Europium Stearate Increases the Oxidation Resistance of UHMWPE

Laurent, P M; Gallardo, LA; Kunze, J; Wimmer, MA
†Rush University Medical Center, Chicago, IL, USA; ‡Technical University Hamburg-Harburg, Germany

Introduction: Ultra-high molecular weight polyethylene (UHMWPE) has been ubiquitous as a bearing surface material in joint arthroplasty for decades. Yet, its vulnerability to wear and fatigue failure following oxidation remains a major concern. Although significant gains in wear reduction and oxidation resistance have been achieved with a combination of cross-linking and heat treatments, these gains have been made at the cost of mechanical properties such as ductility and resistance to crack propagation. α-Tocopherol, while an effective antioxidant additive for UHMWPE, has the disadvantage of interfering with cross-linking [1]. Alternative methods for improving the oxidation resistance of UHMWPE are therefore warranted. We have successfully tested europium, a representative element from the lanthanide group, as a stabilization agent to preserve the mechanical properties of UHMWPE subjected to an oxidative challenge [1]. In this study, we hypothesized that the effectiveness of the europium additive is associated with decreased oxidation of UHMWPE.

Material and Methods: Europium(III) stearate synthesized by reaction of europium nitrate with sodium stearate was intimately mixed with GUR 1050 UHMWPE powder at concentrations of 750 and 7500 ppm. These powders, as well as nondoped material, were each compression-molded into a slab from which 80 mm x 30 mm x 25 mm cuboids were machined. Two cuboids from each slab were gamma-irradiated to 3.5 Mrad in a nitrogen atmosphere. One cuboid for each dopant concentration (0, 750, 7500 ppm) was subsequently subjected to accelerated aging in oxygen at 5 atm at 70°C for 14 days per ASTM-F2003-02. Six material conditions were thus obtained, entailing the three dopant concentrations and the two aging conditions.

The mechanical properties were compared through load-displacement curves obtained from small punch tests (ASTM-F2183-02) aged and non-aged cuboids of all three conditions. Initial peak load, failure load, deformation, and work-to-failure were evaluated for miniature disk samples (n=5). These properties were evaluated as relative conditions, i.e., as a ratio of aged to non-aged state to determine the proportion of each property that was retained after aging for each material condition.

Thin film (0.2 mm) transverse sections of each cuboid were profiled for surface oxidation index per ASTM-F2102–06, to a depth of 3 mm, using a window was 0.2 mm x 0.2 mm.

Statistics: Average and standard deviations are reported. The Student t-test was used to compare averages using a significance level of p ≤ 0.0500

Results: The loss of mechanical properties was markedly less for the europium stearate-doped materials than for the nondoped control, as determined from the retained failure load, failure deformation, and work-to-failure values (Fig. 1). Aging was 0.074 ± 0.021, 0.074 ± 0.007, and 0.051 ± 0.018, resp. The three materials exhibit a similar carbonyl peak envelope in the 1695 to 1775 cm⁻¹ infrared region, with the most intense peak being the saturated ketone carbonyl (Fig. 3). Peaks corresponding to carboxylic, aldehyde, and ester carbonyl stretching frequencies are also clearly discernable.

Discussion: The addition of europium(III) stearate to UHMWPE led to a marked increase in the oxidation resistance of the polymer and concomitant better preservation of mechanical properties, confirming our hypothesis. Interestingly, lower dose of 750 ppm of dopant was almost as effective as the much larger dose of 7500 ppm, suggesting that the europium may act as renewable free-radical chain inhibitor. Trivalent lanthanides compounds have been used as polyvinyl chloride (PVC) thermal stabilizers where it is thought they act as free-radical chain terminators by being able to transiently lose or gain f-shell electrons and by inhibiting dehydrochlorination [2, 3]. Indeed, besides the known stability of Eu(II), there is also evidence for Eu(IV) [4]. The lanthanides also strongly coordinate to oxygen and have high coordination numbers, typically greater than 6. Ceria nanoparticlest have been reported to have hydroxyl scavenging properties [5] and to be neuroprotective by acting as direct antioxidants to limit the amount of oxygen species reaching the cells [6].

Europium stearate has been shown to be an effective wear tracer [7] and to have low cytotoxicity coupled with anti-inflammatory behavior [8]. Hence lanthanide stearates may serve as a multifunctional additive. Further investigation is required to determine the antioxidant mechanism of the lanthanide dopants in UHMWPE and to optimize their concentration.


Acknowledgements: This study was supported by the Grainger Foundation.