The Efficacy of Vitamin E and a Hindered Amine Light Stabilizer in stabilizing UHMWPE from Oxidation

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Statement of Purpose: Oxidative degradation due to the presence of free radicals in irradiated ultra-high molecular weight (PE) components of total joint replacement prostheses have led to incorporation of antioxidants in PE, such as Vitamin E (or alpha-tocopherol) [1-3]. However, a concentration dependent decrease in crosslink density of PE has been observed if Vitamin E is incorporated prior to radiation since it is a radical scavenger and suppresses crosslinking. This would have a deleterious effect on wear resistance of PE, which is needed for the in vivo longevity of the PE component. A recent study showed that hindered amine light stabilizers (HALS) can prevent oxidation in PE without significant suppression of crosslinking since they only become radical scavengers upon irradiation [4]. In this study, we quantified the oxidation resistance and crosslink density for irradiated PE containing Vitamin E and a HALS stabilizer at a specific concentration in order to evaluate their relative efficacy for this application.

Methods: Compression molded sheets of GUR 1020 containing 0%, 0.75% Vitamin E and 0.75% of Chimassorb® 2020 (HALS1) were prepared. The relatively high weight percentage of 0.75 was chosen in order to be able to study small differences in the crosslink densities of irradiated GUR 1020 PEs. Discs of each sample of approximately 3 mm thickness were electron beam irradiated to a dose of 100 kGy and then subjected to accelerated aging in a convection oven for 8 weeks, sectioned and then subjected to Fourier Transform Infrared Spectroscopy (FTIR) using a Nicolet Magna 860 spectrometer (n=6). The oxidation index, OI, was defined to be the ratio of the area under 1740cm^{-1} carbonyl and 1370 cm^{-1} methylene stretching absorbance. Equilibrium swelling experiments were performed on pre-weighed cubic samples [n=6] of approximately 20 mg weight by immersing into Xylene maintained at 130ºC using a silicone oil bath for a period of 3 hours. The solvent swollen samples were sealed into pre-weighed glass vials and re-weighed. Swell ratio (q_{eq}) crosslink density (ν) and molecular weight between crosslinks (M_c) were calculated using the following equations:

(1) q_{eq} = [Volume of absorbed xylene + Initial volume of sample] /Initial volume of sample

(2) ν=_[ln(1-q_{eq}^{-1}) + q_{eq}^{-1} + Xq_{eq}^{-2}]/ $V_1 q_{eq}^{-1/3}$

(3) $M_c=(\nu\nu_d)^{-1}$ where V_1 = 136 cm^3/mol , X = 0.33 + 0.55/q_{eq} and ν_d= 920 g/dm^3 [5].

Results: FTIR showed no statistically significant difference (ANOVA, p>0.05) between the peak oxidation indices of HALS1 and Vitamin E while the control aged, irradiated PE was severely oxidized, indicating comparable oxidative stability in PE containing the stabilizers at a weight percentage of 0.75 (see Figure 1). GUR 1020 PE had the highest crosslink density as shown in Table 1. There was no statistically significant difference (ANOVA, p>0.05) in the swell ratio, crosslink density and molecular weight between crosslinks between control PE and PE containing HALS1. In contrast, PE containing 0.75% Vitamin E had a 62 % higher swell ratio, a molecular weight between crosslinks 2.4 times that of control PE and 59% lower crosslink density than control PE.

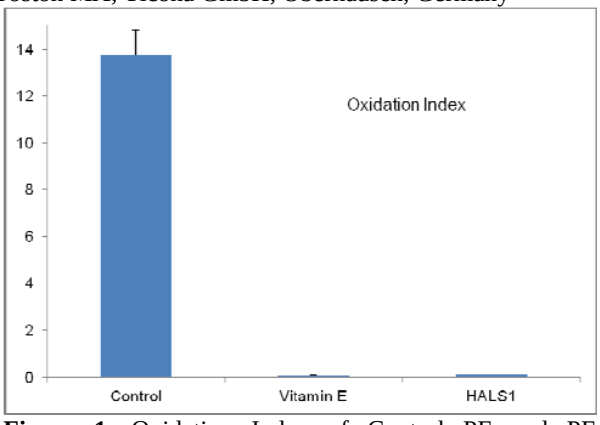

Figure 1. Oxidation Index of Control PE and PE containing 0.75% Vitamin E and HALS1 respectively

Table 1. Swell ratio (SR), Crosslink density (ν) and Molecular weight between Crosslinks (Mc) for control, 0.75% Vitamin E and 0.75% HALS1 stabilized PE respectively (mean ± standard deviation)

Sample	q_{eq}	ν [mol/dm^3]	M_c [g/mol]
Control	2.89 ± 0.03	0.227 ± 0.004	4063 ± 85
Vitamin E	4.67 ± 0.10	0.093 ± 0.003	9861 ± 347
HALS1	2.86 ± 0.05	0.231 ± 0.009	3981 ± 153

Conclusions: This study showed that there was a large decrease in crosslink density in PE containing 0.75% Vitamin E. In contrast, HALS1 stabilizer showed no statistically significant suppression of crosslinking while inducing a comparable oxidative stability in PE at an identical concentration as Vitamin E. This suggests that HALS may be preferable a stabilizer for GUR 1020 PE compared to Vitamin E purely from the standpoint of suppression of crosslinking and when the stabilizers are premixed into PE prior to irradiation. It must however be noted that 0.1% Vitamin E is deemed sufficient to induce oxidative stability in irradiated PE for implant application, and, at such a low concentration, is known to suppress crosslinking to a substantially lower extent than at 0.75% concentration [6]. Further studies must be conducted at various concentration of each stabilizer with molecular, morphological, tribological, mechanical and especially, biocompatibility assessment prior to implementation of an antioxidant, such as HALS1 for this clinical application requiring the maintenance of a high level of crosslinking in irradiated PE.

References: [1] Tomita, N, et al., J Biomed Mat Res 1999 48(4): 474-8 [2] Oral E, et al. *Biomaterials* 26(2005): 6657-6663 [3] Oral E, et al. *Biomaterials* 2004;25:5515-22 [4] Gijsman P et al, *Biomaterials* 2010; 31(26):6685-91 [5] ASTM standard F2214-02 [6] Ngo, H et al, Trans Orthop Res Soc, 2012; 37:2059.