

## Effects of Natural Antioxidants on Polyethylene Radicals in UHMWPE

M. Shah Jahan<sup>1</sup>, Benjamin M Walters<sup>1</sup>, M. Azam Ali<sup>2</sup> and Arun Ghosh<sup>2</sup>

<sup>1</sup>Department of Physics, The University of Memphis, Memphis, TN 38152, USA

<sup>2</sup>Proteins & Biomaterials Team, AgResearch, Lincoln Research Centre, Christchurch 8140, New Zealand  
e-mail: mjahan@memphis.edu

**Statement of Purpose:** In an effort to improve wear properties of the load-bearing polyethylene (PE) components of total hip- and knee-joint replacement devices, antioxidants such as vitamin E ( $\alpha$ -tocopherol ( $\alpha$ -T)) have been incorporated into the PE matrix [1]. While the oxidation resistance of gamma-irradiated ultra-high molecular weight polyethylene (UHMWPE) has increased, it is not clear if vitamin E remains effective as a radical quencher after irradiation is complete. This question is frequently asked because, in presence of oxygen (air), the primary radicals are found to decay to a relatively stable long-lived radical whether UHMWPE contains vitamin E or not [2]. In this study, we investigated the effect of two natural antioxidants on the alkyl and allyl radicals. Low concentrations of 0.1% weight are typical of vitamin E-blended polyethylene because higher concentrations have been determined to prevent satisfactory crosslinking (at room temperature) [1]. The purpose of this study, however, is to investigate radical activity associated with two new antioxidants (AO1 and AO2), so their concentrations were prepared at higher levels (2.0 %) to better detect their corresponding radical activity; a similar approach was used by Jaworska et al. [3] who used 0.5% and 10% antioxidant (Irganox) in low density PE.

**Methods:** UHMWPE powder (GUR 1020) was blended with vitamin E and also with two other natural antioxidants – called here “AO1” and “AO2.” The blends were prepared and consolidated by AgResearch Ltd. in New Zealand: Six different disks were made with: 1) no additives (control); 2) 0.1%  $\alpha$ -T; 3) 2.0% AO1; 4) 2.0% AO2; 5) 0.1%  $\alpha$ -T and 2.0% AO1, and 6) 0.1%  $\alpha$ -T and 2.0% AO2. For production of alkyl radicals (-CH<sub>2</sub>-\*CH-CH<sub>2</sub>-), the test samples were irradiated for 30 min with X-rays (50 kV and 45 mA) in air at room temperature, and electron spin resonance (ESR) signals were recorded immediately after irradiation in air at room temperature using an X-band (9.8 GHz) ESR spectrometer (Bruker, EMX 300). To induce (predominantly) allyl radicals (-CH=CH-\*CH-), the samples were gamma-irradiated to approximately 30kGy in nitrogen and in air.

**Results:** First-derivative ESR spectra of each sample are presented in Figure 1; each exhibit characteristic features of an alkyl radical (a six-line pattern). No major differences are observed among the spectra, but the samples containing AO1 or AO2 show additional weak lines around the center of the spectrum. Gamma-irradiated samples were exposed to air and ESR spectra (allyl (not shown)) of each were recorded for up to 39 days. Figure 2 shows the radical concentration in each sample (spins per gram) as a function of sample type and storage time. While all samples show a gradual decay of the radicals, samples containing AO1 or AO2 retain a greater amount.

**Conclusions:** Polyethylene radicals were detected in UHMWPE (GUR 1020) containing natural antioxidants AO1 and AO2 and/or vitamin E. X-irradiated samples (with or without AO1 or AO2) produced similar radical concentrations, though the spectral features of the AO1 and AO2-containing samples were different. Allyl radicals generated by gamma irradiation decayed to more stable radicals, as reported before [2], in all samples. Slightly higher concentration of radicals in the AO1- and AO2-containing samples could arise from the antioxidant molecules themselves becoming radicals. Results of this study suggest that post-gamma decay of radicals in the presence of oxygen does not depend on the antioxidants.

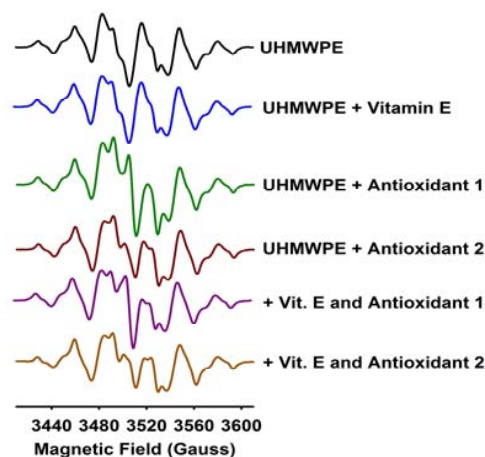


Figure 1. ESR spectra of blends of GUR 1020 as labeled.

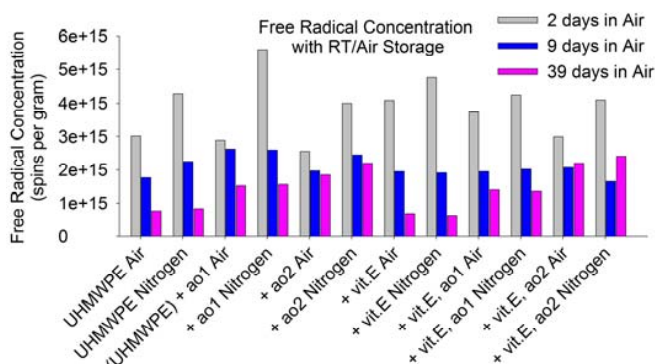


Figure 2. Radical concentrations after gamma-irradiation (30 kGy) in air or nitrogen, as labeled on the x-axis.

- References:** [1] E. Oral et al. 2004, 25, 5515.  
[2] Jahan, M.S. et al. Radiat. Phys. Chem. 2010, 62, 141.  
[3] E. Jaworska et al., Radiat. Phys. Chem., 1991, 37, 285.