading at 37 ^{o}C and 1Hz, and subsequently subjected to hexane (16h) or heptane (6h) Sohxlet extraction (Table 2). Unaged and No-soak samples were used as control.

Aging Process	Soaking	Extraction (wash)
14 days, ambient	No-soak	Heptane, 6 h
ASTM F2003: 14 days, 5 atm O_2, 70 ^{o}C	2280 N, 1 Hz, 37 ^{o}C, bovine synovial fluid	Hexane, 16 h

Table 2: *Treatments*

FTIR analyses (128 scans/spectra, 4 cm^{-1} resolution) were performed using both peak height at and peak area centering 1714 cm^{-1} for OI (normalized using 1368 cm^{-1} peak height/area) measurements from disc cross-sections with 150 μm film thickness.

Data were collected after 1 million cycles (mc) of dynamic load-soaking or equivalent time (11.57 days) in control groups.

Student t-test was used with a significant level of $p < 0.05$.

Results:

Extraction using hexane or heptane promoted elevation of OI regardless of FTIR analysis methods (Area, A or Height, H) in all HXLPE groups (Fig. 1), including No-soak control (Fig. 2). OI computed using peak area is significantly higher than that computed using peak height. Solvent extraction did not significantly increased OI in GammaAirPE.

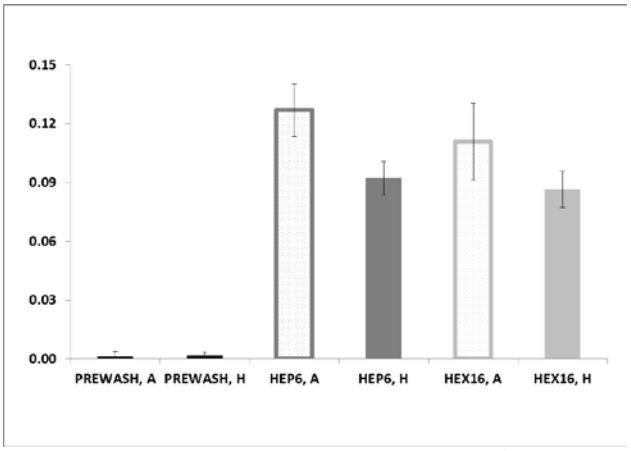

Fig.1: *Both hexane and heptane extraction promoted artificially elevated OI in Post-F2003, soaked HXLPE sample groups.*

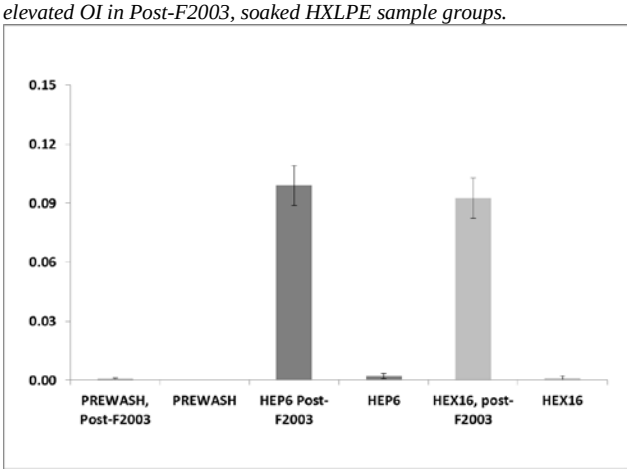

Fig.2: *Elevated OI was observed in NO-soak RM-HXLPE controls both pre- and (more noticeable) post-F2003 aging.*

Discussion:
Unlike legacy gamma-in-air sterilized UHMWPE, the remelted highly cross-linked UHMWPE showed a significantly higher level of OI after exposure to bovine synovial fluid, accelerated aging and solvent extraction. Future work will explore and propose an alternative method to correct these artifacts.

Acknowledgements: The authors thank C. Aponte and R. Baez for sample microtome support.

[1] *Le, K-P. et al. ORS 2013 Poster 1235*

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In vivo oxidation in sequentially irradiated and annealed UHMWPE components

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Introduction: Highly cross-linked polyethylene was developed to improve the wear resistance of UHMWPE bearing surfaces in total joint arthroplasty. First generation irradiated and annealed polyethylene, used exclusively in acetabular liners, showed high oxidation *in vivo,* largely attributed to only the partial-quenching of free radicals, along with additional radicals generated during terminal gamma sterilization[1,2]. A second generation, three-step sequential irradiation and annealing method was advanced for both hip and knee arthroplasty with the promise of better oxidative stability and improved mechanical properties[3-4]. The suitability of highly cross-linked UHMWPE as a bearing surface in knees has been highly debated, with concerns that the reduced mechanical properties associated with radiation cross-linking would not be sufficient to avoid fatigue fracture under the loading conditions of the knee[5,6]. While pre-clinical reports have shown mechanical properties and simulator wear rate results commensurate with conventional polyethylene, these studies were performed with never-implanted material[1,2]. Recent studies examining highly cross-linked retrievals have reported a loss of oxidative stability in UHMWPE during *in vivo* service characterized by the formation subsurface carbonyl peaks below the articular surface as early as two years[7]. Currier et al reported higher levels of oxidation at early time points in knees as opposed to hips[7,8]. This raises additional concerns that significant subsurface oxidation in tibial inserts may lead to delamination and loss of mechanical properties, affecting both mechanical stability, wear rates and overall clinical performance. Sequentially irradiated and annealed components are of particular concern due to the presence of free radicals, which we hypothesize may accelerate and contribute to *in vivo* oxidation.

Methods and Materials: Twenty-nine acetabular liners with *in vivo* durations between 0.1-77 months and twenty-four tibial bearings with *in vivo* durations between 0.4-61 months, made from sequentially irradiated and annealed, gas plasma-sterilized UHWMPE (X3™, Stryker, Mahwah, NJ), were surgically retrieved and analyzed. Four never implanted acetabular liners with a minimum of one year shelf-storage were analyzed as controls. Thin sections were cut with a microtome from across the thickness of the component below the articular surface and below an unloaded surface. Xylene etching was used, by exposing thin sections to boiling xylene fumes for 45 seconds, to identity regions of polymer degradation.

Fourier transform infrared microscopy was used to evaluate oxidation, per ASTM F2102, and hydroperoxides. Hydroperoxides were measured after hexane-extracted thin sections were exposed to 16 hours in a pure nitric oxide environment. Gravimetric swelling analysis assessed cross-link density, per ASTM 2214, and differential scanning calorimetry was used to measure crystallinity. Statistical significance was measured using Welch's t-test; regression analysis was used to assess correlations between data sets and least-squares values calculated.

Results: There was detectable oxidation (OI > 0.1) in 37 of the 51 retrievals with as little as 2 weeks of *in vivo* service. Of those retrievals, 87% of tibial bearings and 67% of acetabular liners showed detectable oxidation. Maximum oxidation values in oxidized retrievals ranged from 0.10-1.59 (Fig 1).

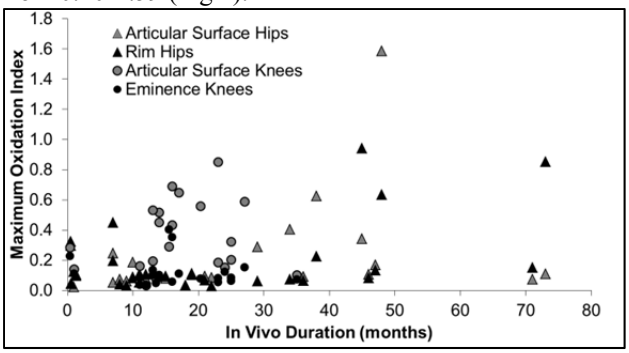

Figure 1. Sequentially irradiated and annealed retrievals showed measurable oxidation well above detection limits (OI=0.1) in *both* the unloaded and loaded regions of the components. Oxidation developed earlier and at higher levels in the articular surface of tibial inserts than in acetabular liners.

Oxidation profiles were predominantly characterized by subsurface oxidation peaks approximately 1-2 mm below the surface, in both the articular surface and rim, along with a pattern of embrittlement induced white banding as shown through xylene etching in several highly oxidized liners (Fig 2). Hydroperoxide profiles were characterized by subsurface peaks or bulk increases, corresponding with their individual oxidation profiles. Oxidation showed a positive linear correlation with increasing hydroperoxide levels, (R^2=0.64), and a negative linear correlation with cross-link density (R^2=0.32), where 14 retrievals showed a greater than 25% decrease in crosslink density compared to the never-implanted control showing no shelf oxidation (0.260 ± 0.001 mol/dm^3).

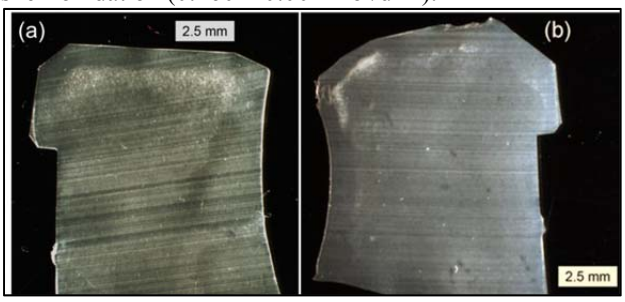

Figure 2. White banding can be seen on the rim cross sections of (a) a six year acetabular retrieval with an MOI=0.85 and (b) four year acetabular retrieval with an MOI=1.6 after xylene etching.

One 3.9 mm-thick acetabular retrieval, with 26.6 months in vivo service, showed deep yellowing of the backside and articular surface, along with heavy scratching, deformation and wear at the center of the dome (Fig 3). The component was revised as part of a modular stem recall in which heavy neck-taper corrosion was present and resulted in embedded metal debris at the articular surface. The retrieval showed a subsurface oxidation peak approximately 0.6 mm below the articular surface with an maximum oxidation index of 0.21. No regional change in cross-link density was measured throughout the component (0.222 ± 0.010 mol/dm^3).

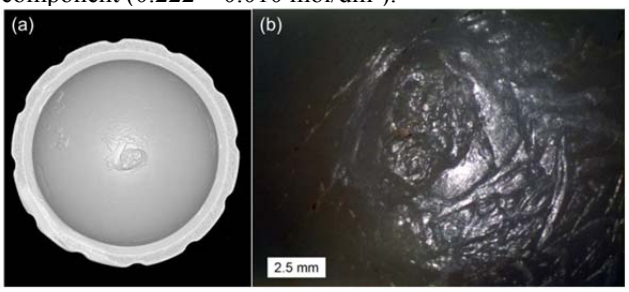

Figure 3. After 26.6 months of in vivo service, this implant was revised due to the excessive corrosion of the neck-taper junction in its recently-recalled modular femoral component. Significant surface damage can be seen across the articular surface and prominently at the dome from the (a) microCT scan and (b) optical image.

Nine tibial inserts showed an elevated oxidation index in the bulk of the component thickness (Figure 4). Of the nine, six showed subsurface peaks in addition to this bulk increase, while three exhibited overall bulk oxidation with less than 1.5 years, includiing a two-week *in vivo* duration liner showed oxidation and degradation of material properties throughout the bulk (Figure 5a).

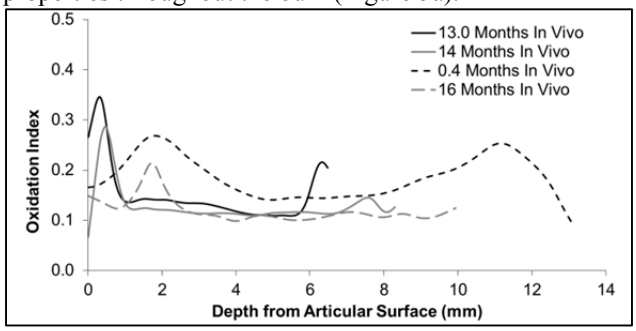

Figure 4. Splined-average articular surface profiles from four tibial inserts showing subsurface oxidation peaks as well as detectable bulk oxidation.

Three of four never-implanted liners, with up to five years shelf storage, also showed bulk oxidation (Max OI ≤ 1.5; Figure 5b), loss of cross-link density (41-71%) and increased hydroperoxides (4-9 times) compared to the one never-implanted liner showing no shelf oxidation (OI=0.03 ± 0.00), uniform crosslink density (0.260 ± 0.001 mol/dm^3) and hydroperoxide levels (HI=0.60 ± 0.02).

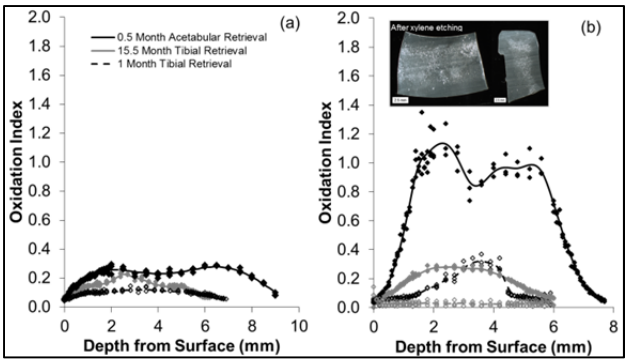

Figure 5. (a) Three of four never-implanted, shelf-stored components show bulk oxidation, (b) while three short duration retrievals display similar bulk oxidation with a little as 2 weeks in vivo, suggesting that they were oxidized prior to implantation (inset: xylene etching of articular surface cross-section of the never-implanted acetabular liner showing greatest oxidation).

Discussion: High levels of detectable oxidation, subsurface oxidation peaks, and white banding were all identified in sequentially irradiated and annealed UHMWPE retrievals with short *in vivo* durations. Studies examining the effect of in vivo lipid absorption and cyclic loading make a strong case for higher oxidation levels present at the articular surface. However, sequentially irradiated and annealed retrievals are displaying equally significant subsurface oxidation at both their loaded and unloaded regions. We hypothesize that this is a result of the maintained presence of free radicals, which either accelerated the lipid and mechanically-induced oxidation and/or oxidized the polymer independently, contributing to the overall in vivo oxidation.

Oxidation measured in shelf-stored, never implanted liners also raises concerns that liners may already be oxidatively compromised before being implanted into patients. Evidence of this was seen in retrievals demonstrating bulk oxidation after extremely short implantation periods. Due to gas plasma sterilization methods, these free-radical containing liners are packaged and stored in air, likely resulting in a pre-implantation oxidation effect similar to that historically reported in gamma-in-air sterilized UHMWPE[9].

These results raise concerns about the long-term oxidative stability, as well as the impact upon clinical performance of these materials. Longer-term retrievals are needed to better understand the progress of these in vivo changes and whether or not it will compromise the durability of the bearing surface in both knees and hips.

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He ion implantation as a barrier to squalene effects in UHMWPE

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Introduction: Elimination of free radicals to prevent oxidative degradation of highly cross-linked ultra-high molecular weight polyethylene (UHMWPE) is one of the most relevant concerns in joint arthroplasty. It was expected that cross-linked remelted UHMWPEs could maintain oxidative stability in vivo comparable with its stability during shelf storage. However, these materials show a measurable and unexpected oxidation in vivo [1], attributed by the presence of synovial liquid lipids, such as squalene (SQ). This lipid is known to absorb into polyethylene *in vivo* [2] and could act as a pro-oxidant in cross-linked UHMWPEs [3].
Ion beam implantation has been successfully applied to the modification of polymers for improving their surface properties such as wear resistance, mechanical properties and biocompatibility [4]. This study aims to assess the effect of helium ion implantation on the squalene and oxygen diffusion in UHMWPE. The hypothesis of the present work was that the diffusion of squalene into polyethylene will decrease due to the ion implantation process.

Materials and Methods: The raw material used in this study was a ram-extruded bar of GUR 1050 UHMWPE resin (Perplas Medical Ltd, UK). Discs 3 mm thick and 20 mm in diameter were machined from this bar and polished to a surface roughness equal to 0.15 ± 0.06 μm. The helium implantation in UHMWPE was carried out in AIN (Pamplona, Spain) at doses of 10^{16} ions/cm^2 with energy of 50 keV. After implantation process, some discs were soaked in squalene at 120 ºC during 2 hours in nitrogen gas atmosphere.
To study the oxidative behaviour of the squalene diffused samples, the dealt materials underwent an ageing protocol under air at 120 ºC for 36 h. One sample from each specimen group was cut and microtomed at the center of the discs to obtain a transversal section to the surface. The microtomed sections, 150 mm of thickness, were analyzed using a Perkin–Elmer 1600 infrared spectrometer (range: 4000–400 cm^{-1} and resolution 4 cm^{-1}). The depth profile of squalene was quantified by normalizing the area under 1150 cm^{-1} absorbance to the area under the internal reference methylene vibration at 1895 cm^{-1}. Also, the oxidation indices were calculated using the guidelines provided in ASTM F2102.

Results and Discussion: In general, He^+ implanted surfaces undergo chemical, physical and microstructural changes associated with dehydrogenation, amorphous graphitization and cross-linking. The results demonstrated that this surface modification produced a change in the adsorption and bulk diffusion of synovial fluid component into polyethylene. Figure 1a shows the concentration profiles of the squalene after diffusion. Thus, he lipid index measured in the raw specimen sample was higher than in the ion implanted one. This decrease can be attributed to the increase of crosslinking and crystallinity on the surface due to the ion implantation process, what is based on the increase of hardness and surface elastic modulus [5]. As the diffusion of the lipid molecules is mostly restricted to the amorphous domains, an increase in the crystallinity would decrease the extent of lipid diffusion into polyethylene [6].

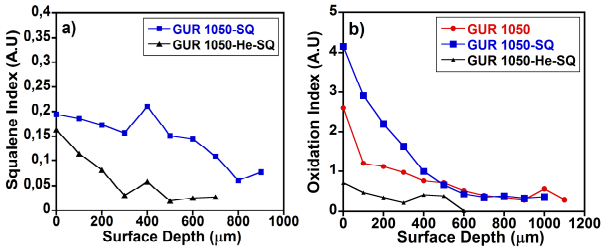

Figure 1: a) Squalene index profiles, b) Oxidation index after aging protocol.

On the other hand, the oxidation index after the aging protocol was lower for the ion implanted sample than the obtained for the no implanted one and even for the raw material (Figure 1b). These findings show that the presence of a thin region of helium ions in the surface of polyethylene can be also acts as oxygen barrier.

Conclusions:
This study has shown that ion implantation represents a powerful tool on modifying UHMWPE surface producing and decrease of both, squalene diffusion and oxidative behavior of UHMWPE components in total joint replacements at the regions out of the bearing zones where the ion layer keeps.
We plan to extend the research to the effects of the ion implantation technique in the squalene diffusion into gamma irradiated UHMWPEs.

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Dielectric effects induced by gamma irradiation and vitamin E in ultra high molecular weight polyethylenes

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Introduction: Dielectric relaxation spectroscopy (DRS) is a powerful tool to study the molecular dynamic in polymers. This technique has also been used in polyethylenes in spite of the non polar character of their molecular structure. Different processes like consolidation, irradiation, aging, chemical treatment of fiber/polyethylene composites introduce traces or polar groups in the polyethylenes, which affect the α, β and γ relaxations [1]. In contrast to HDPE, LDPE or LLDPE, few works [2] appeared in the literature concerning to the UHMWPE. This study aims to assess the use of this technique to observe the changes introduced by gamma irradiation and by the presence of vitamin E on the relaxations.

Methods and Materials: The raw material was medical grade GUR 1050 UHMWPE (Orthoplastics, UK). The antioxidant, vitamin E, was incorporated by blending with UHMWPE powder at 0.1 wt% in compression molded blocks. These blocks were subsequently irradiated by electron beam to 75, 150, 225 and 300 kGy (MIT, Cambridge, MA) to study the influence of irradiation doses. To separately study the effects of vitamin E concentration, 0.2 mm sections were microtomed from the compression molded GUR 1050 without antioxidant and soaked in a bath of vitamin E (α-tocopherol, Aldrich Chemicals) at 120 ºC in a nitrogen gas atmosphere for different times and further homogenized to obtain finally 1.5, 4.4 and 7.9wt% of vitamin E.
Dielectric measurements were performed using a dielectric spectrometry setup (Novocontrol BDS4000). The complex dielectric constant was obtained by sweeping the frequency range 0.01 Hz to 1 MHz at different stabilized temperatures by heating from –70 ºC to 120 ºC in temperature steps of 6 ºC. The samples were disks of 0.2 mm of thickness, which were held between the condenser plates (golden brass circular electrodes, diameter 10 mm).

Results and Discussion: The γ relaxation is not observed in any of the dealt materials, because it appears in the polyethylenes around 190 K, which is below of our initial temperature. The β relaxation is not detected either in GUR 1050. Only the α and α´ relaxation, commonly attributed to the relaxation mechanisms in the crystalline region, are observed in all the materials overlapped by a low-frequency dispersion behavior. The influence of the antioxidant vitamin E is reflected by means of the appearance of a relaxation between -30 to -0 ºC (Figure 1). This relaxation is only detected at vitamin E concentration above 1 wt%. The frequency dependence of the dielectric complex was described by the Havriliak-Negami (HN) and Fouss-Kirkwood (FK) equations, after subtracted the term associated with the AC conductivity. The obtained relaxation time, τ, and the temperature of the maximum value of ε´´ at isochrone conditions, T_{max}, follow an Arrhenius behaviour with an activation energy around 195 kJ/mol and 183 kJ/mol for HN and FK approaches, respectively. These values are in agreement with the values calculated from DMTA measurements [3].

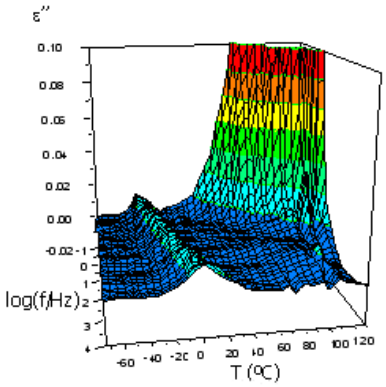

Figure 1: Dielectric loss ε´´(ω,T) for UHMWPE with 7.9 wt% of vitamin E.

Gamma irradiation introduces changes in the molecular structure which are reflected in the DSR data by means of changes in the dielectric constant, positive or negative depending of the temperature. On the other hand, an AC conductivity is present about 60 ºC, which increases with radiation dose and temperature. This conductivity could be associated with an increase of the carrier charge density as a result of an increase in free radicals, unsaturated bonds, defects, which may be generated by gamma irradiation.

Conclusions: The presence of vitamin E introduces a relaxation in vitamin E containing UHMWPE, which can enable us to study the grafting effects of vitamin E in UHMWPE. DRS measurements can detect the influence of gamma irradiation via a dose and temperature dependence of AC conductivity.

