Published in final edited form as:

J Biomed Mater Res B Appl Biomater. 2009 August ; 90(2): 720–729. doi:10.1002/jbm.b.31340.

EFFECT OF CROSSLINK DENSITY ON THE HIGH PRESSURE CRYSTALLIZATION OF UHMWPE

Ebru Oral, PhD^{a,b}, Christine Godleski Beckos, BS^a, Bassem W. Ghali, BS^a, Andrew J. Lozynsky, BS^a, and Orhun K. Muratoglu, PhD^{a,b,*}

^a Massachusetts General Hospital, Department of Orthopaedic Surgery

^b Harvard Medical School

Abstract

Ultrahigh molecular weight polyethylene (UHMWPE) is a bearing surface material for total joint implants. It is radiation cross-linked for high wear resistance and is melted or treated with vitamin E for oxidative stability. We investigated high pressure crystallization (HPC) of irradiated UHMWPE as an alternative method to improve the mechanical strength while stabilizing the residual free radicals from radiation crosslinking. HPC of uncross-linked UHMWPE has resulted in the formation of extended chain crystals and increased crystallinity, leading to improved strength. We hypothesized that increased cross-link density would hinder crystallization during HPC due to decreased chain mobility. Therefore, we investigated the crystalline structure and tensile mechanical properties of high pressure crystallized 25-, 65- and 100-kGy irradiated UHMWPE. We also determined free radical content and wear. The strength of 25- and 65-kGy irradiated UHMWPEs was improved by HPC with increased crystallinity and crystal size. 100-kGy irradiated UHMWPE did not show improved strength, supporting our hypothesis that decreased chain mobility would hinder crystal formation and strength improvement. None of the HPC irradiated UHMWPEs contained detectable free radicals and their wear properties were maintained, suggesting oxidative and mechanical stability in the long term. Therefore, HPC can be used effectively for imparting oxidative stability while strength improvement can be achieved for irradiated UHMWPE with low to moderate crosslink density.

Keywords

Joint arthroplasty; polyethylene; crystalline; wear; radiation; implant

Introduction

Ultra-high molecular weight (UHMWPE) is the material of choice for total joint arthroplasty bearings. Radiation cross-linking is used to reduce the wear of UHMWPE, which has been associated with peri-prosthetic osteolysis in the long-term¹⁻³. Cross-linking is achieved by the recombination of free radicals induced by irradiation on the polyethylene chains in the amorphous phase. However, free radicals formed in the crystalline phase cannot recombine and are trapped. In the long-term, these free radicals migrate into the amorphous phase and cause embrittlement through reactions with diffused oxygen. In order to eliminate this possibility, radiation cross-linked UHMWPEs are thermally treated after irradiation. One approach is to thermally anneal cross-linked UHMWPE below the melting point. While this

* Corresponding Author: Orhun K. Muratoglu, PhD, Orthopaedic Biomechanics and Biomaterials Laboratory, Massachusetts General Hospital, 55 Fruit Street, GRJ 1206, Boston, MA 02114. Tel: (617) 726-3869, Fax: (617) 643-2521, omuratoglu@partners.org.

method prevents complete melting and preserves the crystallinity and mechanical properties of cross-linked UHMWPE, it does not eliminate all free radicals, resulting in long-term oxidation^{4,5}. Another approach is to melt the crystalline regions completely. This method removes the oxidation potential but also reduces the mechanical properties due to decreased crystallinity caused by post-irradiation melting⁶.

UHMWPE exhibits a hexagonal phase at high temperature and high pressure (Fig 1), where crystal stems are randomly rotated and their mobility is increased. As a result, the increased mobility allows the growth of 'extended chain crystals', which are larger in size than the 'folded chain crystals' exhibited by UHMWPE crystallized from the melt at ambient pressure. In addition, the overall crystallinity of the material is increased, thereby increasing its yield strength and ultimate tensile strength⁷.

