A New Method of Stabilizing Irradiated UHMWPE Using Vitamin E and Mechanical Annealing

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Introduction

First generation highly crosslinked ultra high molecular weight polyethylenes (UHMWPEs) have been used successfully in total hip arthroplasty for nearly a decade. Next generation highly crosslinked UHMWPEs have improved the properties of their first-generation counterparts: sequentially irradiated and annealed materials have less residual free radicals than irradiated and once-annealed materials [1], and irradiated materials stabilized with α-tocopherol (Vitamin E) have better mechanical properties than irradiated and melted materials [2].

We propose another next generation highly crosslinked material candidate for total joint arthroplasty. Mechanical annealing has shown promise in eliminating residual free radicals while retaining good mechanical properties [3]. We propose eCIMA: an irradiated and mechanically annealed α-tocopherol blended UHMWPE. Mechanical annealing after irradiation would reduce the initial free radical concentration and create an oxidation-resistant material while retaining good mechanical properties. α-Tocopherol would serve as an active stabilizer – that is, the α-tocopherol would protect the material *in vivo* where it will be exposed to lipids and cyclic loading, the latter of which has been shown to accelerate oxidation [4]. We hypothesize that eCIMA will have good mechanical and wear properties and excellent resistance to oxidation, even under aggressive aging conditions.

Materials and Methods

eCIMA was manufactured by irradiating 0.1 wt.% α-tocopherol blended UHMWPE to 150 kGy. The irradiated material was then mechanically annealed by compressing in a hydraulic press (Carver, Inc., Wabash IN) to a compression ratio of 2.5. The compressed material was subsequently thermally annealed at 130°C for 16 hours to recover its shape. In addition to eCIMA, two other materials were tested: 1) Annealed vPE – virgin UHMWPE (containing no α-tocopherol) that was irradiated to 100 kGy and thermally annealed at 130°C for 16 hours, and 2) Melted vPE – virgin UHMWPE (containing no α-tocopherol) that was irradiated to 100 kGy and subsequently melted at 160°C. All of the above samples were made with GUR1020 resin.

Specimens (n=3) were cut from the samples and analyzed by Electron Spin Resonance (ESR) on a Bruker EMX EPR system (Bruker BioSpin Corporation, Billerica MA) at the University of Memphis to determine the free radical concentration in all sample groups.

Bidirectional pin-on-disk (POD) wear testing was conducted on cylindrical pins (n=3). Samples were subjected to a Paul-type load curve with a peak stress of 6.5 MPa while travelling in a 10×5 mm rectangular path at 2 Hz in undiluted bovine calf serum. Wear was quantified gravimetrically on daily basis between 0.500×10^6 and 1.128×10^6 cycles.

Tensile specimens (Type V, n=5) were stamped out of 3.2 mm thick sections and tested using an Insight 2 Electromechanical load frame (MTS Systems, Eden Prairie MN) at a crosshead speed of 10 mm/min, per ASTM D638. Ultimate Tensile Strength (UTS) and Yield Strength (YS) were determined with a 5000N load cell; Elongation at Break (EAB) was determined with a laser extensometer (LX300, MTS Systems) attached to the Insight 2 load frame.

Two types of accelerated aging were performed on 1 cm cubes from all sample groups (n=3 each). The first was the standard ASTM F2003 aging, where samples were placed in a pressure vessel under 5 atm of pure oxygen and heated to 70°C for 14 days. The second doped the sample with squalene – a lipid found in synovial fluid – and then aged in a pressure vessel under 5 atm of pure oxygen and heated to 70°C for 6 days. Squalene, in our yet unpublished data, showed accelerated oxidation of polyethylene: its carbon-carbon double-bonds, which oxidize readily, created free radicals on the squalene molecules which transferred over to the polyethylene molecules, oxidizing it in turn.

After both types of accelerated aging, microtomed thin films (~150 μm) from all samples were boiled in hexane for 16 hours to remove any absorbed species and subsequently analyzed by FTIR (Varian FTS2000, Palo Alto CA) to quantify oxidation, per ASTM F2102.

Results and Discussion

The free radical content, POD wear rate, and mechanical properties are given (Table 1), and the oxidation profiles after ASTM F2003 aging (Fig 1) and after squalene doping and aging (Fig 2) are shown.

Table 1: Results from ESR, POD, and Tensile Testing from all groups.

Sample	FRC (spins/g)	Wear Rate (mg/MC)	UTS (MPa)	YS (MPa)	EAB (%)
eCIMA	0.9×10^{14}	1.2 ± 0.2	50 ± 4	23 ± 0	256 ± 10
Annealed vPE	11×10^{14}	1.4 ± 0.3	56 ± 1	22 ± 0	315 ± 5
Melted vPE	***	1.7 ± 0.1	43 ± 4	19 ± 0	303 ± 13

**** Below detection limit*

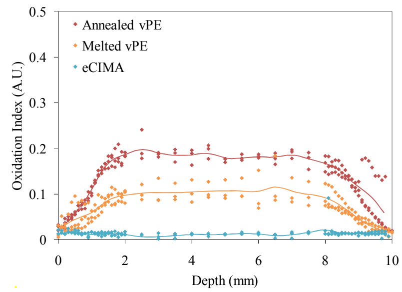

Fig 1: Oxidation profiles after ASTM F2003 aging. Actual data from all samples in a group is represented by the individual data points; the splined average of the three profiles in each sample group is shown as the solid line.

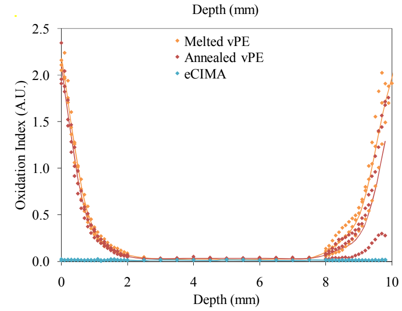

Fig 2: Oxidation profiles after squalene doping and pressure vessel aging. Actual data from all samples in a group is represented by the individual data points; the splined average of the three profiles in each sample group is shown as the solid line.

eCIMA showed that mechanical annealing did not have an adverse effect on the wear or mechanical properties. eCIMA had higher UTS and a slightly lower wear rate as compared to the irradiated and melted material; the annealed vPE material had superior mechanical properties but had a free radical content an order of magnitude larger.

ASTM F2003 aging yielded very little oxidation in all materials. The annealed virgin polyethylene had the highest oxidation, as expected due to its higher free radical content. After squalene doping and aging, both the melted and annealed virgin polyethylene materials showed extremely high oxidation as the oxidation of the absorbed lipid induced oxidation on the polyethylene, even in melted vPE, which initially had no detectable free radicals. In contrast, the α-tocopherol in eCIMA presumably protected this material from oxidation, even under such adverse aging conditions.

The reduced free radical content imparted by mechanical annealing coupled with the active protection of α-tocopherol makes eCIMA a good candidate as a load bearing material due to its excellent mechanical, wear, and oxidation-resistant properties.

References

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