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Effect of Antioxidant on Polyethylene Particle Induced Inflammation and Cellular Activation

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Introduction:

Wear particles derived from ultra-high molecular weight polyethylene (UHMWPE) implants can provoke inflammatory reaction and cause osteolysis in the surrounding bone, which can ultimately lead to aseptic implant loosening. Antioxidants, e.g. vitamin E, have been incorporated into UHMWPE with the intention to improve long term oxidative stability of UHMWPE implants and reduce wear. Since antioxidants have been shown to have anti-inflammatory properties, it is of great interest to determine if the incorporation of an antioxidant into UHMWPE implants can reduce wear particle induced inflammation. The objective of the study was to evaluate the effect of 2 different antioxidants, i.e. cyanidin and vitamin E, on UHMWPE induced macrophage activation and on aseptic inflammation using a well-established air pouch model.

Methods and Materials:

Polyethylene particles: 4 types of UHMWPE materials were used: (1) compression molded conventional GUR1020 (PE); (2) compression molded GUR1020 blended with 300 ppm cyanidin (C-PE); (3) compression molded GUR1020 blended with 1000 ppm α-tocopherol (BE-PE); and (4) compression molded GUR1020, gamma irradiated at 100kGy, diffused with α-tocopherol, and sterilized at 30kGy (DE-PE). Each material was sectioned into 2mm cubes before cryomilling. The cryomilled particles were washed twice in 70% ethanol solution and dried overnight in a sterile hood. Particle count, size, and aspect ratio were determined for each material using SEM and Image Pro.

In vitro cell activation assay: A mouse macrophage cell line (RAW264.7) was cultured with 4 different particle concentrations (0.625, 1.25, 2.5, and 5 μg/mL) of each material in a standard medium for 4 days. Cell numbers were quantified using MTT assay. Cytokine gene expression (IL-1β, TNFα, and IL-6) in the cells was measured using RT-PCR and cytokine release in the medium was measured using ELISA.

In vivo air pouch inflammation assay: Particles of each material were suspended in PBS at 2 concentrations (0.2 or 1 mg) and injected into pre-established, subcutaneous air pouches in BALB/c mice (n=6/material). Control animals were injected with PBS alone. Air pouches were harvested 6 days post-injection. Half of the air pouches were fixed with formalin and processed for histology. Histological sections were stained with H&E and examined for membrane thickness and inflammatory cell quantity. Remaining air pouches were frozen and analyzed by ELISA for cytokine production.

Statistical analysis: Data were compared using one-way ANOVA with post hoc (LSD) testing. $P<0.05$ was considered significant.

Results:

Particle characterization

All 4 materials yielded similar particle size, shape and distribution after cryomilling (Table). Particle size ranged from 1 to 19 μm for all materials with 33% of particle population smaller than 2 μm.

Material	Diameter (μm)	Aspect Ratio	Roundness
PE	4.7±3.9	2.02	1.65
C-PE	4.1±3.3	1.92	1.59
BE-PE	4.5±3.6	1.95	1.63
DE-PE	3.7±2.8	1.94	1.60

In vitro macrophage activation

All particle groups supported RAW264.7 cell proliferation during the 4-day culture period. There was a slight inverse correlation between proliferation rate and particle dose in all 4 materials. No significant difference was observed between PE and other antioxidant containing materials. Gene expression of IL-1β and TNFα also showed an inverse correlation with particle dose. Expression of IL-1β, TNFα, and IL-6 appeared lower in cells cultured with C-PE than the other 3 materials. The accumulative protein productions of IL-1β and TNFα were significantly lower while IL-6 production was moderately lower in C-PE, BE-PE and DE-PE when compared to PE.

In vivo inflammation

Injection of polyethylene particles increased the air pouch membrane thickness significantly compared to the PBS control regardless of particle type and dose. Higher particle dose induced thicker membrane in all 4 materials while little difference was observed between the materials. A similar trend was also observed in the percentage of inflammatory cell infiltration in the pouch membrane. Additionally, at low dose, C-PE and DE-PE particles induced lower levels of IL-1β and TNFα in the air pouch membrane than PE. At high dose, only C-PE particles induced lower level of IL-1β and TNFα than PE. IL-6 production was similar between PE and the antioxidant containing particles.

Discussion:

Antioxidant incorporated in UHMWPE did not alter the level of macrophage proliferation and air pouch inflammation induced by UHMWPE particles, although it reduced cytokine gene expression in these models. Future investigation in a synovial joint environment is desired to evaluate the chronic inflammation response to antioxidant containing UHMWPE wear particles and to verify the effect of antioxidant in UHMWPE properties.

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Toughness Changes with Radiation Dose in an Antioxidant Stabilized UHMWPE

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Introduction: Antioxidant-stabilized ultra high molecular weight polyethylene (**UHMWPE**) materials are increasingly being regarded as effective against long-term lipid and load-induced oxidation in orthopaedic joint replacement components[2,3]. An antioxidant-stabilized UHMWPE, generated by the incorporation of a hindered phenol antioxidant, tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate], **PBHP**, into GUR 1020 UHMWPE that was compression molded and irradiated to various radiation doses, is described here for its toughness response to gamma irradiation dose.

Methods and Materials: GUR 1020 (Ticona, US) UHMWPE material stabilized with 0.075% (w/w) PBHP was consolidated by compression molding (MediTECH, IN). Samples were machined, washed, vacuum foil packaged and crosslinked using gamma radiation dose in the range 75-135 KGy and marked as **AO-75**, **AO-80**, **AO-115**, **AO-125,** and **AO-135**. The following fracture resistance and toughness evaluations were conducted to characterize differences in response as a function of radiation dose: fatigue crack propagation resistance; uni-axial tensile toughness and ductility; and, double notched Izod impact toughness. The difference in the response elicited by these various testing modes is expected to facilitate a better and fundamental understanding of material behavior.

Results: With increasing radiation dose, there is a progressive loss of fatigue crack propagation resistance, da/dn versus ΔK (i.e., the curves shift to the left). This is not unexpected as increasing radiation dose results in increased crosslinking and consequently, reduced ductility. However, upon comparison with toughness measured from tensile and impact tests, the reduction noted in fatigue crack propagation resistance is less than that obtained from the other modes of toughness. This may be due to the increase in crystalline domains with increasing radiation dose that serve to blunt the crack propagation more effectively than what is warranted by the loss in ductility[4]. The % crystallinity appears to plateau off at approximately 61 ~ 63% beyond 115 KGy. This could explain the progression of ΔK_{Incep} loss beyond 115 KGy through 135 KGy as there is no further increase in crystallinity to counter the increase in crosslinking due to increasing radiation dose.

The benefit provided by antioxidants incorporated into UHMWPE devices is the avoidance of oxidative degradation in UHMWPE devices that results in embrittlement of the polymer. Such degradative changes in UHMWPE can lead to brittle fracture. The findings of this study support that crystallinity changes associated with the increased radiation dose in this family of hindered phenol antioxidant UHMWPE materials mitigates the loss in fatigue crack propagation resistance associated with increased crosslinking. This interesting and somewhat unexpected result may be significant since the long-term clinical mode of mechanical failure, in the absence of oxidative degradation, may be primarily due to fatigue failure caused by the cyclic nature of loading experienced by the devices in-vivo.

Discussion/Conclusion: The semi crystalline, crosslinked, hindered phenol antioxidant-stabilized UHMWPE shows smaller changes in fatigue crack resistance as a function of increasing gamma radiation dose when compared with the changes in other modes of ductility and toughness such as uni-axial tensile and double notched Izod toughness.

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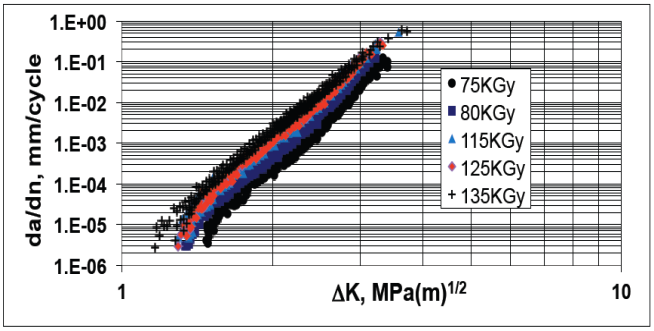
Table 1 – Mechanical Properties with Radiation Dose

Property	AO-75	AO-80	AO-115	AO-125	AO-135
ΔK_{Incep}, MPa(m)$^{1/2}$	1.5	1.5	1.4	1.3	1.2
Tensile Toughness, MPa	93 ± 4	86 ± 2	79 ± 3	75 ± 4	64 ± 3
Elongation at break, %	335 ± 11	300 ± 6	276 ± 9	267 ± 11	229 ± 8
DNI Toughness, kJ/m^2	74 ± 4	71 ± 1	57 ± 1	53 ± 2	51 ± 1
% Crystallinity	58.7 ± 0.7	63.1 ± 0.6	63.0 ± 2.0	63.7 ± 2.0	61.3 ± 1.2



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Mediators of the inflammatory response to joint replacement devices

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Introduction: Biomaterials that are engineered for medical applications have greatly improved, or even replaced, previously lost organ functions. The field of orthopedic surgery has been particularly transformed by biomaterials, engineered to replace hips and knees affected by severe arthritis. As much as biomaterials have transformed organ replacement therapy, issues of biocompatibility often arise that require a closer look at the interactions between biomaterials and the immune system. Issues of biocompatibility have been noted with several of the orthopedic implant devices including polyethylene and ceramic. However, they were generally regarded as low frequency long term complications. Recently, patients implanted with a new generation of hip and knee devices of the "Metal on Metal' type (MoM) have been shown to develop an accelerated inflammatory reaction frequently associated with tissue necrosis and cellular toxicity. This response was particularly puzzling since components, such as Cr and Co, which are the metal alloy utilized in the MoM implants, have been used in the manufacture of implant devices for several years without causing the massive inflammatory and necrotic reaction observed in patients implanted with the MoM type. Thus, at the moment the correlation between metal composition of the implants and the resulting immunological response is not clear. The sense of urgency in determining the molecular association between implant type and immune response relates to the fact that there are over 20 million people with hip and knee replacement devices containing Cr and Co. Since joint replacement devices will be used for many more years to come, an understanding on how implant composition affects immune response is pivotal for the design of biomaterials with increased performance and decreased immune reactions.

Methods and Materials: Cr and Co ion concentrations were determined in different biological tissue and bodily fluid from patients with different type of implants, containing different levels of Cr/Co alloy. Both spectroscopic and X-ray absorption near edge structure (XANES) analyses was employed to determine the oxidation state of Cr and Co ions present in these specimens.
As a read out of oxidative stress, *in vitro* and *in vivo* levels of protein oxidative damage was analyzed using biochemical (protein derivatization, SDS-PAGE) and biophysical assays (Mass Spectrometry). Potential correlations between tissue metal ion concentrations, oxidative stress and tissue damage (necrosis and inflammation) was analyzed by ICP/MS, immunohistochemistry and ultrastructural analysis.

Results: We determined that the particulate metals released from the wear and tear of joint implants were readily phagocytosed by tissue resident macrophages and transported in endosomal and lysosomal compartments. In endosomal compartments, due to the presence of an acidic pH, the transition metals released Cr and Co ions with different positive valences. The metal ions catalyzed the breakdown of hydrogen peroxide (H_2O_2) into reactive hydroxyl radicals ($HO^{\bullet}$) in a chemical reaction known as the Fenton reaction. The hydroxyl radicals formed by the metal-catalyzed Fenton reaction caused deleterious biological effects and irreversible damage by promoting protein, lipid, carbohydrate and DNA oxidation. Free metal ions could also directly bind and likely oxidize biomolecules. Extensive oxidative modifications resulted in protein fragmentation, sub-unit dissociation, unfolding, and aggregation, with an overall loss of biological function.

Discussion: Our data provide the first biochemical mechanistic explanation for how different types of implants with similar element composition, albeit at very different ratios, have such a different outcome in terms of biocompatibility. By using a series of biochemical and biophysical assays, we investigated the formation and oxidation states of the Cr and Co ions released by the metal implants and correlate the presence and concentrations of these metals with the cellular and tissue proteome and any resulting oxidative damage. Altogether, our research provides a comprehensive mechanistic analysis of the interaction between body tissues and Cr and Co ions that are released from implants.

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Characterization of High-Density Polyethylene Changes Induced by Gamma Irradiation

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Introduction: High-density polyethylene with ultrahigh molecular weight (M_w = 2–6 × 10^6 g/mol) has been widely used in arthroplasty as a bearing material in total joint replacements (TJRs). In order to improve life-limiting factors of the arthroplasty component, the polymer is crosslinked by ionizing radiation and thermally treated and/or stabilized with vitamin E [1]. Ultrahigh molecular weight of the polymer, together with the complexity of modifications process, makes data interpretation difficult in some cases. Namely, the determination of the extent of crosslinking is difficult. Therefore, we crosslinked two lower molecular weight polyethylenes (high-density polyethylene and very high molecular weight polyethylene) and tested the radiation-induced changes in their structure by means of several microscopic techniques (scanning and transmission electron microscopy, infrared microscopy, microhardness, and microcreep measurements). We plan to extrapolate the observed effects of the model lower-molecular-weight PEs and compare measured properties with real-arthroplasty-application UHMWPEs.

Materials and methods: Two types of HDPE with different M_w were used PE1 (Liten DMJ, Litvinov, Czech Republic; standard high-density PE; $M_w \approx 5 \times 10^4$ g/mol) and PE2 (Liten DSX, Litvinov, Czech Republic; very high molecular weight PE; $M_w \approx 1 \times 10^5$ g/mol). The granulated polymers were compression molded at the HDPE melting temperature and then slowly cooled to laboratory temperature. Some of the prepared plates were then gamma-irradiated (^{60}Co γ-emitter in Nuclear Research Institute Řež, Czech Republic; laboratory temperature, radiation dose 100 kGy, low oxygen atmosphere). After irradiating and between all experiments, the irradiated samples were stored in dark cold place (~5°C).

Scanning Electron Microscopy. In order to visualize an arrangement of crystalline lamellae in the amorphous matrix, the etched surfaces of HDPE samples were observed in a scanning electron microscope (SEM). Small samples were prepared by microtomy at laboratory temperature and etched with permanganic mixture (a 1:1 mixture of concentrated H_2SO_4 and concentrated H_3PO_4, containing 1 wt.% of $KMnO_4$). Immediately after etching the samples were washed with four solutions [2]. The etched and washed samples were fixed to copper supports, sputtered with platinum (4 nm; Vacuum sputter coater SCD 050, Balzers) to avoid charging, to decrease sample damage due to electron beam, and to increase resolution. SEM micrographs were obtained with a microscope Quanta 200 FEG (FEI, Czech Republic) using secondary electron imaging at 5 kV.

Transmission Electron Microscopy. Lamellar structure of HDPEs was studied by transmission electron microscopy (TEM) using a microscope Tecnai G2 Spirit (FEI, Czech Republic). All micrographs were taken at an acceleration voltage of 120 kV. Specimens for TEM were prepared by ultramicrotomy (microtome Leica UCT with cryo attachment, diamond knife, sample and knife temperature –100°C and –50°C, respectively). In order to visualize the crystalline lamellae, the sampes were stained with oleum (SO_3 in concentrated H_2SO_4) for four days as described in our previous study [3].

Infrared microscopy. Oxidation index (OI), trans-vinylene index (VI) and degree of crystallinity (%C) profiles were determined by infrared (IR) according to Medel et al. [4]. Infrared spectra of all HDPE samples were measured with infrared microscope Nicolet Continuμm ™.

Differential scanning calorimetry. Melting points (T_m) and crystallinities (CR) were determined from DSC as described elsewhere [2].

Microhardness. Microhardness (MH) was measured by means of a microhardness tester (VMHT AUTO man; UHL) using Vickers method (square pyramid indentor of diamond with angles between non-adjacent faces 136° is forced against flat surface of the specimen). For each sample, at least 30 indents were made (3 smooth surfaces prepared by microtomy, 10 indents on each, load F = 50 gf; load time t = 6s), average diagonal length (d = average of the two diagonals of the indent) was measured with a light microscope and the final MH value was calculated [5]:

$$\mathrm{MH} = H[\mathrm{MPa}] = 1.854 \times F[\mathrm{N}]/d^2[\mathrm{mm}^2] \quad (1)$$

Microcreep (MC) was determined from MH values (H, Eq. 1) measured at different load times (t). The relationship between H and t is described by time law (Eq. 2a) as described by Balta-Calleja et al. [5] We define microcreep as the creep constant from the above mentioned time law (Eq. 2b):

$$H = H_0 t^{-K} \quad (2a)$$
$$\mathrm{MC} = -K \quad (2b)$$

Results: Scanning electron microscopy proved that the two lower-molecular weight polyethylenes (PE1 and PE2) exhibited spherulitic structure (Fig. 1). The concentric circles on the SEM micrographs indicated that under given preparation conditions, both PE1 and PE2 crystallized in the form of banded sherulites, in which the lamellae are twisted [6]. The spherulitic structure is

different from UHMWPE, which contains randomly oriented crystalline lamellae in the amorphous matrix.

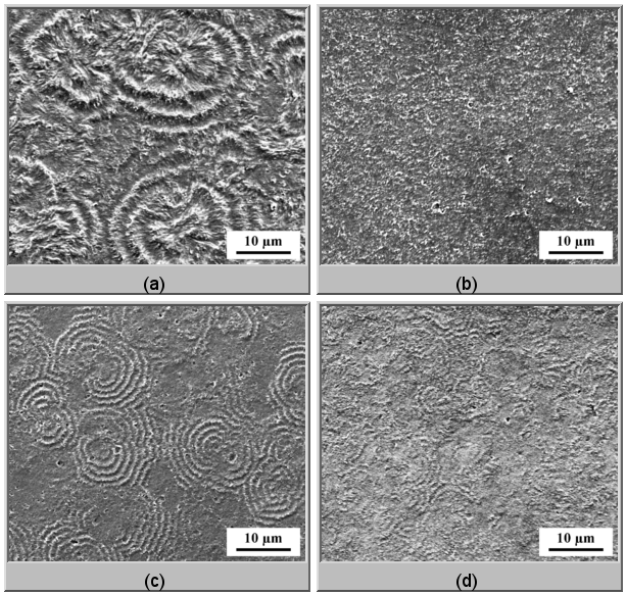

Figure 1. SEM micrographs showing crystalline lamellae in amorphous matrix of all studied HDPEs (a) non-irradiated PE1, (b) non-irradiated PE2 and (c) 100kGy-irradiated PE1, (d) 100kGy-irradiated PE2.

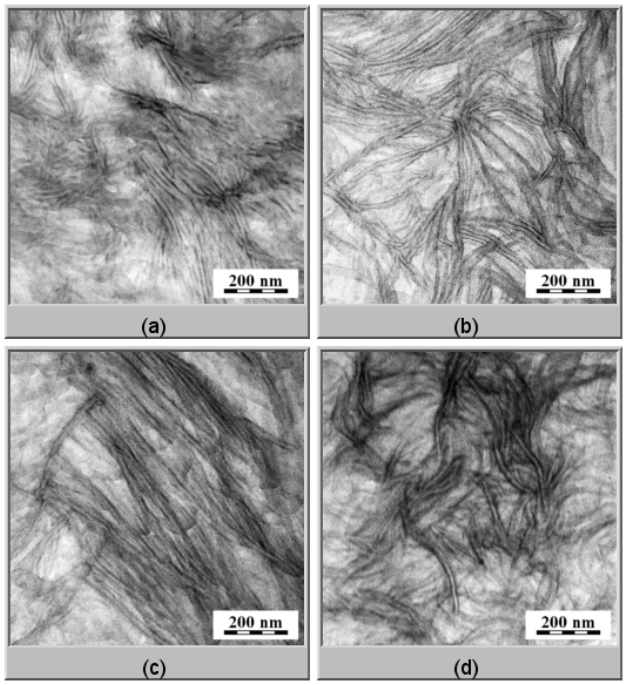

Figure 2. TEM micrographs showing all studied HDPE (a) non-irradiated PE1, (b) non-irradiated PE2 and (c) 100kGy- irradiated PE1, (d) 100kGy-irradiated PE2 samples stained only with oleum.

It is worth noting that irradiation changed the spherulitic morphology significantly, although it was not followed by thermal treatment. According to DSC and IR, overall crystallinity (CR) was inversely proportional to the molecular weight (PE1 ~80 %; PE2 ~70 %) and decreased after irradiation (by ~8 % in both PE1 and PE2). TEM micrographs (Fig. 2) suggested that the average thickness of the lamellae did not change significantly.

The results from SEM, DSC and IR were correlated with the changes of micromechanical properties. Microhardness (MH, Eq. 1) and microcreep (MC, Eq. 2a,b) at various loads are shown in Fig. 3. Microhardness (absolute values in Fig. 3) increased with CR, which is in agreement with literature [5]. Microcreep (slopes in Fig. 3) decreased with increasing molecular weight. Our tentative explanation is that higher concentration of entanglements (due to higher M_w) and crosslinks (due to irradiation) increased the creep resistance.

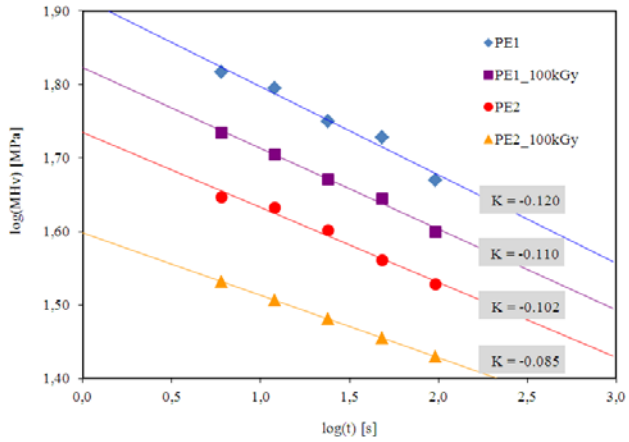

Figure 3. Microcreep of non-irradiated (PE1, PE2) and irradiated (PE1_100kGy, PE2_100kGy) samples .

Discussion and conclusion: We characterized HDPEs with lower molecular weight than standard UHMWPE for total joint replacements. We showed that microhardness and microcreep are sensitive to both M_w and CR of the samples, as well as to irradiation-induced changes of supermolecular structure. Moreover, we verified that our oleum staining technique [3], originally developed, optimized and tested on UHMWPE, was applicable also to lower molecular weight polyethylenes.