Our aim was to improve the mechanical strength of UHMWPE joint implants while maintaining or improving their oxidation and wear resistance. Currently, satisfactory wear resistance is achieved by radiation cross-linking of UHMWPE^{8,9}. However, radiation cross-linked UHMWPE is not oxidation resistant unless the residual free radicals trapped in its crystalline domains are stabilized⁴. An alternative method to post-irradiation melting to achieve oxidative stability is the stabilization of the free radicals by the incorporation of an antioxidant such as vitamin E, which can be blended with UHMWPE powder prior to consolidation and radiation cross-linking^{10,11} or can be diffused into consolidated and irradiated UHMWPE^{12,13}. Using both methods, an oxidation resistant UHMWPE with comparable crosslink density and wear resistance to the irradiated and melted UHMWPEs can be achieved^{10,14}. Furthermore, mechanical strength is improved compared to irradiated and melted UHMWPE because post-irradiation melting is not necessary to stabilize the free radicals and the associated mechanical strength loss due to the reduction in crystallinity is spared¹⁴. We are seeking alternative mechanisms and methods by which mechanical strength of UHMWPE joint implants can be further improved without sacrificing or improving the wear and oxidation resistance.

One approach is to high pressure crystallize radiation cross-linked UHMWPE¹⁵. The presence of cross-links are expected to adversely affect high pressure crystallization. The formation of extended chain crystals requires chain mobility to allow reptation of the molecules. When the chains are crosslinked the mobility is compromised, and thus high pressure crystallization will not be as effective. Therefore, we hypothesized that UHMWPEs with lower crosslink density would show improvement in mechanical properties due to HPC because of higher chain mobility similar to unirradiated UHMWPE. It is not known if extended chain formation in radiation cross-linked UHMWPE would compromise wear resistance. To test our hypothesis, we high pressure crystallized 25-, 65- and 100-kGy irradiated UHMWPE and determined the crystallinity, mechanical and fatigue properties, cross-link density and wear resistance of these radiation cross-linked HPC UHMWPEs.

Materials and Methods

Preparation of radiation cross-linked, high pressure crystallized UHMWPE

Slab compression molded GUR1050 UHMWPE (Orthoplastics, Lancashire, UK) was packaged in vacuum. Packaged material was irradiated to 25-, 65- and 100-kGy by gamma irradiation (Steris Isomedix, Northborough, MA).

Blocks (approximately 5 × 5 × 10 cm) were cut from radiation cross-linked UHMWPEs. One block was placed in a custom-built high pressure chamber (High Pressure Equipment Co., Erie, PA) in deionized water for each radiation dose. The chamber was heated to 200°C. The sample was allowed to melt at this temperature for at least 5 hours. Then, the

chamber was pressurized to 380 MPa by pumping additional water (SC hydraulics, Brea, CA). The sample was kept at 200°C and 380 MPa for 5 hours, then the sample was cooled under pressure to about 25-60°C and the pressure was released. In this text, we refer to these materials as 'irradiated, melted, HPC UHMWPE'.

One set of unirradiated UHMWPE was also high pressure crystallized using the same procedure. This sample was referred to as 'unirradiated HPC UHMWPE'. Two sets of controls were used; one set were 25-kGy, 65-kGy and 100-kGy irradiated UHMWPE without further treatment. This set was referred to as 'irradiated' or 'irradiated non-HPC' UHMWPE. Another set was melted in argon gas at 200°C, this set was referred to as 'irradiated, melted UHMWPE' (Table 1).

Determination of crystalline content

The DSC specimens were weighed with a Sartorius CP 225D balance to a resolution of 0.01 milligrams and placed in aluminum sample pans. The pan was crimped with an aluminum cover and placed in a Q-1000 Differential Scanning Calorimeter (TA Instruments, Newark, DE). The sample and the reference were then heated at a heating rate of 10°C/min from -20°C to 180°C. Heat flow as a function of time and temperature was recorded.

Crystallinity of the samples (n=3 each) was determined by integrating the enthalpy peak from 20°C to 160°C, and normalizing it with the enthalpy of melting of 100% crystalline polyethylene, 291J/g. The peak melting point is also reported here.

Determination of tensile mechanical properties

Thin sections (3.2 mm) were machined from the cross-linked HPC UHMWPE (Eastern Tool, Medford, MA). Dogbone specimens (n=5 each) were stamped from these sections in accordance with ASTM D638, standard test method for tensile properties of plastics. These samples were then tested in accordance with ASTM D-638 using a MTS II machine (Eden Prairie, MN) at a crosshead speed of 10 mm/min. The engineering ultimate tensile strength (UTS) and work-to-failure (WF), calculated as the area under the engineering stress-strain curve, and yield strength (YS) are reported. In addition, the true elongation at break (EAB) was determined using a laser extensometer.

