Radiation-Induced Free Radicals in UHMWPE: A Comprehensive study for a period of 25 Years

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Introduction

In the body, joints such as hips and knees can degrade over time, requiring medical intervention to restore them. A common restoration method is to replace the joints altogether with artificial implants, known as arthroplasty. The success or failure often depends on whether osteolysis occurs. Osteolysis is caused by wear particles that stimulate inflammatory biological response of surrounding tissues [1]. The osteolysis-causing wear particles occur from oxidized polyethylene. Before even that, when the polyethylene is new, before becoming oxidized, there may be free radicals in the polyethylene; these free radicals later react with oxygen, which leads to the oxidation at the beginning of events. So, the problem originates with free radicals.

Gamma-induced crosslinking, followed by annealing, has been reported to improve fatigue strength of the polyethylene components of medical implants [2]. An example is the liner which is commonly made of Ultra High Molecular Weight Polyethylene (UHMWPE) and serves in the cups of hip replacements as the contact surface. UHMWPE also serves similar purposes in implants of the knee, ankle, elbow, and shoulder. Therefore, many major medical implants depend on UHMPWE (therefore, also on free radicals which may or may not exist in it).

Gamma radiation creates free radicals, which may lead to oxidation and related wear debris, for which the annealing is meant to get rid of (quench) the free radicals. However, the annealing may not quench all, and some radicals could remain in the UHMWPE. Besides annealing, the addition of vitamin E (Alpha-Tocopherol) into UHMWPE can stabilize the trapped free radicals.

The ongoing effort to improve the performance and durability of these implants requires a comprehensive study of free radical reactions over the full lifetime of the polyethylene used in them. This knowledge is still limited, at most covering only a partial lifetime. This study is focused to detect and analyze, via Electron Spin Resonance (ESR) technique, the radicals which still remain from the initially-produced primary radicals, about 25 years ongoing, in gamma-sterilized medical grade UHMWPE. This is closer to covering a full lifetime of an implant than has been done before.