Acknowledgement:
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Wear and deformation of novel anti-oxidant UHMWPE acetabular cups for total hip replacement under standard gait and adverse loading conditions

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Introduction: Crosslinking of ultrahigh molecular weight polyethylene (UHMWPE) by gamma or electron beam radiation has been shown to reduce the wear rate of acetabular cups but adversely affect the ductility and fatigue resistance[1,2]. Furthermore, the crosslinking process produces free radicals that leave the material at risk to oxidation. Stabilisation of UHMWPE can be provided by the addition of anti-oxidant agents such as hindered phenols, thus reducing the need to expose the material to post-irradiation thermal treatments of varying degrees of effectiveness which may further compromise mechanical properties. Hip joint simulator studies have previously shown that wear is increased when hard on hard bearings are subjected to edge loading, highlighting the importance of testing new materials under a wider range of loading conditions. The aim of this study was to investigate the wear and deformation of two designs of metal-backed stabilised UHMWPE acetabular cups tested under standard gait conditions and under conditions of microseparation where the femoral head contacts the rim of the UHMWPE cup.

Methods and Materials: In both test groups the bearing surface comprised of four 36mm hindered phenol anti-oxidant stabilised GUR 1020 UHMWPE acetabular liners (irradiated to 115kGy) articulating with a 36mm cobalt chromium femoral head supplied by DePuy Synthes, UK. In one group the liner was compatible with a commercially available modular acetabular shell (Pinnacle™) and in the second group the UHMWPE was direct compression moulded into a metal shell. Both groups were tested on a hip simulator (Prosim, UK) replicating a physiologically relevant wear pattern under standard gait conditions and then dynamic microseparation conditions, reflecting translational malposition of the acetabular cup with the head contacting the rim of the cup.[3] The Pinnacle compatible liners were assessed for volumetric wear both gravimetrically and geometrically using a coordinate measuring machine. The compression moulded cups were only assessed geometrically. Geometric assessment determined volume change in the cup, which is comprised of wear volume and creep deformation. The worn surface was analysed using SR3D mapping software to analyse the wear area and penetration into the bearing surface and cup rim. All volumetric wear rates were calculated between one and five million cycles to obtain the steady state wear rates and to minimise the contribution of creep in the first million cycles. Statistical analysis to compare wear rates by design and loading condition was performed using a one-way ANOVA (significance $p<0.05$).

Results: Creep had a significant influence on the volume change of the cups for both standard gait and microseparation conditions, particularly during the first million cycles of each test condition. Under standard gait conditions the compression moulded cups were significantly ($p=0.002$) lower wearing than the Pinnacle compatible cups. However, under microseparation conditions there was no statistical difference ($p =0.09$). For the Pinnacle compatible liners, the mean steady state wear rate under microseparation conditions was not significantly different ($p=0.06$ for geometric measurements) to the mean steady state wear rate under standard loading conditions (Figure 1). For the compression moulded cups, the mean steady state wear rate under microseparation conditions was significantly lower ($p=0.04$) than under standard gait conditions. Neither acetabular cup design showed signs of rim fracture or cracking at the end of the test, although there was some rim deformation. The geometrical measurement of the bearing surface showed the penetration and orientation of the wear areas and confirmed that supero-lateral rim deformation had occurred during the microseparation test (Figure 2).

Discussion: This study has shown that the wear rates for both acetabular cup designs are comparable to those observed in previous studies of crosslinked UHMWPE ($8.1mm^3$/million cycles)[4] and lower than those observed previously for conventional non-crosslinked UHMWPE ($34.3mm^3$/million)[2]. Creep influenced the total volume change for both cup designs. However, this was more marked for the Pinnacle compatible liners than the compression moulded cups and could be attributed to the non-conforming nature of the removable liner, which allowed UHMWPE to flow more readily. Edge loading and microseparation conditions did not increase the wear of either acetabular cup design and in fact may have resulted in a decrease in wear rates of the compression moulded cups. The observations made

during this study suggest that these novel anti-oxidant UHMWPE acetabular cups offer good wear resistance relative to similar liners and unlike hard on hard bearings wear was not significantly increased by edge loading conditions.

Significance: Anti-oxidant stabilised UHMWPEs provides good wear resistance and offer protection from oxidative degradation. This study shows the importance of testing under clinically relevant loading conditions such as edge loading to ensure these conditions do not accelerate wear or result in failure of the components.

Acknowledgements: This work was supported by the LMBRU. Components were supplied by DePuy Synthes, UK. JF is an NIHR senior investigator.

GHI is a paid employee of DePuy Synthes. JF and SW are paid consultants of DePuy Synthes.

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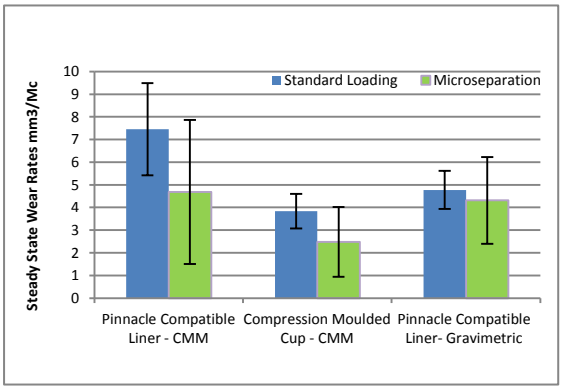

Figure 1 Steady state wear rates for Pinnacle compatible liners and compression moulded cups under standard and microseparation conditions measured geometrically (CMM) and gravimetrically (mean± 95% confidence limits, n=4)

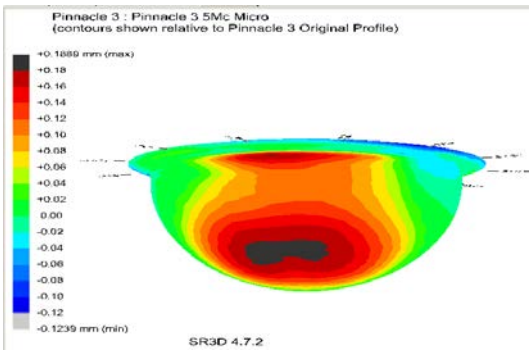

Figure 2 SR3D reconstruction of the bearing surface of a Pinnacle compatible liner showing penetration and orientation of the area of volume change following 5Mc of standard gait and 5Mc of microseparation conditions

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Preparation and characterization of sodium alginate modified UHMWPE

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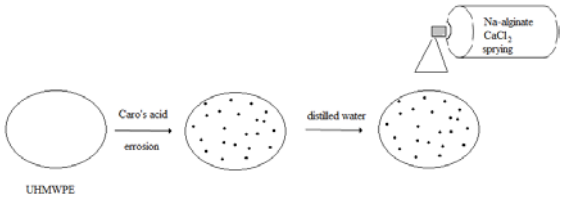
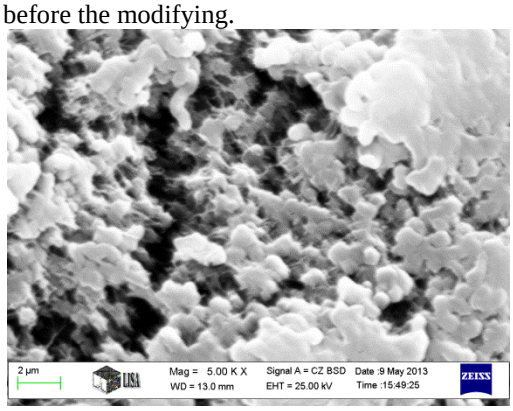
Introduction: The basic idea came from the theme of E-vitamin-filled Ultra High Density Polyethylene (UHMWPE). Read from Sodium alginate [Jian-ping Wang, Xing-Xiang-Zhang, Xue-Chen Wang, Preparation, characterization and permeation of calcium alginate macro-capsules containing shape- stabilize phase change materials, Renewable Energy, vol.36 (2011)pp.2984-2991] and its special properties that it behaves like an egg box and able to trap different cations. We believe that applied a special preparation on the surface of the UHMWPE powder the sodium alginate form a layer which could hold calcium from calcium solution. The UHMWPE main application is hip joint cup. If we could implanted to calcium ions by using alginate, the calcium maybe reduces the risk of rejection.
Many problems incurred by the preparation of the samples. The first is how can be applied coating surface of the UHMWPE because it is a very stable and inert material. The second at higher temperatures the alginate is decomposes or not and can withstand 20 kGy gamma radiation. This irradiation was exactly the same as the one used for sterilizing UHMWPE implants.

Methods and Materials: The used UHMWPE is GUR 4120 (Average molecular weight: 5×10^6 g/mol(Mw)) powder. In first stage the surface of the polymer powder was treated by etching Caro' s acid (1:1 v/v cc.H2SO4 : 30 v/v % aqueous solution H2O2). The surface modifying hold different times.
After modifying followed a thorough cleaning with distilled water.

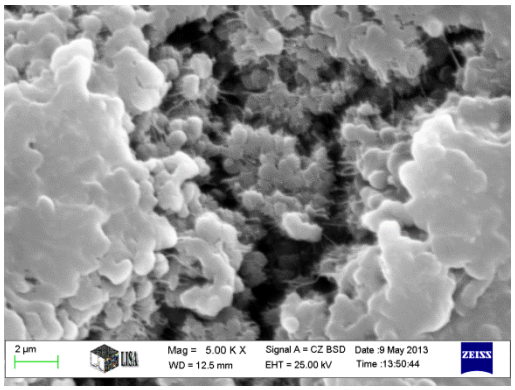


The erroded surface of the polymer particles become visible under the Scanning Electron Microscope.
The sodium alginate (ISP Alginates) alcohol solution (0,5 wt% water solution with alcohol) and calcium chloride and calcium carbonate (commercial product) (20 wt% water solution) spayed onto the modified polymer powder. The samples were heated 50°C for 1 hour. Then the samples cooled and controlled with Scanning Electron Microscopy and X-ray Microanalysis.

The Differential Scanning Calorymerty (DSC) analysis of the sodium alginate was performed before the modifying.



Untreadted UHMWPE powder



Treated UHMWPE powder

DSC methods are used to track the thermodynamics of structural changes and relaxation processes within polymers. Based on the measurements the sodium alginate it does not decompose.

Results: The treatments which we have done proved to be suitable for the surface treatment of UHMWPE. The polymer is capable of binding to the surface of the sodium alginate and the calcium. The presence of calcium on the surface checked for X-ray Microanalysis measurements.

Discussion: The next examinations are thermal properties of the alginate modified UHMWPE. Preventive DSC measurements showed that sodium alginate not decompose under 150°C. The UHMWPE powder press into sheets at 175 ° C. After the pressing method follows the gamma radiation. To further examine that after pressing and radiation the planted calcium found in the UHMWPE sheets. We would like to carried out the tests in UHMWPE hip joint cups too.

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Radiation-induced graft polymerization of UHMWPE fiber and dying application

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Introduction: Ultra high molecular weight polyethylene (UHMWPE) fiber is a material that maximizes polyethylene (PE) strength and modulus of elasticity. The theoretical strength and theoretical modulus of elasticity for PE are potentially high in a fiber macromolecule [1]. The theoretical strength of PE is approximately 30 GPa, which is high compared with the theoretical strength of steel fiber (3 GPa). However, the actual strength of PE fiber is hundreds of MPa lower than the theoretical values. To close the gap between the theoretical strength and theoretical modulus of elasticity, the orientation of a macromolecule with a high molecular weight must be optimized, and experiments for high strength and high elasticity fibers by super-extending UHMWPE have been conducted since the 1970s. To enhance super-extension in the gel-like fiber to 20% or more at a suitable temperature using a semi-dilute solution of UHMWPE, samples were generated with a strength of 4.4 GPa and a modulus of elasticity of 114 GPa [2]. One requirement for this technique is a dilute solution of UHMWPE; thus, the compression of a molecule chain decreases. Super-extension was generated for the first time using this method, and an ideal structure for a high molecular weight molecule chain in the proper orientation was obtained. Because the UHMWPE fiber is lightweight and strong, it is used for fishing lines, tether lines, tire cords, and sails, among other applications. The UHMWPE does not have a polar group in the polymer chain, but its surface is hydrophobic and lacks adhesive properties or dye affinity. Thus, to improve such characteristics, the surface was treated. Graft polymerization is an excellent method for maintaining the effect of processing. This research aimed to improve dye affinity for grafted UHMWPE fiber.

Methods and Materials: Materials and irradiation:
UHMWPE samples from Dyneema SK60, TOYOBO, were used for the experiments. Acrylic acid (AA) and styrene (St) (Kanto Kagaku Co., Ltd.) were reagent grade and used as received. The UHMWPE samples were irradiated using γ-rays from a Co-60 source in air at room temperature with a 1.6 kGy/h dose rate. The total doses were 25 kGy. Electron beam irradiation was performed using a 25 kGy dose under 200 kV of accelerating voltage and a nitrogen atmosphere.
Graft polymerization: The AA monomer was added to the methanol solution, which included Mohr's salt and concentrated sulfuric acid. The St monomer was used without additives. The AA were graft polymerized for 1, 2 and 3 hours in a water bath at 70°C. St was graft polymerized for 10 hours in a water bath at 70°C. To remove unreacted monomers and homopolymers after the grafted reaction, the grafted samples were extracted.
Dyeing procedure and color measurement: The grafted and untreated UHMWPE fibers were dyed using a 0.02% cationic dye solution (Color Index, Basic Red 46). The fiber dye concentrations were measured using a GretagMacbeth spectrophotometer (ColorEye 7000), which generated the color strength (*K*/*S*) values. The *K*/*S* value is proportional to the fiber dye concentration.
Tensile strength test: The strength changes caused by irradiation and graft processing were measured using a Shimadzu autograph (AG-X). The fracture point load was investigated for a 200-nm sample length, 100-mm/min test-rate, and 10 kN load. In addition, ESR and X ray diffraction experiments were performed.

Results and Discussion: Graft polymerization: For the graft polymerization experiments herein, peroxide radicals generated by irradiation in air and air storage were used as the precursor. The results from the graft polymerization of AA and St to UHMWPE fibers as a function of storage time after irradiation are shown in Figure 1 and Figure 2, respectively.

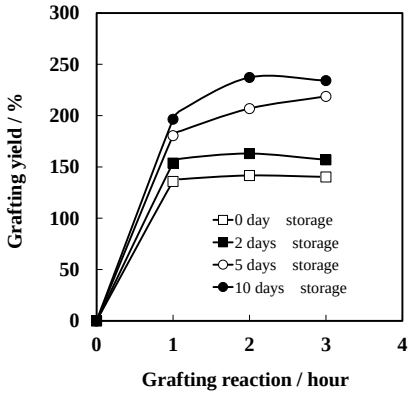

Figure 1 Graft polymerization of AA to irradiated UHMWPE fibers at 70 °C for 1-, 2- and 3-hour reactions. The dose was 25 kGy in air with several days of storage in air.

As shown in Figure 1, for graft polymerization of AA to UHMWPE fibers, the grafting yield was higher as the storage time increased. Regardless of the reaction time, the grafting yields were similar for samples with a short storage time. This result is contrary to the tendency of such radicals to disappear upon irradiation and shows that the decomposition radical from hydroperoxide and AA reacts easily. Moreover, because AA reactivity is high, if the radical concentration is high, a homopolymer is generated, and because graft chain growth is insufficient, the grafting yield will likely be low. In Figure 2, the grafting yield for St was low compared with that of AA, and the reaction time required for a substantial grafting yield was longer. The grafting yield decreased with storage time. For graft polymerization of St to the irradiated UHMWPE, to generate a homopolymer, the

grafting time is likely lower than for AA. Our results are consistent with previous findings [3].

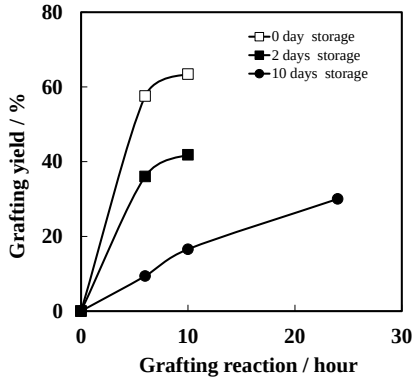

Figure 2 Graft polymerization of St to irradiated UHMWPE fibers at 70 °C for 5-, 10- and 24-hour reactions. The dose was 25 kGy in air, and the samples were stored in air for several days.

Color measurements: The surface-dye concentrations for the grafted fibers using the cationic dye are shown in Figure 3. The St-grafted fibers were prepared through sulfonation using chlorosulfonic acid in carbon tetrachloride (1:100) at room temperature for 24 hours. The surface-dye concentration (K/S value) was determined using the Kubelka-Munk relationship. The K/S relates the absorption and scattering coefficients, as well as the colorant concentration in the sample, with its overall reflectance. Although the concentration was high and resulted in high grafting yields at 135% and 230% for the AA grafted fiber, the concentrations were not observed at levels similar to the grafting yield differences. However, although the grafting yield for St was 22%, it was dyed at a high concentration through sulfonation. This result is attributed to the different reactivities between the carbonyl and sulfo groups.

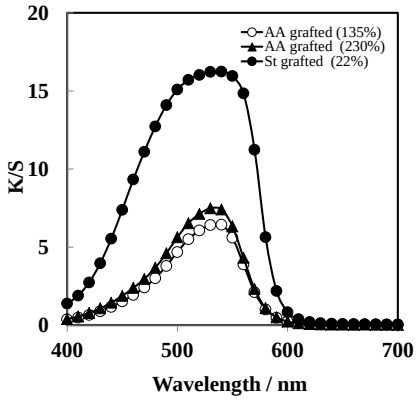

Figure 3 The K/S value from the AA- and sulfonated St-grafted UHMWPE fibers dyed using cationic dye (C.I., Basic Red 46).

Tensile strength: The tensile strengths for untreated fibers, irradiated fibers and grafted fibers were investigated. The results are shown in Figure 4. The strength of the sample stored post-irradiation for 10 days decreased by approximately 20% relative the untreated sample because of γ irradiation, and a strength reduction of approximately 10% was observed using electron beam irradiation. The strength differences between the materials treated with γ ray and electron beam irradiation decreased; the former was irradiated 16 hours in air, and the latter was irradiated for 1 or 2 seconds in nitrogen gas. Therefore, the degrees of oxidation of the samples were different. The strength reduction was likely not influenced by graft polymerization because the strength of the UHMWPE fiber used for graft polymerization by AA was comparable to the sample at room temperature that was stored in air for 10 days. From these results, the strength degradation of the UHMWPE fiber likely arises primarily from oxidization. However, after strength reduction, if the sample is compared with other fibers, its high strength is observed to be maintained.

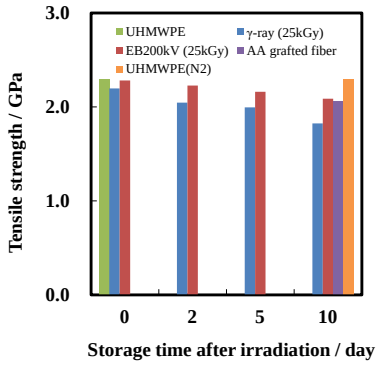

Figure 4 The tensile strength results for unirradiated UHMWPE fibers, irradiated fibers and AA-grafted fibers.

Conclusions: The graft polymerization of UHMWPE fibers stored in air after irradiation was investigated. For graft polymerization of AA, a high grafting yield was achieved with longer storage times, and the AA-grafted fiber was dyed with cationic dye. However, the grafting yield from St after 10 days of storage and 10 h of reaction was only 22%, whereas the sulfonated grafting fiber was intensely dyed with cationic dye. The surface treatment of UHMWPE fiber by graft polymerization using peroxide is a realistic treatment, and its utility is clearly indicated herein.

Acknowledgements: This work was supported by Grants-in-Aid for Scientific Research (Grant Number 24500935) from the Japan Society for the Promotion of Science (JSPS).

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Similar surface damage observed in XLPE acetabular liners across manufacturers

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Introduction: Crosslinked UHMWPE (XLPE) was introduced to decrease in vivo wear compared to conventional polyethylene. Previous work from our implant retrieval laboratory demonstrated that retrieved remelted XLPE acetabular liners demonstrated lower average damage scores than their conventional counterparts from the same manufacturer, and that these damage scores were time dependent, increasing with time in vivo [1]. With the various crosslinking methods, we sought to expand our damage analysis of XLPE acetabular liners to other XLPE designs, specifically those of sequentially annealed XLPE acetabular liners. We sought to evaluate the in vivo performance of the annealed XLPE acetabular liner and determine if patient and implant factors such as length of implantation, component position, and polyethylene liner thickness influence the damage mode and severity observed on retrieved components.

Methods and Materials: Utilizing our institutional IRB approved implant retrieval program, 54 sequentially annealed XLPE acetabular liners (X3®, Stryker, Mahwah, NJ) were identified. Seven liners were excluded from the analysis, leaving 47 liners remaining in the cohort. Patient demographic data, including length of implantation (LOI), body mass index (BMI), reason for revision, and patient age, were collected from medical records (Table 1). The articular surface, backside, and rim of each retrieved component were assessed for damage. Grading for damage scores was performed on the articular and backside surfaces, for eight damage modes, assigning a score from 0 to 3 on the extent of damage coverage in each zone [2]. Grading was conducted by two independent graders. Light microscopy was used to evaluate rim impingement, the presence of furrowing, and backside screw-hole creep. Pre-revision radiographs were reviewed by two independent surgeons for implant abduction angle using Spectra IDS7 imaging software (Spectra Medical AB, Linkoping, Sweden). Comparisons in damage scores were made using the Mann-Whitney rank sum test. Correlations between damage scores and patient factors were examined using a Pearson or Spearman Rank Order correlation where appropriate.

Results: Patient demographics were collected and reviewed (Table 1). The most common reason for revision was instability (62%), followed by infection (13%) and aseptic loosening (9%). Abduction position was categorized as acceptable (30-50°) in 74%, vertical (>50°) in 15% and horizontal (<30°) in 11% of retrieved components. The most common femoral head size was 32mm (range 28-44mm). The median XLPE liner thickness was 7.9mm (3.9-14.7, range). Of the 47 liners, 16 had an elevated rim. The most prevalent modes of damage were scratching, burnishing, and pitting. The average damage score for the articular surface was 21.3 ± 4.7. The backside showed less damage with an average damage score of 8.5 ± 3.5. Thirty-three liners showed evidence of backside screw-hole creep. A majority of the liners had marks of rim impingement (44 of 47). Of the elevated liners, 14 of 16 had impingement; an additional 9 had impingement lesions within the elevated region. Furrowing was seen in 23 of the 47 liners (Fig. 1). No correlation was found between damage scores and LOI, BMI, or component position. Thickness of the acetabular liner did not influence the articular surface damage.