Determination of fatigue crack propagation resistance

Fatigue crack propagation testing was done following ASTM E-647. Compact tension (C(T)) specimens (n=3) were pre-cracked at the notch using a razor blade. Testing was conducted at a sinusoidal load cycle frequency of 5 Hz and stress ratio of 0.1 in tension. Crack length was monitored optically every 20,000 cycles. The average of the crack length on both sides of the C(T) specimen was used as the representative crack length for the computation of crack growth rates. Stress intensity factor ranges at crack inception (ΔK_I) were reported in MPa•m^{1/2} at a threshold crack growth rate of 10⁻⁶ mm/cycle. All testing was done in an aqueous bath at 40°C to simulate the physiologic temperature of the joint.

Determination of cross-link density

Crosslink density measurements were performed by thermal mechanical analysis (DMA 7e, Perkin Elmer, Wellesley, MA). Thin sections machined from radiation cross-linked, high pressure crystallized UHMWPE were melted at 170°C under partial vacuum to remove any stresses residual from the consolidation process that might result in additional swelling during cross-link density measurements.

Small sections were cut out by razor blade from these thin sections to be analyzed (approximately 3 mm by 3 mm, n = 3 to 5 each). These small pieces were placed under the

quartz probe of the DMA (10 mN) and the initial height of the sample was recorded after about 10 minutes. Then, the probe was immersed in xylene, which was subsequently heated to 130°C and held for at least 100 minutes. The UHMWPE samples swelled in hot xylene until equilibrium was reached. The final height was recorded.

The cross-link density of the samples was calculated as described previously¹⁶ and are reported as mol/m³. Measurements were made on radiation cross-linked UHMWPE before and after HPC.

Electron spin resonance

An approximately 3×3×10 mm section was cut from each block. The sections (n=2) were analyzed by a Bruker EMX EPR system (Bruker BioSpin Corporation, Billerica, MA) at the Department of Physics at the University of Memphis (Memphis, TN). The free radical content of all samples was calculated by double integration of the ESR signal over the magnetic field and normalizing by the sample weight.

Bidirectional pin-on-disc wear testing

Three cylindrical samples (9 mm in diameter and 13 mm in length) each of irradiated, melted, HPC UHMWPEs (25-kGy, 65-kGy and 100-kGy irradiated) were used for POD wear testing. Three samples each of irradiated non-HPC UHMWPEs were tested as controls. The pins were tested on our custom-built bi-directional POD tester at a frequency of 2 Hz for 2 million cycles with gravimetric assessment of wear at every 0.5 million cycles. Undiluted bovine serum was used as lubricant with 33 ml penicillin-streptomycin solution per 500 ml as antibacterial agent and 1 mM EDTA as chelating agent. The wear rate was determined by linear regression of the weight change of each pin over 0.5 to 2 million cycles.

Transmission electron microscopy (TEM)

The test samples were stained to increase the contrast between the crystalline and amorphous phases when examined in a transmission scanning electron microscope. A small piece of each sample was cut with a scissor, placed in a small glass vial, covered with chlorosulfonic acid and kept at 60°C for 6 hours. The sample was then washed in sulfuric acid and water and subsequently dried. The dry sample was embedded using a room temperature curing epoxy in a silicone mold and left overnight. This sample block was then trimmed with a razor blade to expose the sample and ultra-microtomed at room temperature. The resulting sections, approximately 70nm thick, were collected on 300 mesh copper grids and post stained with a 7% aqueous solution of uranyl acetate for 3 hours. The sections were then imaged on a Philips 420T TEM using 100kV accelerating voltage.

In all studies in which there were at least three samples, statistical analysis was performed using a Student's t-test for two-tailed distributions with unequal variance.

Results

The irradiated UHMWPEs showed clear and detectable free radical signals (Fig 2a-2c inset). The free radical signals of irradiated UHMWPEs were not detectable after HPC (Fig 2a-2c).

