Oxidative Analysis of Retrieved Moderately Cross-linked UHMWPE Acetabular Bearings After 10 Years In Vivo

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Statement of Purpose: Radiation cross-linked polyethylene is currently the most widely used bearing surface in total hip arthroplasty [1]. Irradiation generates residual free radicals which are known precursors to oxidative instability [2]. One method used to eliminate free radicals and provide oxidative stability is through post-irradiation melting [3]. However, recent retrieval studies have reported oxidation in some irradiated and melted UHMWPE bearings after long *in vivo* durations [4-5], and significant oxidative degradation after shelf-storage [6]. Since radiation-induced free radicals are eliminated during the manufacturing process, these results suggest *in vivo*-mechanisms initiating this oxidation with potential for material property changes. This study investigates whether these changes occur in a subset of moderately irradiated and melted acetabular liners with up to ten years of *in vivo* duration.

Methods: Twenty-nine surgically-retrieved 50kGy gamma-irradiated and remelted, gas plasma-sterilized UHMWPE (Marathon™, DePuy Inc., Warsaw, IN) acetabular liners with *in vivo* durations up to ten years (0.3-116 months) and one never-implanted liner were analyzed. Three retrievals were shelf-stored in air for 10-11 years while the remaining 26 were vacuum sealed and frozen at -20°C until analysis. The never-implanted liner and 6 retrievals with *in vivo* durations < 4 years (10.8-42 months) and no detectable oxidation were accelerated aged (5 atm O_2 at 70°C; ASTM F2003). FTIR was performed on articular surface and rim thin sections before and after 16hr hexane extraction. Carbonyl indices (CI), used to calculate lipid absorbance and oxidation, were calculated from FTIR spectra per ASTM F2102-$01^{\varepsilon 1}$. Hydroperoxides (HI) are considered to be indicative of oxidation potential [8] and were calculated, after 16hr nitric oxide staining, by normalizing the nitrate peak height at 1630 cm^{-1} to the peak height from the polymer backbone at 1895 cm^{-1}. Crystallinity measurements were performed using differential scanning calorimetry. Cross-link density was calculated using gravimetric swelling analysis per ASTM F2214.

Results: The never-implanted liner served as a baseline comparison for oxidation (CI=-0.11±0.00), lipid content (CI=0.01±0.00), hydroperoxides (HI=0.38±0.01), cross-link density (0.250±0.005mol/dm^3) and crystallinity (57.4±0.1%). All liners absorbed lipids, with higher absorption levels and penetration rate at the bearing surface than the rim. Four retrievals with *in vivo* durations greater than 4 years exhibited measurable subsurface oxidation (Max CI=0.10-0.41; Fig 1) with no correlation to *in vivo* duration nor any concomitant change in crystallinity or crosslink density. All retrievals showed an average increase of 15% in hydroperoxides compared to the fresh liner. Only one shelf-stored retrieval showed surface oxidation (MCI=2.10; Fig 1), accompanied by a 4x increase in hydroperoxides, a 53% decrease in cross-link density at the oxidized surface, and an increase (8.6%) in crystallinity with high variability.

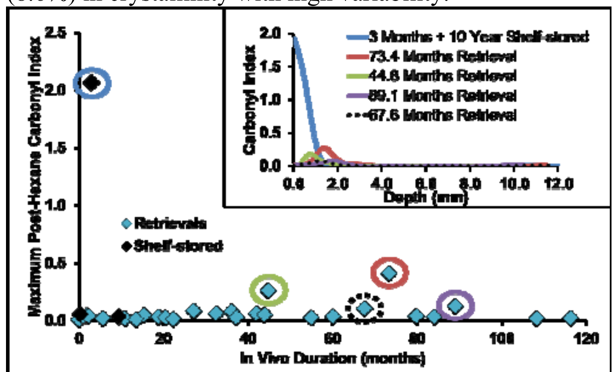

Figure 1. Four retrievals showed detectable subsurface oxidation (CI>0.1), while one showed *ex vivo* surface oxidation after shelf-storage. Inset: Carbonyl profiles for all liners showing oxidation.

All accelerated aged retrievals regardless of lipid levels showed surface oxidation (MCI=0.32-1.81; Fig 2) and decreased cross-link density (41-90%). No detectable oxidation was measured in the never-implanted acetabular liner after aging.

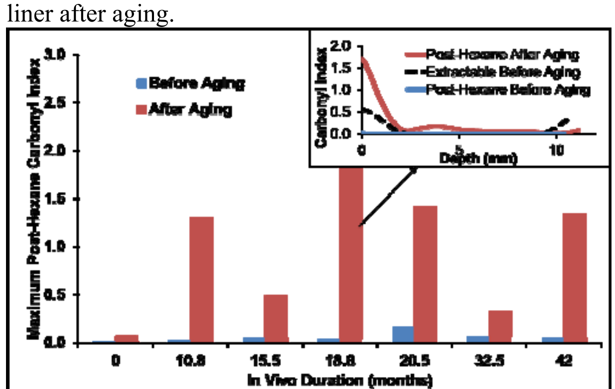

Figure 2. Retrievals with no *in vivo* oxidation showed high oxidation after accelerated aging. Inset: Aging-induced oxidation occurred at the surface of retrievals where lipids were absorbed *in vivo*.

Conclusions: Retrievals with up to 10 years *in vivo* showed low-to-no measurable oxidation with no associated material property changes that would impact wear resistance or clinical performance. However, shelf-aging and accelerated aging of retrievals evidenced oxidative degradation, indicating that exposure to *in vivo* loading and lipids impacted the oxidative stability of the material. Further investigation is required to assess the exact role of lipids and mechanical loading in the formation of subsurface carbonyls, and to determine the long-term impact of these preliminary changes on clinical performance over the next decade of service.

References: [1] Kelly. Am J Orthop. 2009;38:E1-4. [2] Muratoglu. Biomaterials. 1999;20:1463. [3] Muratoglu. JOA. 2001;16:149. [4] Currier. JBJS. 2010;92:2409-2418. [5] Rowell. 2010 ORS Annual Meeting. Paper #358. [6] Muratoglu. JBJS. 2010;92(17):2809-16. [7] James. Biomaterials. 1993;14(9):643-647. [8] Costa. *Biomaterials*. 1998;19(7–9):659–68.