Table 1: Patient Demographics	
Demographics	
Age (Years)	69.7 ± 10.9
Male:Female	17 : 37
Right:Left	24 : 23
BMI (kg/m^2)	26.3 ± 5.5
LOI (months)	16.8 ± 22.14

Discussion: While the clinical performance of XLPE acetabular liners has excellent at long-term clinical follow up, we sought to assess in vivo damage on retrieved sequentially annealed XLPE liners. Comparison of raw damage scores of the current series of annealed liners with previously published data from remelted XLPE liners from a different manufacturer [1] showed no significant difference; similar damage modes were seen on both. Although poorly understood from a mechanistic standpoint, furrowing was seen in 23/47 liners. Mechanical failure has been a concern with XLPE [3]. With the annealed liners, no instances of rim crack were seen; in our previous series rim cracks were seen in 5 of 39 retrieved components, though the difference may be design dependent. Recent concerns with XLPE liners have surfaced regarding optimal polyethylene thickness. While we saw no correlation with increased damage scores in thin liners, our cohort was largely comprised of 7.9mm acetabular liners. The number of liners with impingement lesions was striking, which could be associated with the high number of implants revised for instability. While no difference was noted in the damage on the bearing surfaces of the liners with impingement, the combination of liner thickness and impingement could prove troublesome. Continued long-term retrieval analysis is necessary to determine the in vivo performance of XLPE acetabular liners.

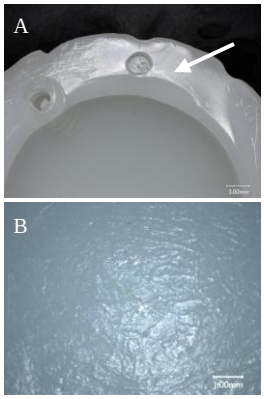

Figure 1: (A) Impingement lesion and (B) furrowing seen on retrieved X3® XLPE liners.

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Impact resistance and fractography in highly crosslinked polyethylenes

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Introduction: First and second-generation of highly cross-linked ultra high molecular weight polyethylenes represent different via to enhance the performances of the conventional UHMWPE [1]. While wear resistance and chemical stability has been significantly improved, some concerns must be considered about ductility, fatigue resistance and especially toughness [2]. We used the double-notched impact Izod test to assess the fracture resistance of XLPEs. Although the impact energy cannot be considered as an intrinsic property of the material, its value is unquestionable from a comparative point of view. Additionally, it could be correlated with the tensile energy to fracture [3].
This work aims to study the influence of the microstructural parameters on the impact toughness. Fractography is also used to study the mechanism involved during the impact. Thus, different UHMWPE medical resins including neat, ^{3}-irradiated and thermal treated were chosen to elucidate the relationship between microstructure and impact response.

Methods and Materials: Three UHMWPE medical grades manufactured in the form of compression-molded sheets were used. GUR 1050 and GUR 1020VE (blended with 0.1 wt% vitamin E) were supplied by Orthoplastics (Bacup, UK), and MG003VE (blended with 0.1 wt% vitamin E) was provided by DSM Biomedical (The Netherlands). Besides, specimens were also prepared for further gamma-irradiation in air at 90 kGy (Aragogamma, Spain). One of them, GUR 1050 resin, was remelted at 150 °C in a vacuum oven (LTE, UK) at 8 and 16 hours, before and after γ irradiation.
Differential Scanning Calorimetry (DSC) were performed (n=3) heating in air from 20 to 200 °C at 10 °C/min in a Q200 Thermal Analysis DSC. Double-notched Izod impact strength was measured by an instrumented CEAST 9050 motorized pendulum. Fractographic analysis were conducted on fracture surfaces from impact specimens and also on these surfaces after an etching process [4] with a Field Effect Scanning Electron Microscope (FESEM) model Gemini (Carl Zeiss AG, Switzerland). Additionally, Transmission Electron Microscopy (TEM) images with a Jeol 100CX TEM was used to determine the lamellar thickness.

Results: The integration of load-deflection, F-´, curves obtained from the Izod impact test revealed remarkable differences in the total impact energy among the different as-received resins. The best tough response, 176.5 kJ/m^2, appeared in the GUR1020VE, followed by the GUR 1050, 94.9 ± xx kJ/m^2, and ended by the MG003VE, 51.0 kJ/m^2. Irradiation effect provided a strong decrease of the impact strength.. Remelting processes led to higher impact energies, which is more relevant for the neat GUR 1050 that for the γ-irradiated specimen. On the other hand, the F-δ curve in GUR 1050 presented several steps or load drops as it could be observed in Fig. 1, which also appeared in the remelted neat resins.

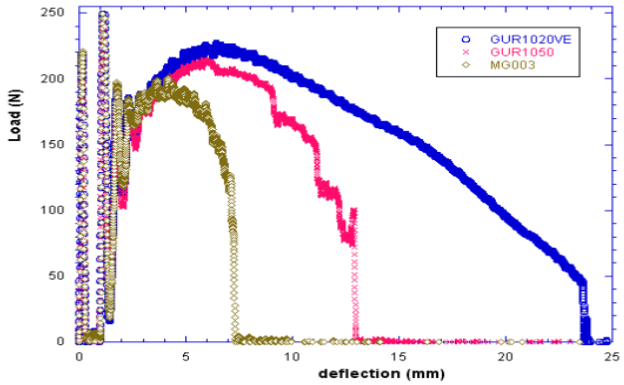

FIGURE 1. Load-deflection curves for the neat resins.

Fractographic studies revealed a fringed structure, which consist of sequential dark and light grey bands, for the neat resins and the non-irradiated and melted GUR 1050. However, monotonic fracture surfaces were obtained for the irradiated samples, regardless of the thermal treatment. The number and size of fringes varied with the type of resin, as can be seen in Fig 2. The higher the number of fringes, the lower impact energy was reached.

a) MG003VE b) GUR1050 c) GUR1020VE

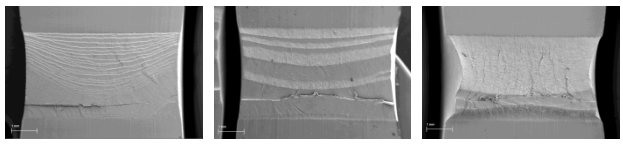

Figure 2. SEM micrographs (x15) of the pristine resins.

Discussion: The fringed structure is associated to ductile and brittle fracture steps, due to a lumpy morphology appears at the highest magnifications in the dark zone and a banding-like structure perpendicular to the impact direction in the light one. We correlate each ductile-brittle transition to the discontinuities appeared in the F-´ impact curve, which could correspond to the initial fast propagation fracture region. The irradiation results in a decrease of impact toughness of the materials, removing the fringed structure and leading to smoother surfaces in the fracture. Additionally, remelting processes resulted in an improved impact behavior which could be explained by the ability of the treatment to remove consolidation defects in the line of [5] and to release internal tensions in the material. Its microstructural analysis reveals shorter lamellar length and thinner lamellar thickness compared to the neat material, besides the appearance of a more

star-like lamellar configuration, which could play a relevant role in the final fracture behavior, in addition to the cross-linking degree and the molecular chain length.

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Wear Performance of MPC-grafted UHWMPE for Total Hip Replacement

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Introduction: With the advent of crosslinking and antioxidants, wear and inflammatory response to wear debris continue to be clinically relevant issues for total hip arthroplasty. Previously, biocompatible phospholipid polymer 2-methacryloyloxyethyl phosphorylcholine (MPC) has been grafted to the surface of UHMWPE to improve its tribological properties[1]. The objective of this study was to explore the wear performance of MPC-grafted UHWMPE acetabular liners against cobalt chrome and ceramic femoral counterfaces.

Methods and Materials: Four test groups (n = 3 per group) were total hip wear tested to determine the wear rates of UHMWPE material with and without MPC grafting against both cobalt chromium and zirconia toughened alumina ceramic femoral heads (Table 1).

Table 1. Study Design.

Study Group	Resin	Crosslinking Dose (kGy)	MPC Grafting	Sterilization	Femoral Counterface	Wear Stations	Load Soak
1	GUR 1020	75	No	Gas Plasma	CoCr	n = 3	n = 2
2	GUR 1020	75	No	Gas Plasma	Ceramic	n = 3	n = 2
3	GUR 1020	50	Yes	25 kGy γ-irradiation	CoCr	n = 3	n = 2
4	GUR 1020	50	Yes	25 kGy γ-irradiation	Ceramic	n = 3	n = 2

For study groups 1 and 2, compression-molded GUR 1020 bar stock was gamma irradiated using 75 kGy and annealed at 120 °C. Acetabular liners were then machined and sterilized using gas plasma. For study groups 3 and 4, compression-molded GUR 1020 bar stock was gamma irradiated using 50 kGy and annealed at 120 °C. Liners were machined from this bar stock, coated with benzophenone and immersed in a solution of MPC (0.5 mol/L). Photo-induced graft polymerization of the liner surface was completed using ultraviolet (350 nm wavelength) irradiation of 5 mW/cm^2 at 60°C for 90 min. Lastly, MPC-grafted UHMWPE liners were sterilized using gamma irradiation at a dose of 25 kGy. Samples were then paired with their respective femoral counterfaces and tested using the waveforms provided in ISO 14242-1 using an AMTI 12 station total hip wear simulator. Testing was conducted to 10 million cycles, stopping every 0.5 million cycles for interval analysis. Interval analysis consisted of gravimetric assessment of the components, photodocumentation, and bovine serum collection and replacement. The gravimetric methods included a standardized cleaning, drying and desiccation procedure for all components and the final mass losses of the wear components were corrected using the load soak components. All testing was conducted in 37 ± 2 °C bovine serum with a protein content of 30 g/L. The resulting mass loss for each component was plotted versus cycle count and a linear regression analysis performed to determine mass wear rate over the 10 million cycle experiment. A student's t-test was used to assess statistical differences between the wear rates for each study group using a significance level of $p \leq 0.05$. Fluid samples from each bearing couple at 1.0 MC, 5.0 MC and 10.0 MC were analyzed using the recommendations in ASTM F1877.

Results: After 10 million cycles of wear testing, the mass wear rate for the non-MPC liners were 4.5 ± 0.67 mg/MC and 1.9 ± 0.40 mg/MC against cobalt chrome and ceramic, respectively. The mass wear rate for the MPC liners were 1.5 ± 1.0 mg/MC and 0.15 ± 0.52 mg/MC against cobalt chrome and ceramic, respectively. The mass loss versus number of cycles has been provided as Figure 1. For both femoral counterfaces the wear rate for MPC grafted UHMWPE was statistically lower than the non-MPC material ($p \leq 0.015$). For the non-MPC material the wear rate was significantly lower for the ceramic femoral counterface ($p = 0.0042$) whereas for the MPC material no statistical difference was observed between the two counterfaces ($p = 0.21$). The average, median and range of the equivalent circular diameter resulting from the particle analysis have been summarized at Table 2. The particles were consistently present in a bimodal distribution, with the majority of particles found in the 0.1-0.2 µm bin and 1.0- 2.0 µm bin for all bearing couples. Additionally, the majority of particles were polymeric, as confirmed using EDS, and were smooth and round in morphology.

Discussion: The hip wear simulation of MPC-grafted UHMWPE demonstrates the material's increased wear resistance under controlled laboratory conditions. Whether the material is paired with cobalt chrome or ceramic femoral counterfaces, the mass wear rate was lower compared to non-MPC crosslinked UHMWPE tested under the same conditions. However, bench testing is the first step in assessing a material's clinical potential and further *in vivo* studies will be required to assess the material's performance clinically.

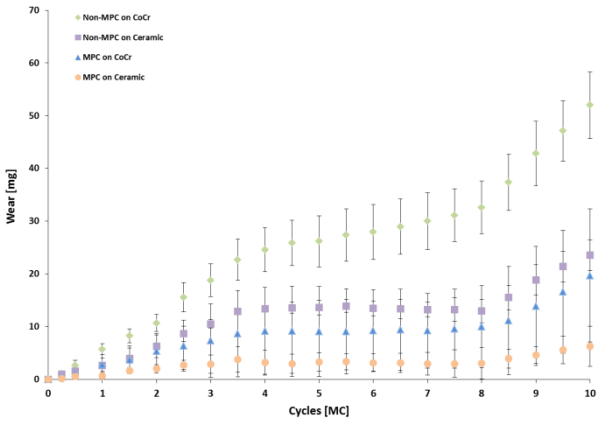

Figure 1. Wear versus number for cycles for all test groups.

Table 2. Particle ECD Results.

Cycle	Head Material	Liner Material	Avg+Stdev [um]	Median [um]	Range [um]
1MC	CoCr	Non-MPC	0.54 ± 0.90	0.20	0.10 - 16.82
1MC	CoCr	MPC	0.60 ± 0.82	0.26	0.10 - 7.51
1MC	Ceramic	Non-MPC	0.65 ± 1.28	0.21	0.10 - 22.96
1MC	Ceramic	MPC	0.57 ± 1.04	0.24	0.10 - 18.26
5MC	CoCr	Non-MPC	0.55 ± 1.10	0.21	0.10 - 18.71
5MC	CoCr	MPC	0.74 ± 1.40	0.27	0.10 - 13.10
5MC	Ceramic	Non-MPC	0.59 ± 0.78	0.22	0.10 - 7.52
5MC	Ceramic	MPC	0.86 ± 1.18	0.32	0.10 - 11.61
10MC	CoCr	Non-MPC	0.31 ± 0.55	0.17	0.10 - 9.99
10MC	CoCr	MPC	0.40 ± 0.70	0.17	0.10 - 6.60
10MC	Ceramic	Non-MPC	0.55 ± 1.13	0.21	0.10 - 22.04
10MC	Ceramic	MPC	0.53 ± 0.75	0.20	0.10 - 8.00

Acknowledgements: Funding and materials for this study were provided by KYOCERA Medical Corporation.

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The relationship between graft polymerization to UHMWPE and the depth distribution of hydroperoxide

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Introduction: Ultra high molecular weight polyethylene (UHMWPE) is an indispensable material in industry and orthopedic medical treatment because it is strong and resistant to wear, among other properties. To use this material in a wider range of fields, the surface treatment must have a higher affinity for other materials. Among the various surface treatment methods, radiation-induced graft polymerization is useful for maintaining the effect of a surface treatment over a long period of time. Although γ-ray sterilization processing is performed using 25 kGy in UHMWPE for medical polymer materials, radicals are generated in such samples through processing for a long period of time, and oxidation slowly promotes degradation [1]. Radicals generated through irradiation react with oxygen first and produce a peroxidation radical. This product further abstracts a hydrogen atom from the PE and generates hydroperoxide. Hydroperoxide can generate a graft reaction as a precursor. However, when it is generated in the atmosphere after UHMWPE treatment in inert gas and introduction of the sample to air or when the radical is a precursor for graft polymerization, such as an early-generated radical, peroxyradicals and peroxide are intermingled, which alters the reaction rates as a function of time [2]. For an especially thick sample, the composition of the surface differs from that of the inside. For a sample in which two or more radicals are used as the precursor for graft polymerization, such radicals have not been studied in detail regarding polymerization. Thus, the research herein aimed to clarify the reaction mechanism of graft polymerization through irradiation and storage in air.

Methods and Materials: Materials and irradiation: UHMWPE sheet (GUR415) samples (1-mm thick) were used. The UHMWPE samples were irradiated with γ-rays from a Co-60 source in air at room temperature using a 1.6 kGy/h dose rate. The total doses were 10 kGy, 25 kGy and 40 kGy. The irradiated samples were stored in air at room temperature in the dark.

Graft polymerization: The methyl methacrylate monomer (MMA) was added to the methanol solution, which included Mohr's salt and concentrated sulfuric acid, and solutions with the following concentrations were generated: 5.6×10^{-5} mol/cm^3, 2.5×10^{-6} mol/cm^3 and 1.0×10^{-4} mol/cm^3. The MMA graft polymerizations were conducted for 2, 4, 6 and 8 hours in a water bath at 70°C. To remove unreacted monomers and homopolymers after the grafting reaction, the grafted samples were extracted using a Soxhlet apparatus for 24 hours and dried in a vacuum oven.

Fourier-transform-infrared-spectroscopy measurements: A Shimadzu AIM8000M microscopic infrared spectrophotometer was used for FT-IR absorption-spectrum measurements. The samples were cut 500-μm thick using a microtome. The sample X-Y stage was moved every 25 μm, and a spectrum was measured from the inside relative to the sample surface. The depth distribution was determined using the oxidization index (OI). The absorption peak for hydroperoxide at approximately 3400 cm^{-1} is weak. Therefore, the UHMWPE sample was exposed to nitrogen monoxide gas (NO), and the height of the absorption peak for nitrate at 1631 cm^{-1} was measured [3]. The graft products were compared with the area under the carbonyl absorption peak at 1731 cm^{-1}, which appears between 1689 cm^{-1} and 1778 cm^{-1}.

Results and Discussion: Graft polymerization: After irradiation, the UHMWPE samples were stored at room temperature in air from day 0 (immediately after irradiation) to day 21. Graft polymerization was performed for 8 hours at 70℃. Figure 1 shows the relationship between the grafting yield and the storage time after irradiation. The grafting yields increased as the dose increased, and the maximum grafting yield according to the storage duration is shown. In the 25-kGy sample, an 8-hour reaction time produced 87%, 120% and 143% of the maximum grafting for 5, 7, and 10 days of storage, respectively.

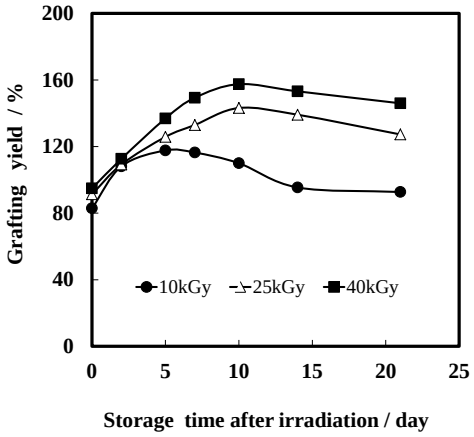

Figure 1 Effect of storage time on the grafting yield of MMA to UHMWPE irradiated with 10 kGy, 25 kGy and 40 kGy in air and stored in air. Graft polymerization was performed for 8 hours at 70°C.

Oxidation distribution: The depth profiles for oxide distribution in irradiated UHMWPEs are shown in Figure 2. The profiles in Figure 2 show a clear symmetry around the center. Immediately after irradiation, the OI gradually decreased to 200 μm and then steeply decreased before leveling out at 400 μm. Although the samples stored for 10 and 21 days maintained symmetry, the OI increased in the central area to more than half of the surface OI. The surface OI increased by approximately 60–70% after 10 and 21 days of storage. When a polymer is irradiated in air at room temperature, the oxygen reacts with radicals

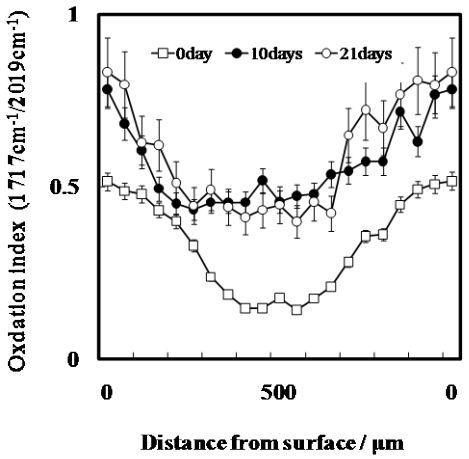

Figure 2 Oxidation profiles plotted as a function of distance from the surface for UHMWPE stored in air after irradiation with 25 kGy for 0 days, 10 days and 21 days. Sample: UHMWPE (500-mm thick and 1-mm wide).

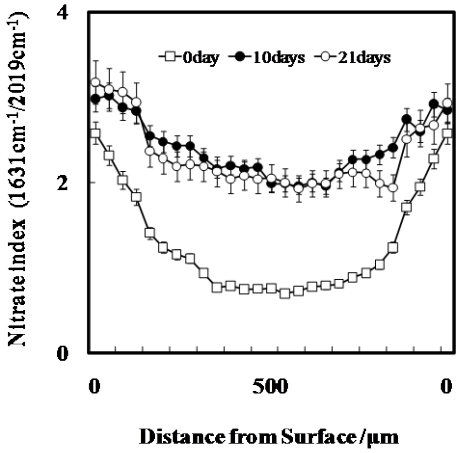

Figure 3 Nitrate from hydroperoxide profiles plotted as a function of distance from the surface for UHMWPE after 25 kGy irradiation in air followed by 24 h of NO exposure for 0 days, 10 days and 21 days. Sample: UHMWPE (500-mm thick and 1-mm wide).

on the polymer backbone to form diperoxides (POOP) and hydroperoxides (POOH). Although these peroxides are stable, heat regenerates the radicals. Diperoxides are typically more stable than hydroperoxides. Therefore, the hydroperoxide behavior is important in graft polymerization to UHMWPE. Although the absorption band of hydroperoxide is in the 3400-cm^{-1} region, the direct measurement of this band in a sample irradiated with 25 kGy is unsuitable because it has a weak absorption coefficient. Nitric oxide gas (NO) treatment can convert the hydroperoxide to its nitrate, which can be measured using FT-IR. The depth profiles for the distribution of nitrates from hydroperoxides were also measured, as shown in Figure 3. The nitrate index in Figure 3 shows the distribution of peroxides only, whereas the OI in Figure 2 shows all of the oxide types, including peroxides. The depth profiles for the grafting products are shown in Figure 4. The absorption spectrum of the MMA carbonyl group is almost flat up to 100 μm from the surface. Almost no carbonyl product is formed in the region between 400 and 600 μm from the surface. This observation differs from the hydroperoxide distribution profiles, as shown in Figure 3. Thus, the grafted MMA molecules are likely bulky and form a barrier to further MMA supply from the surface to the deeper regions. These results strongly suggest that the peroxides are the primary precursors of the grafting reaction. To support this proposition, the peroxide thermal stability was investigated. It was observed that heat treatment for a few hours decreases the peroxide levels.

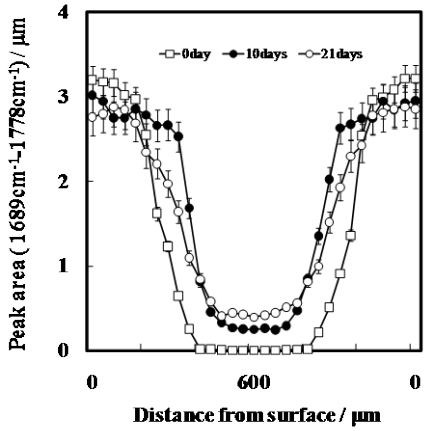

Figure 4 Depth distribution profile for MMA grafted to UHMWPE for 8 hours at 91.4 wt% (0 days), 143.2 wt% (10 days) and 127.3 wt% (21 days). The peaks extend from 1689 cm^{-1} to 1781 cm^{-1} and were acquired from FT-IR measurements of 30-μm sliced films.

