Electron Beam Warm Irradiation Improves Oxidative Resistance and Grafting of Blended Vitamin E Polyethylene

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Statement of Purpose: Vitamin E (VE) has been shown to be an efficient stabilizer for preventing oxidation of crosslinked UHMWPE via addition to the polyethylene either before (blending) or after (infusion) consolidation and irradiation [1, 2]. An additional benefit afforded by both methods is the ability to stabilize the polyethylene without melting after irradiation, thus avoiding a reduction in mechanical properties. VE is a highly efficient free radical scavenger, and has potential for reducing the crosslinking achieved at a given irradiation dose. Irradiation also has potential for reducing the ability of the VE to serve as an oxidative stabilizer. Our hypothesis was that warm irradiation would result in higher levels of detectable VE after aging and extraction, which would improve oxidative stability.

Methods: A design of experiments (DOE) approach was utilized. The factorial design had 42 conditions with four numerical variables (pre-conditioning temperature, irradiation dose, dose rate and VE level) and one categorical variable (resin type, Ticona GUR 1050 or GUR 1020). Films microtomed from the compression molded and e-beam irradiated UHMWPE-VE blends were evaluated for vitamin E index (VEI), the FTIR ratio of peak areas (VE)1275-1245 to (PE)1985-1850 cm^{-1}, after crosslinking, after accelerated aging, and after aging followed by extraction with 16 hours refluxing hexane. Films were also evaluated for oxidation after aging with subsequent extraction per ASTM F2003-02.

Results: Material pre-conditioning temperature was the most significant factor for oxidation index (OI) after aging/extraction based on contribution to the model, see Figure 1. The effect of VE blend level on OI was much smaller, and included an interaction with irradiation dose rate. Higher VE levels lowered OI, and higher irradiation dose rates reduced OI at lower VE levels. Irradiation dose had no statistical significant effect on OI. The non-extractable or "grafted" VE was determined by two methods for VE content via FTIR where the Δ1 % grafting was determined as the ratio of VEI for aged, extracted material to VEI for non-aged, non-extracted material, and the Δ2 % grafting was determined as the ratio of VEI for aged, extracted material to VEI for aged, non-extracted material. The Δ1 response depended mostly on the starting VE level. Irradiation dose had greater effects at higher VE levels, where % grafting increased with increasing dose levels. The Δ2 response also depended mostly on starting VE level, but had a stronger dependence on irradiation dose level, where higher dose levels increased the % grafting at both low and high VE levels, see Figure 2. All figures are plotted with 95% confidence interval error bars. It can be seen that at lower levels of starting vitamin E, a high percentage of grafting occurs. Increasing irradiation dose, which also increases temperature during irradiation, serves to increase the amount of VE that is non-extractable, i.e. grafted, after aging as shown in Figure 2, even at lower VE levels.

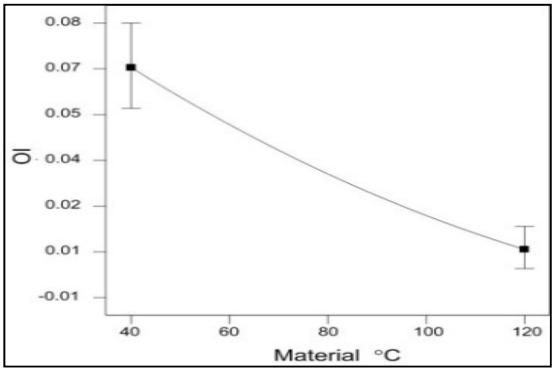

Figure 1. Oxidation vs. Pre-conditioning Temperature

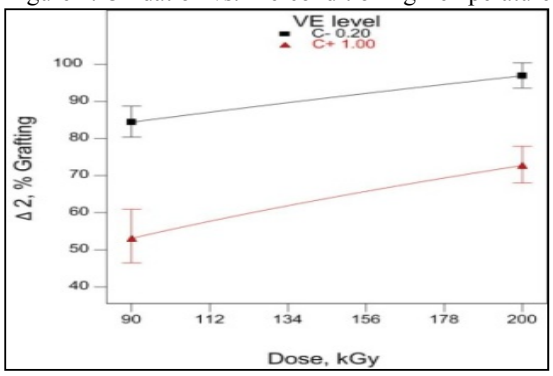

Figure 2. % Grafting vs. Irradiation Dose

Discussion:

Warm irradiation preserves a more active form of VE as shown in Figure 1, since oxidation can only be reduced by an active form of antioxidant. The non-extractable VE has been grafted to the polyethylene chain, as VE has been shown to be readily extractable from non-irradiated compression molded material manufactured from UHMWPE blended with VE. [3]. Electron beam irradiation is completed within seconds, and there is a significant amount of energy that manifests itself as heat (1 Gy = 1 J/kG), so the temperature achieved during irradiation is dependent on both temperature of the material just before irradiation, and the irradiation dose level. For this experiment, the temperature is therefore confounded with irradiation dose level.

Conclusions: Irradiation conditions can have significant effects on the oxidative stability and level of non-extractable (grafted) antioxidant for highly crosslinked VE-UHMWPE blends. Higher e-beam irradiation dose levels, resulting in higher temperatures during irradiation, increased the amount of grafted, non-extractable active VE after aging at all levels of VE examined.

References: [1] Wolf et al, J Mater Sci: Mater Med 13 (2002) 185–189 [2] Oral et al, Biomaterials 26 (2005) 6657–6663 [3] Braithwaite et al, paper 562, AAOS Annual Mtg, 2013(in publication).