The crystallinity of all high pressure crystallized irradiated UHMWPEs were higher compared to both the irradiated non-HPC UHMWPEs with the corresponding radiation dose and their melted counterparts (Fig 3). Similarly, the peak melting point (PMT) of 25 and 65-kGy irradiated HPC UHMWPEs were higher than both irradiated non-HPC UHMWPE and irradiated and melted UHMWPEs irradiated at the same dose (Fig 4), whereas that of 100-

kGy irradiated HPC UHMWPE was comparable to that of the 100-kGy irradiated UHMWPE and higher than that of the 100-kGy irradiated and melted UHMWPE. Irradiated UHMWPEs showed single, narrow crystal melting peaks (Figs 5a-5c). Melting at ambient pressure shifted this narrow peak to lower temperatures and caused slight to moderate broadening, whereas melting and HPC shifted the peaks to higher melting temperatures. In addition, after melting and HPC, 25-kGy irradiated UHMWPE showed a narrow peak with a lower melting shoulder (Fig 5a).

While post-irradiation melting decreased the ultimate tensile strength (UTS), yield strength (YS) and work to failure (WF) of irradiated UHMWPE at all radiation doses, subsequent HPC increased all of these properties at both 25 and 65 kGy (Fig 6-8). HPC had little or no effect on the UTS, YS and WF of 100 kGy irradiated, melted UHMWPE (Figs 6-8). Only at 25 kGy, there was also a statistically significant increase in UTS with HPC in comparison to the irradiated UHMWPE (Fig 6). Similarly, only at 25-kGy, the WF of irradiated, melted, HPC UHMWPE was comparable to irradiated UHMWPE, and was lower for 65 and 100-kGy irradiated UHMWPEs (Figs 7 and 8). In contrast to the other mechanical properties, elongation to break (EAB) of UHMWPE was decreased with HPC after melting at all radiation doses (Fig 9). The elastic modulus of irradiated UHMWPEs did not change significantly as a function of increasing dose (Table 2). The modulus was decreased as a result of melting at ambient pressure for 25 and 100 kGy irradiated UHMWPE and did not change for 65-kGy irradiated UHMWPE. Melting followed by HPC did not change the modulus of 25-kGy irradiated UHMWPE but increased that of 100-kGy irradiated UHMWPE significantly (Table 2).

Melting at ambient pressure decreased the fatigue crack propagation resistance of irradiated UHMWPEs as previously reported (Fig 10; ⁶). On the other hand, the fatigue crack propagation resistance of irradiated, melted, HPC UHMWPE was comparable to irradiated UHMWPE and higher than irradiated, melted UHMWPE for all radiation doses (Fig 10).

Transmission electron micrographs of high pressure crystallized unirradiated UHMWPE showed the presence of extended chain crystals, which are apparent from their larger size and thickness compared to irradiated, non-HPC UHMWPE (Figs 11a and 11b). Of note are bands vertical to the crystal growth direction within the crystalline lamellae in the HPC UHMWPE. The larger crystal size was also apparent in 25-kGy and 65-kGy irradiated, melted, HPC UHMWPE compared to irradiated, non-HPC UHMWPE (Figs 12a, 12b, 13a and 13b) as well as some occurrence of the vertical bands. For 100-kGy irradiated UHMWPE (Figs 14a and 14b), the change in the crystal size was not as pronounced from the TEM micrographs; the vertical bands were still apparent only in the HPC treated UHMWPEs.

The crosslink density of radiation cross-linked UHMWPE was slightly increased after high pressure crystallization, this increase was significant only for 25 kGy irradiated UHMWPE (Fig 15). The bidirectional POD wear rates of HPC UHMWPE were slightly lower than non-HPC UHMWPE (Fig 16).

Discussion

In this study, we investigated high pressure crystallization (HPC) of radiation cross-linked UHMWPE as a function of radiation dose. Irradiated, melted, HPC UHMWPEs were expected to be oxidation resistant because they are molten before crystallization at high temperature, therefore allowing the recombination of the residual free radicals from irradiation (Figs 2a-2c). Non-HPC irradiated and melted UHMWPEs irradiated to the same dose were used as control for mechanical strength since these samples do not contain

detectable free radicals and were expected to be equivalent to irradiated, melted HPC UHMWPE in terms of oxidation resistance. In addition, we have used irradiated non-HPC UHMWPEs to determine the direct effects of the HPC on irradiated UHMWPE.