Conclusions: In this research, the depth distribution of the oxide and peroxide from an irradiated UHMWPE was investigated, and the relationship between MMA grafting and oxides was clarified. It was concluded that the change in hydroperoxide depth profiles as a function of storage time after irradiation affects the grafting yields for radiation-induced polymerization of MMA to UHMWPE.

Acknowledgements: This work was supported by Grants-in-Aid for Scientific Research (Grant Number 24500935) from the Japan Society for the Promotion of Science (JSPS).

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Effect of mechanical activation on UHMWPE-based composites perspective for cartilage defects replacement

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Introduction: The use of dispersion-strengthening can significantly improve mechanical properties of UHMWPE. However, attention must be paid to the formation of the microstructure of the composite material, which directly affects the resulting mechanical properties. In this work microstructure and mechanical properties of UHMWPE composites filled with Al_2O_3 nanoparticles and microspheres after mechanical activation were investigated.

According to the reptation model of de Gennes and "tube"-model of Doi-Edwards the movement of the molecular chain of the polymer is limited by topological barriers, "tubes", made of the neighboring molecular chains, so the chain can relax only along the "tube". For the long molecular chains of UHMWPE it takes a long time for sintering diffusion. Because of high molecular weight, melted UHMWPE has a very high viscosity and very low self-diffusion parameters of the molecular chains, which leads to difficulty in consolidation and homogenization during sintering. As a result, structural defects in UHMWPE products can occur.

The mechanical properties of UHMWPE composites can be enhanced by accelerating the diffusion of molecular chains in the interparticle boundaries. It was shown, that mechanical activation leads to the formation of low molecular weight chains, which help to increase the speed of inter-diffusion between the boundaries of the polymer particles and hence establishes molecular connectivity between them, consequently, improves the mechanical properties**.**

Methods and Materials: The UHMWPE powder (JSC "Kazanorgsintez", 2×10^6 g/mol) was used as the polymer matrix. Al_2O_3 in the form of nano-powder (average particle size of 20 nm) or microspheres (average particle size of 1 micron) was used as a filler. The initial UHMWPE powder (dried at 100 ºC) and fillers were processed in the planetary mill Fritsch Pulverisette 5, equipped with agate bowl (500 ml) and corundum grinding balls 10 mm in diameter. Thermopressing of mechanically activated mixtures was carried out under a load of 76 MPa with holding at 160 ºC for 50 min and cooling under pressure.

Studies of the chemical bonds of the mechanically activated powders UHMWPE were carried out by IR spectroscopy. To study the effect of shock and shock-shear deformation on degradation and the degree of crystallinity of UHMWPE has been applied differential scanning calorimetry (DSC). Mechanical testing was performed on a universal testing machine Zwick/Roell Z 020. The impact strength was determined by the Charpy-method. The fracture surface was studied by scanning electron microscopy at Hitachi TM-1000 microscope with an accelerating voltage of 5 kV.

The tribological tests were carried out in the mode of friction in distilled water by pin-on-disk method on CETR-UMT-3 (load 50-200 N, T=37 °C). Comparison samples were made from knee and shoulder cartilages of dogs .

Results and Discussion: In all cases, it should be noted, that the ultra-fine particles remain on the surface of polymer particles ("grains") after the mechanical activation. Their homogeneous distribution is hampered by the fact that they do not penetrate into the "grain" body after mechanical activation or hot pressing. When a certain degree of powder filling in the composite is reached, the particles on the surface can form a monolayer completely covering the surface of the polymer powder. As a result, the bonds between individual powder particles can be extremely low. This can be observed when a degree of UHMWPE filling is far from the critical, when the failure mechanism changes.

Due to a high melt viscosity of UHMWPE, the polymer particles retain the shape of initial particles after hot pressing. The mechanical activation in certain modes can contribute to obtaining more dense structure of the composite by changing the shape of initial UHMWPE particles. The reinforcing phase particles, which are much smaller than the original polymer particles, are distributed only over the UHMWPE surface and, therefore, enhance only the boundary strength. The boundary structure and mechanical properties only slightly dependent on the initial dispersion of the powder, due to the aggregation of the filler in the mills of any power density.

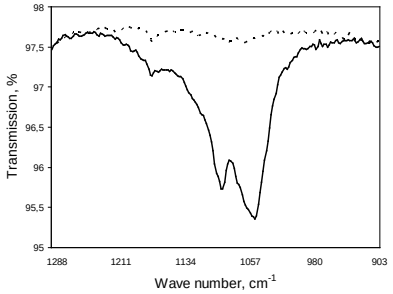

Fig.1 IR spectra of UHMWPE after mechanical activation in a planetary mill for 3 hours

After processing UHMWPE for 3 hours in a planetary mill three new lines appear on IR-spectra (1055 cm^{-1}, 1090 cm^{-1} and 1170 cm^{-1}) associated with increasing of C-O bonds (Fig.1, solid line). This indirectly indicates the rupture of molecular chains of UHMWPE during mechanical activation. According to the DSC analysis the degree of crystallinity of UHMWPE may vary due to the

influence of shear-shock deformation during mechanical activation. Melting point strongly depends on the length of the polymer molecular chain. The decrease in the melting temperature of 1,8 °C indicates the formation of low-molecular chains due to their scissoring during mechanical activation. Low molecular chains contribute to a better sintering of the particles of UHMWPE. The destruction of crystalline formations UHMWPE can be seen in decreasing of the degree of crystallinity of 9%. The increase in quantity of the amorphous phase can have a positive effect on reducing the sintering time due to the fact that the diffusion of macromolecules UHMWPE realized through the amorphous regions.

Elongation at break can be an indicator of structural defects elimination. Microstructure of composites after mechanical activation is more homogenous and elongation is higher in 2 times (Fig.2).

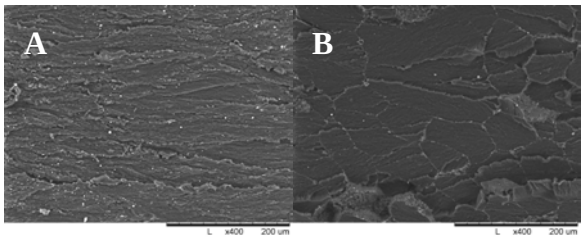

Fig.2 Microstructure of UHMWPE-composites' break surface after tensile-tests. Composites (A) with mechanical activation, (B) without mechanical activation

The destruction of UHMWPE, like other amorphous-crystalline polymers, can be performed by the mechanism of microcracks propagation. "Grains" of UHMWPE are insulated with ceramic dispersed particles, preventing the spread of cracks in the unfilled areas in this regard. Because of this fact, in these composites an intergranular fracture is mainly observed. As a consequence, there was a significant increase in impact strength of the composite by increasing the mass fraction of ceramic particles. Hollow spherical particles can behave as pores and increase the angle of a crack and prevent propagation of microcracks.

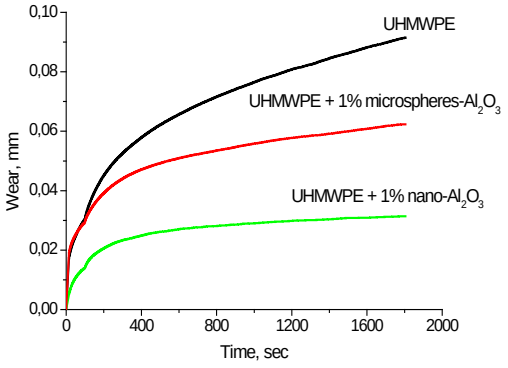

Fig.3 Wear of UHMWPE and UHMWPE-based composites filled with Al_2O_3 of different types

Reduce of wear of UHMWPE filled with Al_2O_3 (Fig.3), also accompanied by a decrease in the coefficient of friction. The composite UHMWPE+3%microsheres-Al_2O_3 has the most low coefficient of friction. Average coefficient of friction was equal to 0.056 and was the closest to the value of the coefficient of friction of joint tissue (Fig.4). The friction coefficient becomes stable sooner than the cartilage tissue - after 15 minutes of friction. Continuous transfer film was observed for all types of samples except UHMWPE filled with Al_2O_3 nanoparticles. It may be due to abrasion of a surface.

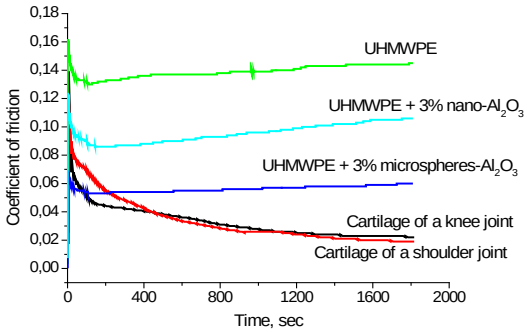

Fig.4 Coefficients of friction of various materials

The friction coefficient of the composite materials based on UHMWPE decreases when the load increases, due to reduced adhesive component of the coefficient of friction. Hardness increases by increasing the degree of filling of UHMWPE, causing a reduction of the deformation component and decrease of friction coefficient. This dependence is observed up to 3% wt. When there is a greater degree of filling the friction coefficient and the wear are increasing, due to the fact that the nano-particles cover a polymer particle with a monolayer, deteriorating sintering of UHMWPE "grains".

Biocompatibility of the material was studied in vitro and in vivo. Also a hemispherical samples 1.0×1.8 mm were implanted in the knee joints of rats. Histology of implanted samples and the surrounding tissues was studied. Important indicators are the state of the cartilage surface that contacts with the implant and a motor activity of the animals. There were no signs of acute rejection and no macrophages in the contact zone. It should be noted that during functioning of implant in the joint for 3 months there were no motor activity disorders.

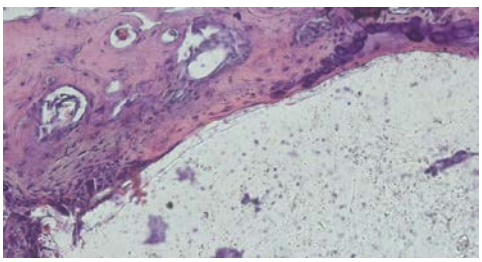

Fig.5 The boundary between the surface of the implant and surrounding tissues

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Fracture of highly cross-linked UHMWPE liners: An analysis of 75 reports of a single design to the FDA

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Introduction: Cross-linking improves wear resistance but has been associated with decreased mechanical properties and reports of polyethylene fracture. We reviewed the reports of fractures to the US Food and Drug Administration (FDA) observed with a single type of highly cross-linked UHMWPE (HXLPE) acetabular liner. Our goals were to more accurately understand the incidence and cause of these fractures as well as to determine any factors that could minimize the likelihood of this complication.

Methods and Materials: A search of the FDA Manufacturer and User Facility Device Experience database was carried out for a single type of HXLPE acetabular liner. Catalog numbers, event date, need for re-operation, description by the submitting party, and manufacturer narrative, were evaluated.

Results: Among 420 records of adverse events, 75 reported on an unequivocal fracture of this type of liner. The reports of fractures increased from 2 observed from 1999 to 2003 to 37 between 2009 and 2012. The average time-in-situ of the liners was 27 months (1 to 96). The polyethylene thickness in the weight-bearing portion was <= 6 mm in 60 cases and <= 7 mm in 69 cases. The polyethylene thickness at the rim where most of the fractures occurred, was <= 3.7mm in 62 liners, and <= 4.7mm in 71 liners. Sixty five cups had a diameter of <=56 mm; and 56 fractured liners were articulating with large diameter heads (>=36mm) (Table 1). Following fracture, all patients required revision surgery for instability or pain, and articulation of the metal shell and prosthetic metal head was common.

Table 1: Analysis of Liner Variables

Variable		n	Unknown
Head size (mm)	28	4	2
	32	13	
	36	52	
	40	3	
Cup size (mm) *	48	7	2
	50-52-54	43	
	56	14	
	58	6	
	60	1	
	62	1	
WB PE thickness	<=6mm	59	2
	>6mm	13	
Rim PE thickness	<=4.6	68	2
	>4.6	4	
Geometry	Standard	37	3
	10	31	
	20	3	
Hx of fall		6	
Hx of dislocation		18	

Discussion: While only 6 fractured HXLPE acetabular liners of this design have been reported in the orthopaedic literature, 75 have been reported to the FDA. This suggests that the orthopaedic community underestimates the prevalence of this complication. Thin HXLPE liners, articulating with large diameter heads were prevalent in this series and should be avoided whenever possible. A minimum polyethylene thickness of 4.7 mm at the rim may provide substantial protection against fracture. After liner fracture, the unnatural articulation of the prosthetic head with the backside surface of the shell produces metalosis and implant damage, and expeditious revision surgery is required.

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Effect of Gamma Irradiation and Head Size on the Wear of Moderately Crosslinked UHMWPE Inserts with EtO Sterilization in a Hip Simulation Study

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Introduction: Moderately crosslinked polyethylene maintains a balance of wear resistance and mechanical properties. The GVF poly was manufactured from GUR1020 UHMWPE bars, sealed in vacuumed foil package, and gamma sterilized at 4 Mrads. The MARATHON® polyethylene inserts were manufactured from GUR1050 UHMWPE bars, crosslinked by gamma irradiation at 5 Mrad, and followed by a remelting process that eliminates free radicals. The final sterilization method is gas plasma (GP) or ethylene oxide (EtO). Both methods will not introduce free radicals.

Previous studies have shown MARATHON polyethylene (GP sterilized) with 83% lower wear than conventional polyethylene in a simulation test [1], compared to a 10-year clinical study that showed 77% wear reduction [2]. There is no study to compare the wear performance of MARATHON (EtO sterilized) and conventional poly.

In the current study, effect of slightly increased gamma irradiation on wear reduction was investigated by comparing MARATHON (EtO) to conventional poly (GVF). With the wear reduction in MARATHON, one can afford to use larger head size, which has the dual benefits of increased joint stability and improved head/shell ration for better range of motion.

Materials and Methods: Four groups of polyethylene inserts (Table 1) were paired with matching femoral heads that were manufactured from CoCrMo (ASTM F1537) with diameters of 28, 32, and 36 mm. The inserts were chosen to have similar thickness at the dome for MARATHON, while for GVF it was the largest head size available.

Group	Material	ID/OD* (mm)	Dome Thickness (mm)
A	GVF	32/52	6.9
B	MARATHON	36/52	5.5
C	MARATHON	32/48	5.9
D	MARATHON	28/44	5.6

Table 1. Summary of test groups (ID = insert inner diameter; OD = outer diameter of the backing shell)

Wear testing was performed on a 12-station hip simulator (AMTI, Watertown, MA) per ISO 14242-1 standard [3] at 1Hz using the described inputs (Table 2), which provide a larger range of motion than the ISO standard. The cups were mounted in accordance with ISO 14242-1 using custom fixturing and secured with cement while the femoral heads were mounted on a vertical taper support. Testing was performed in 25% bovine calf serum (Hyclone Laboratories, Logan UT) at 37±2°C with sodium azide (0.2%wt) and EDTA (20mM). At 0.5 Mcyc intervals, the components were cleaned for analysis and the serum was replaced. Wear of the inserts was determined gravimetrically at 0 Mcyc and then after each 0.5 Mcyc interval using a digital balance (XP250, Mettler-Toledo). A corrected wear value was computed by incorporating the apparent weight gain of non-articulating loaded soak controls. Finally, wear rates were calculated by linear regression and then compared between the groups using ANOVA analysis (α=0.05).

	Forces and Motions
Vertical Force	300N – 3000N
Flexion/Extension	±23°
Abduction/Adduction	±9°
Inward/Outward Rotation	±10°

Table 2. Test inputs

Results: The total wear over 5-million cycles and the wear rate of each group is in Figure 1. The wear of GVF (Group A) was the highest over that of the MARATHON (Groups B, C and D), with a wear reduction of 53%, 61%, and 74%, respectively. For MARATHON, there was a 7% wear increase per mm increase in head size ($p<0.01$).

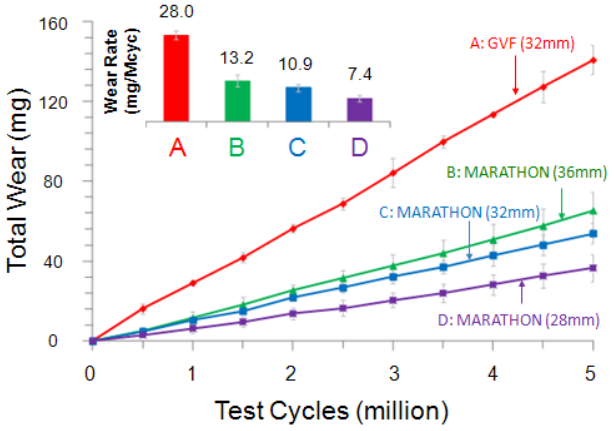

Figure 1. Cumulative wear for the GVF and MARATHON ETO polyethylene inserts. The inset graph reports mean wear rates. All error bars represent 95%CI.

Discussion: The fact that the wear of MARATHON was at least 53% lower than that of GVF suggested that the poly wear was primarily affected by gamma-irradiation dose used for crosslinking of the polyethylene. In addition, the lower wear of MARATHON provides an option of using large head size which has the dual benefits of increased joint stability and improved head/shell ratio for better range of motion.

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Influence of radial mismatch and UHMWPE additivation on glenoid liner wear performance

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Introduction: Shoulder joint is a non conforming coupling, and as such, restoring its functionality with artificial replacements has been a challenge for many years. Currently, there is no consensus in the literature about the ideal mismatch between a prosthetic humeral head and a UHMWPE glenoid component in total shoulder replacement systems (TSRs). It has been indicated in several studies that a radial mismatch of 4 mm [1-4] allows to simulate the best glenohumeral kinematic. From a literature overview, to avoid joint instability and wear, the recommended radial mismatches varies between 2 and 10 mm [5, 6]. From a tribological point of view, it is believed that having high values of radial mismatch will imply a higher wear rate. For this reason, a limited mismatch is generally suggested. In case of a metal backed system, having an excessive wear rate will lead to the risk of un-permitted metal back articulation against the humeral head, and consequently to metal wear and ion release. Therefore, verifying that the chosen radial mismatch ensures not only a proper biomechanical restoration, but also does not compromise the *in vivo* performance of the whole system in terms of wear and degradation is a key factor.
The aim of this study is to compare the influence of radial mismatch on the wear between different materials in UHMWPE metal backed glenoid liners.

Methods and Materials: UHMWPE formulations (standard and vitamin E crosslinked blended and irradiated), with different wear resistance properties were tested. 2+2 soaking controls (loaded and unloaded) UHMWPE liners (SMR System - Limacorporate, IT) were tested in a wear testing apparatus against two different CoCr humeral heads sizes, Ø40mm (smallest diameter available) and Ø54mm (largest diameter available). Two coupling configurations were chosen for each humeral head size, by varying the liners UHMWPE type (standard, and vitamin E crosslinked blended 75kGy irradiated).
Radial mismatches for the Ø54mm and the Ø40mm couplings were 8mm and 13mm respectively.
Component positioning and loading, as well as angular motions and translations, were applied to the coupling according to previous similar studies [7]. The glenoid liner components were horizontally upwards oriented with a constant force vector vertically downwards applied (750N). Rim loading was achieved at maximum abduction and at maximum adduction. Moreover kinematic simulations were performed to check test parameters. Table 1 summarizes the input parameters for the test apparatus. Wear was evaluated by gravimetric weight loss, by measuring liners weight with an high precision balance (Sartorius BP211D) at 100k, 200k, 500k and 1M cycles. Test environment, liner cleaning procedure and soaking controls were realized as indicated in the reference standards [8].

Wear Test Parameter	
Force maximum	0,75 KN
Frequency	1,0 Hz
Elevation	+11,5°/-11,5°
Flexion-extension	+23°/-23°
Abduction-adduction	+23°/-23°
Test-fluid	Newborn calf serum
Test fluid temperature	37°C±2°C

Table 1. Wear test parameters

Results: Figure 1 shows the wear amount for all the configurations tested. With Ø40mm humeral head, weight loss for standard, and vitamin E irradiated UHMWPE was 0,019 and 0,008 g/10^6cycle, respectively. With Ø54mm humeral head, the reached values were instead 0,056 and 0,016 g/10^6cycle respectively.

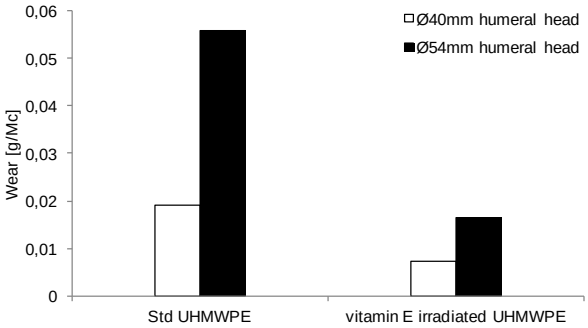

Figure 1. Wear test results

It can be observed that standard UHMWPE showed the highest wear values for both humeral heads sizes, while vitamin E crosslinked blended and irradiated UHMWPE showed a considerably lower wear rate. Further, the measured weight loss was higher for Ø54mm heads, for the two material tested.

Discussion: Our findings clearly indicate that the choice of a smaller humeral head size (i.e. higher mismatch) allows to obtain lower wear.
The lower wear rate obtained for a higher radial mismatch coupling is not in agreement with results published on knee prosthesis. Biomechanical wear tests on knee prosthesis indeed showed that increased congruency (i.e. lower radial mismatch) contributes to reduction of contact stresses resulting in a reduced wear rate (9-11). Conversely, a higher radial mismatch implies a reduction

of the contact areas, with consequent increase of local contact stresses up to values that could exceed mechanical strength of UHMWPE. For the Ø40mm humeral head-liner coupling (higher radial mismatch), the combination of a reduced sliding contact area and local stresses not exceeding the material yield strength may be factors that contributed to the lower wear rates observed in this case [12]; further investigation and biomechanical tests will be required to assess which parameters may play a major role for the observed behavior. In order to further minimize wear rate, a proper material choice should be considered. In this sense, vitamin E additivated UHMWPE has shown to be a valid solution for the *in vivo* performance of the TSR systems.

