Surface Crosslinking of Vitamin E Blended UHMWPE via Spatial Extraction of Vitamin E Through High Temperature Processing

[1,2] Gupta, C; +[1,2]Oral, E; [1,2]Muratoglu OK
+[1]Harris Orthopaedic Laboratory, Massachusetts General Hospital, Boston, MA; [2]Department of Orthopaedic Surgery, Harvard Medical School
eoral@partners.org

Statement of Purpose Radiation crosslinking is used in ultrahigh molecular weight polyethylene (UHMWPE) joint implants to improve wear resistance [1]. Wear is a surface phenomenon [2] and increased cross-linking is detrimental to strength [3]. Thus, limiting cross-linking to the articular surface of implants is desirable to improve wear resistance without sacrificing mechanical strength. A method of surface cross-linking is via the spatial control of the anti cross-linking agent vitamin E (also an antioxidant) during irradiation [4]. We hypothesized that a surface cross-linked UHMWPE with high wear resistance could be obtained by extracting vitamin E from the surface of vitamin E-blended UHMWPE at high temperature by evaporation and subsequent irradiation.

Methods Medical grade UHMWPE (GUR1050) was blended with 1 wt% vitamin E and molded (10 cm dia., ~1 cm thickness), which were annealed to remove residual stresses. Machined cubes (1cm) were heated to 180, 250 and 290°C for 90 minutes to determine the effect of extraction temperature on the vitamin E concentration. Another set was heated to 290°C for 90, 210 and 290 minutes to determine the effect of extraction time.

Two pucks were placed on top of each other and masked on all sides except one circular surface. They were heated at 290°C in N_2 for 290 min with the unmasked surface exposed. Samples were subsequently irradiated to 175 kGy with the extracted surface the electron beam (10 MeV). Uniformly blended 0.1 wt% vitamin E-blended UHMWPE irradiated to 100, 150 or 200 kGy and a 'conventional' virgin UHMWPE without antioxidant irradiated to 25 kGy were controls. Before machining, 1 mm was machined from the surfaces.

Thin sections (150 microns) were cut from the extracted UHMWPEs. Fourier Transform Infrared Spectroscopy (FTIR) analysis was performed at every 100um from the surface. A vitamin E index was obtained by normalizing the area under the absorbance at 1260 cm^{-1} (1245-1275cm^{-1}) against that at 1895 cm^{-1} (1850-1985cm^{-1}). Wear testing was performed [4] in undiluted bovine serum. Wear was measured gravimetrically at 0.5 million cycles (MC), and every 0.16 MC until approximately 1.2 MC. Testing was repeated after milling off 100, 300, 600 and 1000 micron from the original surface. Small sections (3×3×1 mm, n=3) were cut at 1.5 mm, 5.5 mm and 8.5 mm away from the surface and swollen in xylene at 130°C to measure the cross-link density [5]. One thin section (3.2 mm thick) was machined from the surface (2-5 mm) and bulk (6-9 mm) of the extracted and irradiated puck. Dog-bones were stamped and tested at 10 mm/min in tension according to ASTM D-638 (Type V; n=4).

Results The extracted surface of 1 wt% vitamin E-blended pucks was defined as the depth (at x=0) at which the vitamin E index was below 0.04. Vitamin E concentration was not significantly depleted at 180°C but as the temperature increased from 250°C to 290°C, the surface increased from 0.4±0.1 mm to 1.0±0.0 mm (Fig 1a). When extraction increased at 290°C from 90 to 210 and 290 minutes (Fig 1b), the surface increased from 1.0±0.0 mm to 1.4±0.2 and 1.9±0.1 mm.

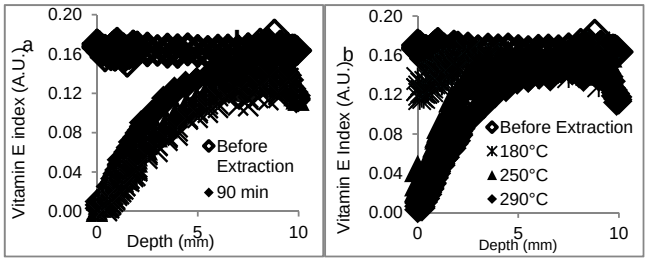

Figure 1. The vitamin E concentration profile of 1 wt% vitamin E-blended UHMWPE exposed to (a) 90 minutes at 180, 250 or 290°C (b) at 290°C for 90. 210 and 290 minutes.

Vitamin E blended UHMWPE had increasing weight loss with increasing temperature in contrast to virgin UHMWPE. The weight loss at 180, 250 and 290°C for 90 minutes was 0.1±0, 0.5±0 and 0.7±0 % whereas that of virgin UHMWPE was 0.1±0 % for all temperatures. The loss in the vitamin E index also correlated well with weight loss (R^2 = 0.91), further suggesting evaporation. These results supported our hypothesis that evaporation of vitamin E occurred at sufficiently high temperature and that the concentration profile of vitamin E could be controlled by high temperature exposure.

Irradiation of the extracted surface resulted in high cross-link density and low surface wear. The surface cross-link density was higher (208 mol/m^3; x=1.5mm) compared to the bulk (114 mol/m^3; x=8.5mm) (p<0.01) and to 25-kGy irradiated conventional UHMWPE (81 mol/m^3; p<0.01). It was equivalent to a 0.1% vitamin E blend irradiated to 116 kGy (intrapolated from controls). The extracted, irradiated UHMWPE had a surface wear rate of 2.7±0.4 mg/MC, which was lower than conventional UHMWPE (8.2±1.3 mg/MC, p<0.01) and between 0.1 wt% vitamin E-blended, 100 and 200-kGy irradiated UHMWPE (4.4±1.1 mg/MC, p=0.03 and 1.1±0.2 mg/MC, p<0.01).

Bulk crosslinking was lower than that of the surface; resulting in higher tensile strength (41 vs 31 MPa; p<0.01) and elongation-at-break (327 vs. 226%; p<0.01).

Conclusions This study showed that high temperature extraction of a vitamin E-blended UHMWPE and its subsequent irradiation could result in a surface crosslinked UHMWPE with low wear rate and high tensile strength.

References 1. McKellop et al. J Orthop Res, 1999. 17(2): p. 157-167. 2.Edidin et al. J Arthroplasty, 1999. 14(5): p. 616-27. 3. Baker et al. J Biomed Mater Res, 2003. 66A: p. 146-154. 4. Oral et al. Biomaterials, 2010. 31: p. 7051-7060. 5. Bragdon et al. J Arthroplasty, 2001. 16(5): p. 658-65.