Radiation-Induced Free Radicals in UHMWPE: A Comprehensive Study for a Period of 25 Years

Afsana Sharmin[1], Benjamin M Walters[1], Farhan Azim[1] and M. Shah Jahan[1]

[1]*Biomaterials Research Lab, Dept. of Physics and Material Science, The University of Memphis, USA*

Purpose: Ultra High Molecular Weight Polyethylene (UHMWPE) has been in use as a component material for articulating surface of total joint arthroplasty (TJA) since 1962 [1]. While the clinical performance of UHMWPE was limited due to the wear debris of the material and delamination wear associated with oxidation, radiation-induced crosslinking followed by annealing (heating below melting point), introduced in 1998, has shown to increase the longevity of the load bearing components by circumventing the abrasive wear [2]. However, free radicals, resulting from gamma sterilization, were found to be responsible for the subsequent oxidation process which can lead to osteolysis and overall implant failure. Over the period of time, addition of vitamin E into UHMWPE was found to reduce the rate of oxidation by stabilizing the free radicals [3]. While this process has improved the life expectancy of the prostheses, long term clinical studies are ongoing. This study is focused to detect and analyze the long-lived free radicals inside gamma sterilized medical grade UHMWPE using Electron Spin Resonance (ESR) technique.

Methods: The solid medical grade UHMWPE samples used in this study were machined from ram extruded rod and prepared into a size appropriate for ESR testing. All the samples were irradiated with 30 kGy gamma radiation to achieve sterilization as well as crosslinking. Out of two, one group of samples were carefully prepared and annealed at different temperatures (23°C, 37°C and 75°C) in open air (in presence of oxygen) and sealed (inert gas, argon or nitrogen) environment for about 25 years. This study was initiated in 1998 as a part of a project between the State University of New York at Buffalo (SUNY Buffalo) and the University of Memphis under the sponsorship of the NSF Center for Industry/University Collaborative Research on Biosurfaces. Another group of UHMWPE samples, tested in this study, contained vitamin E (alpha-tocopherol) (%) as antioxidant and aged for 17 years at room temperature. The third group of samples were kept in Bovine solution for 25 years at room temperature. The free radical type and concentration (FRC) were analysed using an X-band Bruker EMX spectrometer operating at 9.8 GHz microwave frequency and 100 kHz magnetic field modulation frequency. The UHMWPE samples and the ESR system used in this study are shown in Fig.-1.

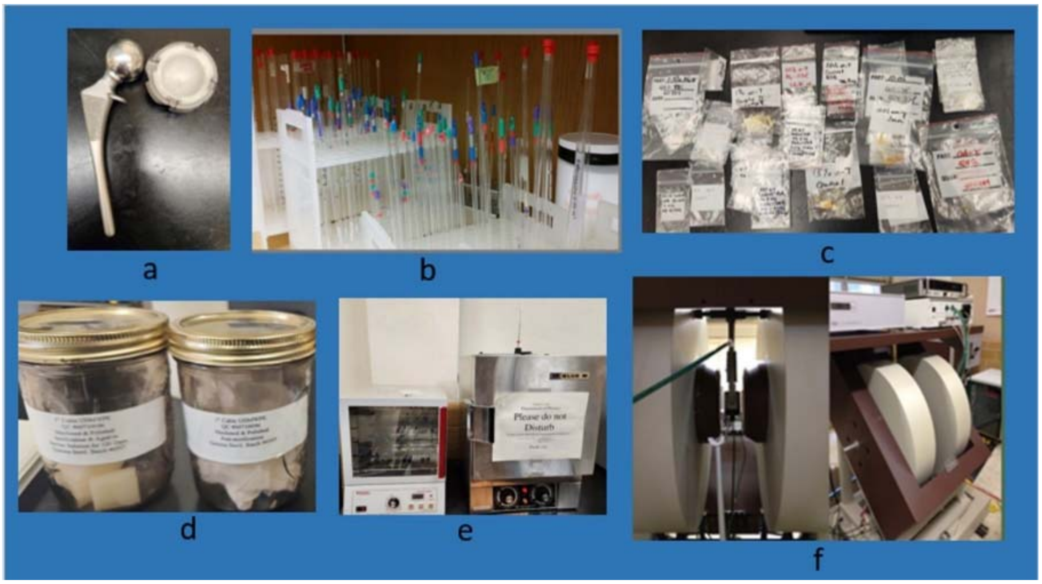


Figure 1: (a) UHMWPE components of total hip joint replacement. (b) Inert sealed UHMWPE samples at room temperature. (c) Shelf storage UHMWPE samples blended with vitamin E. (d) UHMWPE aged in Bovine solution at room temperature. (e) UHMWPE samples stored in oven at higher temperature, and (f) ESR system used in this project.

