

Analyses of Oxygen-Induced Radicals in UHMWPE

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In this report we conducted free radical measurements on UHMWPE following sterilization with gamma rays (Co-60) at room temperature in open air, vacuum, nitrogen, or argon and subsequently aged at room temperature, 37°C or 75°C for approximately 10 years. Measurements made on vitamin E-mixed UHMWPE powder as well as compression-molded bulk materials are also presented. Additionally, this report includes data obtained from measurements on retrieved acetabular cups and tibial inserts. All free radical measurements were conducted using X-band (~9 GHz) electron spin resonance (ESR) technique.

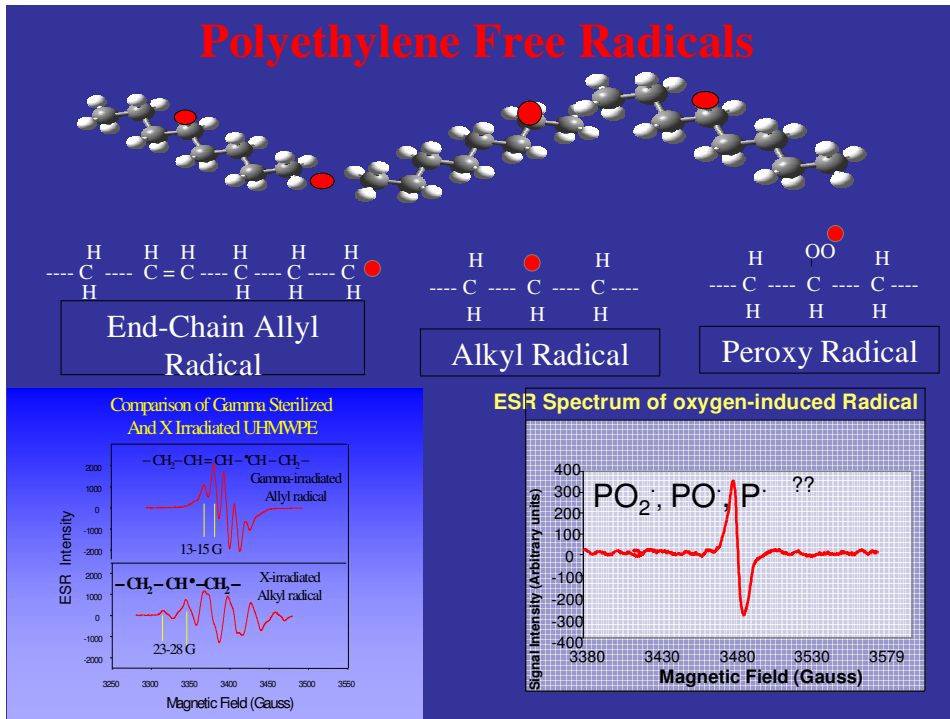
When annealing is performed at 75°C in inert environments, PE free radical number is reduced significantly (~98%). However, the residual radicals (remaining 2%, approximately) produce oxygen-induced radical (OIR) upon subsequent exposure to oxygen (open air). OIRs are also detected in acetabular cups and knee-joint plateaus retrieved 6-8 years following implantation.

Two groups of vitamin-E samples were investigated. In one group, samples were prepared from blends of α -T and UHMWPE powder (α -T-P), and in the second group, from compression molded blocks (α -T-B). In each group, samples were gamma-irradiated in sealed packages filled with N₂, or in open air, and free radicals were measured in open air environment as a function of time. PE radicals were found to be quenched by α -T in presence of oxygen (open air) but not in packages containing N₂. Furthermore, like in control, OIR were formed in N₂-packaged α -T-P as well as in α -T-B.

Acknowledgements: Work was supported in part by funds from the NSF Industry/University Center for Biosurfaces and the University of Memphis.

Structure and electron spin resonance (ESR) spectra of PE free radicals at X-band microwave frequency 9.5-9.8 GHz and amplitude 2.0 mW, 100 kHz magnetic field modulation and signal detection frequency, and 5.0 G modulation amplitude.

