Absorption of Physiologically Relevant Compounds in UHMWPE

[1]Berlin, J B; +[1]Braithwaite, G J C; [1]Spiegelberg, S; [2]Knight, J; [2]Pletcher, D; [2]Rufner, A.
+[1]Cambridge Polymer Group, 56 Roland Street, Suite 310, Boston, MA, [3]Zimmer, Inc., 1800 West Center Street, Warsaw, IN 46580
gavin.braithwaite@campoly.com

P 1297

It is well known that there are number of chemical species that absorb into UHMWPE implants during in vivo use, such as fatty acids and other lipids. It has also been suggested that these absorbable species may play a role in biodegradation of UHMWPE [1-4]. While this has been studied to some extent in first and second generation UHMWPE implants, little is known about the effect of antioxidant stabilizers on the absorption of species into UHMWPE. To further investigate this, we have studied the absorptivity of one representative material, isopropyl myristate (IM), into various UHMWPE formulations. Isopropyl myristate has a similar chemical structure to many biological compounds that might be absorbed into polyethylene, such as triglycerides and fatty acids (see Figure 1). Various UHMWPE formulations were soaked at elevated temperatures for up to six weeks in IM and then the relative bulk concentration of IM was determined using FTIR.

(a) Squalene

(b) Isopropyl Myristate

(c) Hexadecanoic acid, methyl ester

Figure 1: Chemicals (a) and (c) have been extracted from explanted UHMWPE [2]. Isopropyl myristate (b) was used as a model compound in this study.

Materials

Consolidated GUR 1050 material was prepared using five different processing conditions as described in Table 1. Three highly crosslinked materials were prepared (VE-HXPE, HXPE, Extracted), as well as two gamma sterilized formulations (VE-PE, UHMWPE). Two of the formulations contained similar amounts of vitamin E (VE-HXPE, VE-PE), two contained no vitamin E (HXPE, UHMWPE), and one originally contained vitamin E (VE), but was post-extracted such that the final vitamin E content is assumed to be minimal (Extracted).

Table 1: Description of 5 UHMWPE GUR 1050 materials examined in the study.

Material	Description
VE-HXPE	0.27% VE blended; 200 kGy e-beam crosslinked
HXPE	100 kGy gamma crosslinked; post-melted
Extracted	0.27% VE blended; 200 kGy e-beam crosslinked; post-extracted with hexanes (3 days) and isopropyl alcohol (3 days)
VE-PE	0.28% VE blended; 28.1-31.4 kGy gamma sterilized
UHMWPE	25-37 kGy gamma sterilized

Methods

Three 3 mm cube samples of each material were analyzed for crosslink density by swell ratio according to ASTM F 2214-02 [5] before aging. Crystallinity was measured in the bulk of the samples prior to aging by differential scanning calorimetry (DSC) according to ASTM F 2625-07 [6]. When possible, samples were vacuum-packaged and stored in a 0°C freezer to minimize the possibility of unintended degradation or aging. Five 10 mm cubes of each material were aged in 100% isopropyl myristate solution (Sigma-Aldrich, St. Louis, MO) in a 60°C oven. Care was taken to ensure that all surfaces of the cubes were equally exposed to the aging environment. One cube of each material was removed at 1, 2, 3, 5, and 6 weeks. 200 mm thick slices were microtomed from the center of each cube for FT-IR analysis. The IM index was calculated as the ratio of the height of the IM peak at 1738 cm^{-1} to the height of the polyethylene peak representing C-H overtones at 4322 cm^{-1}, and was reported from the bulk of the material (approximately 4.8 mm from the edge of the microtomed specimen).

Figure 2: Ratio of IM peak at 1738 cm^{-1} to PE peak at 4322 cm^{-1} as a measure of IM absorption versus aging time.

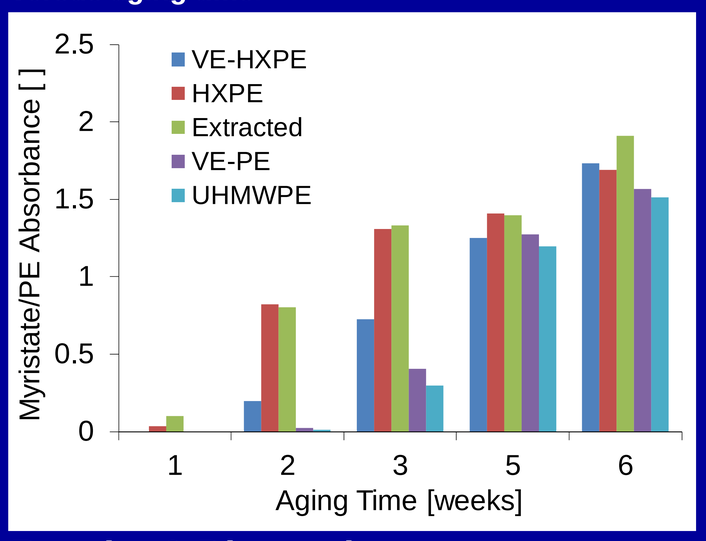


Figure 3: Crosslink density of IM aged materials prior to aging. Error bars = 1σ.