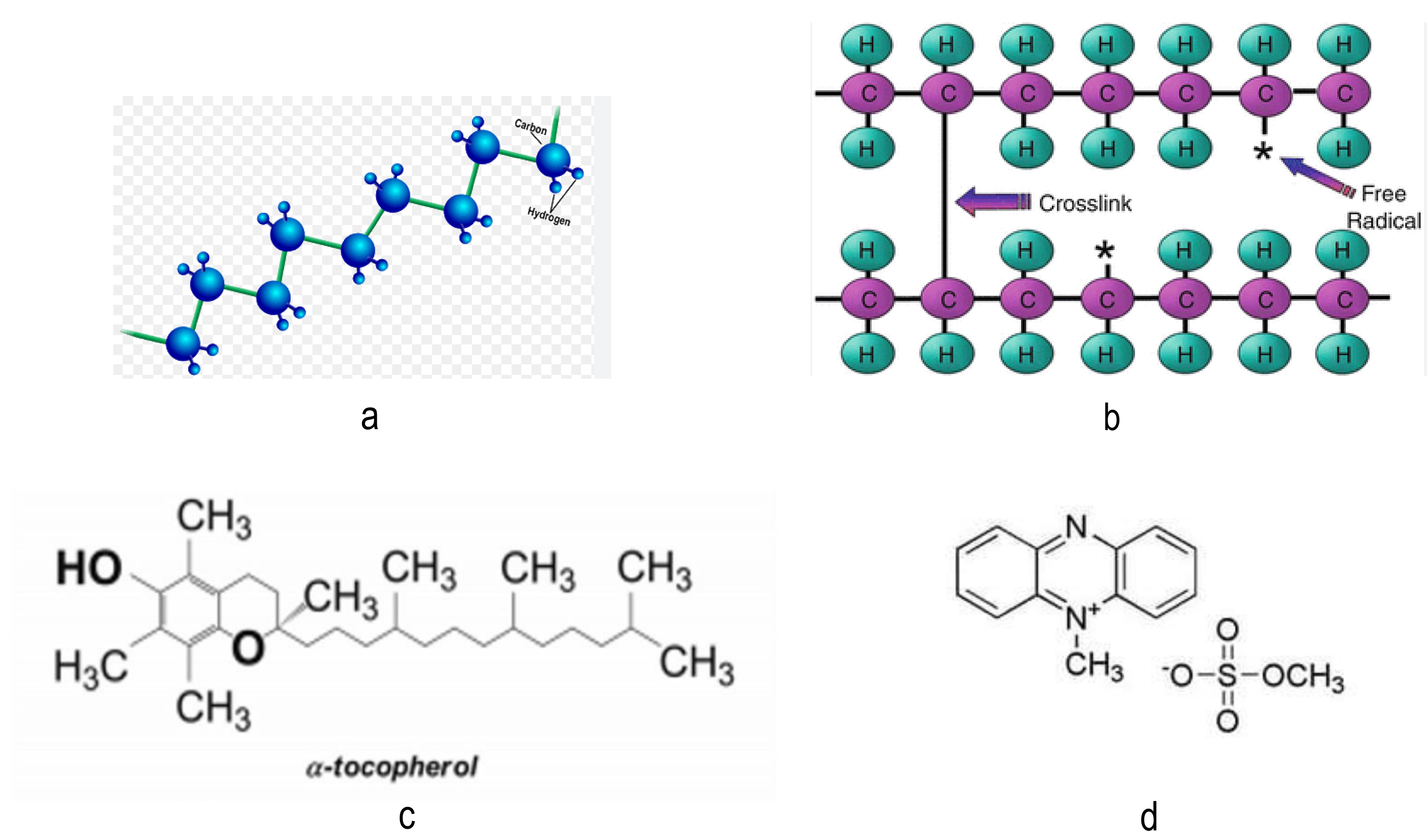


Figure 1: a. Ultra High Molecular Polyethylene (UHMWPE) chain (CH_2-CH_2)n, where n is >1million; (Image source: https://archimorph.com/2010/05/26/uhmwpe-gel-spinning/; Date retrieved: 4/23/2024) **b.** Schematic view of crosslinking showing residual free radicals, (Image source: Aiguo Wang et al., Ultra-High-Molecular-Weight Polyethylene (UHMWPE) as a Bearing Material in Hip Joint Replacements, pp 3933–3939, Fig-2 (2013). **c**. Molecular structure of Vitamin E (Alpha Tocopherol). **d**. Molecular structure of Bovine Serum Albumin solution. (Figure source: https://www.fishersci.com/shop/products/bovine-serum-albumin-sol-50ml-1/NC1578322 ; Date retrieved: 4/23/2024)

Materials and Methods

All solid UHMWPE samples (GUR 4150,Himont 1900, GUR 1020) were irradiated with 30 kGy gamma radiation to achieve sterilization, as well as crosslinking.

The first group of samples were annealed at 23°C, 37°C, and 75°C in open air (in presence of oxygen) and sealed (inert/without oxygen) for 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.

The second group contained vitamin E (alpha-tocopherol) as antioxidant and aged in open air for 17 years at room temperature.

The third group of samples (not containing vitamin E) was kept in Bovine solution in open air 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.