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Regulation of radical reactions in electron-beam irradiated *dl*-α-Tocopherol blended Ultra High Molecular Weight Polyethylene

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Introduction : *dl*-α-Tocopherol blended Ultra-High Molecular Weight Polyethylene (UHMWPE) was originally developed as a material for total knee arthroplasty (TKA) , and various results have demonstrated that the material reduces the incidence of delamination failure and lowers the amount of wear produced during knee simulator testing. (1, 2) In addition, it was found that the wear particles from *dl*-α-Tocopherol blended UHMWPE elicited a reduced biological response compared to conventional UHMWPE.(3)

In order to use *dl*-α-Tocopherol blended UHMWPE in total hip arthroplasty (THA), electron-beam irradiation has been utilized to achieve crosslinking. However, it is hypothesized that *dl*-α-Tocopherol radicals, which are formed during irradiation, may alter the biological activity of the material. Additionally, subsequent reactions can lead to the formation of α-Tocopheryl quinone and multimeric complexes that can also influence the biological behavior of the material. In this study, different attempts were made to regulate the formation and subsequent transformation of *dl*-α-Tocopherol radicals within electron-beam irradiated *dl*-α-Tocopherol blended UHMWPE.

It is well known that the *dl*-α-Tocopherol radicals are reduced by antioxidants like vitamin C and ubiquinol in vivo. However, this reaction has not been clarified in polyethylene. Therefore, as a preliminary experiment, ascorbic acid 6-palmitate was used to dope electron-beam irradiated *dl*-α-Tocopherol blended UHMWPE in an attempt to reduce *dl*-α-Tocopherol radicals. In addition to this, cold temperature irradiation was used in an attempt to regulate the formation and preservation of *dl*-α-Tocopherol radicals within electron beam irradiated *dl*-α-Tocopherol blended UHWMPE.

Materials&Methods : For the *dl*-α-Tocopherol blended samples, UHMWPE resin powder was mixed with *dl*-α-Tocopherol at 0.3 wt% and direct compression molded in a vacuum at 25 MPa and 220°C, while non-blended (Virgin) samples were produced similarly, but without the addition of *dl*-α-Tocopherol . Cylindrical pins (length : 40 mm, diameter : 3.5 mm) were then machined from these bulk samples, packaged in a vacuum, and irradiated by electron-beam at 300 kGy.

For the doping experiments, samples were doped with ascorbic acid 6-palmitate at room temperature under hydrostatic pressure (100 MPa) for 1 and 2 weeks. Ascorbic acid 6-palmitate solutions were produced by dissolving ascorbic acid 6-palmitate powder into ethanol. As a control, samples were also placed in undiluted ethanol.

For the cold temperature irradiation experiments, cylindrical pins were produced as above, and subsequently irradiated at 25°C or -80°C using frozen carbon dioxide.

For both the doping and cold temperature irradiation experiments, Electron Spin Resonance (ESR) was used to measure *dl*-α-Tocopherol radicals, while High Performance Liquid Chromatography (HPLC) was used to measure the amount of *dl*-α-Tocopherol following chloroform extraction.

Results : Under hydrostatic pressure, the samples doped in ascorbic acid 6-palmitate displayed increased *dl*-α-Tocopherol radical reduction compared to the samples placed in ethanol (Fig.1). Samples doped with ascorbic acid 6-palmitate under hydrostatic pressure also exhibited greater amounts of *dl*-α-Tocopherol compared with samples placed in ethanol (Fig.2).

Fewer *dl*-α-Tocopherol radicals were observed in the samples irradiated at -80°C compared to those irradiated at 25°C (Fig.3). Additionally, radiation at -80°C resulted in an increase in the amount of *dl*-α-Tocopherol relative to irradiation at 25°C (Fig.4).

Discussion : Due to the increased amount of *dl*-α-Tocopherol and the reduction in *dl*-α-Tocopherol radicals for the ascorbic acid 6-palmitate doped samples under hydrostatic pressure, it is thought that the ascorbic acid 6-palmitate was successful in reducing at least some *dl*-α-Tocopherol radicals. However, it is necessary to confirm these results with a larger number of samples, and perform a quantitative analysis with respect to biological response. Specifically, it is necessary to consider the total amount of reduced *dl*-α-Tocopherol and whether such an amount will influence the biological activity of the material.

There are several possible mechanisms by which the amount of *dl*-α-Tocopherol radicals was lower and the amount of *dl*-α-Tocopherol was higher for the samples irradiated at -80°C. First, it is thought that the initial formation of *dl*-α-Tocopherol radicals can be inhibited through irradiation at low temperatures. Other ESR and FT-IR results (not shown) also showed the presence of polyethylene alkyl radicals and a lower double bond index for specimens irradiated at -80°C. Therefore, it is also possible that polyethylene radical- *dl*-α-Tocopherol radical reactions were enhanced. More work, however, is necessary to further clarify these mechanisms.

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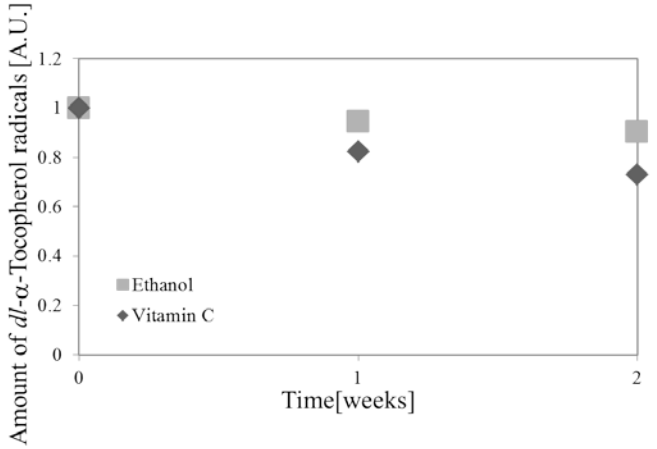

Fig.1 Amount of *dl*-α-Tocopherol radicals in electron beam-irradiated *dl*-α-Tocopherol blended UHMWPE under hydrostatic pressure (100MPa) with and without doping with ascorbic acid 6-palmitate.

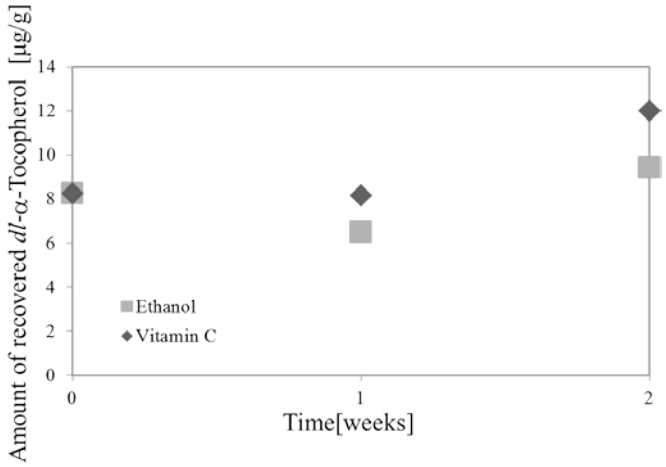

Fig.2 Amount of *dl*-α-Tocopherol in electron-beam-irradiated *dl*-α-Tocopherol blended UHMWPE under hydrostatic pressure (100MPa) with and without doping with ascorbic acid 6-palmitate.

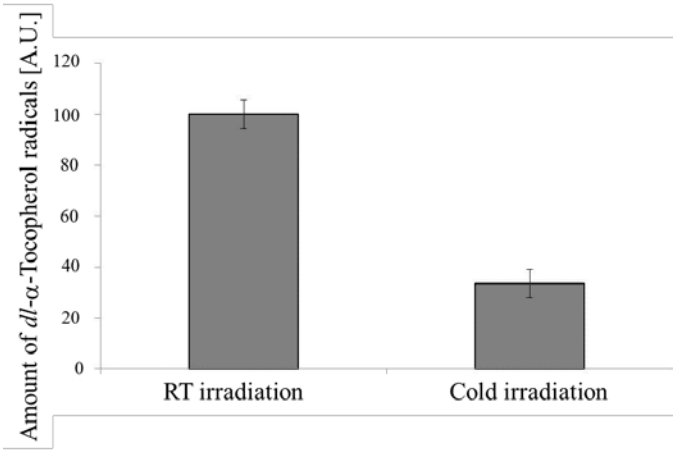

Fig.3 Comparison of amount of *dl*-α-Tocopherol radicals for samples irradiated at 25°C and at -80°C.

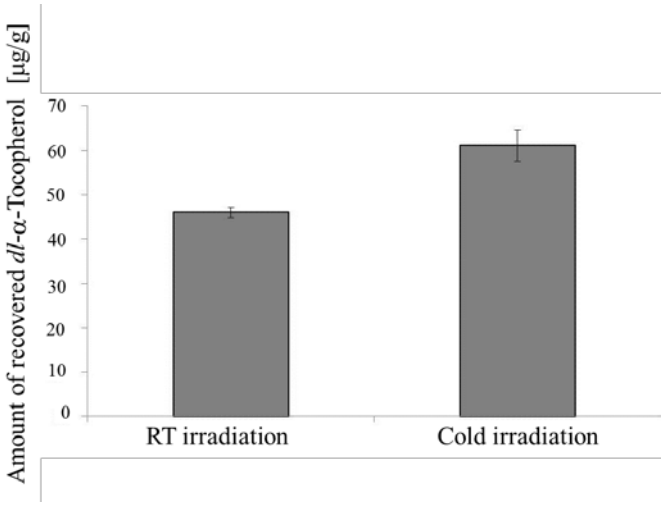

Fig.4 Comparison of amount of *dl*-α-Tocopherol for samples irradiated at 25°C and at -80°C.

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THE EFFECT OF SAMPLE PREPARATION AND MEASUREMENT SETUP, ON OXIDATION INDEX AND TRANS-VINYLENE INDEX ANALYSIS OF UHMWPE.

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INTRODUCTION

The definitions within ASTM F2102 for Oxidation Index and ASTM F2381 for Trans-Vinylene Index, do not specify the equipment setup (e.g use of a BaF_2 crystal) or the sample preparation methodology. This study investigates the effects of FTIR analysis on UHMWPE containing 0.1% Vitamin E material (namely Ticona GUR1020-e).

MATERIALS AND METHODS

The equipment used during the evaluation was a NICOLET iN10 FTIR and OMNIC Picta Software. The Crystal used was Barium Fluoride Crystal. The UHMWPE GUR1020-e materials were processed by compression moulding techniques at Orthoplastics Ltd. In addition cross-linked materials were Gamma irradiated within a range 70-80kGy. Test specimens were microtomed from a 10mm cross section to a thickness of 200µm and 270µm.

Four different variants were assessed during the study;

CONTROL

Microtomed specimen

LENS CLEANER

Surface cleaned using a Whatman Lens Cleaning Tissue

LIGHTLY SANDED

Sanding with light pressure to the surface of the sample using 600 Wet & Dry Sand paper.

SANDED

Sanded with heavy pressure until sample was opaque using 600 Wet & Dry Sand paper.

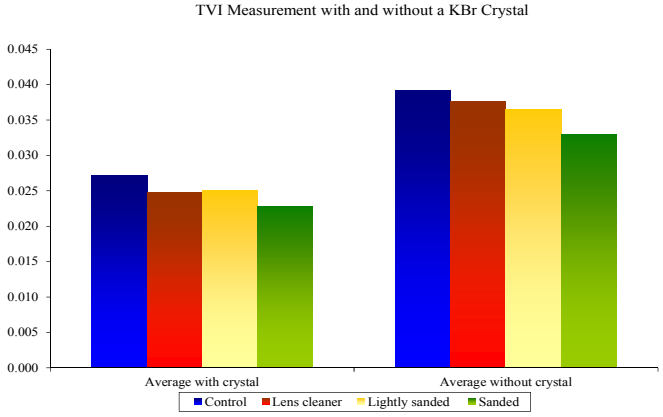
ANALYSIS

The samples were tested using 32 scans in transmission, and the peaks were measured using a macro at the following points.

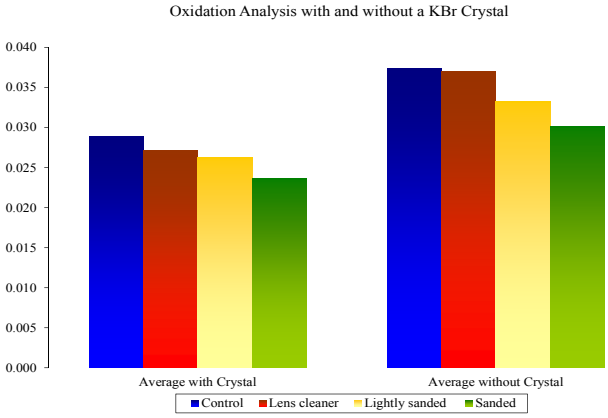
	Orthoplastics Ltd	ASTM
OI	1708cm^{-1} – 1728 cm^{-1}	Centered @ 1720 cm^{-1}
TVI	945cm^{-1} – 980 cm^{-1}	Centered @ 965 cm^{-1}
Normalisation Peak	1370 cm^{-1}	Centered @ 1370 cm^{-1}

RESULTS AND DISCUSSION

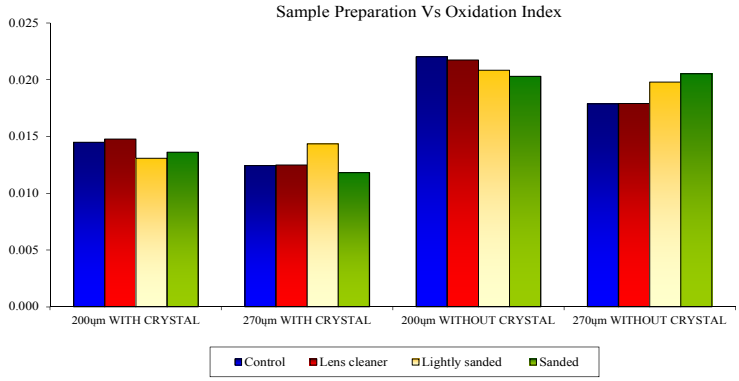
The TVI results show a significant difference when using a BaF_2 crystal. This effect is also noted when analysing the different sample preparation techniques/variables.

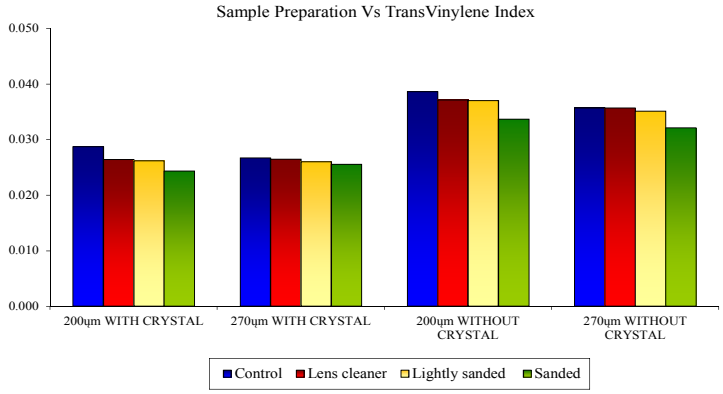


The effect of using a crystal in determining oxidation characteristics is also evident



Specimen thickness was evaluated with and without the BaF_2 crystal @ 200µm and 270µm; As you can see on the two graphs, the results show little difference between the two thicknesses for both Oxidation and TVI with and without using a BaF_2crystal.





CONCLUSIONS

Evaluation of Trans-Vinylene and Oxidation Index via FTIR within the study concludes the following;

The use of a BaF_2 crystal during the analysis significantly affects the reported data, showing both higher TVI and OI values.

Sample preparation is critical when chemical characterising a UHMWPE material via FTIR and should be included within the reporting of any values.

FURTHER STUDIES

- The using of complex macros in evaluation of peak area.
- Sample conditioning and time to analysis.
- ATR Vs Transmission

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Third Body Wear of Vitamin E Blended Highly Cross-linked Polyethylene in a Hip Simulator

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Introduction: In total hip arthroplasty (THA), accelerated wear will be observed when third-body particles migrate into the bearing surface. Third-body particles can be defined as a contamination of the bearing environment with debris not originating from the femoral head–acetabular liner articulation [1]. Gozzini et al. [2] reported small ceramic particles within XPE liners which were retrieved from a THA system used after replacing a fractured ceramic femoral head by a CoCrMo alloy femoral head where the well-fixed acetabular component was not replaced. The ceramic particles ranged from 2 µm to over 100 µm. Head subluxation is assumed to increase the number of third-body particles that enter the otherwise closely conforming articular bearing space and become embedded in the liner, when compared to level-walking cycles alone [3]. However, within this *in vitro* study no additional subluxation cycles were simulated.
The purpose of this study was to investigate the wear behavior of the Trinity™ THA system consisting of vitamin E-blended highly cross-linked polyethylene inserts in a) a "clean" test environment (group 1) and b) in a "contaminated" test environment (group 2) to evaluate the affect of severe head damage on polyethylene wear.
The particle size and Al_2O_3 concentration used for test environment contamination were based on pilot studies conducted by Bragdon et al. [4] resulting in similar wear rates and surface wear features to those seen in retrieval studies of polyethylene components known to have been subjected to third-body wear [5]. Smaller particles can be assumed to easily enter to the bearing space during simulated level walking even without applying subluxation cycles.

Methods and Materials: ECiMa™ polyethylene inserts with an articular diameter of 40mm were articulated against CoCrMo femoral heads. ECiMa™ is highly cross-linked polyethylene containing vitamin E consolidated through direct compression moulding. The material (GUR 1020) is processed through steps of cold irradiation (120kGy) followed by mechanical annealing (CiMa) [6] allowing the material to be processed below the melting temperature thereby maintaining crystallinity and mechanical properties, including fracture toughness [7]. . The inserts were fixed within Trinity™ cluster shells (size 56 mm). Al_2O_3 particles (particle size of 1 µm, deagglomerated alpha alumina; Micropolish® II, Buehler, Lake Bluff, IL, USA) with a concentration of 0.15 mg/cm³ test fluid were used for test environment contamination [4].

All specimens were tested according to ISO 14242-1 (2012) using the EndoLab® hip joint simulator. Each group consisted of six specimens (n=6) plus two loaded soak controls. Inserts of group 2 ("contaminated" test environment) were artificial aged by heating to 70°C under 5.03bar O_2 for 14 days according to ASTM F 2003-02 prior to wear testing. Inserts of group 1 ("clean" test environment) were not artificially aged. Group 1 was tested to 5 million load cycles and group 2 was tested to 3 million load cycles. The test fluid was exchanged every $5x10^5$ cycles.

To maintain the third-body particle suspension in the test fluid, the test fluid of each test chamber was circulated by peristaltic pumps (see Figure 1).

Figure 1: EndoLab® six station hip joint simulator according to ISO 14242-1 modified with two peristaltic pumps.

Results: After 5 million cycles the ECiMa™ inserts of group 1 showed a mean wear rate of 1.84 mg per million cycles (StdDev. 1.02). A mean wear rate of 92.29 mg per million cycles (StdDev. 24.58) was established for the ECiMa™ inserts of group 2 after 3 million cycles. Figure 2 (group 1) and Figure 3 (group 2) show the average wear of the inserts tested as a function of the number of cycles.
After testing, all components were examined under light microscopy. ECiMa™ inserts of group 1 showed polishing with slight scratching and original machine mark residuals evident at the contact area. All ECiMa™ inserts of group 2 showed a polished scuffed surface with heavy irregular scratches. Femoral heads of group 2 showed areas with dull appearance and slight matting of the surrounding contact area. A representative photograph of one femoral head is shown in Figure 5.

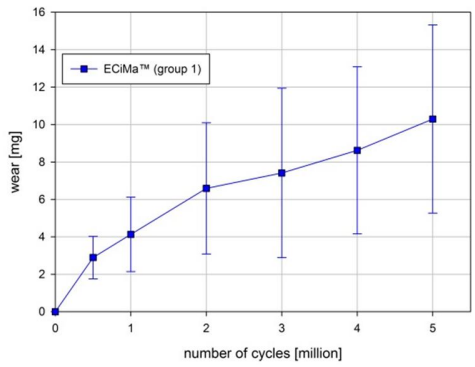

Figure 2: Mean wear (n=6) vs. number of cycles of the ECiMa™ inserts of group 1 ("clean" test environment).

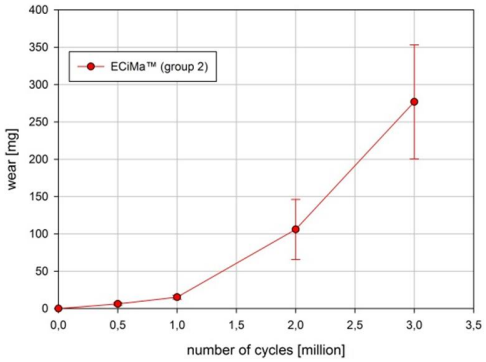

Figure 3: Mean wear (n=6) vs. number of cycles of the ECiMa™ inserts of group 2 ("contaminated" test environment).

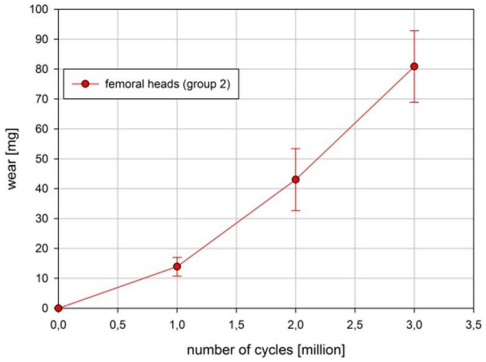

Figure 4: Mean wear (n=6) vs. number of cycles of the femoral heads of group 2 ("contaminated" test environment).

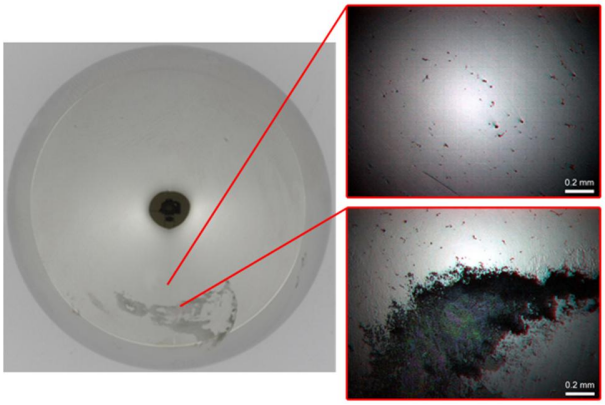

Figure 5: Representative femoral head of group 2 after 3 million cycles. The anterior position is orientated to the right side of the picture.

Discussion: ECiMa™ test results of group 1 indicated ultra low wear rates; 95% reduction compared to UHMWPE and 83% reduction compared to HXLPE [6] with the potential to reduce wear-related osteolysis i*n vivo*.

