Radiation-Induced Radicals in Polyaryletheretherketone (PEEK)

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Statement of Purpose: PEEK is a member of the polyaryletherketone (PAEK) polymer family that has been used for orthopedic and spinal implants and known to be radiation resistant [1]. However, a recent study detected free radicals in plasma-treated PEEK at room temperature; the lifetimes of the radicals were about 24 hours [2]. Li et al. observed radicals at liquid nitrogen-temperature (77 K); the gamma- and e-beam-induced radicals then decayed in less than 20 minutes at room temperature, and the UV-induced radicals decayed in about 24 hours [3]. In our report, we also show the free radicals in as-received, unirradiated, neat (unfilled) PEEK (which we will call "R1"), as well as an additional radical type (which we will call "R2"). We have observed these radicals for much longer than any radiation-induced radicals in PEEK previously reported, to our knowledge.

Methods: 10 mil. (0.254 mm) neat (unfilled) PEEK film and medical-grade PEEK granules were tested. UV- and X-irradiation was performed by us in-house. Gamma was performed by Steris Isomedix. Free radicals were detected at 23°C using an X-band electron spin resonance (ESR) spectrometer (EMX300, Bruker). fitted with a mixed mode resonance cavity, operating at 9.8 GHz microwave frequency, and 100 KHz modulation and detection frequencies. For calibration of the spectral splitting factor, g-value, an organic free radical DPPH (2,2-diphenyl-1-picrylhydrazyl) with g factor value of 2.0036±0.0002 was used; for free radical concentration, a ruby standard by NIST was employed.

Results: From Figure 1, it is clear that an additional radical type (we call here "R2") is created; this radical is distinguished from R1 by a higher g-value, causing the additional feature ((a) of Fig.1) in the spectra, and slight shift to the left (higher g-value). Similar results were obtained whether using film or granules. The R2 features are seen in UV- and X-irradiated samples even after three weeks (figure 2). After 1 year post-gamma, the features are less prevalent, but are significantly distinguishable; Fig. 1(c) actually three samples of each; lines very close/overlaying. Still, entire project repetitions are needed to more confidently conclude gamma-related findings. The R2 quantities were found to increase with UV-exposure time and X-irradiation. Experimental methods may be employed to isolate R2 from R1. The radical R1 was found to be very stable.

Summary: UV-, X-, and gamma-radiation appear to produce the same type of (R2) radicals, which are observable for longer times than previously reported, to our knowledge. Additional work is needed to further characterize R2 – e.g., molecular structure and long-term effects. This report primarily shows that radiation-induced radical formation may be more significant than previously thought. Additional work may provide more insight into the aging processes occurring in PEEK.

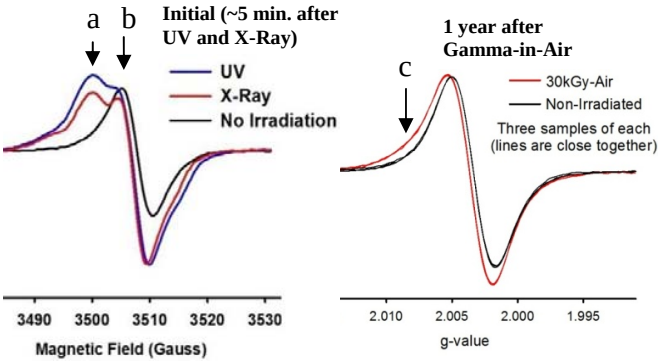

Figure 1. ESR spectra of PEEK. (a) points to a feature of the "R2" radical. (b) identifies a peak of the "R1" radical. (c) shows R2-features 1 year after gamma.

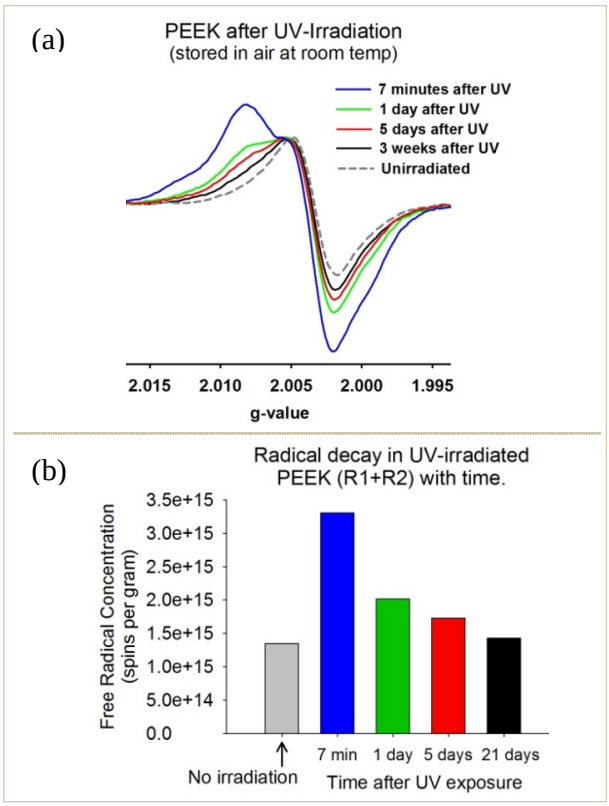

Figure 2. (a) ESR spectra showing radicals after UV-irradiation and (b) corresponding radical concentrations. The grey line/bar represents the R1-only radical of PEEK before irradiation.

References: [1] Kurtz (ed), PEEK Biomaterials Handbook, 2012. [2] Awaja et al., Plasma Process. Polym. 2012, 9, 174-9. [3] Li et al., IEEE Trans. Dielectr. Electr. Insul., 1999, 6, 295-303.