

## Observation of New Residual Radicals in Irradiated UHMWPE

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**Introduction:** Residual radicals, also known as oxygen-induced radicals (OIR), are observed in UHMWPE if the primary radicals are not quenched (by heating near melting temperature) after radiation sterilization or crosslink processes. They are very long-lived (20 years in this laboratory), and are observed in shelf-aged as well as in retrieved hip- and knee-joint components [1].

Electron spin resonance (ESR), the only technique that can directly detect free radicals, has been used extensively to study primary as well as secondary radicals in UHMWPE. However, the type or the properties of the *residual radicals* are not fully understood. Under normal operating conditions, ESR signal produces a single-line spectrum which had been tentatively attributed to radical specie such as alkoxy (PO•), or polyenyl (P•), although some have attributed it to peroxy (PO<sub>2</sub>•) radical [2]. In this ESR study, we applied microwave power saturation technique at low (-133°C to 23°C) temperature to resolve the single-line, for the first time, into two distinct resonance signals, each one has its own characteristic ESR parameters. Dependence of the *residual radicals* on crystallinity, and their decay behavior in the temperature region 75-140°C were also explored.

**Materials and Methods:** UHMWPE samples used in this study were made from ram extruded GUR4150 resin, and each sample was approximately 3 mm thick and 3x9 mm<sup>2</sup> in size. Majority of the measurements were conducted on high-dose (1000 kGy) samples because they produced very strong ESR signals. They were irradiated in air at room temperature with gamma rays using a <sup>60</sup>Co source in 1988. Since then, all samples were kept in open air at room temperature. For comparison, few measurements were also conducted on low-dose (30 kGy) samples. Measurements were also made on highly crystalline fibers (98% cryst), 55% crystalline solids, and low crystalline (<30%) powder. Each of these latter samples was gamma irradiated (500 kGy) in air in 1997, and the ESR signals at this time show the presence of residual radicals only.

For free radical measurements, an ESR spectrometer (Bruker EMX 300) was used. The spectrometer is fitted with a high-sensitive, mixed mode cavity and operates at 9.8 GHz microwave frequency (X-Band) and 100 kHz modulation and detection frequencies. While the modulation amplitude was kept between 1 and 5 G, microwave power was varied from 0.01 mW to 160 mW. For low temperature measurements, a computer-controlled gas-flow (N<sub>2</sub>) system (Bruker) was employed, and ESR signals were recorded at fixed temperatures between -133°C and 23°C. For high temperature measurements, samples were placed in an oven (Model 20 GC Quincy Lab, Inc., Chicago, IL, USA) at various temperatures (75-140 °C) for different intervals of time, and ESR signals were recorded at room temperature.

**Results and Discussion:** Figure 1 shows ESR signal of the residual radicals recorded at different operating conditions. Under standard operating conditions (1 mW microwave power 1-5 G modulation amplitude) at room temperature (23°C), a single line with broad shoulder is observed (b). At low microwave power, 0.01 mW, a well-defined symmetric single line with no shoulder was produced (a). The peak-to-

peak width of the line  $\Delta H_{pp} = 5.5$  G and the spectral splitting factor g-value is 2.0044. This isolated single line is attributed to a carbon-centred radical, R1. At microwave power 160 mW, the weak shoulder increased and the single line due to R1 reduced (c), and at -133°C, the intensity of R1 was further reduced and, as a result, a broad resonance signal with multiple weak lines (5 lines with separation 4.86 G) became clear (d). This resonance signal has a g-value of 2.0056, and it is attributed to a second radical R2. ESR intensity plotted as a function of square root of power, shown in Fig. 2, clearly shows that the power dependence of R1 is different from that of R2.

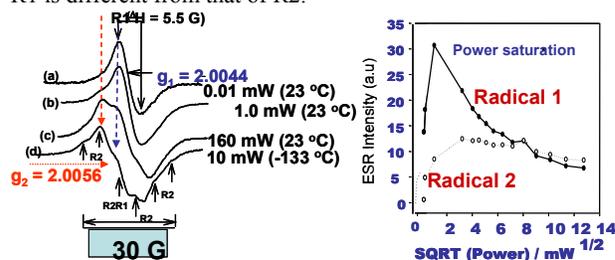


Fig. 1

Fig. 2

When heated for fixed time at 75°C, 100°C and 130°C, R2 suffered more loss (decayed) than did R1. At 140°C both R1 and R2 decayed completely in about 18 min (see Figs. 3 and 4).

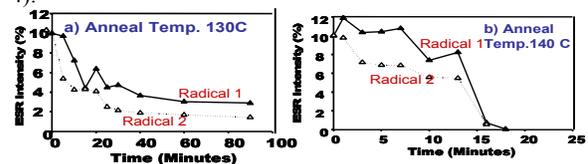


Fig. 3

Fig. 4

Residual radical concentrations (RC) in fiber, solid and powder were found to follow this relation:  $RC_{\text{fiber}} > RC_{\text{solid}} > RC_{\text{powder}}$ .

**Conclusions:** Following observations are made:

1. Residual radicals (R1 and R2) reside primarily in the crystalline environment of UHMWPE.
2. Heating experiments suggest that R1 resides fully and R2 partially inside the crystalline regions.
3. Microwave power saturation tests (R2 saturates at higher power and R1 at lower) suggest that R2 is oxygen-centered (-PO•).
4. Based on spectral characteristics, R1 is attributed to polyenyl (highly conjugated with  $m > 3$ , in  $(-\text{CH}=[\text{CH}=\text{CH}]_m-)$ ) and R2 to oxygen-centered di- or tri-enyl ( $m=2$  or 3) *dangling* radical.

In conclusion, ESR resonance signal due to *residual radicals* was resolved, for the first time, and two radicals were identified.

**References:**

- [1] Jahan et al., J. Biomed. Mater. Res., 25 (1991) 1005.
- [2] P. O'Neill et al. Poly. Deg. Stabl. 63 (1999) 31.

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