A New Technique for Surface Cross-linked UHMWPE by Diffusion of Peroxides

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Introduction: Crosslinking of ultrahigh molecular weight polyethylene (UHMWPE) is used to decrease wear [1]. Limiting crosslinking to the surface is desirable, as crosslinking leads to decreases in mechanical strength and toughness [2]. Peroxides have been used to crosslink polyolefins by blending during consolidation [3]. We hypothesized that surface diffusion of peroxides followed by heating to decompose the peroxide could cross-link UHMWPE. One of the drawbacks of peroxides is oxidative degradation. We hypothesized that antioxidant stabilization can prevent against oxidation.

Methods: Medical grade UHMWPE (GUR 1050) was mixed with vitamin E at 0.1 wt%. The blend was compression molded and cubes (1 cm) were machined. Dicumyl peroxide (DCP) or 2,5-di(*tert*-butylperoxy)-2,5-dimethyl-3-hexyne (P130) were used. Cubes were doped with the peroxide under argon gas and heated to decompose the peroxides. Cubes were weighed at each step. To determine the effect of doping temperature on cross-linking, cubes (n=3) were doped with DCP at 60, 80 or 100^{o}C for 4 hours followed by heating at 130^{o}C for 4 hours. Another set of cubes (n=3 each) were doped with P130 at 80, 100 or 120^{o}C followed by heating at 180^{o}C. To determine the effect of decomposition temperature on cross-linking, cubes doped with DCP at 80^{o}C for 4 hours were heated at 130 or 140^{o}C. Another set of cubes (n=3 each) doped with P130 at 80^{o}C were heated at 150, 165 or 180^{o}C. Wear testing pins were machined from oversized blocks (11×11×15 mm) were doped with DCP at 100^{o}C for 4 hours followed by heating at 130^{o}C for 4 hours, and with P130 at 120^{o}C for 4 hours followed by heating at 180^{o}C for 4 hours. The pins had one doped surface without machining maintained as the wear surface. A surface section (n=6; 1 mm deep and 3 × 3 mm) was swollen in xylene at 130°C. The cross-link density was calculated as previously described [4]. Pin-on-disc (POD) wear testing was performed on cylindrical pins (n=3) as previously described [5]. 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 done in a pressure vessel at 5atm oxygen at 70°C for 14 days. Thin sections (150µm) were cut and analyzed using Fourier Transform Infrared Spectroscopy (FTIR) at an interval of 100µm as a function of depth. Oxidation index was calculated by normalizing the area at 1700 cm^{-1} (1680-1780cm^{-1}) to that at 1370 cm^{-1} (1330-1390cm^{-1}). **Results:** Our hypothesis that UHMWPE could be cross-linked by diffusing peroxides and elevating the temperature to decompose the peroxides tested positive (Fig 1a and 1b). The decomposition temperature (measured as the temperature at which half of the peroxide is decomposed in 1 hour) was 137°C for DCP, which enabled doping and decomposition below the peak melting point of UHMWPE. The decomposition temperature was 152°C for P130, which required decomposition above the melting point of UHMWPE. The amount of DCP in doped cubes was 0.3, 0.8 and 2.3 wt% at 60, 80 and 100^{o}C, respectively. The amount of P130 in doped cubes was 0.4, 1.0 and 4.6 wt% at 80, 100 and 120^{o}C, respectively. Decomposition at higher temperature increased the cross-link density of both types of peroxide cross-linked UHMWPEs (Figs 1a and 1b).

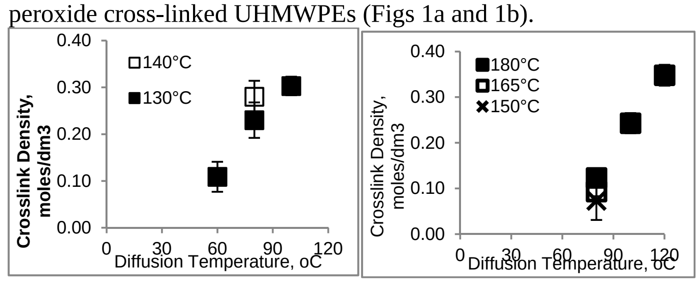

Figure 1. (a) Crosslink density as a function of dicumyl peroxide (DCP) doping temperature and subsequent peroxide decomposition temperature; (b) Crosslink density as a function of Peroxide 130 (P130) doping temperature and peroxide decomposition temperature.

The achieved cross-link density of peroxide-diffused vitamin E-blended UHMWPE was comparable to that of 100-kGy irradiated and melted virgin UHMWPE (~0.26 mol/dm^{3}), which has excellent wear resistance *in vivo* [6]. The wear rates of peroxide-crosslinked UHMWPEs (1.5±0.9 and 1.6±0.6 mg/MC, respectively for DCP and P130-doped samples) were lower than their non-cross-linked counterpart (13.6±0.1 mg/MC). After aging, the negligible oxidation (surface 1 mm of DCP doped blend was 0.01±0.003 and that of the P130 doped blend was 0.00±0.007) supported our hypothesis that vitamin E can improve the oxidation resistance of peroxide cross-linked UHMWPEs.

Significance: A novel method of limiting crosslinking to the surface of vitamin E-blended UHMWPE by diffusion and decomposition of organic peroxides is presented for the first time, providing a feasible alternative of making a wear and oxidation resistant cross-linked UHMWPE for total joint implants. **References:** 1. McKellop et al. JOR 17: 157-67 (1999); 2. Baker et al. JBMR 66A: 146-54 (2003); 3. Gul J Mater Sci 19: 2427-35 (2008); [4] Oral et al. Biomaterials 31: 7051-60 (2010); [5] Bragdon et al. J Arthroplasty 16: 658-65 (2001); [6] Muratoglu et al. Biomaterials 20: 1463-70 (1999).