**Diffusion of Vitamin E in High Temperature Melted and Radiation Cross-linked UHMWPE**

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**Introduction:** Highly cross-linked ultrahigh molecular weight polyethylene (UHMWPE) joint implants are stabilized against oxidation either by post-irradiation thermal treatment (annealing or melting) or antioxidant stabilization [1]. Antioxidant stabilization can be achieved by post-irradiation diffusion of vitamin E to prevent oxidation. This process comprises doping with vitamin E to obtain a high surface concentration followed by homogenization to distribute the surface vitamin E into the entire component. Both processes take place at below but close to the peak melting temperature of irradiated UHMWPE (120-130°C) to enhance diffusion without melting the cross-linked polymer [2], which is known to decrease mechanical strength and toughness[3].

High temperature melting (HTM) of UHMWPE at very elevated temperatures (280-340°C) prior to radiation cross-linking has been shown to improve the toughness of cross-linked UHMWPE without sacrificing the wear rate. The goal here was to study the effect of HTM on the diffusion behavior of vitamin E after radiation cross-linking.

**Methods:** Sample Preparation: Virgin UHMWPE blocks (7.3 x 4 x 3.1 cm) (GUR 1020 medical grade, Biomet, IN) were machined from compression molded bar stock. These were HTMed at 320°C for 6 hours in nitrogen, followed by irradiation to 175 kGy by gamma radiation (Biomet, IN), denoted as ‘HTM samples’. The virgin UHMWPE irradiated to 100 kGy using gamma radiation served as a control. The irradiated blocks were machined into 1 cm cubes, which were doped in vitamin E with stirring under argon flow at 120°C for 3 hours. The cubes were allowed to cool to room temperature and excess vitamin E was wiped off their surfaces. After doping, one set of control cubes (n=2) was homogenized under argon, at ambient pressure, at 130°C for 8 hours. Four sets (n=1, each) of the HTM doped cubes were homogenized at 150°C for 1 or 2 hours and 180°C for 30 mins or 1 hour, respectively. The wear and mechanical properties of both the HTM and control samples were measured prior to doping and homogenization. Another set of controls were irradiated HTM blocks (n=1 each) that were melted at 180 and 220°C for 6 hours, simulating homogenization, to test the effect of high temperature melting on mechanical properties.

**Characterization:**
Vitamin E concentration index: Thin sections (150 μm) were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) and a vitamin E index was calculated by normalizing the absorbance at 1265 cm-1 (1245-1275cm-1) by that at 1895 cm-1 (1850-1985cm-1). The penetration depth of vitamin E was calculated as the depth up to which the vitamin E index of the sample was ≥ 0.02. Wear Rate: Pin-on-disc wear testing was performed on cylindrical pins (dia. 9mm, height 13mm) as previously described at 2 Hz [3]. Wear was measured gravimetrically every ~0.16 MC and the wear rate was measured by a linear regression from 0.5 to 1.2 MC. Tensile Mechanical Properties: Type V tensile specimens (n=5) according to ASTM-638 were stamped out of 3.2 mm thick sections and tested with a crosshead speed of 10mm/min. Statistical Analysis: Statistical significance was calculated using a Student t-test. Significance was assigned to < 0.05.

**Results:** The penetration depth of vitamin E increased from 1.0 ± 0.0 mm after doping to 3.8 ± 0.3 mm for the 100 kGy irradiated control samples homogenized at 130°C for 8 hours (p=0.003, Fig. 1), while for the HTM samples it increased from 0.9 ± 0.0 mm after doping to 2.5 ± 0.0, 3.5 ± 0.0, 3.0 ± 0.0 and 4.2 ± 0.3 mm for samples homogenized at 150°C for 1 hr, at 150°C for 2 hours, at 180°C for 30 mins and at 180°C for 1 hour, respectively (p= 0.000004, 0.000002, 0.0002 and 0.0025; Fig. 1). The wear rate of the 100 kGy irradiated control prior to doping, (1.7 ±0.2 mg/MC) was comparable to that of 175 kGy irradiated HTMed sample(2.1 ± 1.3 mg/MC); (p= 0.67). The elongation-at-break (EAB) and work to failure of the HTM sample prior to doping was higher than the control sample (p= 0.003, 0.053 respectively, Table 1). The ultimate tensile strength (UTS) of the HTM sample prior to doping, was comparable to the control sample (p= 0.049, Table 1). The HTM samples melted at 180 and 220°C for 6 hours showed significantly higher EAB as compared to the control sample (p= 0.009 and 0.002 respectively). The UTS of the HTM samples after melting at 180 and 220°C was slightly lower than the control sample (p= 0.008 and 0.012 respectively) while the work to failure was higher than the control sample (p= 0.078,0.05 respectively, Table 1).

**Discussion:** We manipulated the morphology of UHMWPE by using HTM, to achieve increased toughness of cross-linked UHMWPE. Our goal here was to study its effect on the diffusion of vitamin E. Doping and homogenization of vitamin E is typically performed below the melting point of cross-linked UHMWPE to maintain its mechanical properties by avoiding the decrease in crystallinity associated with melting in the presence of cross-links. However, HTM prior to crosslinking improves the toughness
of UHMWPE mostly due to significantly increased elongation. Thus, exposing the HTMed and irradiated UHMWPEs to homogenization temperatures above the melting point of UHMWPE may be less detrimental to their resultant mechanical properties.

Increasing the homogenization temperature to 180°C for the HTMed, irradiated UHMWPE decreased the required homogenization time 8 fold while achieving similar penetration depths compared to the control sample homogenized below the melt. Despite melting at 180 and 220°C, the HTMed, irradiated samples showed improved toughness compared to irradiated control as measured by the tensile work-to-failure and EAB. In addition, the wear resistance of the HTMed, irradiated UHMWPE was comparable to the irradiated control, suggesting that HTM before radiation cross-linking followed by doping with vitamin E and homogenization at above-the-melt temperatures may be a feasible alternative to fabricating total joint implants without sacrificing crucial properties.

This study is limited by our use of HTMed irradiated samples before vitamin E doping and homogenization for testing wear resistance. While we plan on confirming our results after vitamin E incorporation, the effects of post-irradiation melting on wear properties was shown to be insignificant.

Significance: The required time to diffuse the antioxidant vitamin E into radiation cross-linked UHMWPE was shortened markedly by high temperature melting it prior to irradiation without sacrificing the toughness and wear resistance.

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Table 1. Elongation-at-break, UTS and yield strength values of all the test and control samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elongation-at-break (%)</th>
<th>UTS (MPa)</th>
<th>Work to Failure (kJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 kGy - Control</td>
<td>272 ± 14</td>
<td>46.4 ± 1.2</td>
<td>1557 ± 77</td>
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<tr>
<td>175 kGy - HTM</td>
<td>318 ± 7</td>
<td>43.1 ± 0.8</td>
<td>1758 ± 48</td>
</tr>
<tr>
<td>175 kGy – HTM – Melted @ 180°C – 6h</td>
<td>292 ± 4</td>
<td>40.1 ± 1.0</td>
<td>1684 ± 75</td>
</tr>
<tr>
<td>175 kGy – HTM – Melted @ 220°C – 6h</td>
<td>301 ± 4</td>
<td>40.6 ± 0.5</td>
<td>1786 ± 38</td>
</tr>
</tbody>
</table>

Figure 1. The vitamin E index profile of the non-HTM and HTM doped control and doped and homogenized samples.