Suppression of Crosslinking and Increase in Tensile Elongation in Irradiated, Remelted Polyethylene Containing Vitamin E

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Introduction: Ultra-high molecular weight polyethylene (UHMWPE) has been used as a bearing material in total joint replacements since 1962. It is currently subjected to radiation crosslinking followed by a post-radiation thermal treatment in order to quench free radicals that can lead to oxidative degradation, resulting in a substantial increase in wear resistance over uncrosslinked UHMWPE [1-2]. In recent years, Vitamin E has been introduced as an antioxidant in UHMWPE in order to avoid post-radiation thermal treatments since both radiation and the thermal treatment can decrease several mechanical properties [1-6]. While efforts are being made to avoid post-radiation melting or annealing by incorporation of antioxidants, there conceivably is a need for even post-radiation remelted or annealed UHMWPE to contain antioxidants since it has been shown that cyclic stress [7] and components of synovial fluid can promote oxidation even if there are no detectable free radicals present in the UHMWPE [8]. However, the presence of antioxidant in UHMWPE prior to irradiation can suppress crosslinking [6]. In this study we evaluated the mechanical properties and crosslink density suppression of irradiated and remelted UHMWPE containing various amounts of Vitamin E. We hypothesized that the presence of excess Vitamin E may affect tensile properties as well as crosslink density. Tensile tests and crosslink density measurements validated our hypothesis showing most of the tensile properties and crosslink density measurements depended on Vitamin E concentration in UHMWPE prior to irradiation and remelting.

Methods: GUR 1020 UHMWPE powder (Hoechst-Ticona, Houston, TX) was blended with a-tocopherol (Fisher Scientific, Houston, TX), which is a synthetic form of Vitamin E, and compression molded into 2 mm thick sheets. The concentration at which a-tocopherol was incorporated in the UHMWPE was 0, 0.1, 0.25, 0.5, 1, 1.5, 2, & 3 wt%, respectively, with the 0% a-tocopherol serving as a control. The sheets were then subject to 5 Mrad electron beam radiation, and then post-radiation melted at 180°C for 6 hours to remove free radicals. Crosslink density experiments were performed on pre-weighed cubic samples [n=6] of approximately 20 mg weight by immersing into xylene maintained at 135°C using a silicone oil bath for a period of 3 hours. Swell ratio (qeq), crosslink density (nd), and molecular weight between crosslinks (Mc) were calculated using the following equations: (1) qeq = (Volume of xylene absorbed + Initial volume of sample)/Initial volume of sample; (2) nd (mol/cm^3) = \_ \[ln(1-qeq-1) + qeq-1 + Xqeq-2] / V1(qeq-1/3 - qeq-1/2) and (3) Mc = (nd)-1 where V1 = 136 cm3/mol, X = 0.33 + 0.55/qeq [2,9] and n= 920 g/dm3 [10]. Uniaxial tensile testing was performed on ASTM D638-Type V specimens [n=8] using an Admet universal tester operating at 10 mm/min crosshead speed to measure tensile properties. A Q-2000 differential scanning calorimeter (DSC) was utilized to determine the percent crystallinity for all samples [n=3] using a heat of fusion of 289.3 J/h for polyethylene.

Results: Equilibrium swelling experiments showed that there was a general decrease in crosslink density with increase in Vitamin E content, as shown in Figure 1. There was a significant difference in the crosslink density between the Control UHMWPE with 0% Vitamin E and all other groups (p<0.05, ANOVA) as well as the following pairs: 0.1% Vitamin E UHMWPE - 3% Vitamin E UHMWPE and 0.25% Vitamin E UHMWPE - 3% Vitamin E UHMWPE. There was no trend in crystallinity observed with Vitamin E content and the crystallinity ranged from 39.6 ± 2.0 to 43.7 ± 2.2. Similarly, there was no trend in the Tensile Modulus, Yield Stress and Ultimate Tensile Stress, but a systematic increase was observed in Maximum Strain with Vitamin E content, as shown in Figure 2. There were no statistically significant differences observed in Maximum strain for the following pairs: 0 and 0.25% Vitamin E, 0.1 and 0.25% Vitamin E, 0.5 and 1% Vitamin E, 0.5 and 1.5% Vitamin E, 1 and 1.5% Vitamin E, 1 and 3% Vitamin E, and 2 and 3% Vitamin E UHMWPEs. The maximum strain for all other pairs showed statistically significant differences (p<0.05, ANOVA).

Discussion: This study showed that for 5 Mrad irradiated and remelted UHMWPE, crosslink density decreases with increasing Vitamin E content, while simultaneously increasing the maximum tensile strain (or elongation). The decrease in crosslink density with Vitamin E content is expected since it is known that Vitamin E is a radical scavenger and can suppress crosslink density. These results are in agreement with a study that has shown a decrease in crosslink density with increasing Vitamin E content for Vitamin E blended and irradiated UHMWPE with no post-thermal treatment [6]. This study also showed that tensile elongation increased with increasing Vitamin E content. This can also be expected to result from a suppression of crosslinking with increase in Vitamin E content. The change in elongation or maximum strain was highest up to 0.5% Vitamin E content and then the elongation appeared to level off, as shown in Figure 2. This is probably due to a leveling off of crosslink suppression under these conditions of crosslinking and processing, as shown in Figure 1. This indicates that an excess of Vitamin E beyond a 0.5 weight %
does not have any significant consequence for crosslink density suppression and elongation for a 5 Mrad irradiated and then remelted UHMWPE, but can possibly fortify it from oxidative degradation due to non-radiation factors such as cyclic loads [7] and synovial fluid absorption [8]. The oxidation resistance due to the presence of Vitamin E in irradiated, remelted UHMWPE must however be verified by accelerated and real time aging under conditions that simulate cyclic loads and oxidation associated with components of the synovial fluid or bovine serum, its analog. Optimization of Vitamin E in irradiated, remelted UHMWPE would also require a more comprehensive evaluation of mechanical and tribological properties of these crosslinked UHMWPEs prior to clinical use.

**Significance:** This study shows that Vitamin E, an antioxidant used in total joint replacement prostheses, can decrease the crosslink density and increase tensile elongation with increase in content in irradiated UHMWPE which is further remelted to remove free radicals. There is a clinical consequence to changes in crosslink density since crosslink density directly correlates with wear rates in total joint replacement prostheses while Vitamin E content may protect UHMWPE components of joint replacement prostheses from oxidative degradation.

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Figure 1: Inverse Correlation of Vitamin E Weight Fraction with Crosslink Density of UHMWPE.

Figure 2: Direct Correlation of Vitamin E Weight Fraction with Maximum Strain of UHMWPE.

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