We have previously shown that HPC of unirradiated UHMWPE increases its mechanical strength significantly⁷. The mechanical strength increase accompanies an increase in crystallinity and crystal size as determined by differential scanning calorimetry and transmission electron microscopy. Therefore, the increase in the mechanical strength was attributed to the presence and abundance of these extended chain crystals. It is believed that extended chain crystal growth occurs in the hexagonal crystalline phase. The stable hexagonal crystalline phase, as determined by in situ thermal analysis experiments, lies above about 210°C and 340 MPa^(17,18, Fig 1). However, it has been shown that extended chain crystals can be obtained in a 'transitional' hexagonal phase above about 190°C and 200 MPa¹⁹. In our previous studies with uncross-linked UHMWPE (GUR1050, 6 million g/mol), we were able to obtain extended chain crystals and increased crystallinity at 180°C and 310 MPa. The phase diagram of radiation cross-linked UHMWPEs has not been determined. In this study, we proposed that increased cross-link density would shift the hexagonal phase transition to higher temperature and pressures and thus, we performed our experiments at 200°C and 380 MPa.

Extended chain formation is highly dependent on the chain mobility of the semi-crystalline network. While chains which were crystallized within the orthorhombic lamellae are rotated randomly at chain stems and can slide past each other to obtain the more mobile hexagonal phase, it is also important that the amorphous phase be mobile as the growing crystals would incorporate more chains and chain segments into the lamellae from the amorphous network. Our goal is to improve the mechanical strength of radiation cross-linked UHMWPE by extended chain growth during HPC, but we proposed that there would be a cross-link density, above which the network would be too constrained by cross-links to form additional crystals. Therefore, we hypothesized that UHMWPEs irradiated with low radiation dose and having low crosslink density would benefit more from the HPC.

This hypothesis was supported by the presented data. The mechanical strength, as measured by the ultimate tensile, and yield strength of the 25-kGy and 65-kGy irradiated UHMWPEs improved significantly over their counterparts melted at ambient pressure while that of 100-kGy was unchanged (Figs 6 and 7). We and others have previously shown the effect of post-irradiation melting on crystallinity and mechanical properties^{6,20,21}. Due to a decrease in chain mobility due to crosslinking, the crystallinity and peak melting point of irradiated UHMWPEs are decreased after melting (Figs 3-5). In contrast, the crystallinity of irradiated, melted HPC UHMWPEs were increased, presumably due to the formation of extended chain crystals during HPC. The increase in the peak melting point of 25- and 65-kGy irradiated UHMWPEs point to the formation of larger crystals but this value is much less than the peak melting point achievable by the HPC of uncross-linked UHMWPE, around 146°C. In addition, only 25-kGy irradiated, melted HPC UHMWPE exhibited a crystal population distribution resembling that of unirradiated HPC UHMWPE (not shown) with a shoulder at 137°C (Fig 5a), presumably due to chain mobility comparable to that of unirradiated UHMWPE.

Although the lamellar thicknesses, as observed by TEM, increased after HPC for 25- and 65-kGy irradiated UHMWPE (Figs 12b and 13b), they were much smaller in comparison to non-irradiated HPC UHMWPE, which had an approximate lamellar thickness of 100 nm for a specimen with an average crystallinity of 70% and an average peak melting point of 146°C (Fig 11b). This is presumably due to the decreased chain mobility in the amorphous regions of radiation cross-linked UHMWPEs, limiting the growth of the lamellae.

Although not quite as apparent as the uncross-linked UHMWPE, the TEM images of 25- and 65-kGy irradiated, melted, HPC UHMWPEs also showed increased lamellar thickness (Figs 12 and 13) whereas there was no discernable difference in the size of the lamellae for 100-kGy irradiated, melted, HPC UHMWPE (Fig 14). One feature observed in the lamellae of all samples that have gone through HPC were the bands within the crystal perpendicular to the plane of the lamellae. We propose that these are due to lamellar twisting of the crystals which are placed under stress during the high pressure crystallization process. Lamellar twisting has been associated with the increased surface stresses induced by the surrounding melt or the separation between the crystals and regions of uncrystallizable polymer²². Increasing crosslink density in the amorphous phase was expected to increase uncrystallizable regions in the polymer. This may be the reason why 100-kGy irradiated UHMWPE also showed increased twisting despite no significant changes in the peak melting point and lamellar thickness.