An alkyl radical produces six lines with separation between the lines 23-28 G and allyl produces seven or five lines with separation 13-15 G. The single line produced by the residual oxygen-induced radical (OIR) has been attributed by many to peroxy (PO₂·), alkoxy (PO·) or polyenyl (P·).

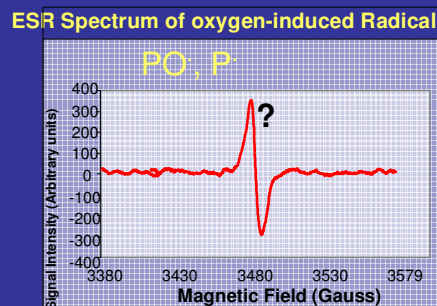
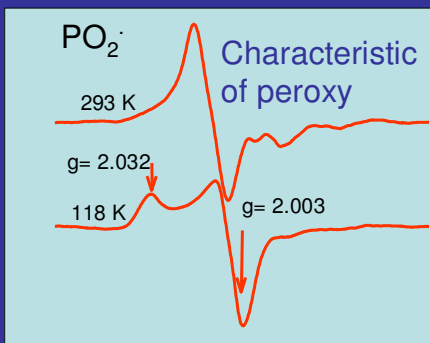


Introduction (contd): Polyethylene Free Radicals

ESR spectrum due to peroxy radicals exhibits a single line at room temperature (293 K) whose asymmetric feature with characteristic g-values, $g_{\perp} = 2.003$ and $g_{\parallel} = 2.032$, is resolved at low temperature (118 K) [J. Durant, M.S. Jahan, NIMB, 236 (2005) 160].

The single-line spectrum produced by the residual OIR in UHMWPE does not exhibit characteristic feature of a peroxy radical at room or low temperature.

The objective of this report is to determine the type/structure of the OIR by analyzing its ESR spectrum.



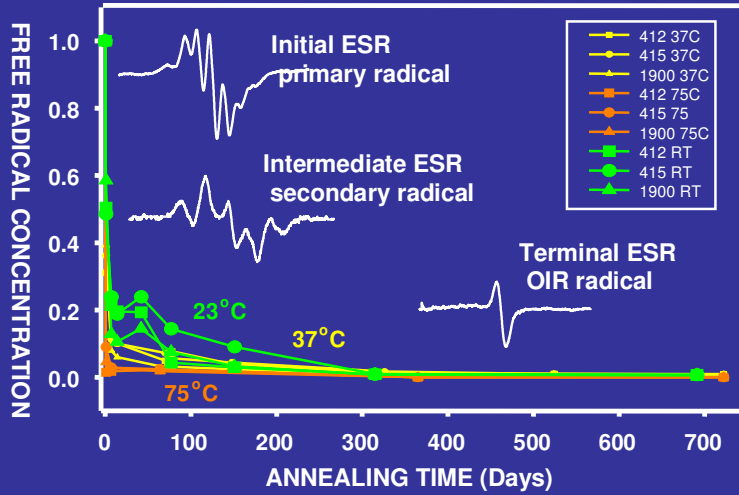
Background 1: free radical decay in open air as a function of time following gamma sterilization (3 MRad) in air.

UHMWPE Resins: GUR 412, GUR 415, Himont 1900

Storage/annealing temp.: room temperature (RT), 37°C, 75°C

Storage/annealing time.: 750 days

Result: Production of oxygen-induced radical (OIR)



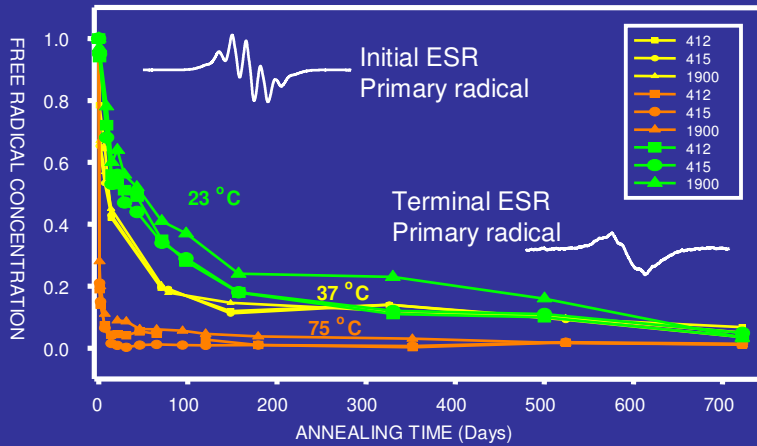
Background 2: free radical decay in sealed ESR tubes (argon, nitrogen or vacuum) as a function of time following gamma sterilization (3 MRad) in the same tube.