Results: The ESR spectra of UHMWPE samples aging in open air for 25 years indicated strong presence of oxygen-induced radicals whereas the inert storage samples aging for the same period indicated presence of primary (initially produced by gamma sterilization) radicals suggesting the oxidation protection effect inside the sealed environment, as shown in Fig.-2. In addition, R1 (carbon centered) and R2 (oxygen centered) radicals (shown in Fig.-3) were detected for the open air samples aging for 25 years. The primary radical types could be clearly detected and estimated for a typical sealed sample at 37°C, as shown in Fig.-4. The effect of annealing in reducing the number of trapped free radicals in open air samples aging for 25 years was found to be less in room temperature (23 °C) and higher at body temperature (37 °C), as shown in Fig.-5. There were no detectable free radicals observed in the samples stored in elevated temperature (75 °C) (Fig.-5). The antioxidant effect of vitamin E was found to be slightly higher in 0.5% (compared to 1%) following 17 years of aging in open air at room temperature as shown in Fig.-6. This effect was significant in the samples aged in bovine solution for 25 years (Fig.-6). The free radical concentrations of all open air samples were found to be reduced by at least 10^4 over 7 years, as shown in Fig.-7.

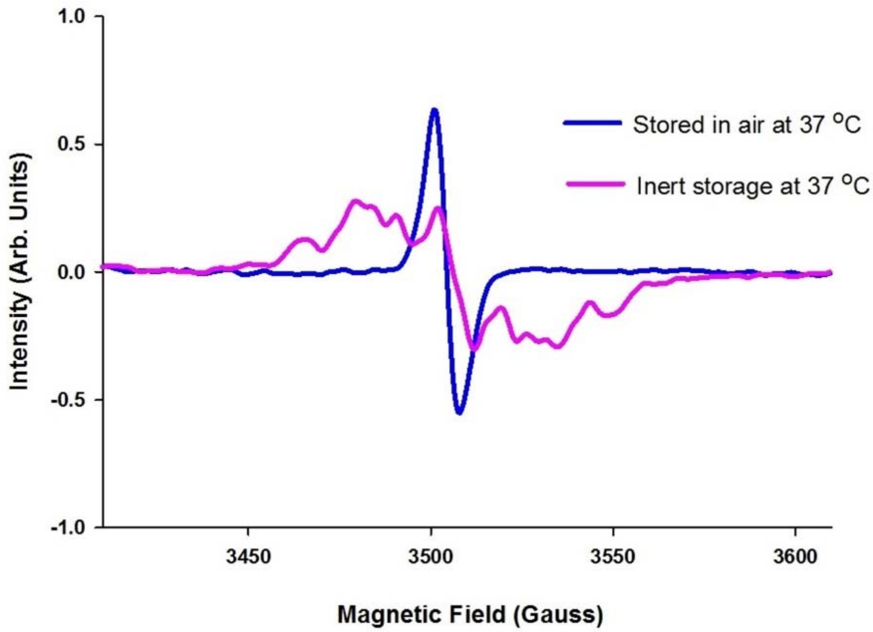


Figure 2: Comparative ESR spectra of open air and sealed UHMWPE samples after 25 years of aging.

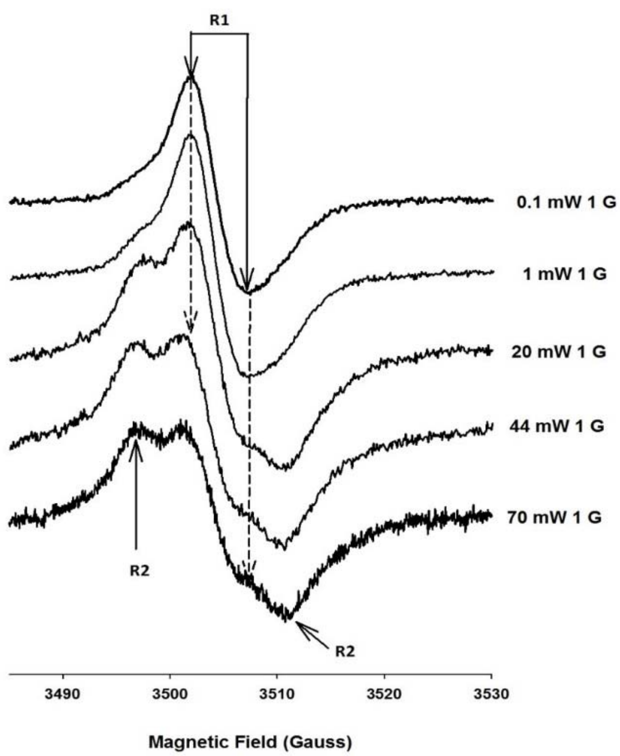
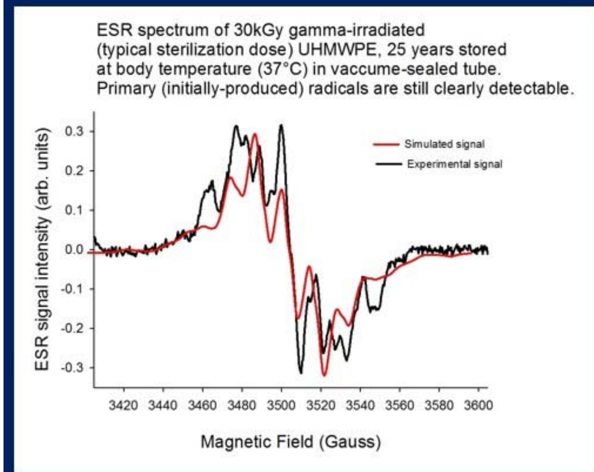


