# Oxidation Resistant Peroxide Crosslinked UHMWPE

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**Introduction:** Crosslinking of polymers using peroxides is used in polyolefins by blending into the resin before processing [1]. Peroxide crosslinking by blending was also shown to lower the wear of ultrahigh molecular weight polyethylene (UHMWPE*)* for orthopedic implants [2]. But, there is concern about the oxidation of these materials due to peroxide decomposition. The antioxidant vitamin E was successfully used to stabilize UHMWPE against oxidation [3]; but, since it is a free radical scavenger, its presence with peroxides may disrupt crosslinking [4]. We hypothesized that the desired crosslinking and oxidation resistance can be achieved by peroxide crosslinking of UHMWPE with vitamin E.

**Methods:** Medical grade UHMWPE (GUR 1050) was mixed with vitamin E and 2,5-di(*tert*-butylperoxy)-2,5-dimethyl-3-hexyne (P130). The mixture was molded into pucks (10 cm dia., ~1 cm thickness) under 15- 26 MPa for 2 hours. Both virgin and 0.1 wt% vitamin E-blended resins were processed with 1 wt% P130. To determine the effect of consolidation temperature, 0.1 wt% vitamin E-blended UHMWPE was processed with 0.5 wt% P130 at 170, 180, 190, 200 or 210$^{o}$C.
Crosslink density was measured by swelling cubes (n=6; 3 mm) in xylene at 130°C and the cross-link density was further calculated as previously described [5]. Type V tensile specimens (n=6) according to ASTM D638 were stamped out of 3.2 mm thick sections and then tested at 10 mm/min. The ultimate tensile strength (UTS) was reported. True elongation at break (EAB) was determined using a laser extensometer. Pin-on-disc (POD) wear testing was performed on cylindrical pins (n=3) as previously described at 2 Hz [6] for 1.2 million-cycles (MC). Wear was measured gravimetrically every ~0.16 MC and the wear rate was measured by the weight change from 0.5 to 1.2 MC. Accelerated aging was conducted on 1 cm cubes (n=3) in a pressure vessel at 5 atm oxygen at 70°C for 14 days. Thin sections (150µm) were cut from an inner surface of the cubes, and analyzed using Fourier Transform Infrared Spectroscopy (FTIR) at an interval of 100µm from the surface along the depth of the sample. An oxidation index was calculated by normalizing the absorbance at 1700 cm$^{-1}$ (1680-1780cm$^{-1}$) against that at 1370 cm$^{-1}$ (1330-1390cm$^{-1}$).

**Results:** Our hypothesis that crosslinking using a peroxide can be achieved in the presence of an antioxidant free radical scavenger was confirmed (Table 1). The lower value of the crosslink density of vitamin E blended UHMWPE compared to virgin UHMWPE is presumably due to vitamin E's free radical scavenging ability similar to its effect during radiation cross-linking [4] ($p$<0.0001).

| | **Virgin UHMWPE** | **0.1 wt% vitamin E-blended UHMWPE** |
|---|---|---|
| Cross-link Density, moles/dm$^3$ | 0.343±0.005 | 0.301±0.005 |
| Ultimate tensile strength, MPa | 32.9±3.8 | 26.7±3.3 |
| Elongation at Break, % | 234±17 | 251±15 |
| Average Oxidation Index | 0.27±0.05 | 0.04±0.01 |

Table 1. Crosslink density, ultimate tensile strength, elongation at break, and average oxidation index of peroxide-crosslinked virgin and 0.1 wt% vitamin E-blended UHMWPEs.

For peroxide cross-linking of polymers, the consolidation was optimized to address two main concerns; (1) to avoid premature crosslinking than can lead to incomplete consolidation and (2) to ensure oxidative stability due to peroxide decomposition. As the consolidation temperature increased from 170 to 180, 190, 200 and 210$^{o}$C for 0.1 wt% vitamin E-blended UHMWPE, the crosslink density was similar; 0.269±0.007 to 0.256±0.003, 0.250±0.004, 0.245±0.003 and 0.242±0.004 moles/dm$^3$, respectively. The processing temperature also did not have an effect on the UTS (35-37 MPa) or EAB (304-333%). These results suggested that P130 was a suitable peroxide for cross-linking vitamin E-blended UHMWPE.

Due to its high cross-link density, the wear rate of 0.5 wt% P130, 0.1 wt% vitamin E-blended UHMWPE processed at 180 and 210$^{o}$C was 1.9±0.3 and 1.8±0.2 mg/MC compared to 0.1 wt% vitamin E blend with no peroxide at 13.6±0.1 mg/MC.

After aging, the oxidation index of 0.1 wt% vitamin E-blended, 1 wt% peroxide cross-linked UHMWPE was 0.04±0.01 compared to 0.27±0.05 for virgin UHMWPE cross-linked with peroxide.

**Significance:** Peroxide cross-linking of vitamin E-blended UHMWPE was achieved, resulting in a wear and oxidation resistant cross-linked UHMWPE with good mechanical properties. This may present a convenient and economical alternative of crosslinking UHMWPE for total joint implants.

**References:** 1. Morshedian et al. Iranian Polymer Journal 18: 103-28 (2009); 2. Gul J Mater Sci 19: 2427-35 (2008); 3. Bracco et al. CORR 469: 2286-93 (2011); 4. Oral et al. Biomaterials 29: 3557-60 (2008); 5. Oral et al. Biomaterials 31: 7051-60 (2010); 6. Bragdon et al. JOA 16: 658-65 (2001); 7. Muratoglu et al. Biomaterials 20: 1463-70 (1999).