Oxidative Stability of Highly Crosslinked Vitamin E UHMWPE Blends in Extreme and Physiological Accelerated Aging Conditions

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Antioxidant stabilized polyethylenes offer increased oxidative stability for implantable devices and are beginning to become commercially available. In particular, vitamin E (VE) stabilized materials show promise in extending the life of polyethylene implants *in vivo*. Historically, VE stabilized materials have been aged in conventional environments [1-3], but have not been in clinical use long enough to assess *in vivo* implant longevity. In this study we examine the accelerated aging of a highly crosslinked VE stabilized material relative to highly crosslinked and conventional ultra-high molecular weight polyethylenes. The materials are aged in the standard ASTM F 1980 [4] and F 2003 [5] accelerated aging environments, as well as in an accelerated bovine synovial fluid (BSF) environment intended to provide a more clinically relevant aging medium. Aging was performed up to 24 weeks to test the theory that VE stabilized polyethylene shows improved oxidative stability as compared to predecessor materials and that choice of aging medium can affect the physiological relevance of UHMWPE oxidation.

Materials Methods

Consolidated GUR 1050 was either gamma sterilized to 25-37 kGy (UHMWPE), e-beam irradiated to 100 kGy and melted (HXPE), or stabilized with 0.27 % VE by powder blending and e-beam irradiated to 200 kGy (VE-HXPE). Samples were packaged in vacuum-sealed bags and stored in a freezer to minimize unintended degradation or aging between tests. Five to seven 10 mm cubes of each material were aged according to ASTM F 1980 and ASTM F 2003, respectively. Additionally, seven cubes of each material were aged in BSF at 60 ºC 5 atm O_2. All cube surfaces were exposed to the aging environment. One cube of each material was removed at 1, 2, 3, 5, 6, 8, and 24 weeks. ASTM F 1980 samples were run for 6 weeks. Two-hundred micron slices were microtomed from the center of each cube for oxidation induction time (OIT) and oxidation index (OI) analysis. OI was measured according to ASTM F 2102 using FTIR through the full thickness of the samples at intervals of 200 µm. Surface oxidation index (SOI) was measured as the average oxidation index from the surface to 3 mm subsurface. Bulk oxidation index (BOI) was measured as the average oxidation index through the central 0.5 mm of the sample. Two samples were cored from the FT-IR slices post-analysis using a 6 mm punch for OIT analysis. OIT was measured according to ASTM D 3895 using a new analysis method equivalent to the tangent method, but insensitive to misleading/atypical features present in the oxidative exotherm [6]. The FT-IR sample of UHMWPE aged in BSF for 2 months was reflux extracted in hexanes for three days top remove adsorbed species and re-analyzed.

Results & Discussion

Table 1 shows the SOI and BOI for the materials in each environment by time point. Figure 1 shows oxidation index as a function of depth for each aging environment and material at various time points. OI and OIT analysis of VE-HXPE post-aging up to 6 weeks in ASTM F 1980 and up to 24 weeks in ASTM F 2003 and in 60 ºC BSF at 5 atm O_2 indicated minimal oxidative degradation. HXPE showed measurable oxidation by OI analysis after 5 weeks in the ASTM F 2003 environment. By 24 weeks, OI analysis could not be performed on HXPE. High degradation of UHMWPE occurred at 6 weeks in ASTM F 2003 and 24 weeks in BSF, preventing OI analysis. The aging results suggest that VE-HXPE exhibits excellent long-term oxidative stability even in extreme aging conditions and shows improved oxidative stability as compared to HXPE materials.

Table 1: SOI and BOI of accelerated aged UHMWPE samples over 24 weeks. ASTM F 1980 was run only for 6 weeks. Starred (*) samples were not measurable.

	0 wk	1 wk	2 wk	3 wk	5 wk	6 wk	8 wk	24 wk
VE-HXPE								
SOI								
ASTM F 1980	-0.08	-0.06	-0.06	-0.05	-0.07	-0.05	-	-
ASTM F 2003	-0.08	-0.06	-0.06	0.00	-0.02	-0.04	-0.01	0.02
BSF	-0.08	0.01	0.03	0.07	0.02	0.05	0.06	-0.02
BOI								
ASTM F 1980	-0.09	0.09	-0.08	-0.07	-0.07	-0.06	-	-
ASTM F 2003	-0.09	-0.05	-0.05	-0.04	-0.07	-0.03	-0.02	0.00
BSF	-0.09	-0.02	0.00	0.04	0.01	0.03	0.05	-0.03
HXPE								
SOI								
ASTM F 1980	-0.07	-0.07	-0.06	-0.06	0.08	0.22	-	-
ASTM F 2003	-0.07	-0.06	-0.04	0.03	0.66	1.58	4.23	*
BSF	-0.07	-0.05	0.00	-0.07	-0.06	-0.05	-0.05	-0.05
BOI								
ASTM F 1980	-0.06	-0.07	-0.06	-0.05	0.03	0.19	-	-
ASTM F 2003	-0.06	-0.06	-0.04	0.07	0.78	1.84	4.26	*
BSF	-0.06	-0.05	0.00	-0.08	-0.06	-0.05	-0.05	-0.04
UHMWPE								
SOI								
ASTM F 1980	-0.03	-0.01	0.06	0.01	0.15	0.27	-	-
ASTM F 2003	-0.03	0.02	0.08	0.56	3.59	*	*	*
BSF	-0.03	0.02	0.07	0.09	0.12	0.17	0.66	*
BSF (Extracted)	-	-	-	-	-	-	0.73	*
BOI								
ASTM F 1980	-0.03	-0.04	-0.02	0.01	0.03	0.05	-	-
ASTM F 2003	-0.03	0.02	0.20	0.72	2.53	*	*	*
BSF	-0.03	0.01	0.07	0.12	0.31	0.42	1.27	*
BSF (Extracted)	-	-	-	-	-	-	1.40	*

