

## Effects of Vitamin E on the Formation of Residual Radicals in $\gamma$ -Irradiated $\alpha$ -T-UHMWPE

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**Introduction:** Ultra high molecular weight polyethylene (UHMWPE) is a widely accepted material for load-bearing components in total joint replacements.<sup>1</sup> Improved wear resistance by cross-linking UHMWPE (XLPE) is accomplished by irradiating UHMWPE with ionizing radiation such as e-beam or gamma. Ionizing radiation is also used, by some, for sterilization of polyethylene produce free radicals ( $P^{\cdot}$ ) which lead to oxidative degradation of the components if they are not quenched or annealed. Secondary or residual radicals are also known to participate in oxidation. To combat oxidative degradation, vitamin E ( $\alpha$ -Tocopherol ( $\alpha$ -T)) is introduced into polymer matrix as antioxidant.<sup>2,3</sup> However, recent study reports formation of secondary and residual radicals in presence of  $\alpha$ -T without producing significant oxidation as measured by FTIR.<sup>4</sup> This phenomenon has triggered current research to investigate the effects of  $\alpha$ -T on formation of residual or oxygen-induced radicals (OIR) in UHMWPE.

**Materials and Methods:** Consolidation was made with GUR 1020 UHMWPE resin (Ticona). It was mixed with various  $\alpha$ -T concentration ratios ranging, 0.5%, 1.0%, 10.0%, wt. by wt. to create  $\alpha$ -T-PE matrix. Compression molding was performed on a customized Wabash Vantage Series 50 ton heating press with a ramp up and cool down rate of 10°C/min through temperature range (30°C to 190°C ( $\pm$ 10°C)) with a holding time (15 min. @ 190°C), minimum pressure of 1kN was used to sinter the resin powder. For irradiation, samples were packaged in two groups, one group in open air ( $\alpha$ -T-PE-A, C-PE-A) and the other in nitrogen-sealed Mylar foil bags ( $\alpha$ -T-PE-N, C-PE-N). All samples received 32 kGy gamma radiation (<sup>60</sup>Co) provided by Steris-Isomedix Services. Free radical measurements were performed on an X-band electron spin resonance (ESR) spectrometer (EMX 300, Bruker).

**Results and Discussion:** Before irradiation, consolidated  $\alpha$ -T-PE samples show presence of vitamin E radicals ( $\alpha$ -TO $\cdot$ ) whose concentration depends on %  $\alpha$ -T, see Fig. 1. Signals due to  $\alpha$ -TO $\cdot$  can not, however, be observed in irradiated samples, most likely because of strong, overlapping signals due to PE radicals (allyl and alkyl). While the major resonance lines in the initial spectra of  $\alpha$ -T-PE-A and  $\alpha$ -T-PE-N are similar to those of C-PE, each major line in  $\alpha$ -T-PE-N exhibit superhyperfine structure, see Fig. 2. Initial measurements also show significant difference in radical concentration between these samples;  $\alpha$ -T-PE-A has the lowest concentration.

Evidently,  $\alpha$ -T reduces or quenches radicals in  $\alpha$ -T-PE-A and  $\alpha$ -T-PE-N. When ESR spectra are recorded as a function of time in air, all three samples, C-PE,  $\alpha$ -T-PE-A,  $\alpha$ -T-PE-N produce signals characteristic of oxygen-induced terminal-radical, which is shown in Fig. 2(b). Additionally, similar changes occur in the absorption lines, from initial to terminal stage, further suggesting that free radicals go through similar transformation with or without  $\alpha$ -T.

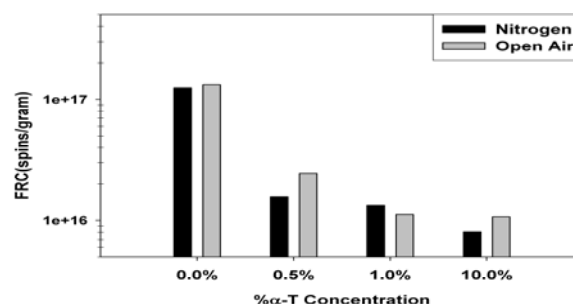


Fig. 1 Free Radical Concentration vs. %  $\alpha$ -T-UHMWPE

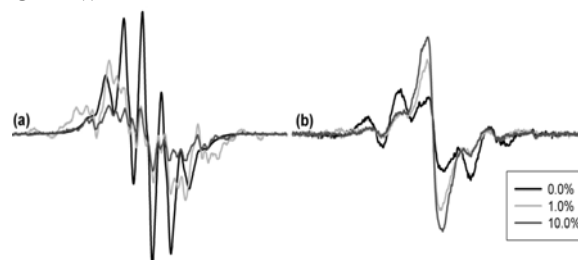


Fig. 2. (a) Initial and (b) 1 month of ESR spectrum as a function of concentration  $\alpha$ -Tocopherol

**Conclusion:** Free radical data suggest that  $\alpha$ -T acts as a quencher of primary/initial radicals. However, long-term reaction of PE radicals in presence of oxygen (air) does not seem to be affected by  $\alpha$ -T. Consequently, as much residual radicals are found in  $\alpha$ -T-PE as in C-PE. Additional work is needed to elucidate radical reaction mechanisms in UHMWPE in presence of  $\alpha$ -T.

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