

Free Radical Activity during Vitamin E Diffusion of Ultra-high Molecular Weight Polyethylene

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Statement of Purpose: Gamma irradiation can be used for cross-linking and sterilizing the ultra-high molecular weight polyethylene (UHMWPE) which is beneficial and necessary for application in orthopedic implants.

However, irradiation with ionizing radiation produces free radicals in the polymer matrix. The formation of these species contributes to the overall degradation of the mechanical properties of UHMWPE [1]. Annealing is traditionally used after cross-linking to eliminate any residual free radicals, but results in a loss of crystallinity and decrease in fatigue resistance. An ideal alternative to annealing would be a process that eliminated free radicals while maintaining crystallinity. Research has shown that antioxidants, particularly vitamin E (alpha-tocopherol, α -T), meet these requirements [1]. Therefore α -T is a valid replacement for post-irradiation annealing. However, the reaction process of α -T with the primary UHMWPE radicals, alkyl or allyl, is not fully explored. In this study, electron spin resonance (ESR) technique is applied to follow the reaction of the alkyl and allyl radicals (P°) in presence of α -T at room temperature (23°C) and 100°C.

Methods: *Sample Preparation & Irradiation:*

Consolidated UHMWPE (GUR 1050) bar stock was machined into 2.5×2.5×8 mm³ blocks. After cleaning, the samples were placed in a nitrogen environment for γ -irradiation (30.1-33.9 kGy) at room temperature. Following γ -irradiation samples were packaged and placed in liquid nitrogen until measurements began.

Sample Treatment: Sample 2 was heated at 100°C ± 3°C without α -T. Sample 3 was heated at 100°C ± 3°C in presence of α -T. Sample 4 received no treatment with heat or α -T; it was kept at 23°C. Sample 5 was kept at 23°C in presence of α -T. All samples were kept in nitrogen environment during the treatments and measurements which lasted for two hours (only one hour data are shown in this report).

ESR Measurements & Data Analysis: Free radical measurements were conducted at 23°C in a nitrogen environment using an X-band (9.8 GHz) ESR spectrometer (Bruker, EMX 300). The ESR signals (first derivative of the absorption signal) were detected at 1.0 mW microwave power and 1.0 G magnetic field modulation amplitude. All samples with α -T were kept in α -T medium throughout the measurements.

Results: Shown in Fig. 1 is the ESR spectrum of the PE radical (P°) recorded before heating or treatment with α -T. Some of the lines due to alkyl and allyl are shown by arrows. Fig. 2 shows the spectrum recorded after the sample was heated at 100°C for two hours (B) in presence (α -TO $^\circ$ + P°) or absence (P°) of α -T. For comparison, a spectrum of the α -T radical (α -TO $^\circ$) is also shown in the same figure (A). Radical decay as a function of time is shown in Fig. 3. During the decay, no change in the radical structure was noticed in the ESR spectra, indicating that alkyl and allyl decayed independently.

Radical stabilization (relatively constant concentration) occurred after 30 minutes of treatment in all but the control sample, where concentration remained constant for the entire period as expected. Within the first five minutes, ~50% of the free radical signal had decayed; over the two hour span, almost 90% of the radical concentration was lost due to heating alone. There was no detectable difference between the decay of the two heated samples, though one was heated in presence of α -T and the other was not. α -T alone caused the radical concentration to decrease by ~40% and have an approximate 35% decay with the first five minutes.

Conclusions: It appears that, for a small sample (2.5×2.5×8 mm³), the free radical stabilization induced by heating overpowers the free radical scavenging ability of α -T. It also appears that heating at 100°C, and the addition of α -T, do not produce a synergistic effect with regard to free radical stabilization. The results, however, suggest that α -T has a stronger effect within the first five minutes of treatment than heating.

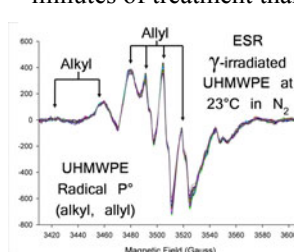


Fig. 1. ESR spectra of the alkyl/allyl radicals in N₂ environment recorded as a function of time (without α -T). The spectra recorded at different times superimposed well.

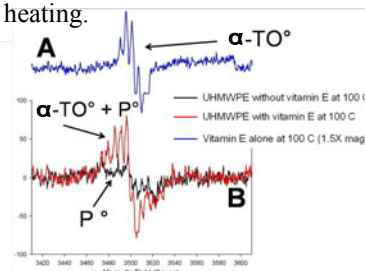


Fig. 2. A. ESR spectrum of the α -T radical (α -TO $^\circ$). B. ESR spectrum of the alkyl/allyl radicals with α -T (α -TO $^\circ$ + P°) and the alkyl/allyl radicals in UHMWPE (P°). Samples were heated at 100°C for 120 minutes in N₂.

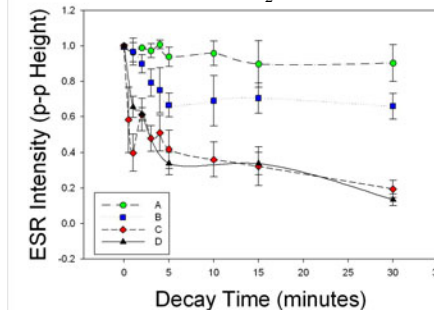


Fig. 3. Decay of the UHMWPE radical (P°) as a function of time in N₂: (a) no α -T and no heating (b) without heating, but in presence of α -T; (c) heated at 100°C in presence of α -T; (d) heated at 100°C in absence of α -T.

References:

[1] E. Oral *et al*, Biomaterials 2007; 28: 5225-5237; Biomaterials 2008; 5: 1-4; Biomaterials 2006; 27: 5580-5587.

Acknowledgements: Work was supported in part by the funds from NSF REU grant, NSF Center for Biosurfaces (IUCB), and the University of Memphis.