Oxidative Stability of First and Second Generation Highly Cross-linked UHMWPE retrievals

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Statement of Purpose: Radiation cross-linked UHMWPEs were developed to address osteolysis-induced joint arthroplasty failure by improving wear resistance and reducing associated particulate debris [1]. Introduced clinically fifteen years ago, they are the primary bearing surface in use with excellent clinical outcomes. First generation materials sought to maintain oxidative stability by reducing or eliminating free radicals through thermal treatments [2], while second generation aimed to further balance oxidation resistance and improve mechanical properties through sequential irradiation and annealing [2] or the incorporation of an antioxidant [3]. Recent reports have identified lipid absorption and cyclic loading as potential *in vivo* oxidation-inducing mechanisms [4]. Surgically-retrieved highly cross-linked components serve to provide the greatest insight into the development of this *in vivo* oxidation and its potential impact on clinical performance. In this on-going retrieval study, we report on the current status of oxidative stability in these two generations of UHMWPE bearings.

Methods: Six types of highly cross-linked UHMWPE bearings used in hip and knee arthroplasty (Table 1) were surgically-retrieved and collected under IRB approval. No revisions were directly attributed to a wear or osteolysis or failure of the polyethylene component, however, Marathon™ and E1™ sample sets both contained retrievals that failed as a result of highly vertical cup positioning and subsequent rim fracture.

Table 1. Retrieval material type, sample sizes and *in vivo* durations

Retrieval Material	n	In Vivo Duration (Years)		
		Average	Max	Median
Marathon™ 50kGy irradiated/melted, gas plasma sterilized acetabular liners (DePuy, Warsaw, IN)	32	4.2 ± 3.1	10.2	3.6
Prolong™ 65kGy irradiated/melted, gas plasma sterilized tibial inserts (Zimmer, Warsaw, IN)	5	8.8 ± 1.9	10.5	9.1
Longevity™ 100kGy irradiated/melted, gas plasma sterilized acetabular liners (Zimmer, Warsaw, IN)	48	3.8 ± 3.6	10.6	2.8
Durasul™ 100kGy irradiated/melted gas plasma sterilized tibial inserts (Zimmer, Warsaw, IN)	6	2.9 ± 2.1	6.1	3.0
X3™ 90kGy (total dose) sequentially irradiated and annealed, gas plasma sterilized acetabular liners and tibial inserts (Stryker, Mahwah, NJ)	62	2.0 ± 1.7	7.1	1.5
E1™ 100kGy irradiated, vitamin E-stabilized 25-30kGy gamma-sterilized acetabular liners and tibial inserts (Biomet, Warsaw, IN)	15	0.8 ± 0.8	3.1	0.7

Standard material analysis was performed on cross-sections of loaded and unloaded bearing surfaces of the components. Thin sections (150 µm thickness) were extracted in boiling hexanes under reflux for 16 hours followed by vacuum drying for 24 hours. Fourier Transform Infrared Spectroscopy (FTIR) was used to evaluate oxidation , which was calculated from post-hexane absorbance spectra by normalizing the area under 1740 cm^{-1} (1680-1780 cm^{-1}) to the area under 1370 cm^{-1} (1330-1390 cm^{-1}), per ASTM F2102-01. Gravimetric swelling of regional cross-sectional blocks (1-2 mm^3) for 2 hours in 130°C boiling xylenes was used to assess cross-link density, per ASTM 2214.

Results: First generation irradiated and melted materials all showed detectable (OI>0.1) low level subsurface oxidation in the articular surface of the retrievals (Table 2; Fig 1). Behavior between materials types differed, however; 48% of Longevity acetabular liners (MOI=0.14±0.19) showed detectable oxidation as opposed to 19% in Marathon retrievals (MOI=0.07±0.08), both with comparable sample sizes and *in vivo* durations. We saw no change in the cross-link density at these regions of oxidative activity in first generation irradiated and melted materials, except in one case where OI>1.0.

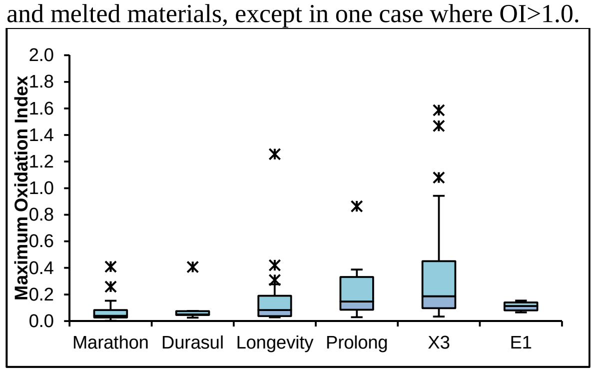

Figure 1. Box plots showing distribution of maximum oxidation indices found in highly cross-linked UHMWPE retrievals.

Sequentially irradiated and annealed retrievals showed the highest incidence of detectable oxidation (89%) higher average maximum oxidation (0.35±0.39) and showed signs of oxidative embrittlement, loss of cross-link density correlated with decreasing oxidation (R^2=0.32) and white banding. Oxidation was present in both loaded and unloaded surfaces. Antioxidant-stabilized E1 retrievals showed low maximum OI values (MOI=0.11±0.03) without change in material properties and a 94% decrease in free radical content.

Conclusions: Irradiated and melted UHMWPE retrievals showed subsurface oxidation, but with little to no impact on material properties detected after the first decade of service with no effect on clinical performance. High levels of detectable oxidation and embrittlement were identified in sequentially irradiated and annealed retrievals with short *in vivo* durations. Residual free radicals and varying levels of pre-implantation shelf oxidation, as a result of their sterilization-required air permeable packaging, are likely the cause behind this more rapid oxidation. Antioxidant-stabilized retrievals showed no change in their oxidative behavior with low baseline OI values in this very short 0-3 year follow-up. Continued analysis is needed to understand the second decade of behavior along with longer-term follow-up with patients to understand if these changes could affect clinical outcomes.

References: [1] Muratoglu. J Arthroplasty 2001;16(2):149-160 [2] Dumbleton. Clin Ortho Rel Res, 2006: 453: 265-271.[3] Oral. Biomaterials 2004;25(24):5515-5522 [4] Muratoglu. JBJS Am 2010;92(17):2809-16

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