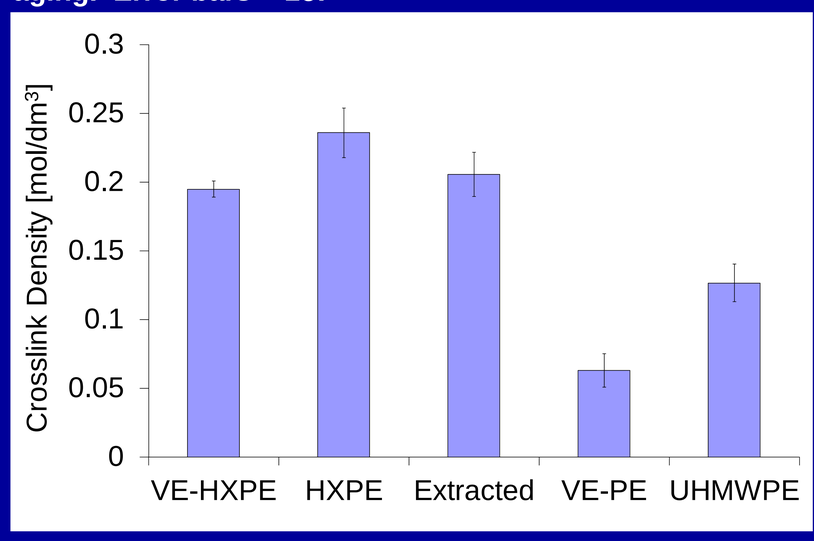
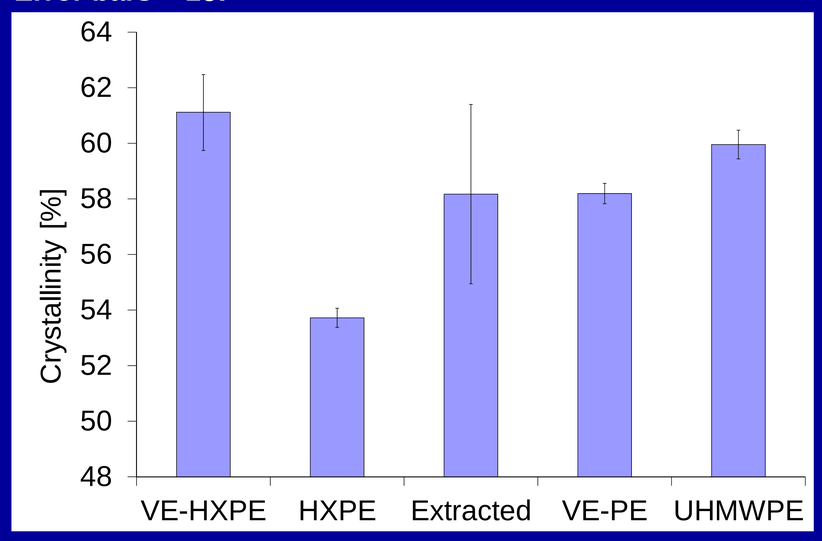


Figure 4: Crystallinity of IM aged materials prior to aging. Error bars = 1σ.



Results & Discussion

Figure 2 shows the absorption of IM into the bulk of each material at aging time points up to 6 weeks. Figure 3 shows the crosslink density of each material pre-aging. Figure 4 shows the percent crystallinity of each material pre-aging. Absorption profiles over the six week aging period in IM show some interesting trends. The HXPE materials show a higher initial absorption rate than the VE materials. While initially counterintuitive, this trend may be explained by increased free volume in crosslinked and melted materials due to either a greater number of chain ends or a reduced degree of crystallinity. The lower crystallinity of the HXPE supports this theory. The blended materials (VE-HXPE and Extracted) were irradiated at levels intended to yield similar crosslink densities to HXPE despite the presence of free-radical scavengers, as supported by Figure 3. The Extracted material indicated similar diffusion rates to the HXPE, which may be due to removal of unbound low molecular weight species leading to more free volume in the sample. However, the VE-HXPE has a lower initial absorption rate than either the Extracted or the HXPE samples, which may suggest that the presence of Vitamin E reduces the absorption rate of otherwise similar materials from surrounding solutions. The two non-crosslinked materials, VE-PE and UHMWPE, exhibited similar absorption rates, which could suggest that the protection against absorption afforded by vitamin E is the result of reduced free volume in highly crosslinked samples.

Although further work is required, these data may indicate that the VE acts to physically protect highly crosslinked polyethylene as well as imparting oxidative stability. After approximately five weeks the levels of IM appear to be similar, suggesting that it is the initial diffusion of the IM that is impacted, and not the equilibrium concentration at long times.

References

[1] Kurtz, SM. 2009. UHMWPE Biomaterials Handbook, 2nd edition. Burlington: Elsevier; p 320-340.
[2] Costa L, Bracco P, Brach del Prever E, Luda MP, Trossarelli L. 2001. Biomaterials 22: 307-315.
[3] Turner JL, Kurtz SM, Bracco P, Costa L. 2003. 49th Annual Meeting of the Orthopaedic Research Society.
[4] Costa L, Luda MP, Trossarelli L, Brach del Prever EM, Crova M, Gallinaro P. 1998. Biomaterials 19: 1371-1385.
[5] ASTM F 2214-02. “Standard Test Method for In Situ Determination of Network Parameters of Crosslinked Ultra High Molecular Weight Polyethylene (UHMWPE)”. 2002.
[6] ASTM F 2625-07. “Standard test method for measurement of enthalpy of fusion, percent crystallinity, and melting point of UHMWPE by means of differential scanning calorimetry”. 2007.

Acknowledgements: Polyethylene materials and funding were provided by Zimmer, Inc.

Cambridge Polymer Group, INC.
Consultation, Testing, and Instrumentation for Polymeric Materials