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A Study Comparing The Relative Efficacies Of Various Antioxidants On The Oxidative Stability Of Highly Cross-Linked Polyethylene (HXLPE).

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Introduction: Ultra high molecular weight polyethylene (UHMWPE) is one of the commonest bearing surfaces used in total joint arthroplasty. It is subjected to radiation crosslinking to produce HXLPE, which has improved wear properties compared to conventional UHMWPE. Free radicals produced by irradiation linger within the substance of HXLPE promoting long-term oxidative degradation. Thermal annealing has been used to quench free radicals but this process reduces the mechanical properties of HXLPE. More recently, antioxidants additives have been used to avoid thermal treatment. However, when blended with UHMWPE prior to irradiation, in quenching free radicals, they also suppress crosslinking. Excessive crosslinking suppression can also reduce the wear properties of HXLPE.

Objectives: This study aims to investigate which antioxidant stabiliser is most effective at improving oxidative stability of HXLPE whilst minimally suppressing crosslinking.

Methods: Medical grade GUR 1020 (Ticona GmbH) UHMWPE powder was blended with 0.1% weight of DL-a-tocopherol (Acros Organics), hindered phenol antioxidant (HPAO) (Irganox 1010, TCI America), butylated hydroxytoluene (Sigma Aldrich) and beta-carotene (Sigma Aldrich). These blends were compression molded to form 2mm thick sheets of Vitamin E-PE, HPAO-PE, BHT-PE, ß-Carotene-PE and Control-PE (no additive) respectively. These were irradiated at 100kGy using electron beam radiation. Equilibrium swelling experiments were performed to calculate swell ratio, crosslink density and molecular weight between crosslinks using hot o-xylene (Sigma Aldrich). Accelerated aging was performed on all samples groups for four weeks in oxygen at a pressure of 5 atmospheres and temperature of 70°C. Fourier Transform Infrared Spectroscopy (FTIR) (ThermoScientific Inc) was used to measure the maximum oxidation index of each blend.

Results: Vitamin E-PE, BHT-PE, HPAO-PE and ß-Carotene-PE all significantly ($p<0.05$, ANOVA) suppressed crosslinking (0.130±0.008, 0.139±0.009, 0.167±0.007 and 0.131±0.010 mol/dm3 respectively) compared to control-PE (0.191±0.010 mol/dm3). ?The maximum oxidation index after 28 days in oxygen for the Control-PE was 0.549±0.020 . All of the antioxidants significantly improved oxidation resistance compared to Control-PE ($p<0.05$, ANOVA) and they were all significantly different from each other. Ascending order of oxidation index is as follows: BHT-PE (0.21±0.03) followed by HPAO-PE (0.28±0.02), Vitamin E-PE (0.29±0.02) and ß-Carotene-PE (0.35±0.03).

Conclusions: The different antioxidants used in this study all significantly improve oxidative stability of HXLPE when subjected to accelerated aging in oxygen and they also inhibit cross linking to varying degrees. The ideal antioxidant stabiliser is one that maximally improves oxidative resistance in HXLPE whilst minimally suppressing crosslinking. HPAO and vitamin E are FDA-approved for use in HXLPE to combat long-term oxidative degradation associated with free radicals generated during radiation crosslinking. This allows preservation of mechanical properties to a greater extent than HXLPE that is later subjected to heat treatments. This study shows that both HPAO and vitamin E are effective antioxidants at 0.1% weight when it comes to balancing the deleterious effects of crosslink suppression when blended with UHMWPE prior to irradiation whilst simultaneously protecting the UHMWPE from oxidative degradation.