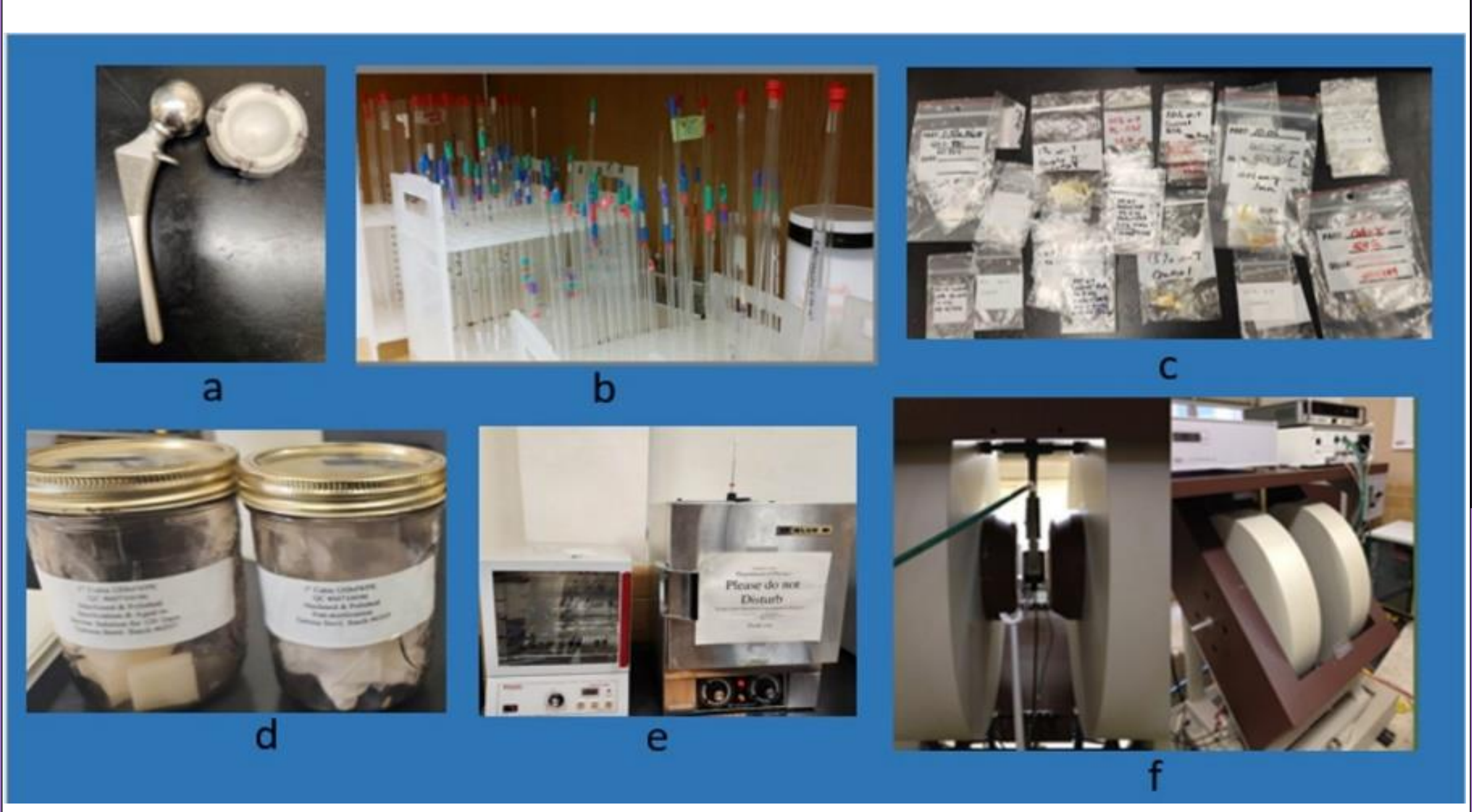


Figure 2: (a) UHMWPE components of total hip joint replacement. (b) Inert sealed UHMWPE samples at room temperature. (c) Shelf storage UHMWPE samples blended with vitamin E. (d) UHMWPE aged in Bovine solution at room temperature. (e) UHMWPE samples stored in oven at higher temperature, and (f) ESR system used in this project.

ESR testing Results

ESR spectra of UHMWPE samples stored in open air showed a strong presence of oxygen-induced radicals at all temperatures except at 75°C in air (although there were still radicals detected for inert-stored samples at 75°C, as well as all other temperatures). Those sealed in an inert environments (without oxygen) showed remaining primary (initially produced by gamma radiation) radicals. Additionally, the R1 (carbon centered radical) and R2 (oxygen centered radical) were also observed in solid UHMWPE after 25 years of aging in open air at room temperature (23°C). The annealing effect in quenching the free radicals was found to be less at room temperature and higher at body temperature (37°C). The antioxidant effect of vitamin E (blended) UHMWPE was found to be about the same 0.5 wt% compared to 1.0 wt% aging for 17 years in open air at room temperature. This effect was also noticeable in the UHMWPE samples aged in bovine solution. The free radical concentrations of all open-air samples were found to be reduced by about 10^4 over 7 years.

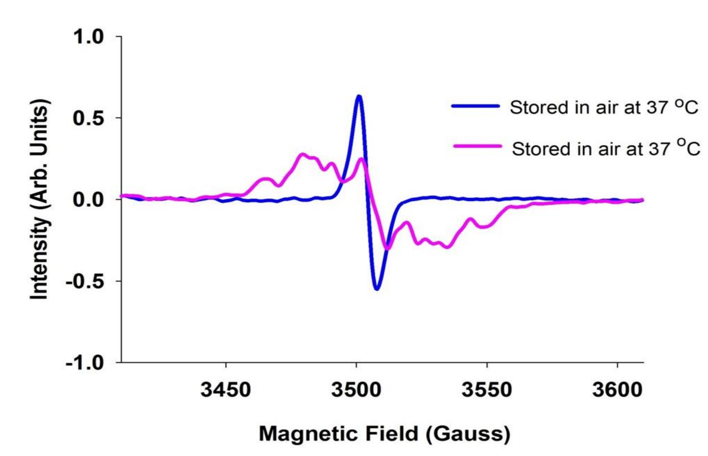


Figure 3: Comparative ESR spectra of open air and sealed UHMWPE samples after 25 years of aging at body temperature (37°C)..

