Characterization of Gamma-Irradiated UHMWPE Stabilized with a Hindered-Phenol Antioxidant

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Introduction

Oxidative degradation in Ultra-High Molecular Weight Polyethylene (UHMWPE) has been the leading cause for delamination and fracture in air-packaged, gamma-sterilized articulating surface components. Post-irradiation re-melting process has been used effectively to quench residual free radicals and enhance UHMWPE oxidative stability [1]. Mori et al. [2] have reported that addition of α-tocopherol to UHMWPE powder prior to consolidation improved its oxidative stability after gamma sterilization. Oral et al [3] have reported that incorporation of α-tocopherol to gamma-irradiated UHMWPE block further enhances its mechanical properties and fatigue strength.

One of the concerns with α-tocopherol, a liquid antioxidant, has been it potential tendency to migrate out of UHMWPE matrix during storage and under loading condition. Therefore, the question of whether α-tocopherol is the most effective antioxidant for UHMWPE implant may be debated.

Hindered Phenol Antioxidants (HPAO’s) has been used to stabilize polyethylene for decades. A typical application is in food-contact package materials. The objectives of this study were to assess efficacy of a representative HPAO as an alternative antioxidant for UHMWPE and to investigate mechanical properties of such a gamma-irradiated, HPAO-stabilized UHMWPE.

Materials and Methods

An antioxidant-stabilized UHMWPE was made from GUR 1020 (Ticona) powder containing 0.075 wt % of a hindered phenol antioxidant, compression molded and gamma-irradiated at a nominal dose of 75 K Gy (Steris) in a vacuum foil pouch. Two control materials were used in this study: (1) conventional gamma-irradiated UHMWPE made from 1020 powder, compression molded and gamma-irradiated at 40 K Gy in a vacuum foil pouch, and (2) crosslinked UHMWPE made from GUR 1020 powder, ram extruded, gamma-irradiated at 50 K Gy in a vacuum foil pouch, and then re-melted at 155°C to quench residual free radicals. Uniaxial tension tests were performed on Type IV specimens per ASTM D 638 and double-notched Izod impact tests were performed per ASTM F 648. The fatigue crack propagation tests were performed using a protocol based on ASTM E 647. Crystallinity and melting point data were generated per ASTM F 2625 while swell ratio data were generated per ASTM F 2214. The wear tests were performed using a bi-directional AMTI pin-on-disk tester with 90% bovine serum as lubricant.

The oxidation resistance of each material group was measured by accelerated aging respective samples for 2 weeks at 70°C in 5-atm oxygen chamber, followed by analysis using a FTIR microscope. An oxidation index was calculated by normalizing the area under the carbonyl vibration to the area under the 1370 cm⁻¹ absorbance. The HPAO molecule contains ester functionalities which contributes to FTIR carbonyl absorption and thus to the calculated oxidation index. A corrected oxidation index for post-accelerated-aged, gamma-irradiated, HPAO-stabilized UHMWPE was calculated by subtracting the baseline HPAO carbonyl absorption of the unaged material from the measured oxidation index average.

Results

Table 1 lists tensile mechanical data, impact strength data and stress intensity factor at crack inception measured during crack propagation experiments for all three material groups. Combination of high radiation dose and HPAO presence has no adverse effect on tensile properties of gamma-irradiated, HPAO-stabilized UHMWPE. The DNI data for gamma-irradiated, HPAO-stabilized UHMWPE is consistent with that of highly crosslinked UHMWPE [4]. Nevertheless, 75 K Gy, HPAO-stabilized UHMWPE shows improved crack growth resistance when compared with that of 50 K Gy, re-melted UHMWPE and 40 K Gy UHMWPE.

Table I Mechanical properties of various crosslinked UHMWPE

<table>
<thead>
<tr>
<th>Dose</th>
<th>40 K Gy UHMWPE</th>
<th>50 K Gy, Re-melted UHMWPE</th>
<th>75 K Gy, HPAO-Stabilized UHMWPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield tensile strength (MPa)</td>
<td>23.0 ± 0.3</td>
<td>21.5 ± 0.3</td>
<td>23.2 ± 0.2</td>
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<tr>
<td>Ultimate tensile strength (MPa)</td>
<td>40.6 ± 0.8</td>
<td>40.1 ± 1.4</td>
<td>46.1 ± 1.4</td>
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<td>Elongation at break, %</td>
<td>339 ± 5</td>
<td>305 ± 5</td>
<td>335 ± 11</td>
</tr>
<tr>
<td>Double-notched Izod impact strength, MPa/m</td>
<td>93.7 ± 1.0</td>
<td>80.2 ± 1.2</td>
<td>73.6 ± 3.7</td>
</tr>
</tbody>
</table>

| Crystallinity, % | 60.0 ± 0.4 | 54.1 ± 1.0 | 58.7 ± 0.7 |
| Melting point, °C | 136.6 ± 0.2 | 134.5 ± 0.4 | 138.2 ± 0.3 |
| Swell ratio | 3.65 ± 0.06 | 3.50 ± 0.01 | 3.73 ± 0.04 |
| POD wear, mg/MC | 8.38 ± 0.13 | 4.29 ± 0.27 | 5.55 ± 0.34 |
| Average oxidation index after acc. aging | 0.506 ± 0.227 | 0.045 ± 0.065* | 0.000* (after correction) |

Discussion

In this study, it has been demonstrated that HPAO’s provide excellent oxidation stability to gamma-irradiated UHMWPE without employing a re-melting process to quench free radicals. This allowed the gamma-irradiated, HPAO-stabilized UHMWPE to provide better tensile strength and fatigue crack resistance relative to the gamma-irradiated, re-melted UHMWPE. Therefore, the study provides strong justification for the employment of a hindered phenol-stabilized UHMWPE for orthopaedic devices with enhanced performance characteristics relative to current UHMWPE materials.

References

4. Internal data

Table II Thermal, chemical, and wear characteristics of crosslinked UHMWPE

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Table II Shows thermal, swell ratio, wear and oxidation resistance characteristics for the three material groups evaluated. Gamma-irradiated, HPAO-stabilized UHMWPE retains its crystallinity and melting point in comparison with gamma-irradiated, re-melted UHMWPE. In addition, it provided improved oxidative stability and wear resistance in comparison with the conventional 40-K Gy UHMWPE (P<0.05).

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