UHMWPE Resins: GUR 412, GUR 415, Himont 1900

Storage/annealing temp.: room temperature (RT), 37°C, 75°C

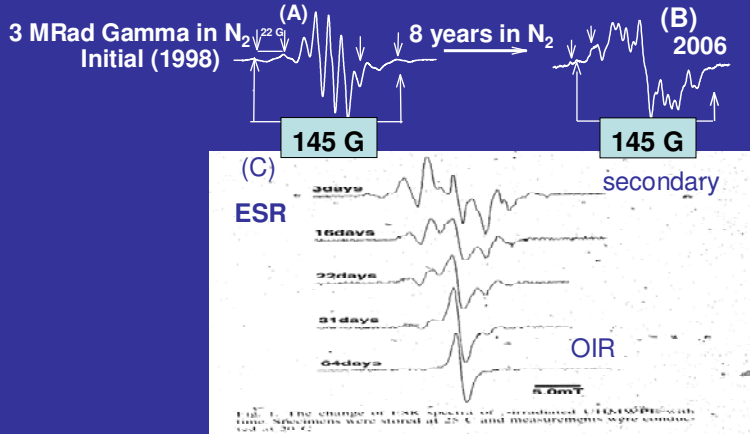
Storage/annealing time.: 750 days

Result: primary radical concentration decreases but no OIR is produced



Background 3: In 8 years in nitrogen ESR intensity is reduced (A-B), but OIR is not formed.

(C): OIR forms in air (oxygen) within 64 days (see references)



K. Nakamura, S. Ogata, Y. Ikada, *Biomaterials* 19 (1998) 2341-2346;

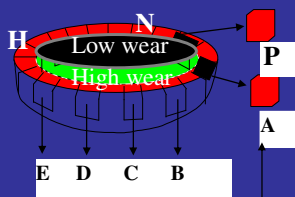
L. Costa, M. P. Luda, L. Trossarelli, E. M. Brach del Prever, M. Crova, P. Gallinaro, *Biomaterials* 19 (1998) 659-668;

P. O'Neill, C. Birkinshaw, J. J. Leahy, R. Barklie, *Polym. Degr. Stabil.* 63 (1999) 31-39].

Background 4: OIR in retrieved acetabular cup

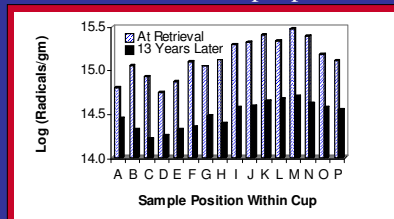
Radical concentration at retrieval (8 years after implantation) and 13 years later