Interestingly, the fatigue crack propagation resistance, which has been shown to increase with HPC in unirradiated UHMWPE^{7,15}, was not significantly changed when compared to before melting and HPC, in contrast to the ultimate tensile strength (Fig 3). The fatigue strength of irradiated UHMWPEs have been shown to decrease with post-irradiation melting at ambient pressure, presumably due to the decrease in crystallinity in the melting and subsequent re-crystallization. However, had crystallinity been the major factor influencing the fatigue strength, the fatigue strength of 25-kGy irradiated, melted HPC UHMWPE would have been higher than that of irradiated UHMWPE and the fatigue strength of 100-kGy irradiated, melted HPC UHMWPE would have been lower. The fact that all irradiated, melted HPC UHMWPEs had improved fatigue strength to the oxidatively equivalent irradiated, melted UHMWPE proved that crystallinity and lamellar size, indirectly shown by the peak melting point, played a significant role, but there were other factors influencing the fatigue crack propagation behavior as discussed below. Similarly, the elastic modulus of 25-kGy irradiated, melted HPC UHMWPE was not significantly different from irradiated, melted UHMWPE despite a large increase in crystallinity (Table 2).

Another important factor is the effect of HPC on the wear resistance of cross-linked UHMWPE for UHMWPE to be used as a joint arthroplasty bearing surface. We determined the cross-link density before and after HPC to assess if the stresses exerted on the tie-chains and cross-linking points during phase transformation and crystallization result in any substantial breaking of chains. The insignificant changes in the cross-link density of irradiated, melted, HPC UHMWPEs (Fig 15) showed that there was no significant chain scission in the network.

Although UHMWPE is considered a low wear material, wear particles of UHMWPE have been closely related to osteolysis and loosening of joint implants. It has been shown previously that increasing cross-link density in non-HPC UHMWPE is directly related to decreasing wear rate^{16,23}. Particles are thought to break up as a result of the orientation of the UHMWPE articular surface in one direction, weakening the oriented material in the transverse direction while under multidirectional motion. Therefore, the mechanism by which radiation crosslinking reduces wear is through the reduction of plasticity. The bidirectional POD wear rates of HPC irradiated UHMWPE were slightly less than the irradiated UHMWPEs (Fig 16). This was likely due to the decrease in the plasticity of the polymer as compared to the irradiated state, as determined by the work to failure (Fig 8; WF) and elongation to break (Fig 9; EAB). These decreases, in turn, were caused presumably by a combination of the increased crystallinity/decreased amorphous content of the polymer and the increased strength. While increased crystallinity could decrease orientation, increased strength could hinder the breakup of the oriented wear fibrils.

Conclusions

We have found that the strength of 25- and 65-kGy irradiated UHMWPEs could be improved through high pressure crystallization, presumably due to increased crystallinity and crystal size. In contrast, the mechanical properties of 100-kGy irradiated HPC UHMWPE were either maintained or decreased, supporting our hypothesis that there is a crosslink density limit in the amorphous content that would not allow additional crystal formation through HPC. None of the high pressure crystallized cross-linked UHMWPEs contained detectable free radicals, which promise the retention of their properties in the long-term. In addition, their wear properties were maintained. Therefore, HPC can be used effectively for imparting oxidative stability and improved strength on radiation cross-linked UHMWPEs with low to moderate cross-link density for total joint implant bearing surfaces.

Acknowledgments

This work was funded by a grant from the National Institutes of Health (AR110542) and a research grant from Zimmer, Inc.