Figure 3: R1 (Carbon-centered radical) and R2 (Oxygen centered radical) observed in UHMWPE after 25 years of aging in open air at room temperature (23°C).



Percent (%) composition of radical types observed for 30 kGy gamma irradiated UHMWPE, after 25 years of aging in vacuum sealed tube at body temperature (37◦C)

Alkyl	8
Allyl	46
Polyenyl	17
Dienyle	23
Trienyle	6
Vitamin E	0
Total	100

Figure 4: Detection of some primary radical types within a sample by comparing simulated and experimental signal.

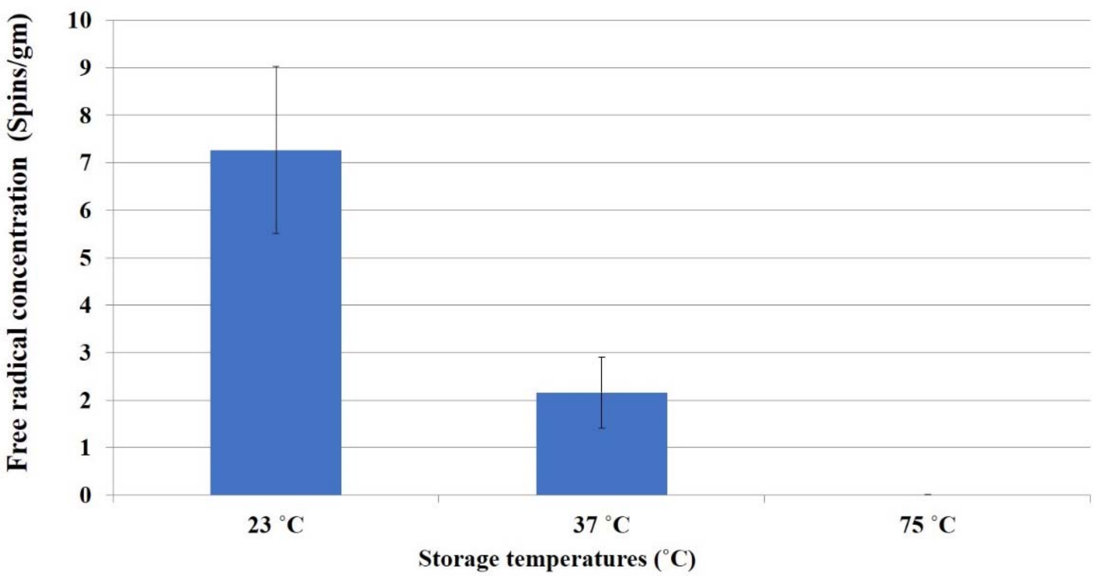


Figure 5: Relative Free radical concentration (FRC) of all open-air UHMWPE samples aging at different temperatures for about 25 years.