Acetabular cup



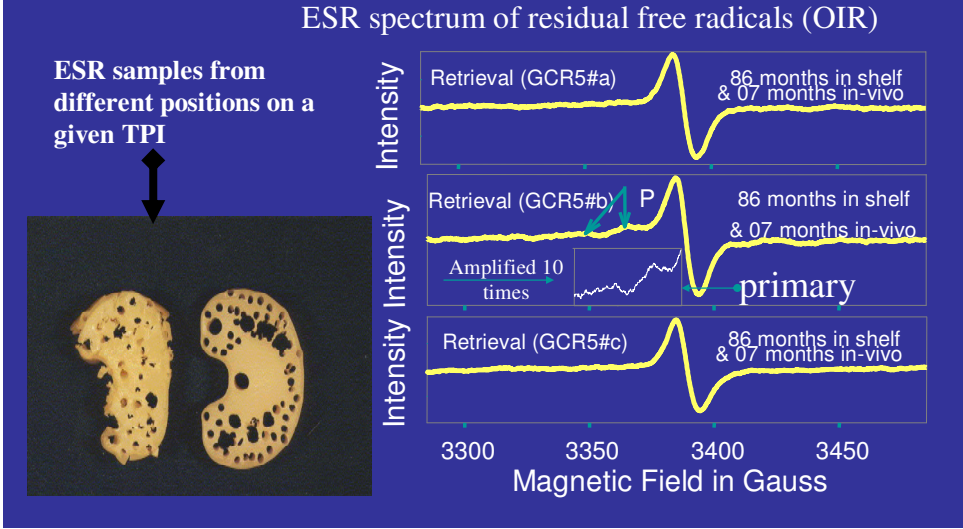
ESR sample

Radical conc. @ sample position



Consistent with SEM results, results of this study show two distinct surfaces, low-radical region (A-G) in the figure correlates with the high wear or superior half separated by a high-radical region (H-P) which correlates with the low wear or inferior half.

Background 5: Examples of OIR in a gamma-sterilized and clinically retrieved TPI (86 months in shelf and 7 months in vivo). Presence of trace amount of primary radicals is also evident.



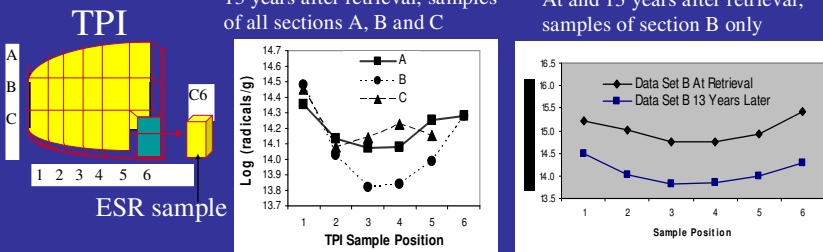
Background 6: Examples of OIR in clinically retrieved TPI retrieved 6.5 years after implantation

ESR data recorded at retrieval and 13 years later

Radical concentration @ sample position

13 years after retrieval, samples of all sections A, B and C

At and 13 years after retrieval, samples of section B only



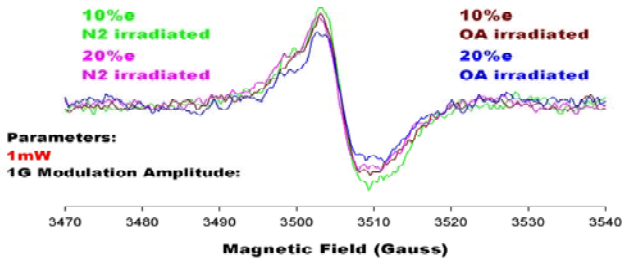
Unlike acetabular cup, tibial plateaus show low radical concentration in the central part of the joint, which is typically the high wear region.

Background 7:

Example of OIR in Vitamin E-doped UHMWPE

Solid samples with Vit E, stored in air. Measurements after 2 years. OA = "open air"

UHMWPE GUR 1020
With vitamin E

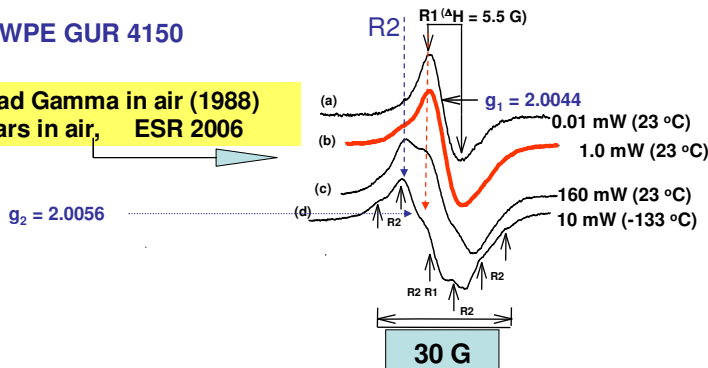


ESR spectrum of OIR in e-PE recorded two years after gamma irradiation in nitrogen or air (OA). Vitamin E concentration used were 10% and 20%