References

1. Jasty M, Smith E. Wear particles of total joint replacements and their role in periprosthetic osteolysis. *Curr Opin Rheumatol*. 1992; 4:204–209.
2. Harris WH. Osteolysis and particle disease in hip replacement. A review. *Acta Orthopaedica Scandinavica*. 1994; 65(1):113–23.
3. Harris W. The problem is osteolysis. *Clin Orthop*. 1995; 311:46–53.
4. Wannomae K, Bhattacharyya S, Freiberg A, Estok D, Harris W, Muratoglu O. In vivo oxidation of retrieved crosslinked UHMWPE acetabular components with residual free radicals. *Journal of Arthroplasty*. 2006; 21(7):1005–1011.
5. Currier BH, Currier JH, Mayor MB, Lyford K, Collier JP, Van Citters DW. Evaluation of oxidation and fatigue damage of retrieved Crossfire polyethylene acetabular cups. *J Bone and Joint Surg*. 2007; 89:2023–2029.
6. Oral E, Malhi A, Muratoglu O. Mechanisms of decrease in fatigue crack propagation resistance in irradiated and melted UHMWPE. *Biomaterials*. 2006; 27:917–925.
7. Oral, E.; Godleski, C.; Malhi, A.; Muratoglu, O. Cross-linking is not necessary to decrease wear of UHMWPE: A Super-tough and low-wear UHMWPE. *Transactions of the 52nd Annual Meeting of the Orthopaedic Research Society* 2006; Chicago, IL. p. 659
8. Muratoglu OK, Bragdon CR, Jasty M, O'Connor DO, Von Knoch R, Harris WH. Knee simulator testing of conventional and crosslinked polyethylene tibial inserts. *Journal of Arthroplasty*. 2004; 19(7):887–897.
9. Digas G, Karrholm J, Thanner J, Herberts P. 5-year experience of highly crosslinked polyethylene in cemented and uncemented sockets - Two randomized studies using radiostereometric analysis. *Acta Orthopaedica*. 2007; 78(6):746–754.
10. Oral E, Greenbaum ES, Malhi AS, Harris WH, Muratoglu OK. Characterization of irradiated blends of alpha-tocopherol and UHMWPE. *Biomaterials*. 2005; 26(33):6657–63.
11. Bracco P, Brunella V, Zanetti M, Luda M, Costa L. Stabilisation of ultra-high molecular weight polyethylene with vitamin E. *Polymer Degradation and Stability*. 2007; 92:2155–2162.
12. Oral E, Wannomae KK, Hawkins NE, Harris WH, Muratoglu OK. α -Tocopherol doped irradiated UHMWPE for high fatigue resistance and low wear. *Biomaterials*. 2004; 25(24):5515–5522.
13. Oral E, Wannomae KK, Rowell SL, Muratoglu OK. Diffusion of vitamin E in ultra-high molecular weight polyethylene. *Biomaterials*. 2007; 28(35):5225–37.
14. Oral E, Christensen S, Malhi A, Wannomae K, Muratoglu O. Wear resistance and mechanical properties of highly crosslinked UHMWPE doped with vitamin E. *Journal of Arthroplasty*. 2006; 21(4):580–591.

15. Simis KS, Bistolfi A, Bellare A, Pruitt LA. The combined effects of crosslinking and high crystallinity on the microstructural and mechanical properties of ultra high molecular weight polyethylene. *Biomaterials*. 2006; 27(9):1688–1694.
16. Muratoglu OK, Bragdon CR, O'Connor DO, Jasty M, Harris WH, Gul R, McGarry F. Unified Wear Model for Highly Crosslinked Ultra-high Molecular Weight Polyethylenes (UHMWPE). *Biomaterials*. 1999; 20(16):1463–1470.
17. Bassett D, Turner B. New high-pressure phase in chain-extended crystallization of polyethylene. *Nature Physical Science*. 1972; 240:146–148.
18. Kurelec L, Rastogi S, Meier R, Lemstra P. Chain mobility in polymer systems: On the borderline between solid and melt. 3. Phase transformations in nascent UHMWPE reactor powder at elevated pressure as revealed by in situ Raman Spectroscopy. *Macromolecules*. 2000; 33:5593–5601.
19. Maeda Y, Kanetsuna H. Crystallization and melting of polyethylene under high pressure. I. Crystallization by slow cooling from the melt. *Journal of Polymer Science:Part B Polymer Physics*. 1974; 12(12):2551–2565.
20. Baker DA, Bellare A, Pruitt L. The effect of degree of crosslinking on the fatigue crack initiation and propagation resistance of orthopedic-grade polyethylene. *J Biomed Mater Res*. 2003; 66A: 146–154.
21. Medel FJ, Pena P, Cegonino J, Gomez-Barrena E, Puertolas JA. Comparative fatigue behavior and toughness of remelted and annealed highly crosslinked polyethylenes. *J Biomed Mater Res B Appl Biomater*. 2007; 83(2):380–90.
22. Schultz J. Self-induced field model for crystal twisting in spherulites. *Polymer*. 2003; 44:433–441.
23. McKellop H, Shen FW, Lu B, Campbell P, Salovey R. Development of an extremely wear resistant ultra-high molecular weight polyethylene for total hip replacements. *J Orthop Res*. 1999; 17(2): 157–167.