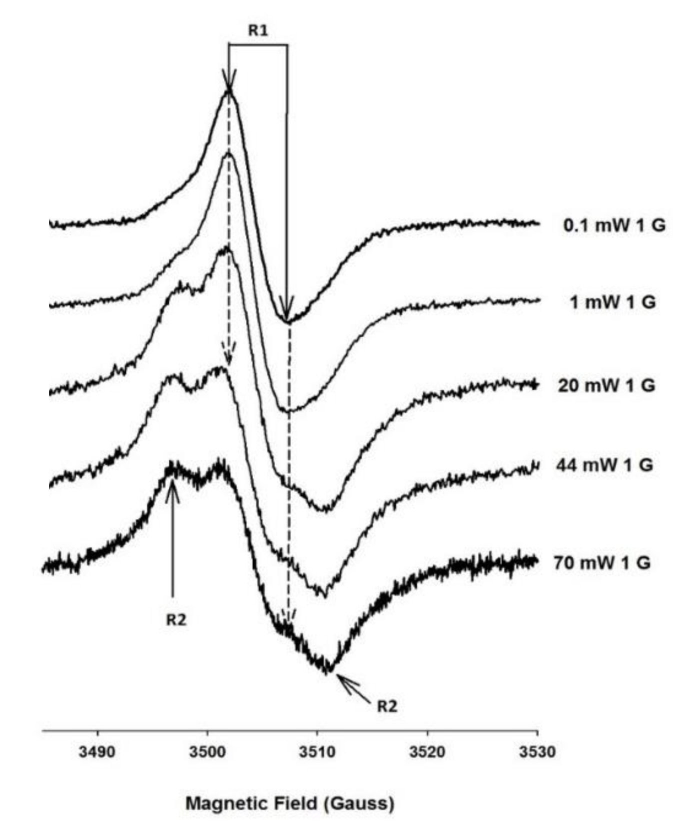
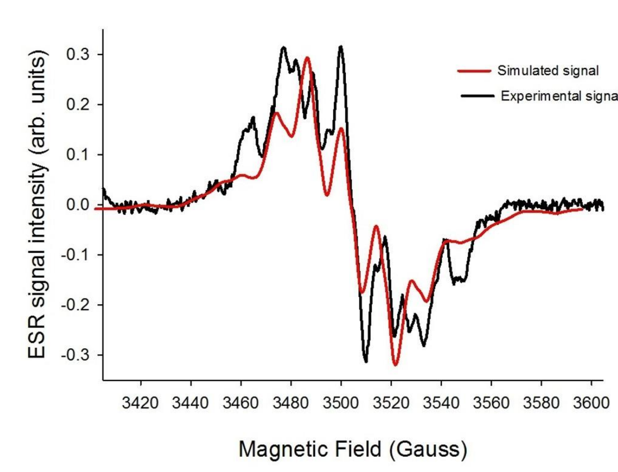


Figure 4: R1 (Carbon-centered radical) and R2 (Oxygen centered radical) observed in UHMWPE after 25 years of aging in open air at room temperature (23°C).



Radical Types	Percent composition (%)
Alkyl	8
Allyl	46
Polyenyl	17
Dienyle	23
Trienyle	6
Vitamin E	0
Total	100

Figure 5: Detection of some primary (initially produced) radical types within a 30 kGy gamma-irradiated UHMWPE, after 25 years of aging in inert sealed tube at body temperature (37 °C).

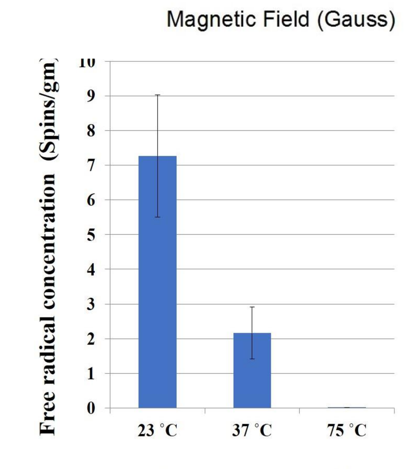


Figure 6: Relative FRC of all open-air UHMWPE samples aging at different temperatures for about 25 years.

