Irradiated, Vitamin E-Stabilized UHMWPE Acetabular Liners: A Retrieval Study

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Statement of Purpose: Radiation cross-linking, used to improve wear resistance of ultra-high molecular weight polyethylene (UHMWPE) bearings used in total joint arthroplasty, generates residual free radicals which are the precursors to oxidative embrittlement [1]. First generation materials adopted thermal treatments to eliminate or reduce free radical content, but came with compromises in reduced mechanical properties or insufficient stabilization [2]. A second generation alternative method infuses an antioxidant, vitamin E, into irradiated UHMWPE to stabilize against irradation- and *in vivo*-induced oxidation while maintaining fatigue strength [3]. *In vitro* studies predict excellent oxidation and wear resistance in vitamin E-stabilized bearings [3], but the long-term *in vivo* oxidation behavior, influenced by lipid absorption and cyclic loading [4], remains largely unknown. Our aim was to investigate *in vivo* changes in UHMWPE surgical explants that were radiation cross-linked and stabilized by vitamin E.

Methods: We analyzed 14 surgically-removed irradiated, vitamin E-doped and inert-gamma sterilized bearings (E1™, Biomet, Inc., Warsaw IN) with *in vivo* durations ranging from 3 days to 36.1 months and one never-implanted component. One retrieval with 2 days *in vivo* was stored on the shelf in air for 1 year before analysis. Total lifetime of components was summed as shelf storage prior to implantation, *in vivo* duration and *ex vivo* duration in air. Analyses were performed through the unloaded rim/eminence and the articular surface of each retrieval. Thin films (150 µm; n=3) were cut and analyzed using Fourier Transform Infrared Spectroscopy (FTIR) as a function of depth from the surface. Carbonyl index (CI) values were calculated from FTIR spectra per ASTM F2102-01ε1, both before and after 16 hour hexane extraction to extract absorbed species. Extracted thin films were also reacted with nitric oxide to quantify hydroperoxides, an intermediate oxidation product associated with oxidation potential. HI was calculated from FTIR spectra by normalizing the nitrate peak height at 1630 cm^{-1} to the absorbance peak height from the polymer backbone at 1895 cm^{-1}. Cross-link density was calculated from gravimetric swelling analysis per ASTM F2214. Crystallinity measurements were performed regionally using differential scanning calorimetry (DSC). Free radical content was measured in E1™ retrievals by electron spin resonance (Memphis, TN).

Results: Retrievals showed scratching at the articular surface, but retained machining marks up to three years *in vivo,* indicative of no measurable wear. Retrievals showed no significant oxidation at the time of surgical removal with maximum post-hexane carbonyl indices in the barely detectable range (MCI=0.029-0.154; Fig 1). Post-hexane carbonyl maxima were located at the surface of retrievals, which is expected as a result of the brief period of exposure to air between irradiation and vitamin E diffusion in the manufacturing process. These carbonyl profiles also differ from reported subsurface *in vivo* oxidative carbonyl peaks seen in long duration retrievals [5-6]. *Ex vivo* oxidation was not observed after 18 months of aging in air at room temperature. There was no average or regional increase in hydroperoxides (never-implanted HI=0.62±0.04; retrieval HI= 0.62±0.04), nor change in cross-link density (never-implanted: 0.275±0.015 mol/dm^3; retrieval: 0.295±0.016 mol/dm^3) or crystallinity (never-implanted: 58.3±1.4 %; retrievals: 60.0±3.5%). Lipid penetration increased with time, showing a higher rate of diffusion in loaded regions.

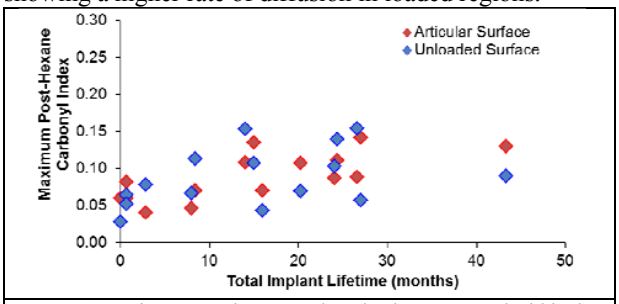

Figure 1. Maximum post-hexane carbonyl values measured within the loaded and unloaded regions of components as function of total implant lifetime, where OI=0.1 is considered the detection limit.

Free radical content was observed to decay with increasing *in vivo* duration ($p<0.05$), and by one order of magnitude (78%) by 19.5 months. A stronger negative correlation ($R^2=0.64$) was observed between the total age of the liner and free radical content (Fig 1).

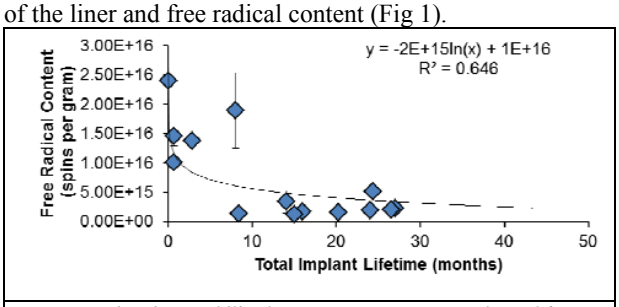

Figure 2. Vitamin E-stabilized UHMWPE components showed free radical content logarithmically decreasing with total lifetime.

Conclusions: The free-radical scavenging activity of the vitamin E appears to successfully prevent both *in vivo* and *ex vivo* oxidation for short durations, while reducing free radical content overall. Without an increase in hydroperoxides, the oxidation cascade initiated by radiation-induced and lipid-derived free radicals appears to have been halted. Retrievals also gave no indication of wear in this timeframe, similar to improved wear resistance seen in first generation materials. Continued monitoring will be necessary at longer implant durations.

References: [1] Sutula. Clin Orthop 1995;(319):28-40 [2] Muratoglu. J Arthroplasty 2001;16(2):149-160 [3] Oral. Biomaterials 2004;25(24):5515-5522 [4] Muratoglu. JBJS Am 2010;92(17):2809-16 [5] Currier. JBJS Am 2010;92A:2409-18 [6] Currier. J Biomed Mater Res Part B, online Sep 21, 2012.