Analysis of ESR spectrum of OIR
Spectrum recorded as a function microwave power and temperature

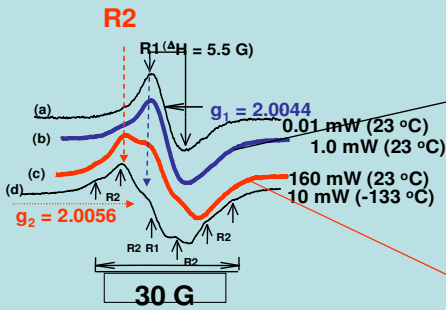
UHMWPE GUR 4150

100 MRad Gamma in air (1988)
18 years in air, ESR 2006



Result: the standard single-line spectrum (b) is reduced to a symmetric single line (a) due to radical R1 at 0.01 mW microwave power, and a spectrum with six weak hyperfine lines at 10.0 mW and -133 °C due to radical R2 (d).

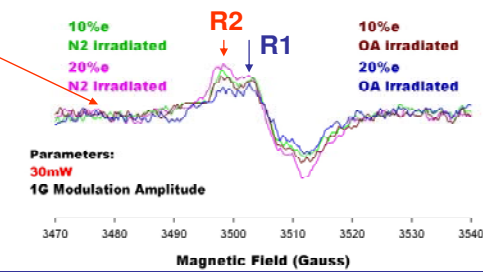
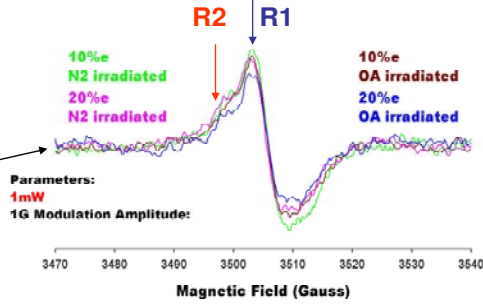
Identical OIR, R1 and R2, are also formed in e-PE



Conventional UHMWPE GUR 4150
Without vitamin E

Solid samples with Vit E, stored in air. Measurements after 2 years. OA = "open air"

**UHMWPE GUR 1020
With vitamin E**



Analysis Test: Radical R1 and R2 have different microwave power saturation behavior

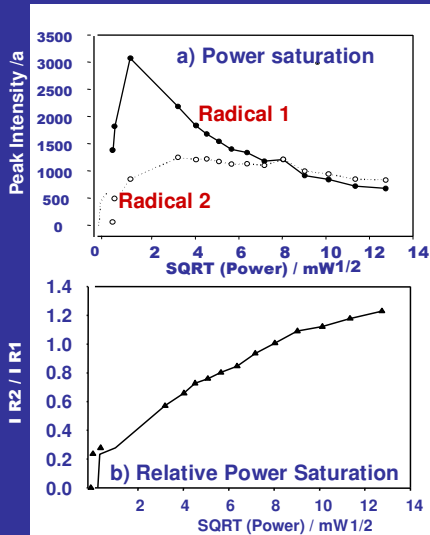
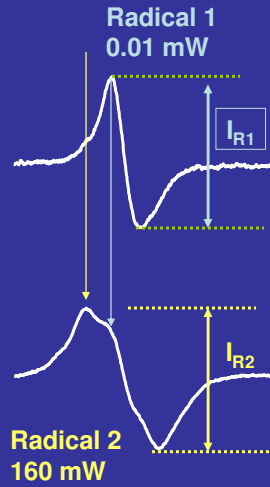


Fig 2: Peak intensity as a function of microwave power
a) Intensity as a function of sqrt μ -wave power
b) Relative Intensity