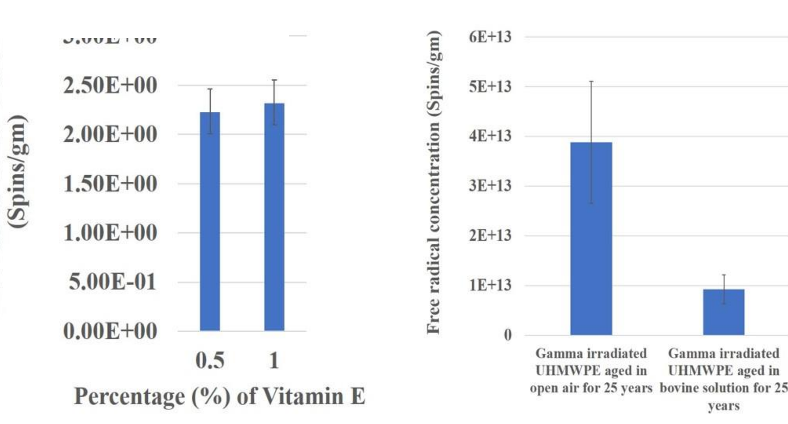


Figure 7: Antioxidant effect of vitamin E (α-Tocopherol) and Bovine solution in UHMWPE after 17 years and 25 years of storage in air, respectively.

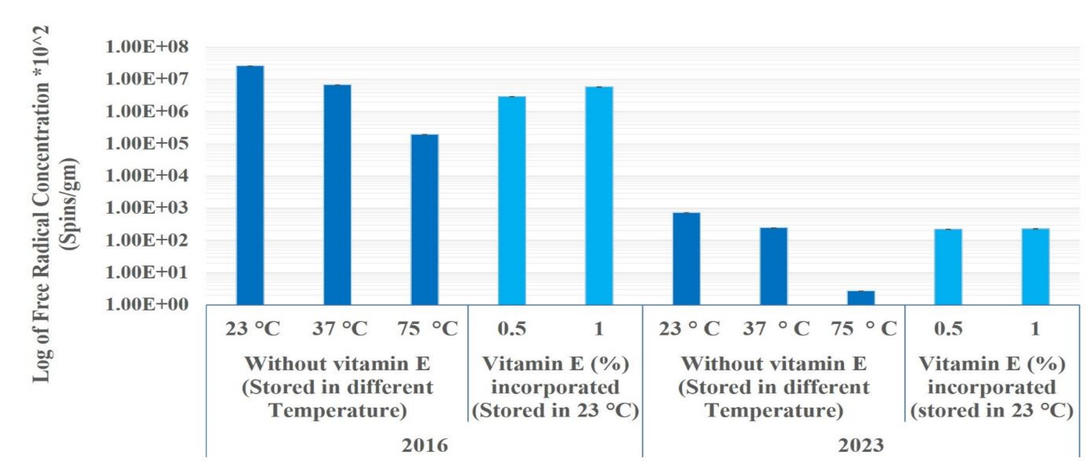


Figure 8: Change in FRC in the UHMWPE samples over 7 years of aging in different temperatures and conditions.

Conclusions

- Except open air at 75°C, all UHMWPE samples (open-air and inert-sealed) showed a detectable quantity of radicals, even after 25 years of storage following 30 kGy gamma irradiation.
- The presence of primary radicals (initially produced) in the inert-sealed UHMWPE samples indicated strong resistance to oxidation which prevented the transition of primary radicals to Oxygen Induced Radical (OIR).
- A typical inert-sealed UHMWPE 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 in UHMWPE samples aged in open-air were found to have become stabilized under thermal annealing. It suggest that the consistent annealing below melting point for long 25 years (closure to the full lifetime) might increase the mobility of the oxygen induced radicals to get recombined.
- About the same amount of residual radicals was observed in 1 wt% vitamin E blended UHMWPE (compared to 0.5 wt%) after 17 years of storage in open air at room temperature. This implies that the effect is not significantly increased at higher percentages than 0.5%.
- The significant reduction of free radicals in gamma irradiated UHMWPE samples diffused in bovine solution for 25 years, implies that, besides the essential nutrients, bovine solution may also possess antioxidant properties due to the presence of antioxidant molecules such as vitamins and trace elements.

References:

[1] Saadi et al. Osteolysis: A Literature Review of Basic Science and Potential Computer-Based Image Processing Detection Methods. Comput Intell Neurosci. 2021

[2] Honglong Wang, Lu Xu, Rong Li, Jiangtao Hu, Mouhua Wang, Guozhong Wu, "Improving the creep resistance and tensile property of UHMWPE sheet by radiation cross-linking and annealing", Radiation Physics and Chemistry, 125, 41–49 (2016).

Acknowledgements: Partially supported by NSF Industry/University Cooperative Center for Biosurfaces (IUCB).