Does In Vivo Oxidation in Highly Crosslinked Acetabular Components Lead to Chain Scission?

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Disclosures: 
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Introduction: The inverse relationship between crosslink density and ketone oxidation has recently been established for highly crosslinked (HXL) polyethylene tibial bearings.[1] In vivo oxidation in HXL components leads to chain scission which yields a decreasing measured crosslink density with increasing oxidation. Since the materials used to produce acetabular components are similar - and in some cases identical - to those used in tibial inserts, one might expect to observe comparable oxidative behavior in retrieved HXL acetabular components. However, several studies have recently established a notable difference in the in vivo oxidation rates of acetabular versus tibial devices. Given the difference in behavior, it is possible that in vivo oxidation in HXL acetabular components does not follow the same mechanism as in tibial devices, and that the relationship between oxidation and crosslink density found in tibial polyethylene components. The aim of this study was to determine whether in vivo oxidation in acetabular materials maintains the observed relationship between oxidation and crosslink density found in tibial polyethylene components. The hypothesis is that while acetabular components oxidize at a slower rate, oxidation will lead to chain scission in a similar manner as in tibial devices, which will result in a similar relationship of decreasing crosslink density with increasing oxidation.

Methods: Sixty-eight HXL acetabular components were used for this study. The set included four materials: AltrX (DePuy-Synthes, Warsaw, IN); Longevity (Zimmer Inc., Warsaw, IN); Marathon (DePuy-Synthes, Warsaw, IN); and X3 (Stryker Orthopaedics, Mahwah, NJ). In vivo duration ranged from 0 to 150 months, with an average of 36.2 months. Three components were removed for dissociation of the polyethylene component (2 AltrX, 1 Marathon) and all other reasons for retrieval were unrelated to the polyethylene bearing. Ketone peak height measured by Fourier transform infrared spectroscopy was used as an indicator of oxidation. The maximum ketone and the average ketone value through the first 2 mm of depth from the articular surface were calculated. Crosslink density was measured by a gravimetric gel swell technique utilizing 2 mm cubes cut from the articular surface. Spearman’s rank correlation was used to assess relationships, with p < 0.05 indicating significance and p < 0.15 indicating a trend.

Results: Oxidation increased with in vivo duration for AltrX, Longevity, and X3 (Figure 1). The relationship for Marathon was not significant (ρ = 0.22, p = 0.52). None of the materials showed a significant relationship between crosslink density and duration (Figure 2), though Longevity did have an apparent trend of increasing crosslink density with time in vivo (ρ = 0.42, p = 0.07). There was a significant negative relationship between crosslink density and average ketone oxidation for X3 (ρ = -0.63, p < 0.005), while Marathon exhibited a trend that was not significant (ρ = -0.55, p = 0.08) and AltrX had no trend (Figure 3). Longevity, on the other hand, exhibited a trend of increasing crosslink density with increasing average oxidation (ρ = 0.36, p = 0.13).

Discussion: Oxidation in terminally γ-sterilized UHMWPE materials is thought to occur by a free radical based mechanism, causing chain scission which ultimately leads to a degradation of mechanical properties. Previously, it has been shown that in vivo oxidation in HXL tibial bearings - which contain few or no free radicals - yields a substantial decrease in crosslink density, indicative of chain scission.

Since the HXL materials used in the hip are processed similarly to those in the knee, though often with higher crosslinking radiation doses, it was hypothesized that in vivo oxidation in HXL acetabular components would result in a decreased crosslink density in the same manner as in tibial materials. Only X3 showed a statistically significant relationship of decreasing crosslink density with increasing oxidation, consistent with the previous study in the knee. There was a notable, though not statistically significant, trend for Marathon as well.

For many of the materials, the statistics may have been limited by the small range of average and maximum ketone levels. In vivo oxidation in HXL materials has been shown to progress more slowly in the hip than in the knee. As a result, ketone values observed in this study were lower than in the previous investigation of HXL tibial components. With such a small range of oxidation values, the statistical power of the study is limited. However, as more and longer duration retrieved devices become available, observed trends may develop into significant relationships.

The most surprising result in this study is the observed trend of increasing crosslink density with either duration or average ketone oxidation for Longevity. While the trends were not significant in either case, the trends warrant further study. Longevity
is unique among the materials investigated in that it is crosslinked using electron beam rather than γ radiation. However, the material has no remaining free radicals following remelting, and to the authors’ knowledge there is nothing about material that should cause it to increase crosslink density over time. Further study may shed light on the oxidation mechanism in Longevity and other crosslinked UHMWPE materials.

**Significance:** While in vivo oxidation in highly crosslinked UHMWPE materials has been well established, the mechanism remains unclear. In light of the negative effects of oxidation in γ-sterilized polyethylene, it is important to monitor the performance of HXL bearings to determine what, if any, effects oxidation is having on the properties of the materials.

**Acknowledgments:**

**References:** 1. Reinitz, S. et al. Oxidation induced changes in crosslink density of retrieved, highly crosslinked UHMWPE tibial bearings. ORS 2013 Annual Meeting, San Antonio, TX 0943
Figure 1: Maximum ketone oxidation (1715 cm⁻¹/1368 cm⁻¹) versus in vivo duration for four highly cross-linked acetabular materials. The relationships of increasing oxidation with increasing duration were statistically significant for AltrX, Longevity, and X3 (p < 0.05) while...
Figure 2: Crosslink density versus in vivo duration for four HXL acetabular materials. No material exhibited a statistically significant relationship, though Longevity exhibited a trend of increasing crosslink density with increasing duration ($r = 0.42, p = 0.07$).
Figure 3: Crosslink density versus average ketone oxidation across the first 2 mm from the articular surface. There was a significant relationship between increasing oxidation and decreasing crosslink density for X3 (ρ = -0.63, p < 0.005) while Marathon exhibited a