

# Detection of Vitamin E Radicals in Gamma-Irradiated $\alpha$ -T-UHMWPE

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**Introduction:** Ultra high molecular weight polyethylene (UHMWPE) is a material of choice for load-bearing components in total joint replacements.<sup>1</sup> To improve wear resistance, cross-linked UHMWPE (XLPE) is produced by irradiating UHMWPE with ionizing radiation such as e-beam or gamma. Ionizing radiation is also used, by some, for sterilization. In either case, polyethylene radicals (P<sup>•</sup>) are produced which then lead to oxidative degradation of the components if they are not quenched or annealed. Recent studies suggest that radical-induced oxidative degradation can be reduced by introducing an antioxidant such as vitamin E.<sup>2,3</sup> Most studies use less than 1% vitamin E ( $\alpha$ -Tocopherol ( $\alpha$ -T)) which may be too low to have its free radical ( $\alpha$ -TO<sup>•</sup>) signal detectable within the overwhelming signal of its host radical (P<sup>•</sup>). In this study, high concentration of  $\alpha$ -T is used for monitoring both radicals at the same time following gamma irradiation.

**Materials and Methods:** Medical grade UHMWPE GUR 1020 resin (Ticona), was mixed with  $\alpha$ -T (95% pure, Sigma Aldridge) at a mixing ratio of 3:1 by volume. After mixing, the matrix was established further by diffusion for eight days at room temperature. ESR samples prepared from the mixture were divided into two groups. Groups received a dose of approximately irradiated to 35 kGy (Steris-Isomedix Services) with gamma rays (<sup>60</sup>Co). Groups of UHMWPE resin,  $\alpha$ -T,  $\alpha$ -T doped UHMWPE resin were irradiated in separated packages of nitrogen-sealed environment and another group in open air. After radiation treatment, free radical measurements were made on all samples as a function of time in air at room temperature. For free radical detection, electron spin resonance (ESR), X-band (9.8 GHz) spectrometer (EMX 300 by Bruker) was employed. FTIR was used for oxidation index measurements.

**Results and Discussion:** Low level vitamin E radical ( $\alpha$ -TO<sup>•</sup>) was found in as-received, non-irradiated  $\alpha$ -T. The concentration of the same radical increased as the sample sat in room environment for 85 days (Fig. 1). When gamma irradiated, concentration was increased by one order of magnitude without forming any new species (Fig. 2). It is to be noted that the seven-line ESR spectrum is a finger print of  $\alpha$ -TO<sup>•</sup>. ESR spectrum of  $\alpha$ -T-doped UHMWPE ( $\alpha$ -T-resin) mixture, irradiated in N<sub>2</sub>, shows the presence of both P<sup>•</sup> and  $\alpha$ -T<sup>•</sup> radicals with significant overlap. If, however, irradiation is performed in presence of oxygen (air), only  $\alpha$ -TO<sup>•</sup> radicals are detected (see Fig. 2). For comparison, Fig. 2 also shows ESR spectrum of an un-doped resin. Apparently, in open air, all P<sup>•</sup> are quenched by  $\alpha$ -T at and/or immediately after irradiation. However, the P<sup>•</sup> radicals that remain trapped in the  $\alpha$ -T-resin following irradiation in N<sub>2</sub> do

not seem to react with  $\alpha$ -T, and they undergo oxidative decay in exactly the same fashion as those present in un-doped resin. This is illustrated in Fig. 3 in which the peak-to-peak height of the rightmost line in the spectrum, representing P<sup>•</sup> radical (alkyl), is plotted as a function of oxidation time. The production of a single-line ESR spectrum (not shown) at the end of decay of P<sup>•</sup> radical further suggests that  $\alpha$ -T does not prevent formation of the long-lived oxygen-induced radical (OIR). Oxidation index obtained from FTIR measurements 85 days after aging in air are as follows: 0.02 (control resin), 0.07 (irrad. resin), 0.89 ( $\alpha$ -T-resin irrad. air) and 1.23 ( $\alpha$ -T-resin irrad. N<sub>2</sub>). These numbers seem to be consistent with the expected oxidation trend of UHMWPE.

**Conclusion:** By using high concentration of  $\alpha$ -T in UHMWPE resin we were able to observe both  $\alpha$ -TO<sup>•</sup> and P<sup>•</sup> radicals at the same time. Results of this experiment suggest that all P<sup>•</sup> radicals can be quenched provided  $\alpha$ -T-UHMWPE mixture is irradiated in open air. When the mixture is irradiated in N<sub>2</sub>, measurable amount of residual or secondary radicals remain trapped in the polymer matrix, and  $\alpha$ -T does not have any effect on them. Furthermore, this study also finds that  $\alpha$ -T can easily transform to its own free radical  $\alpha$ -TO<sup>•</sup> with or without

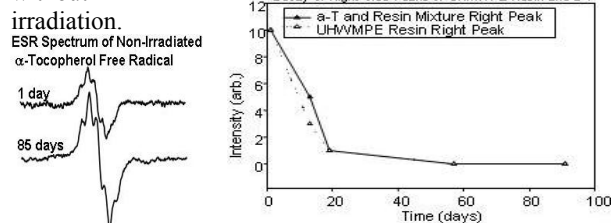


Fig. 2. ESR spectrum recorded in air three days after gamma irradiation. The N<sub>2</sub> represents irradiation in nitrogen and Open Air is irradiation in open air environments.

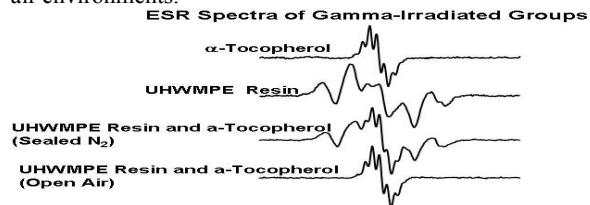


Fig. 3. Decay of secondary alkyl radical as a function of oxidation time in presence (solid line) or absence (dotted line) of  $\alpha$ -T.

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## References:

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