**Analysis Test 2:
Thermal stability**
At 130 °C, ESR
spectrum of R1
reduces slower
than that due R2

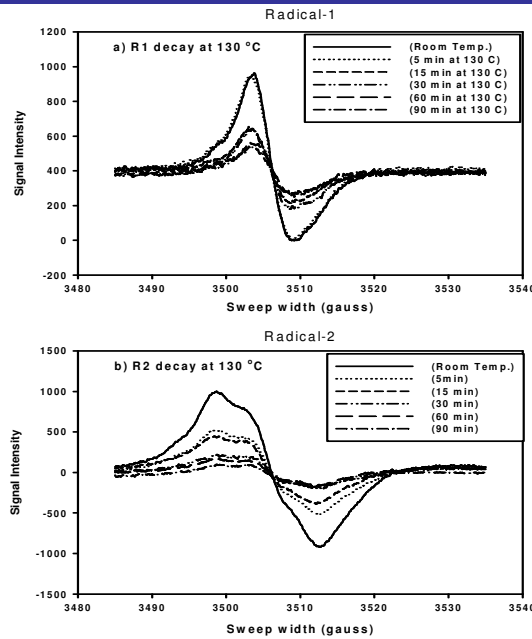


Fig 3: Annealing of R1 and R2 at 130 °C as a function of time. a) Spectra showing decay of single line (R1) b) Spectra showing decay of R2

Analysis Test 2 (contd): Thermal stability
Decay of Radicals R1 and R2 as a function of time at and temp.

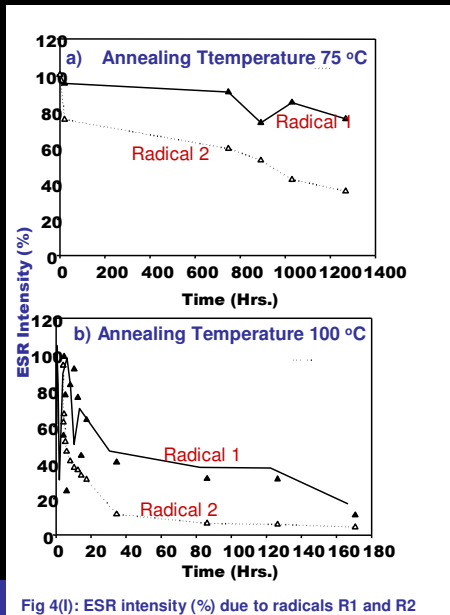


Fig 4(I): ESR intensity (%) due to radicals R1 and R2

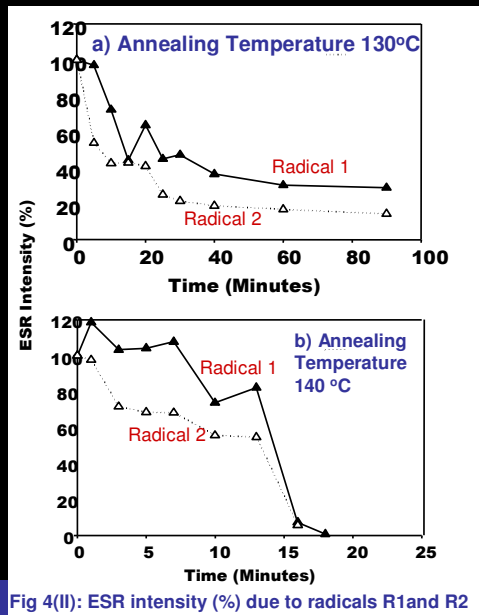


Fig 4(II): ESR intensity (%) due to radicals R1 and R2

summary

Reported for the First time

➤ So called single-line ESR spectrum of the Long-lived oxygen-induced radicals resolved into two resonance signals, produced by two different radicals:

o radical R1: polyenyl radical ($-C^*H-[CH=CH-]_m-$), a radical having a large number (m) of conjugated double bonds

❖ radical R2: oxygen-centred di- or tri-enyl ($-CHO^*-[CH=CH-]_n-$),

o Radical 1 resides in crystalline region of the polymer matrix

❖ Radical 2 resides in near-crystalline region or voids inside crystal, and may have dangling bond for oxygen attachment

❖ Structural stability (high conjugation) may also contribute to the longevity of Radical 2

o Radical 1 and Radical 2 both can be annealed at 140°C

❖ Radical 2 can be annealed at 130°C , below crystal melting temperature

Thank You

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