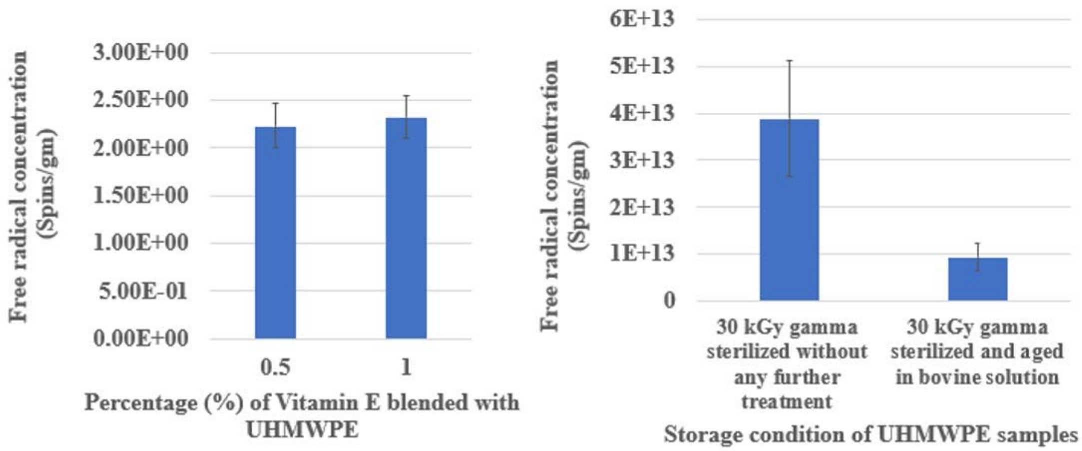


Figure 6: Antioxidant effect of vitamin E (α-Tocopherol) and Bovine solution in stabilizing the gamma induced free radicals inside UHMWPE after 17 years and 25 years of storage in air, respectively.

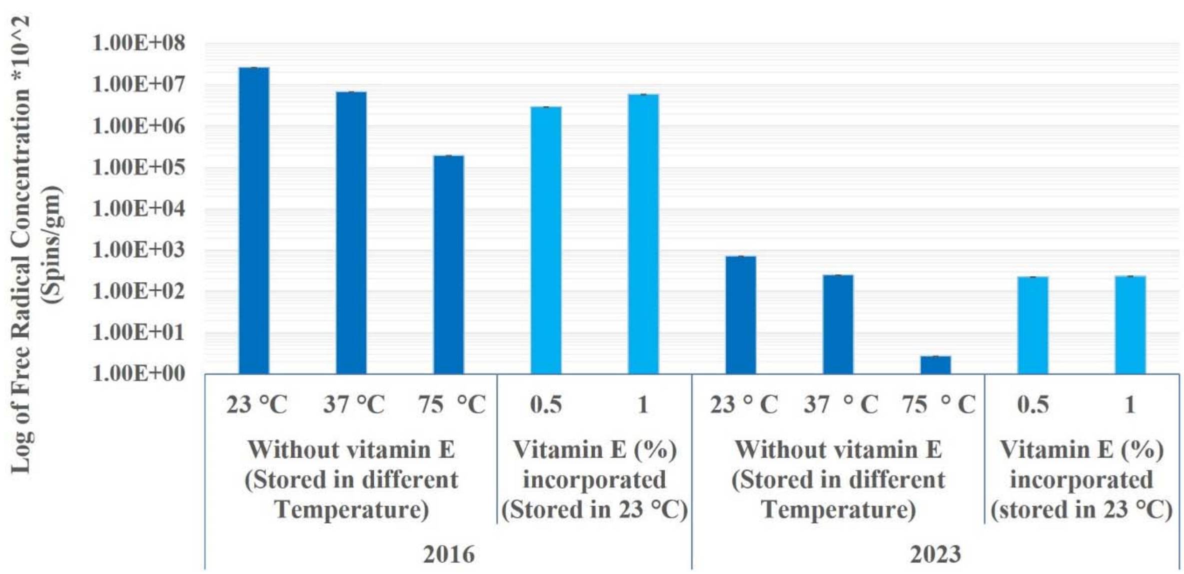


Figure 7: Change in Free radical concentration in the UHMWPE samples over 7 years of aging in different temperatures and conditions.

Conclusion: All samples (open-air and inert-sealed) showed a detectable quantity of radicals, even after 25 years of storage following 30 kGy gamma (sterilization dose). Among those, gamma induced primary radicals are still present in the inert sealed samples indicating the strong oxidation resistance. A typical inert sealed sample aging in 37 °C for 25 years was found to contain 8% Alkyl, 46% Allyl, 17% Polyenyl, 23% Dienyle and 6% Trienyle radical. The free radicals of open air samples were found to get stabilized significantly as a result of thermal annealing, addition of vitamin E and diffusion of bovine solution into the sample, suggesting that annealing below melting point might increase the oxidative stability over long term and the addition of vitamin E can provide a protective effect against oxidation of UHMWPE.

Relevance to CIRMS: This study is a subset of doctoral research of first author with the aim of understanding the ionizing radiations, radiation induced free radicals and the long term effect of radiation induced free radicals on the longevity of polyethylene component acting as articulating surface similar to cartilage. A wide spread research is going on to identify the optimum sterilization process involving ionizing radiations to achieve satisfactory crosslinking ensuring mechanical stability, and minimum concentration of residual free radicals. The CIRMS meeting can be a platform in sharing the benefits and limitations of different ionizing radiations used in sterilization of orthopedic biomaterials.

References:

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