Figure 1: Oxidation index profile of VE-HXPE, HXPE, and UHMWPE in (A) ASTM F 2003 , (B) ASTM F 1980 , and (C) BSF aging environments.

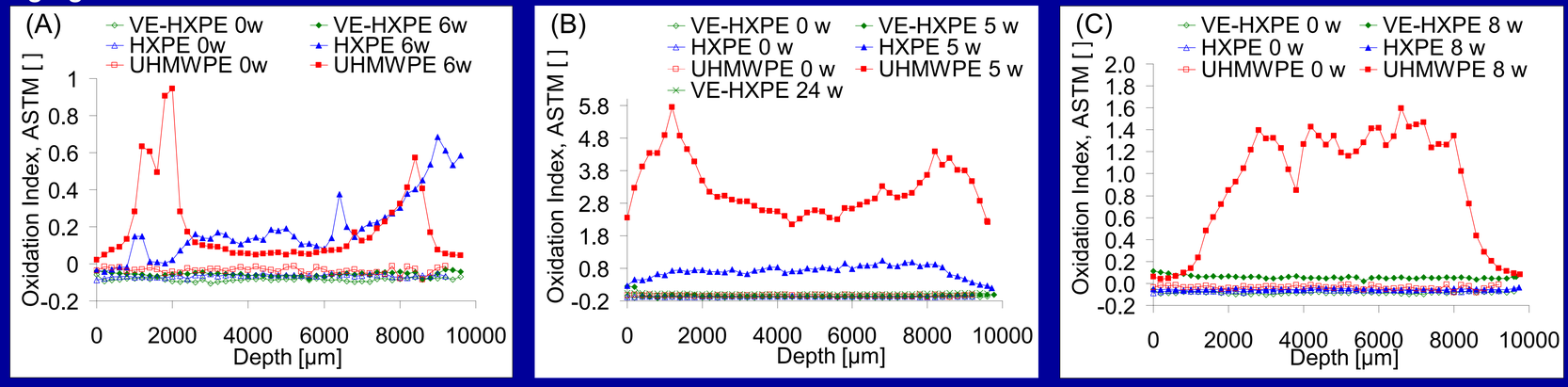
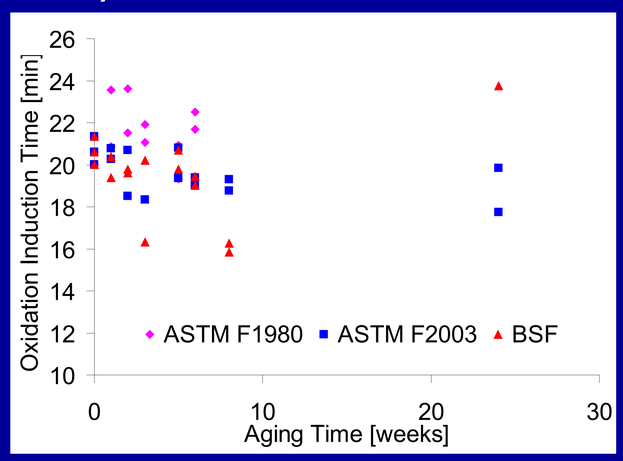


Figure 2: OIT of VE-HXPE at aging time points up to 6 months in each aging environment. VE-HXPE shows little change in OIT with aging time. HXPE and UHMWPE exhibit OIT values below one minute (data not shown).



OIT analysis of the VE material (Figure 2) suggests that there is little change in the oxidative stability of the antioxidant throughout the aging period. OIT provides a measure of stability distinctly different from OI because it measures the ability of the antioxidant to prevent oxidation rather than oxidative degradation of the bulk material. OIT is not currently used as a standard assessment of the long-term oxidative stability of polyethylene devices, and it does have its limitations since OIT values for non-stabilized materials are difficult to interpret given a nearly immediate oxidation reaction after the application of an oxygen purge. However, in this study OIT shows that VE provides antioxidant protection in VE-HXPE even after extreme aging.

The predominance of bulk oxidation of UHMWPE in BSF is also of interest. Oxidation increased alcohol group content in UHMWPE in addition to the usual increase in ketones. It may be that BSF components are stabilizing the UHMWPE surface by preferentially degrading, as has been noted elsewhere [7], but it is unclear what is causing the bulk oxidation effect. Further studies to understand the effects of BSF on oxygen and radical exposure of UHMWPE will be necessary to determine if BSF may be used in a more clinically relevant accelerated aging environment.

References

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Cambridge Polymer Group, INC.
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