Al_2O_3 particles added to the test environment continuously abraded the metal femoral head surfaces with increased cycle count. The wear rate of the ECiMa™ inserts of group 2 increased progressively which correlate to the progressively increased wear of the CoCr femoral heads (see Fig. 3 and Fig. 4). Artificially ageing and adding Al_2O_3 particles to the test environment of group two resulted in a fifty-fold increase in the wear rate of the ECiMa™ when compared to the results of group 1. The wear rate determined for group 2 is approximately 2.3 times higher than the wear rate determined for conventional UHMWPE (GUR 1050) tested in standard conditions ("clean" test environment) [6]. Although the contamination of the test environment by Al_2O_3 particles is not commonly encountered clinically, this could represent a severe case of third body wear [4].

Acknowledgement: The tribology tests were performed at EndoLab® GmbH and were funded by Corin Ltd.

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Correlation between mechanical and oxidative stability of various UHMWPE materials

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Introduction: Wear particle induced osteolysis as a clinical problem has been the driving force behind the advancement in crosslinked Ultra High Molecular Weight Polyethylene (UHMWPE) technologies. Post radiation thermal treatments allow residual free radicals to combine with each other thereby creating an oxidant resistant material. However, these treatments reduce the mechanical properties and fatigue strength of the UHMWPE [1]. The rationale behind stabilizing the residual free radicals in highly crosslinked polyethylene with anti-oxidants was to provide an oxidation and wear resistant material without compromising the mechanical properties. Antioxidants can be incorporated into UHMWPEs either by blending or by diffusion after crosslinking. New research has shown that lipids absorbed into highly crosslinked polyethylene during *in-vivo* use may accelerate the oxidation reaction and lead to a reduction in mechanical properties [2]. This study evaluates the correlation between the oxidative and mechanical stability of various UHMWPE materials in the presence of lipids under long-term aging conditions.

Methods and Materials: *Remelting:* Virgin GUR1020 bars were gamma radiated to a dose of 100kGy and remelted at 150°C. *Blending:* GUR1020 UHMWPE powder was blended with vitamin E to a final concentration of around 0.1 wt %. The blend was then consolidated through a sheet molding process to form bars and was either warm irradiated by e-beam or cold irradiated by gamma at a dose up to 150kGy. Samples of dimension 2 x 1 x 1 cm were machined from the irradiated bar. *Diffusion:* GUR1020 UHMWPE powder was consolidated through Isostatic Compression Molding (ICM), pre-forms machined from the barstock were irradiated to 100kGy by gamma radiation and subsequently diffused with vitamin E. Samples of dimension 2 x 1 x 1 cm were machined from these vitamin-e diffused pre-forms. After machining, the samples were barrier film packaged and gamma sterilized (25-40kGy).

All anti-oxidant materials were soaked in Squalene, a lipid commonly found in synovial fluid, at 120°C for 4 hours. The remelted material was soaked in Squalene for 2 hours at 120°C. After doping, Fourier Transform Infrared Spectroscopy (FTIR) was used to ensure that the amount of squalene absorbed in the samples from the two groups was consistent. The blocks were then placed in an oxygen environment at 5 atm and 70°C for 4 or 6 weeks. Post aging, each sample was cut in the middle along the length using a band saw, and 200µm thick cross sections were microtomed from one half of the sample. The oxidation index through the thickness of the blocks was measured per ASTM F2102 using FTIR. From the other half of the sample, 500µm thick sections were microtomed from the surface of the samples and used for small punch testing per ASTM F2183. Post mechanical testing, pictures of the small punch specimens were taken at a 45° angle at 20X using a light microscope.

Results:
Images of small punch specimens showed no oxidative material degradation of vitamin-e diffused material after 6 weeks of aging. On the contrary, warm irradiated (WR) blended vitamin-e (VE), and cold irradiated (CR) blended vitamin-e showed oxidative material degradation post aging (Figure 1-A, B, C) that presented as cracking and a drop in small punch properties. Note that the remelted material was extremely brittle on the surface and could not be microtomed on the surface for small punch testing. For visual illustration thin sections were microtomed from the bulk of the material for showing the extent of oxidation in the remelted material (Figure 1- D).

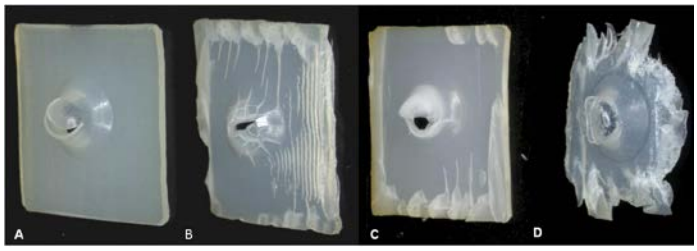

Figure 1: A) Vitamin-e diffused material (6 wks) B) 0.1 wt% WR blended VE (6 wks) C) 0.1wt% CR blended VE (6 wks) D) 100 kGy remelted (4wks)

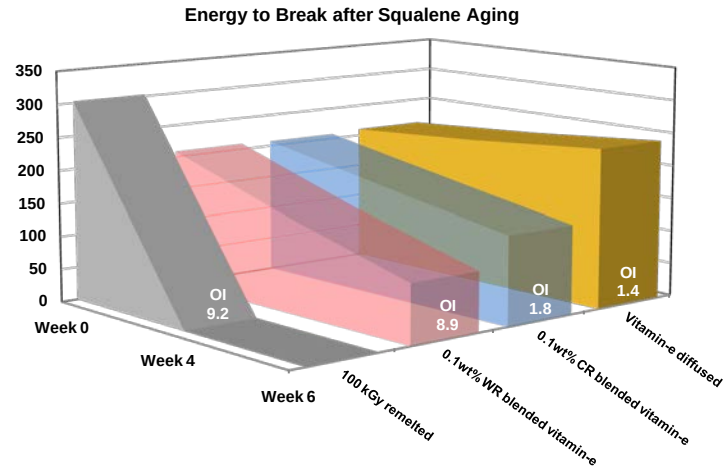

Figure 2: Comparison of energy to break (mJ) small punch test specimens of different UHMWPE materials at time zero, and post 4 or 6 weeks aging in the presence of lipids

When comparing the oxidation indexes, the maximum oxidation index for remelted, WR blended vitamin-e, CR blended vitamin-e, and vitamin-e diffused material was 9.2, 8.9, 8, and 1.4 respectively (Figure 2). Figure 2 also shows that all materials except vitamin-e diffused had a drop in the energy to break small punch property from time zero. Moreover, the remelted material failed at week 4. The percentage drop in the energy to break from week 0 to week 4 or 6 for remelted, WR blended vitamin-e, CR blended vitamin-e, Irganox blended, and vitamin-e diffused material are tabulated in the table below.

Test groups	% drop in energy to break from week 0 to week 4 or 6
100kGy remelted*	100
WR blended vitamin-e	57.07
CR blended vitamin-e	35.62
Vitamin-e diffused	0

**Remelted material failed at 4 weeks*

In addition, there is a strong correlation between the maximum oxidation index and mechanical stability of polyethylene post aging in the presence of lipids. Figure 3 shows that as the oxidation index increases, the mechanical properties are significantly compromised.

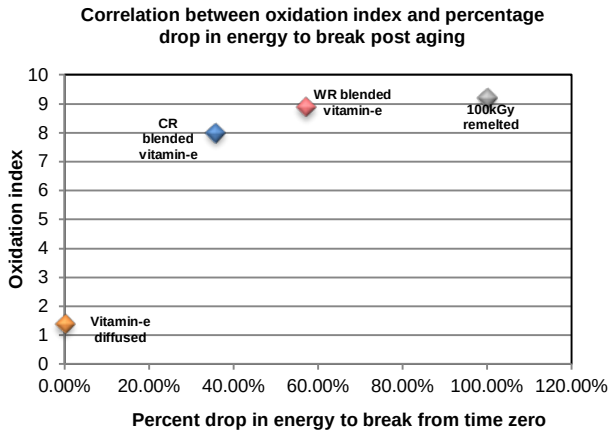

Figure 3: Correlation between maximum oxidation index and percentage drop in energy to break

Discussion: Vitamin-e diffused material had superior oxidative degradation resistance compared to blended vitamin-e and remelted materials [*]. The microscopic images of the small punch test samples show evidence of material degradation in warm radiated blended vitamin-e, cold radiated blended vitamin-e and remelted material in the presence of lipids under long term aging conditions.

The energy to break of vitamin-e diffused samples showed no evidence of oxidation induced mechanical degradation during the small punch test. Whereas, there was a significant reduction in the energy to break in the anti-oxidant blended and remelted samples. Also the drop in the energy to break correlated with the oxidation index of the material. Both remelted and the blended material had higher oxidation indices and the highest drop in the energy to break. This indicates that the oxidation resistance of both the remelted and blended material was less than that of the vitamin-e diffused material.

With recent research studies demonstrating potential for absorbed lipids *in-vivo* to initiate an oxidation cascade, it is important that current and future polyethylene technologies provide enduring protection against material degradation due to oxidation. The results from this study suggest that a vitamin-e diffused material provides exceptional oxidation and mechanical degradation resistance.

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*- Laboratory studies are not necessarily indicative of clinical results

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Can Pin on Disk Testing Be Used to Assess the Wear Performance of Retrieved UHMWPE Liners?

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Introduction: Pin-on-disk (POD) testing currently is used as a screening tool, which can economically identify the most promising bearing couples before expensive joint simulations are warranted. Although earlier POD testers were not capable of facilitating clinically relevant wear mechanisms, multidirectional POD testers are capable of ranking the tribological properties of different formulations of clinically relevant UHMWPE *in vitro* [1]. However, it is not known whether *in vivo* conditions will affect these tribological properties. The ability to perform POD testing on as-manufactured components will enable the direct comparison of the wear rates of materials that have been shelf-aged or retrieved after revision surgery, as well as virgin materials. Thus, enabling the characterization of changes in tribological properties of UHMWPE exposed to in vivo conditions.

The objective of this study was to assess the suitability of using POD testing to ascertain the long-term wear performance of retrieved liners. We also compared the oxidative effects of irradiation in air and in inert gas on the wear resistance of UHMWPE and evaluated the magnitude of these effects on shelf-aged and retrieved implants. We hypothesized that irradiation in inert gas would result in lower wear rates compared to irradiation in air. Our second hypothesis was that retrieved implants would be more wear resistant than shelf-aged implants.

Methods and Materials: Retrieved (n=25) hip liners that were consolidated from GUR 1050 resin and gamma irradiated with a dose of 25-40 kGy were identified from our center's institutional collection of over 2,000 retrieved devices based on their UHMWPE resin (GUR 1050), sterilization method (air vs. inert), and implantation time (>10 years). Shelf aged implants (n=25), which were aged 10-15 years, served as unimplanted controls. In each group, 13 implants were irradiated in air and 12 implants were irradiated in inert gas. Two cylindrical specimens were produced from each implant using a 9 mm diameter core punch. For the 25 retrieved liners, one core was obtained from the superior half and the second core was obtained from the inferior half (n=2 pins per retrieved liner, 50 pins total). The cores were machined on a lathe to ensure flat surfaces. Thus, the measurements pertain to the wear resistance of material near the surface. For the shelf-aged liners, 1 mm of the surface of one core was removed using a lathe to expose the highly oxidized region whereas the second core was lathed similar to the retrieved cores (n=2 pins per shelf aged liner, 50 pins total).

Multidirectional POD wear testing in a physiologically relevant lubricant was conducted on a Super-CTPOD with 100 stations (Phoenix Tribology, England). The counter face disks were wrought CoCr alloy with an average roughness of 4 nm. The lubricant used was Wear Testing Fluid (HyClone, UT) with a protein concentration of 20 g/L. Each pin had its own chamber filled with approximately 15mL lubricant, which was maintained at 37 ± 1^{0}C. An elliptical wear pattern (major axis 10 mm and minor axis 5 mm) was employed to facilitate multidirectional wear. Static loading was applied to generate 2.0 MPa of contact stress. The testing was carried out to 2.5 million cycles at 1.0 Hz. Gravimetric measurements were carried out at 0, 0.25, 0.50, 1.00, 1.50, 2.00, and 2.50 million cycles using a calibrated digital scale (accuracy = 0.01 mg). At each stop, articulating surfaces of pins were photo-documented. The lubricant was replaced every 0.25 million cycles. A load soak station was used to compensate for the absorption of fluid by pins. Wear rates were calculated using a linear regression of volumetric losses.

Results: Volumetric wear rates were found to vary based on the aging environment (i.e., shelf-aged or retrieved, *in vivo*), as well as sterilization environment (i.e. gamma air or gamma inert). Volumetric wear rates were highest for the pins in the shelf-aged gamma air cohort ($p<0.001$; WR = 41.5 ± 18.9 mm^3/MC: Figure 1).

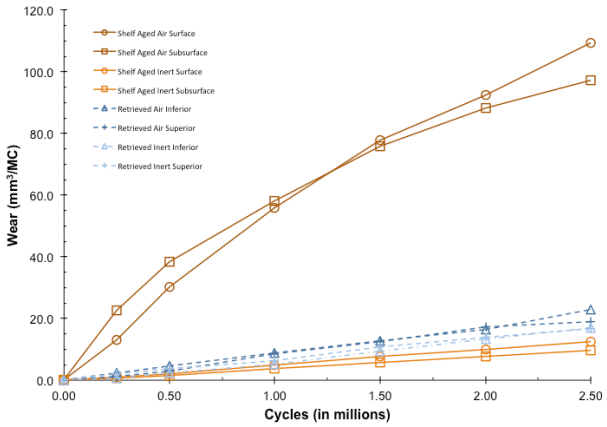

Figure 1: *The relationship between cycle count and volumetric of the pins of all cohorts.*

The retrieved gamma air pins had the next highest wear rates (Wear Rate (WR) = 8.5 ± 7.0 mm^3/MC). Although the gamma inert retrievals had lower wear rates (WR = 7.5 ± 6.9 mm^3/MC), this difference was not statistically significant ($p > 0.6$). The cohort with the least

amount of wear was the gamma inert shelf-aged pins (WR = 4.6 ± 2.1 mm^3/MC).

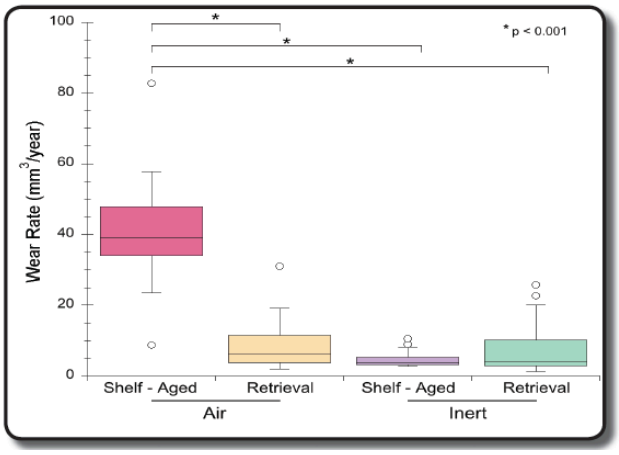

Figure 2: *Box plots illustrating the differences in wear rates amont the 4 tested groups. The shelf-aged gamma air pins had the highest wear rate.*

We were unable to detect statistically significant differences in wear rates between surface/subsurface measurements or superior/inferior measurements when controlling for sterilization environment and aging conditions ($p>0.05$). The shelf aged gamma-air pins (both surface and subsurface specimens) showed evidence of both surface and subsurface cracking (Figure 2). The pins of all specimens showed removal of machining marks as well as burnishing of the articulating surface.

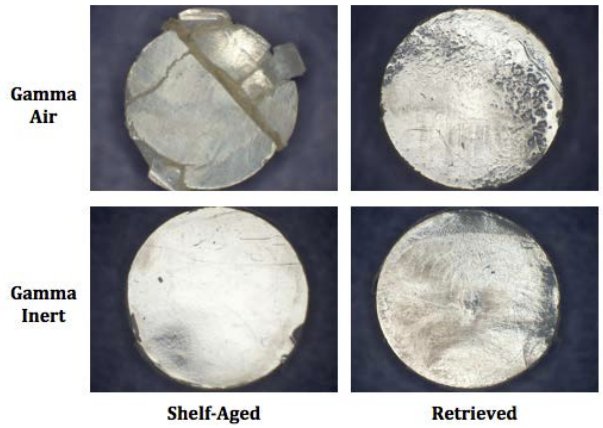

Figure 3: *Example pins from the 4 main cohorts. Note the extensive cracking in the Gamma Air Shelf Aged Cohort.*

Discussion: The results of this study support the the utility of using modern, multidirectional pin-on-disk testing with a physiologic lubricant as an novel method for evaluating the in vivo wear properties of retrieved hip liners. The data also supported the hypothesis that wear rates of gamma inert liners were lower than gamma air liners for both retrieved and shelf aging conditions. The relative oxidative stability of gamma inert UHMWPE, which has been documented in literature [2], probably contributed to the tribological properties measured in this study. Our second hypothesis that shelf-aged UHMWPE would wear more than *in vivo* aged UHMWPE was supported only in the case of gamma air sterilized components. However, gamma inert shelf aged components had the lowest wear rates of all of the components we tested. This suggests that the sterilization in an inert environment, coupled with effective barrier packaging is capable of preserving the tribological properties of UHMWPE even after storage on the shelf for more than 10 years. Another important finding of this study was that long-term aging in air after sterilization in air appears to degrade the wear properties of UHMWPE more aggressively than *in vivo*. This may be due, in part, to the femoral head protecting the articulating surface from oxidizing species in body fluids. Our findings for retrieved conventional liners in the present study will be a useful baseline comparison for evaluating the *in vivo* wear properties of retrieved highly crosslinked polyethylene liners in future research.

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Is In Vivo Oxidation of HXLPE Greater in the Knee than in the Hip?

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Introduction: First generation highly crosslinked polyethylenes (HXPLEs) have proven successful in lowering both penetration and osteolysis rates in total hip arthroplasty (THA). However, little is known about how in vivo oxidation compares in THA and total knee arthroplasty (TKA), because when manufacturers first introduced HXLPEs in the knee, its formulations differed from those used in the hip.

The purpose of this study was to compare in vivo oxidation of HXLPE in the knee to that in the hip. In vivo oxidation of the bearing surface in THA has been shown to be limited by the restriction of oxidizing species and the conforming bearing geometry. The situation is somewhat different in the knee, which has greater nonconformity and higher bearing stresses than in the hip. Therefore, we tested the hypotheses that in vivo oxidation would be greater in the knee than in the hip in loaded regions, but similar in the unloaded regions. To test these hypotheses, we studied matched cohorts of hip and knee retrievals of the same HXLPE formulation.

Methods and Materials: 240 HXLPE hip and knee components (X3, Stryker Orthopedics, Mahwah) were consecutively retrieved during revision surgeries and continuously analyzed in a prospective, IRB approved, multicenter study. We selected a cohort of 35 retrieved TKAs and matched them based on implantation time to a group of 35 THAs. The hip and knee retrievals were matched by implantation time within six months. The clinical characteristics of both cohorts are summarized in Table 1.

	n	Implantation Time	BMI	Gender (%F)	Age (yrs)	UCLA Score
Hip	35	1.8 (0-5.0)	31 (20-49)	44%	59 (32-87)	4 (2-8)
Knee	35	1.9 (0-5.5)	35 (21-48)	86%	57 (36-89)	5 (2-8)

Table 1: *Patient demographics for the matched hip and knee cohorts.*

Thin sections were taken from the acetabular liners (along the superior/inferior axis) and the tibial components (along the medial condyle and central spine) for oxidation analysis and analyzed according to ASTM 2102. Mechanical behavior was assessed via the small punch test (ASTM 2183).

Due to the non-normal distributions of the data, we used nonparametric methods to analyze the data. Specifically, the Wilcoxon test was used to determine differences in continuous variables. For correlations between continuous variables, we utilized the Spearman's Rank Correlation test. A p-value of 0.5 was used for statistical significance. All statistical analysis was performed using commercial software (JMP 10.0, SAS Institute, Cary, NC).

Results: The liners and tibial components fabricated from both HXLPEs were revised predominantly for loosening, instability, and infection (Figure 1).

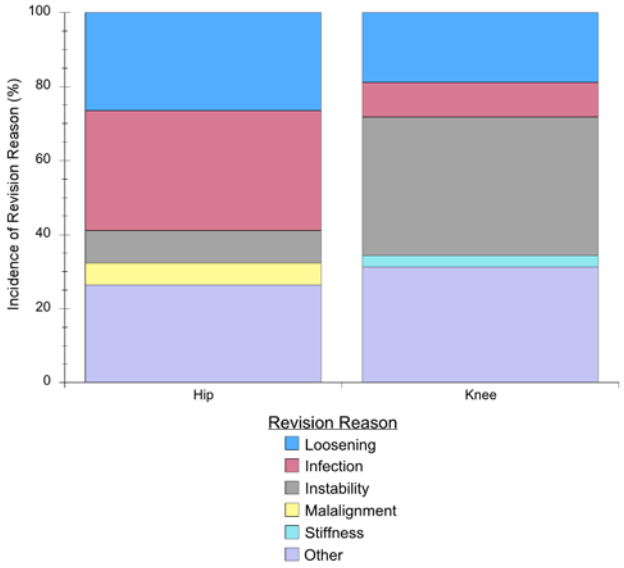

Figure 1*: Reasons for revision for matched hip and knee retrieval cohorts.*

Figure 2: *Stereomicrograph of a Sequentially Annealed acetabular liner that was implanted for 5.0 years.*

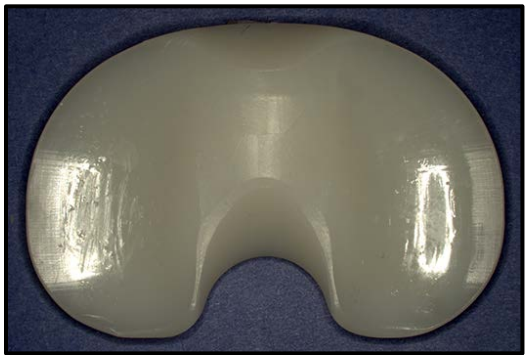

Figure 3: *Stereomicrograph of a Sequentially Annealed tibial insert that was implanted for 5.5 years. Note the burnishing, scratching, and impressions from 3rd body wear.*

The median oxidation indices were low (mean OI≤0.2) and similar between acetabular liners and tibial inserts of at the bearing surface, backside surface, and exposed rim (Figure 4, p≥0.15).

