The initial concentration of vitamin E in irradiated UHMWPE affects vitamin E grafting

[1]Neils, AL; +[1,2]Oral, E; [1,2]Muratoglu OK
[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 Vitamin E-stabilization of radiation cross-linked UHMWPE for oxidation resistant total joint implants can be achieved by blending vitamin E into UHMWPE powder, consolidation of the mixture, and irradiation [1]. This method avoids post-irradiation melting, which decreases the fatigue strength of irradiated UHMWPE [2]. Cross-links are formed during irradiation by the reaction of free radicals and impart increased wear resistance [3]. When vitamin E is present during irradiation, it reacts with free radicals, decreasing crosslinking compared to virgin UHMWPE [4]. Vitamin E may also graft onto the polymer [5], which may be beneficial in preventing elution in the long term.

Grafting of vitamin E was shown in 1 wt% vitamin E-blended UHMWPE. The goal of this study was to determine grafting at the clinically relevant concentrations of 0.1 to 0.3 wt% [6, 7].

Methods Medical grade UHMWPE (GUR1050) was blended with 2 wt% vitamin E and mixed further with virgin (no antioxidant) UHMWPE to obtain 0.1, 0.2, 0.3, 0.5, 0.75, 1 and 2 wt% blends. After compression molding, these blends were irradiated using electrons (10 MeV) to 25, 100, 125, 150, 175 and 200kGy at room temperature.

Vitamin E grafting: Thin sections (150 µm-thick) were cut from the irradiated pucks and Fourier Transform Infrared Spectroscopy (FTIR) was used to obtain spectra every 100µm along the depth. A vitamin E index was calculated as a ratio of the area under 1265 cm^{-1} (1245-1275 cm^{-1}) normalized by 1895 cm^{-1} (1850 – 1985 cm^{-1}), both before and after extraction with boiling hexane for 16 hours. Graft percentage was calculated as the ratio of the post-extraction vitamin E index to that before extraction.

Results The vitamin E was detectable for irradiated UHMWPE with initial vitamin E concentrations of 0.3 wt% or higher. For 0.1 and 0.2 wt% blends, vitamin E could be detected only in unirradiated samples and those irradiated at 100 kGy. The vitamin E index decreased in all irradiated samples; the decrease ranged from 30% for 2 wt% to 75 % for 0.3 wt% vitamin E-blended UHMWPE.

The graft percentage of vitamin E increased with increasing radiation dose (Fig 1). Almost all of the vitamin E in UHMWPE blended with lower concentrations of vitamin E (≤0.3 wt%) was grafted in UHMWPE with radiation doses as low as 100 kGy. Due to the limits of the FTIR, it was not possible to complete the analysis for 0.1 wt% and 0.2 wt% vitamin E-blended UHMWPEs. However, the increasing trend in graft percentage at lower concentrations suggests that most of the vitamin E in these UHMWPEs to be grafted in the range of 90 to 120 kGy, the current radiation dose range used in the fabrication of clinically available implants [6, 8].

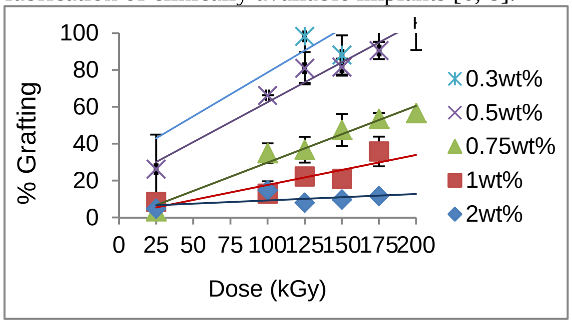

Figure 1. Vitamin E graft percentage as a function of vitamin E concentration and radiation dose.

The mechanism of vitamin E grafting is not known. It appears that there is an amount of vitamin E that gets entangled/grafted regardless of the initial concentration in the polymer (the absolute vitamin E index after hexane extraction was 0.01 to 0.04 in all samples). One limitation of our technique is the indirect analysis of grafting; a direct measurement of grafting is desirable by solid state spectroscopic techniques. Nevertheless, these results suggest that there is a significant amount of vitamin E in vitamin E blended and irradiated joint implants that would not be extractable under clinical conditions.

Earlier results showed improved oxidation resistance of 150 kGy irradiated 0.1 wt% vitamin E blended UHMWPE compared to virgin UHMWPE [9] suggesting that grafted vitamin E was effective against oxidation. A direct comparison of free and grafted vitamin E is difficult since irradiation also produces by-products of vitamin E, which may act as antioxidants with varying efficiency against free radicals and oxygen.

Conclusions The amount of grafted/entangled vitamin E in cross-linked UHMWPE was concentration-dependent with very high graft percentages at clinically relevant vitamin E concentrations and radiation doses. Immobilization of the antioxidant may hinder its elution in the long term.

References 1. Bracco et al. CORR 469:2286-93 (2011); 2. Oral et al. Biomaterials 27: 917-25 (2006); 3. McKellop et al. JOR 17: 157-67 (1999); 4. Oral et al. Biomaterials 29: 3557-60 (2008); 5. Oral et al. JBMR Accepted; 6. Lerf et al. Biomaterials 31: 3643-48 (2010); 7. Teramura et al. JOR 26: 460-4 (2008); 8. Corin, ECiMa™ Vitamin E technology. March 2012; 9. Oral et al. ORS#(2011).