Radiation Cross-linked, High Temperature Melted Vitamin E blended UHMWPE is Stable against Oxidation

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Introduction

Highly cross-linked ultrahigh molecular weight polyethylene (UHMWPE) joint implants are stabilized against oxidation either by post-irradiation thermal treatment (annealing or melting) [1, 2] or antioxidant stabilization by vitamin E [3]. It has been shown that radiation cross-linking reduces the wear but also decreases the mechanical strength of UHMWPE [4]. High temperature melting (HTM) followed by radiation cross-linking of UHMWPE was shown to result in low wear with improved mechanical properties [5].

HTM of UHMWPE eliminates fusion defects by accelerated intergranular diffusion. It also generates vinyl end groups, which upon irradiation lead to a uniquely cross-linked structure with low wear [5]. In this study, we describe vitamin E stabilization of cross-linked HTM UHMWPE. We hypothesize that vitamin E blended in UHMWPE prior to HTM and irradiation will improve the oxidation resistance against accelerated aging with and without synovial fluid lipids known to initiate oxidation of UHMWPE [6].

Materials and Methods

Medical grade GUR1050 UHMWPE was blended with vitamin E at 0.1, 0.2 and 1 wt%, and then consolidated at 181°C and 20MPa (10 cm diameter, 1 cm thickness pucks). These pucks were melted in an inert gas convection oven at 300°C for 5h under nitrogen, then e-beam irradiated at a rate of 25kGy/pass to 150kGy.

Double-notched impact strength measurements were conducted on samples of 63.5×12.7×6.35 mm³ according to ASTM F648. Cross-link densities were measured by swelling cubes (3 × 3 × 3 mm) in xylene at 130°C, as previously described [7]. Pin-on-disc (POD) wear testing was performed on cylindrical pins (dia. 9 mm, height 13 mm) as previously described [8] at 2 Hz for 1.2 million-cycles (MC).

Accelerated aging was done on 1 × 1 × 1 cm cubes in a pressure vessel filled with 5 atm oxygen at 70°C for 14 days with and without squalene doping. Squalene doping was done by immersing the cubes in squalene and heating in a convection oven for 2 hours at 120°C. Thin sections (150µm) were micromotomed from an inner surface of the cubes, boiled in hexane for 16 hours and vacuum dried. An oxidation index was calculated using Fourier Transform Infrared Spectroscopy (FTIR) by normalizing the absorbance at 1610-1769cm⁻¹ to 1330-1390cm⁻¹. The vitamin E content was calculated before hexane extraction by normalizing the absorbance at 1245-1275cm⁻¹ to 1850-1985cm⁻¹.

Results

Cross-link density of irradiated vitamin E-blended, HTM UHMWPEs were similar to irradiated virgin HTM UHMWPEs (p = 0.947, 0.924 respectively for 0.1 and 0.2 wt% blends). Similarly, wear rates of irradiated vitamin E-blended HTM UHMWPEs were comparable to irradiated, virgin HTM UHMWPEs (p = 0.457, 0.347).

The presence of vitamin E did not affect the wear rate of HTM UHMWPEs; therefore, irradiated HTM UHMWPEs were grouped together and compared to irradiated non-HTM UHMWPEs.

Wear rates of irradiated HTM UHMWPEs at 300°C and 320°C (1.7 and 2.2 mg/MC respectively) were similar to irradiated non-HTM UHMWPEs (2.13 mg/MC; p = 0.224, 0.844 respectively; Fig. 1). Similar wear rates were obtained at lower cross-link density for irradiated HTM UHMWPEs at 300°C and 320°C as compared to irradiated non-HTM UHMWPEs (p = 0.0475, 0.00635 respectively).

Pre-irradiation HTM improved the impact strength of irradiated UHMWPEs, which strongly correlated with decreasing cross-link density (Fig 2). Irradiated HTM blends of 0.1 and 0.2 wt% vitamin E did not show an increase in oxidation after accelerated aging for 14 days without squalene (Figs 3 and 5). Similarly, irradiated HTM blends did not show an increase in oxidation after accelerated aging in the presence of squalene (Figs 4 and 6). Overall, the oxidation levels were very low.

Discussion

The goal of this study was to determine the wear rate, mechanical properties and oxidation resistance of vitamin E-stabilized high temperature melted and radiation cross-linked UHMWPE.

Vitamin E blended irradiated HTM UHMWPEs showed wear rates comparable to (Fig 1) and impact strength higher than those of irradiated UHMWPE without HTM (Fig 2). The amount of vitamin E active in the polymer after processing protected it under the aggressive accelerated aging conditions (Figs 3-6), which we know oxidize virgin irradiated and melted UHMWPE severely (Oxidation level: 1.78; [6]). Presumably, this is because at least 65% of vitamin E is preserved in these materials despite the high processing temperature for a prolonged period of time (Fig. 7).

Figure 1: Wear rate of 150 kGy virgin, 0.1wt%, 0.2wt% vitamin E blended UHMWPE.

Figure 2: Impact strength of 150 kGy virgin, 0.1wt%, 0.2wt% vitamin E blended UHMWPE.

Figure 3: Average surface oxidation of 0.1wt% vitamin E blended, irradiated and squalene doped UHMWPE.

Figure 4: Average surface oxidation of 0.1wt% vitamin E blended, irradiated and undoped UHMWPE.

Figure 5: Average surface oxidation of 0.2wt% vitamin E blended, irradiated and squalene doped UHMWPE.

Figure 6: Average surface oxidation of 0.2wt% vitamin E blended, irradiated and undoped UHMWPE.

Figure 7: %Vitamin E graft in 1wt% blend as a function of radiation dose in kGy.

Significance

This study showed that vitamin E blended, high temperature melted, radiation crosslinked UHMWPE is oxidation-resistant with low wear rate and improved impact strength and is a feasible alternative to clinically available UHMWPE total joint implants.

Acknowledgements

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References