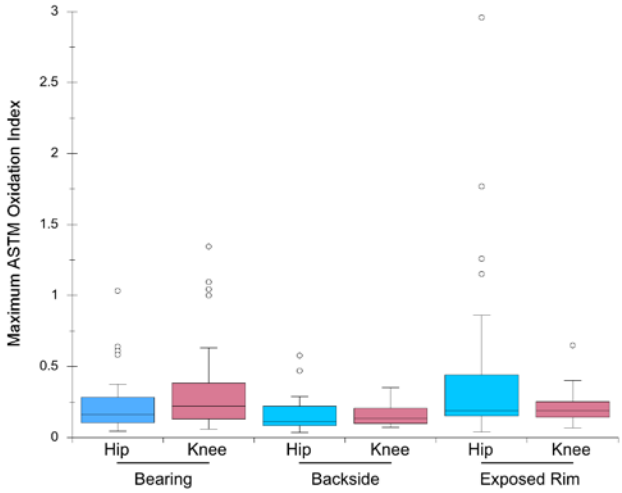

Figure 4: *Regional variations in oxidation.*

Oxidation indices were positively correlated with implantation time at the bearing surface of the knee cohort (Rho=0.58; p=0.0011). Oxidation was not correlated with implantation time at any location in the hip cohort.

The surface and subsurface ultimate loads of the acetabular liners were both statistically higher than the tibial components (p<0.05), however the mean difference was minimal (~6N).

Discussion: This study evaluated the properties of a 2nd generation HXLPE used in THA and TKA. We did not observe a significant difference in oxidative behavior between THA and TKA components. However, the current sample size in this study did not have enough power to detect the minor differences observed (Power = 5 – 55% depending on sample location). In order to detect an oxidation index difference of 0.1 (approximately the difference seen in the current study) at the bearing surface, it is estimated that a sample size of 160 (n = 80 per cohort) will be required to achieve 80% power. Thus, more and longer-term retrievals are necessary to fully assess the oxidative stability of Sequentially Annealed HXLPE used in TKA and THA.

Acknowledgments: This study was supported by NIH R01 AR47904. Institutional support was also received from Stryker, Zimmer, Ceramtec and Formae. Support also provided by the Wilbert J. Austin Chair (CMR).

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24 Weeks Accelerated Aging study for HALS and Vitamin E stabilized 100 kGy irradiated UHMWPE

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Introduction: Several studies have shown that the antioxidant vitamin E effectively scavenges remaining free radicals within irradiation crosslinked UHMWPE materials and thereby preventing oxidative degradation without the need for remelting or annealing (1). However if the vitamin E is applied to the UHMWPE powder prior to the molding and irradiation, it interferes with the crosslink process (2). Part of the vitamin E will be consumed during irradiation, which results in a lower crosslink efficiency. HALS stabilizers have shown not to reduce the crosslink efficiency (3). In this study the chemical and mechanical properties, including wear before and after accelerated aging, are investigated for a 100 kGy UHMWPE containing respectively 0.10 wt.% HALS or Vitamin E.

Methods and Materials: GUR1020 resins doped respectively with 0.10 wt.% HALS or Vitamin E were compression molded into 80 mm thick sheets (Meditech, USA). The material was machined into 1.0 meter bars and then gamma irradiated with 100 kGy (BGS, Germany). After annealing the bars, the test specimens for all subsequent analyses were machined from the bar stock. Accelerated aging was conducted in accordance with ASTM F2003 (70°C, 5 bar O_2). Swell ratio, crosslink density and molecular weight between crosslinks were determined according to ASTM F2214. During aging the oxidation index was followed per ASTM F2102. Tensile properties (yield stress, ultimate stress and percent elongation) were monitored per ASTM D638. The wear resistance was tested using DSM's 100 station POD wear tester (4).

Results: The 100 kGy HALS material was found to have a lower swell ratio, higher crosslink density, and lower molecular weight between crosslinks when compared to the Vitamin E material.

Table 1; Swell ratio, crosslink density and Mw between crosslinks for 100 kGy GUR1020 with HALS and Vitamin E.

Material	Swell Ratio, q_s	Crosslink Density, V_d [mol/dm³]	Molecular Weight Between Crosslinks, M_c [g/mol]
HALS	3.05 ± 0.15	0.205 ± 0.020	4510 ± 430
VITE	4.04 ± 0.07	0.121 ± 0.004	7610 ± 240

Tensile properties were not affected by 24 weeks of aging for both the HALS and Vitamin E materials. The percent elongation values for the 100 kGy HALS material were lower than those for the 100 kGy Vitamin E material for both non-aged and all aged samples. All oxidation values for the 100 kGy HALS and 100 kGy Vitamin E materials, even after 24 weeks of aging, were low (<1.0). In comparison, the control 25 kGy GUR1050 material demonstrated critical oxidation (>3.0) after 4 weeks of accelerated aging (Figure 1). The wear was significantly lower for the 100 kGy HALS material as compared to the Vitamin E material. Both materials' wear rates were not affected by the 24 weeks of accelerated aging (Figure 2).

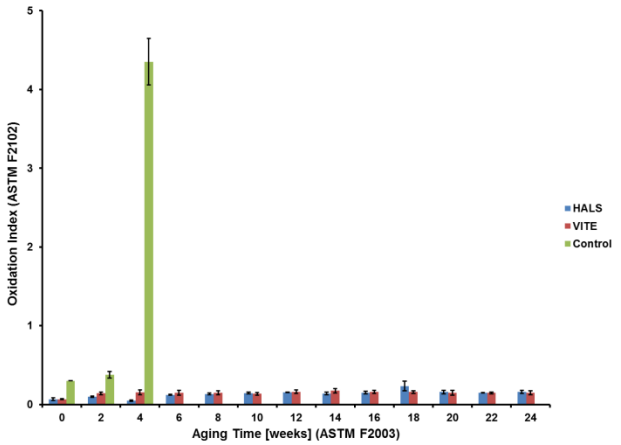

Figure 1: Average maximum OI for the 100 kGy GUR1020 with HALS, 100 kGy GUR1020 with vitamin E, and 25 kGy GUR1050 control materials after accelerated aging. Error bars represent one standard deviation. At six weeks, the 25 kGy 1050 material was too oxidized to perform FTIR.

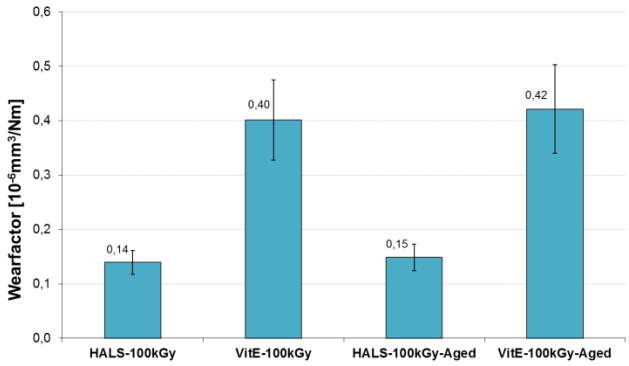

Figure 2; POD wear factor; Total distance 60,480 km (2 million cycles multiaxial motion). Lubricant water-serum (1:1). Pressure on each pin ~70N (~1,1MPa). Test temperature 20°C.

Conclusion: The crosslink density for the HALS material is significantly higher as compared to Vitamin E at the same irradiation dosage of 100 kGy. This is also reflected by the lower elongation values for the HALS material, indicating a higher crosslink density as well. Both HALS and Vitamin E stabilized materials maintained their tensile properties, wear resistance and low oxidation index values even after 24 weeks of accelerated aging. The higher crosslink density resulted in a significantly lower wear for the 100 kGy HALS material as compared to the 100 kGy Vitamin E material.

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Wear, Wear particle Characterization and Biocompatibility of UHMWPE/Multiwalled Carbon Nanotubes Nanocomposites

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Introduction: Metal-on-polyethylene (MoP) has been the bearing combination most commonly used in total joint replacements. However, the degradative oxidation behaviour of ultra high molecular weight polyethylene (UHMWPE) leads to high amounts of wear debris, which contributes directly to the development of aseptic loosening and eventually to the failure of the implant. In order to address this issue, investigations have been focused on developing alternative novel materials with lower wear rates and improved biocompatibility.

An alternative technique for reducing wear is the use of polymer composites. The excellent mechanical properties of multi walled carbon nanotubes (MWCNTs), such as high tensile strength and ultra-light weight, makes them a promising option to improve the performance of UHMWPE.

The aim of this study was to analyse the wear rate and the characteristics, in terms of size and volume distributions, morphology and biocompatibility, of the wear debris generated from a UHMWPE-MWCNTs composite compared with conventional UHMWPE.

Methods and Materials: Two UHMWPE-MWCNTs composites, with 0.5 wt% and 1 wt% MWCNTs were investigated and compared with virgin GUR 1020 UHMWPE. Nanocyl-3150 MWCNTs with a purity of >95%, a particle diameter of 5-10 nm and a length of 1-5 µm were used to prepare the UHMWPE-MWCNTs composites. The composites were manufactured in house under optimized conditions using a ball milling technique.
A six station multidirectional pin on plate wear tester was used under hip kinematics to assess the tribological performance of the UHMWPE-MWCNTs composites and to generate clinically relevant wear particles. Smooth high carbon (>0.2 wt%) cobalt chromium plates with an average surface roughness of 0.01 µm were used as counterface surfaces.
Wear debris from the UHMWPE-MWCNTs 1 wt% composite and GUR 1020 UHMWPE was isolated and characterized and the biological activities of both materials were predicted.
A multidirectional pin on plate wear tester under aseptic conditions was used to generate sterile clinically relevant wear particles. L929 fibroblasts murine cell line was used for culture with UHMWPE GUR 1020 and UHMWPE-MWCNTs 1 wt% particles. The effect of the wear particles on the L929 fibroblasts at different concentrations was monitored for 5 days using the ATP-Lite assay (Perkin Elmer, UK) to assess for possible cytotoxic activity.

Results: The addition of MWCNTs (0.5 wt% and 1 wt%) has been shown to lead to a significant reduction in wear rate, demonstrating up to a 40% reduction in the wear rate compared to virgin GUR 1020 UHMWPE.
Wear debris analysis showed that the addition of MWCNTs did not modify particle morphology but there were some differences in terms of size and volume distributions. Particles from the reinforced polyethylene were found to be larger than those generated from the virgin polyethylene. The volume distribution also showed a lower volume of particles from the reinforced material in the most biologically active size range (0.1-1 µm). This difference, together with the reduced wear factor measured for the MWCNTs reinforced material, was reflected in the functional biological activity (FBA), indicating that the wear particles from the UHMWPE-MWCNT composite had a lower osteolytic potential compared to GUR 1020 UHMWPE.
In addition, clinically relevant UHMWPE-MWCNTs wear particles were not shown to have any adverse effect on L929 fibroblasts cells in culture at any of the concentrations tested over time.

Discussion: The present study has provided an insight into the potential of UHMWPE-MWCNTs composites as an alternative to conventional UHMWPE for use in load bearing applications. The results showed that the MWCNTs have the ability to improve the wear performance of conventional UHMWPE without compromising its biocompatibility. The results of this study are promising; however, further work concerning the long-term performace of UHMWPE-MWCNTs composites and the influence of MWCNTs on human health is necessary.

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Hip Simulator Wear and Lock Detail Performance of Crosslinked UHMWPE Blended with a Hindered Amine Light Stabilizer (HALS)

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Disclosure: *The data presented in this abstract includes information pertaining to a medical device that has not received approval by the FDA or any other regulatory agency. Data presented is strictly for scientific understanding and is not intended to suggest future device performance.*

Introduction: The remelting of crosslinked UHMWPE is known to reduce oxidation potential after gamma irradiation, at the cost of reducing certain mechanical properties. The addition of stabilizers, in the form of antioxidants, may reduce oxidation potential without requiring remelting, retaining some material properties that would be lost during remelting.

This experiment compared the wear performance of 28 mm liners machined from 75 kGy irradiated, remelted UHMWPE and antioxidant-stabilized UHMWPE irradiated to both 75 and 100 kGy. The effect of bearing diameter was also investigated for 100kGy irradiated stabilized UHMWPE.

The lock detail strength of 75kGy remelted and 100kGy stabilized liners was also evaluated.

Methods and Materials: Acetabular liners were manufactured from compression-molded GUR1020. One group was manufactured from GUR1020 that was irradiated with 75 kGy gamma and remelted, the other groups were machined from GUR1020 blended with a hindered amine light stabilizer (HALS), Chimassorb 944, at 1000ppm molded, and irradiated to either 75 or 100 kGy, without subsequent remelting. All groups were EtO sterilized prior to testing.

Wear: Hip wear testing was conducted using a combination of methods outlined in ASTM F1714, ISO 14242-1, and ISO 14242-2. All wear couplings were tested against cobalt chrome femoral heads in an orbital bearing hip simulator (Shore Western) in the anatomically oriented position. A 3 peak Paul gait profile with a minimum and maximum force of 200 N and 2000 N, respectively, was applied to the bearings at a frequency of 1 Hz. The loading was applied to the specimens by a 23° biaxial rocking motion. The lubricant was 25% bovine serum with 0.2% sodium azide, 25 mM EDTA and distilled water. Lubricant volume and concentration was maintained by the continuous addition of distilled water. The test was interrupted at regular intervals for gravimetric assessment of the bearing wear. Each bearing group was tested in conjunction with control load soak specimens to compensate for fluid absorption. Six control and groups of eight, four, and three experimental liners were tested.

Lock Detail: Lock detail testing for push-out, torque-out, and lever-out strength was conducted according to ASTM F1820-13, with minor deviations in liner/shell assembly and lever-out test setup. Three acetabular shells (Dynasty®, Wright Medical) were used (1 per test). All liners and shells were within manufacturing tolerances. Liners were assembled according to surgical technique via impaction instead of the recommended machine assembly to 2000N.

Results: *Wear:* As shown in Figure 1 all groups exhibited steady-state linear wear over 5M cycles. The average wear rate for each group in mg/Mc is taken as the slope and was determined by linear regression. See Figure 1. There was little difference between the two groups of 28 mm liners irradiated to 75kGy, whereas the stabilized 100kGy group exhibited a significant reduction in wear as expected. The 46 mm liners had slightly higher wear than the 28 mm liners, which is consistent with previous results for 75 kGy remelted UHMWPE.

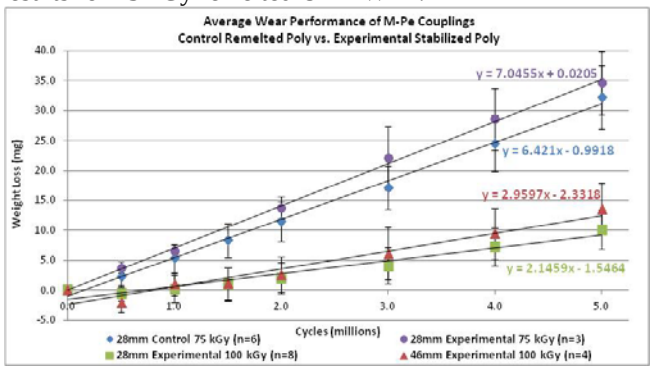

Figure 1: Mass loss vs. number of cycles of wear

Lock Detail: Results were not statistically significant between materials in any test (2 sample t-test, $p > .05$). See table 1 below.

Table 1: Static lock detail testing of 28mm liners

	Remelted 75 kGy	Stabilized 100 kGy
Push-out	720.8 N (93N)	748.0 N (81.5N)
Torque-out	3.479 Nm (0.475 Nm)	3.978 Nm (0.359 Nm)
Lever-out	1423.3 N (89.6 N)	1291.0 N (187.0 N)

Mean failure load or torque. Standard deviations are in parentheses.

Discussion: The wear rate of stabilized, non-remelted liners was equivalent to that of remelted liners at the same radiation dose, which indicates that the HALS molecule does not interfere with cross-linking. As expected, increasing the radiation dose to 100kGy significantly lowered wear due to increased crosslinking. The increase in wear for 46 mm vs. 28mm liners was relatively small considering the large increase in sliding distance and velocity.

The lock detail testing did not show any statistical difference in performance. Eliminating the remelting step would be expected to increase some material properties, while the increased crosslinking dose would be expected to decrease certain material properties. These data suggest that it may be possible to improve wear performance by increasing crosslink density in an acetabular UHMWPE system without significantly degrading lock detail integrity by use of an antioxidant instead of remelting.

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In vitro wear simulation under prolonged ageing and third-body particle conditions of a vitamin E stabilised polyethylene for hip arthroplasty

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Introduction

During the last decade highly cross-linked polyethylenes (XPE) have been clinically established for patients with coxarthrosis or rheumatoid arthritis in total hip arthroplasty (THA). Highly cross-linked acetabular liners have become the material of choice in combination with cobalt-chromium or ceramic heads and have shown substantial benefits in decreasing wear and osteolysis [1,2]. To improve the oxidation resistance highly cross-linked polyethylenes have to be thermally treated after irradiation. Due to a loss of crystallinity during remelting the mechanical properties of XPE are substantially reduced, a possible reason for structural material fatigue, pitting and crack initiation in vivo [3-5]. Due to that the stabilisation of XPE by blending of the antioxidant vitamin E in the polyethylene powder was introduced to enhance oxidation resistance and keep the mechanical properties by avoiding post-irradiation melting [6-8].
The objectives of our study were to evaluate the biotribological behaviour of a vitamin E stabilised polyethylene under conditions of prolonged artificial ageing and third-body particulate debris.

Materials & Methods

In vitro hip wear simulation was performed for 5 million cycles according to ISO 14242-1 on a 6+2 station EndoLab hip simulator. Three different types of polyethylene inserts were made out of GUR 1020:

- $PE_{std.}$ (γ 30 kGy,N_2)
- $XPE_{rem.}$ (γ 75 kGy, remelted, EO)
- XPE_{VitE} (electron-beam 80 kGy, 0.1% vitamin E, EO)

The polyethylene inserts were tested in articulation against femoral heads made out of $CoCr_{29}Mo_6$ (CoCrMo) and ceramic (Biolox® delta) in a diameter 36 mm configuration. The polyethylene inserts were used unaged and after a duration of 42 days of artificial ageing (ASTM F 2003: 70 °C pure oxygen at 5 bar) and soaked prior to wear simulation to allow for saturated fluid absorption. In addition to that the influence of a third-body particulate debris contamination was simulated by adding bone cement particles (Palacos R, size 125-150 µm) in a concentration of 5 g/l. The amount of wear was measured gravimetrically according to ISO 14242-2 with loaded references.

Results

In unaged conditions as reference the cobalt-chromium-on-polyethylene articulations demonstrated comparable average wear rates of 3.4±0.3 mg/mc for $XPE_{rem.}$ and 3.4±0.5 mg/mc for XPE_{VitE}. After 42 days of prolonged artificial ageing $XPE_{rem.}$ showed a significantly increased mean wear rate of 55.4±2.2 mg/mc, but no substantial change was given for the vitamin E stabilised inserts (XPE_{VitE}) with 3.4±0.1 mg/mc.
By adding bone cement as third-body particulate debris the mean wear rate of XPE_{VitE} inserts increased in articulation with Biolox® delta to 7.8±0.5 mg/mc (2.3-fold) and with CoCrMo heads to 47.0±36.1 mg/mc (10.7-fold), respectively.

Conclusion

Vitamin E stabilised polyethylene is effective in preventing oxidation after irradiation cross-linking, which is correlated to low wear in total hip arthroplasty even under prolonged artificial ageing conditions. The articulation of XPE_{VitE} with Biolox® delta heads is comparably less sensitive to third-body bone cement particles.

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Vitamin E Stabilized Polyethylene for Hip Endoprostheses

– Mechanical Properties and Long-term Stability

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Introduction

Hip joint inserts made of highly cross-linked polyethylene (XPE) are clinically well established in reducing wear and hence the risk of osteolysis compared to standard polyethylene (PE_{Std}) [1,2]. To guarantee long-term in vivo oxidation stability, XPE's have to be treated by thermal procedures after irradiation to eliminate residual radicals. On the one hand, remelting of polyethylene ($XPE_{remelted}$) is successful to remove radicals but leads to a decrease of crystallinity hence to a reduction of mechanical properties which results to a structural in vivo failure of the PE insert [3,4,5]. On the other hand, annealing just below the melting area of PE remains the mechanical properties but is not effective enough to eliminate all residual radicals completely. Both, elimination of residual radicals as well as maintenance of the mechanical properties can be achieved by the addition of antioxidant. Due to its outstanding biocompatibility and non-polar character, vitamin E is predestinated as antioxidant for implant grade polyethylene [6,7].

MATERIAL & METHODS

In this study three different types of polyethylene (UHMWPE; GUR1020) were analyzed to compare mechanical properties as well as long-term stability.

- PE_{Std} (γ, 30 kGy, N2)
- $XPE_{remelted}$ (γ, 75 kGy, remelted, EO)
- XPE_{VitE} (β, 80 kGy, 0.1% Vitamin E, EO)

Accelerated aging according to ASTM F2003 (70 °C, O_2 at 5 bar, 14, 28 and 42 days) was used to simulate environmental damage occurring during shelf life or in vivo lifetime. To evaluate the oxidation stability of vitamin E and polyethylene Oxidation-Induction-Time (OIT) was measured by Differential Scanning Calorimetry (DSC) according to ASTM D3895 and Oxidation Index determined by Fourier-Transformation-Infrared-Spectroscopy (FTIR) according to ASTM F2102. Mechanical properties were analysed by tensile- and impact investigations (ASTM D638 and ISO 11542-2) as well as by Small Punch Testing (SPT) according to ASTM F2183.

Results

Even after high dose irradiation the remaining content of vitamin E was effective enough to prevent oxidation in polyethylene. The OIT measurements at aggressive conditions revealed an oxidative protection for more than 8 minutes compared to no protection (0.5 min) of $XPE_{remelted}$. The OI of XPE_{VitE} was below the detection limit of 0.1 even after 3 cycles of accelerated aging. Under the same aging conditions, PE_{Std} and also $XPE_{remelted}$ exhibited severe oxidation with indices higher than 2.
In the unaged state, XPE_{VitE} showed comparable results as $XPE_{remelted}$ regarding yield- and tensile strength as well as elongation at break and Charpy impact strength. But in contrast to $XPE_{VitE,}$ oxidation had a tremendous impact on $XPE_{remelted}$ when the material was aged for 6 weeks. While the tensile stress of $XPE_{remelted}$ was reduced by 50%, the elongation at break and impact strength were diminished close to zero. Comparing findings could be observed regarding the results of Small Punch Testing. After 4 week aging only a slight decrease of peak load, ultimate load, ultimate displacement and energy to failure were found for XPE_{VitE} but partly an enormous reduction for PE_{Std} which was aged in the same matter.

Conclusions

By the addition of vitamin E it was possible to provide a UHMWPE with long term stability after cross-linking with high dose irradiation. No evidence of significant oxidation was found regarding Oxidation Index or Oxidation Induction Time even after excessive aging under aggressive conditions. Both, tensile and impact analysis as well as Small Punch Testing showed no reduction of the mechanical properties after accelerated aging compared to PE_{Std} and $XPE_{remelted}$.

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