Fig 1. Schematic phase diagram of UHMWPE. High pressure crystallization (HPC) is achieved through melting and subsequently pressurizing to transition from the melt to the hexagonal phase.

Fig 2.
Free radical signal of 25-kGy (a), 65 kGy (b) and 100 kGy (c) irradiated, melted, HPC UHMWPEs compared with irradiated non-HPC UHMWPEs.

Fig 3. Crystallinity of irradiated, melted, HPC UHMWPEs as a function of radiation dose. The lines designate data groups between which there are significant differences ($p < 0.05$).

Fig 4. Peak melting point of irradiated, melted, HPC UHMWPEs as a function of radiation dose. The lines designate data groups between which there are significant differences ($p < 0.05$).

Fig 5.

Fig 5a. Differential scanning calorimeter 1st heat thermograms of 25-kGy irradiated (1), irradiated, melted (2) and irradiated, melted, HPC (3) UHMWPEs.

Fig 5b. Differential scanning calorimeter 1st heat thermograms of 65-kGy irradiated (1), irradiated, melted (2) and irradiated, melted, HPC (3) UHMWPEs.

Fig 5c. Differential scanning calorimeter 1st heat thermograms of 100-kGy irradiated (1), irradiated, melted (2) and irradiated, melted, HPC (3) UHMWPEs.

Fig 6. Ultimate tensile strength of UHMWPEs as a function of radiation dose after irradiation, after melting, and after HPC. The lines designate data groups between which there are significant differences ($p<0.05$).

Fig 7. Yield strength of UHMWPE as a function of radiation dose after irradiation, after melting, and after HPC. The lines designate data groups between which there are significant differences ($p < 0.05$).

Fig 8.

Work to failure of UHMWPE as a function of radiation dose after irradiation, after melting, and after HPC. The lines designate data groups between which there are significant differences ($p < 0.05$).

Fig 9.

Elongation to break of UHMWPE as a function of radiation dose after irradiation, after melting, and after HPC. The lines designate data groups between which there are significant differences ($p < 0.05$).

Fig 10.

Fatigue crack propagation resistance of UHMWPE as a function of radiation dose after irradiation, after melting, and after HPC. The lines designate data groups between which there are significant differences ($p < 0.05$).

Fig 11.
Transmission electron micrographs of unirradiated UHMWPE before (a) and after melting and HPC (b).

(a)

(b)

Fig 12. Transmission electron micrographs of 25-kGy irradiated UHMWPE before (a) and after melting and HPC (b).

Fig 13.
Transmission electron micrographs of 65-kGy irradiated UHMWPE before (a) and after melting and HPC (b).

Fig 14.
Transmission electron micrographs of 100-kGy irradiated UHMWPE before (a) and after melting and HPC (b).

Fig 15. Cross-link density of irradiated, melted, HPC UHMWPE as a function of radiation dose. The lines designate data groups between which there are significant differences ($p < 0.05$).

Fig 16.

Wear rate of irradiated, melted, HPC UHMWPE as a function of radiation dose. The lines designate data groups between which there are significant differences ($p < 0.05$).

Table 1

Sample groups

	Radiation Dose (kGy)	Post-irradiation process
Irradiated UHMWPEs		
	25	None
	65	None
	100	None
Irradiated and melted UHMWPEs		
	25	200°C in vacuum
	65	200°C in vacuum
	100	200°C in vacuum
Irradiated, melted HPC UHMWPEs		
	25	200°C, 380 MPa in water
	65	200°C, 380 MPa in water
	100	200°C, 380 MPa in water

Table 2

Elastic moduli of (a) irradiated, (b) irradiated and melted and (c) irradiated, melted, HPC UHMWPEs.

	Modulus (GPa)
25 kGy	
Irradiated	1.37±0.34
Irradiated and melted	1.03±0.07
Irradiated, melted, HPC	0.94±0.53
65 kGy	
Irradiated	1.78±0.30
Irradiated and melted	2.07±0.80
Irradiated, melted, HPC	Not available
100 kGy	
Irradiated	1.63±0.42
Irradiated and melted	1.41±0.50
Irradiated, melted, HPC	4.20±0.32