Diffusion of Vitamin E in Radiation Cross-linked UHMWPE using Homogenization under Pressure

Doshi, Brinda[1]; Oral, Ebru[1,2,+]; Muratoglu, Orhun[1,2]
[1]Harris Orthopaedic Laboratory, Massachusetts General Hospital, Boston MA 02114
[2]Department of Orthopaedic Surgery, Harvard Medical School, Boston MA 02115
eoral@partners.org

Introduction Highly cross-linked ultrahigh molecular weight polyethylene (UHMWPE) joint implants are stabilized against oxidation either by post-irradiation thermal treatment (annealing or melting) or antioxidant stabilization [1]. Antioxidant stabilization can be achieved by post-irradiation diffusion of vitamin E. This process comprises doping and homogenization, both at below the peak melting temperature of irradiated UHMWPE (120-130°C) [2]. We hypothesized that homogenization can be made faster because increasing pressure can enable the use of higher temperatures without melting by elevating the melting temperatures [3].

Methods Virgin UHMWPE (GUR 1050) was irradiated to 100 kGy and machined into 1.5 cm cubes, which were doped in vitamin E under argon at 120°C for 2 hours. One set of cubes (n=3) were homogenized at ambient pressure, at 120°C and 130°C for 24 hours. Two other sets (n=3 each) were placed in a high pressure chamber in water at about 70 MPa and 150°C. The average pressure and temperature were calculated during the dwell cycle as the averages from when the sample reached 130°C upon heating to when the sample cooled to 130°C upon cooling and were 66.2 ± 9.7 MPa and 156 ± 8°C for 'LPA1' and 68.2 ± 8.3 MPa and 154 ± 8°C for 'LPA2', respectively. The dwell time at temperature/pressure was ~24 hours. The samples were cooled and the pressure was released.

Thin sections (150 μm) were cut from the cubes and analyzed by Fourier Transform Infrared Spectroscopy (FTIR) every 100μm along the depth. A vitamin E index was calculated by normalizing the absorbance at 1265 cm^{-1} (1245-1275cm^{-1}) by that at 1895 cm^{-1} (1850-1985cm^{-1}). The penetration depth of vitamin E was calculated as the depth where the vitamin E index was ≥ 0.02. Cross-link density was measured by swelling cubes in xylene at 130°C [5]. Crystallinity (n=3) was determined by integrating the enthalpy peak from 20°C to 160°C using differential scanning calorimetry at 10°C, and normalizing it with the enthalpy of 100% crystalline polyethylene, 291 J/g. Statistical significance was calculated using a Student t-test. Significance was assigned to < 0.05.

Results Our goal in manipulating the morphology of irradiated UHMWPE was to improve the diffusion of vitamin E in irradiated UHMWPE. The hypothesis was that we could achieve faster diffusion at elevated temperature under pressure without significant melting of the irradiated UHMWPE, which can reduce its mechanical strength [4]. The penetration of vitamin E was improved after doping and homogenization at 154-156°C at ~70 MPa (4.7±0.8 to 6.3±1.3 mm for LPA1 and LPA2) compared to that at 120-130° ambient pressure (2.8±0.8 and 4.0±0.5 mm), which is the fabrication method for clinically available implants (Fig 1).

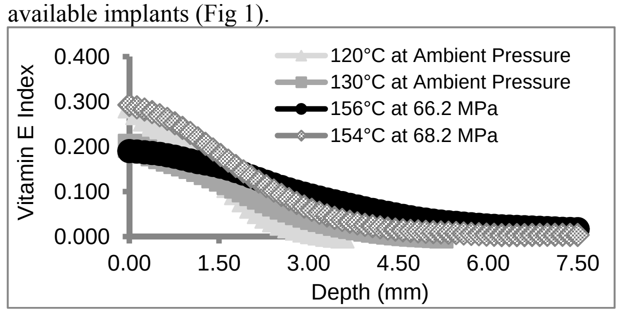

Fig. 1: The effect of annealing under pressure on the vitamin E index in irradiated UHMWPE as compared to diffusion at ambient pressure.

The cross-link density of the samples homogenized under pressure was comparable to the samples homogenized at 120°C (p=0.46, 0.43 for LPA 1 and LPA 2) and 130°C (p=0.45, 0.43 for LPA 1 and LPA 2) at ambient pressure. The crystallinity of the samples homogenized under pressure was comparable to the samples homogenized at 120°C at ambient pressure (p=0.48, 0.09 for LPA 1 and LPA 2) and 130°C (p=0.38, 0.04 for LPA 1 and LPA 2).

Previously, annealing under pressure used to reduce free radicals was accompanied by partial melting of the crystals, which resulted in two distinct crystalline populations [3]. Similar peaks were observed in samples homogenized under pressure, confirming partial melting. The sharp melting peak of irradiated UHMWPE after doping was preserved after homogenization at ambient pressure. (Fig 2).

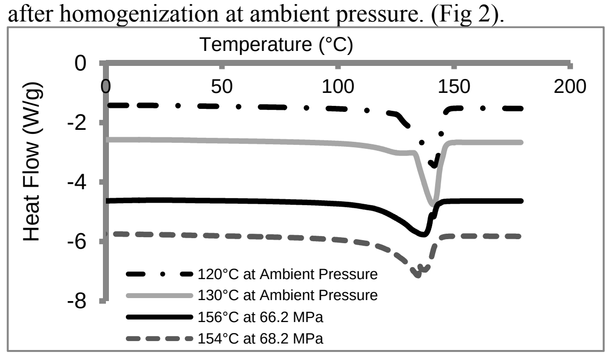

Fig. 2: The effect of annealing under pressure and annealing at ambient pressure on the melting behavior of vitamin E diffused, irradiated

We attribute the increase in the diffusion rate of vitamin E in irradiated UHMWPE partly to the increased energy at high temperature and partly to the increase in amorphous content available for diffusion.

Conclusions Homogenization of radiation cross-linked and vitamin E doped UHMWPE under pressure at about 155°C resulted in higher diffusion rate of vitamin E without decreasing crystallinity.

References 1.Kurtz, S. Biomaterials Handbook, S. Kurtz, Editor. 2009, Elsevier: New York. p. 291-308. 2. Oral et al. Biomaterials, 2007. 28(35): p. 5225-37. 3. Oral et al. JBMR 2011. 97B: p. 167-174. 4.Oral et al. Biomaterials, 2006. 27: p. 917-925.