Surface Cross-linked Ultra High Molecular Weight Polyethylene by Diffusion of Dicumyl Peroxide

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Introduction: Highly cross-linked ultrahigh molecular weight polyethylene (UHMWPE) is the material of choice for total joint arthroplasty due to its highly improved wear resistance. Cross-linking leads to decreased wear but also decreases the toughness of the material [1]. Thus, surface cross-linking is a method that improves the wear resistance on the surface while maintaining the toughness in the bulk of the material [2].

Cross-linking in polyethylene can be achieved during consolidation by using peroxides. We have also shown that an organic peroxide with a low decomposition temperature could be diffused into virgin and antioxidant-blended UHMWPEs, resulting in cross-linking on the surface [3].

In this study, we hypothesized that a low wear rate, high impact strength, surface cross-linked, antioxidant-blended UHMWPE could be obtained by using diffusion of an aqueous emulsion of dicumyl peroxide (DCP). In this manner, a feasible manufacturing method for tougher joint implants could be achieved using peroxides.

Methods: Sample Preparation: Medical grade GUR1020 UHMWPE was blended with vitamin E at 0.1, 0.3 and 0.8 wt%, and then consolidated. These pucks were then machined into 1cm cubes for diffusion. 30mg of DCP/ml was added with 40% Tween 20 into DI water to form a stable emulsion. In emulsions also containing vitamin E, 15mg of vitamin E/ml was added to this emulsion. To determine optimum diffusion durations, the cubes were doped using emulsion at 100°C for different times and decomposed in argon at 150°C for 4 hours to initiate cross-linking. For assessing the properties of a medical preform-size sample (large scale), a 0.3 wt% vitamin E blended UHMWPE (~ 80x60x10 mm) was doped at 100°C using a DCP emulsion containing vitamin E for 16 hours followed by decomposition at 150°C for 4 hours.

To compare its properties to clinically relevant controls, an ‘E1™’ tibial bearing (Biomet, Inc.) was machined for further testing. Another control ‘CISM-100’ was prepared by irradiating UHMWPE (GUR1020) at 100 kGy followed by subsequent melting.

Sample testing: Cross-link density was measured by swelling 3 mm cubes in xylene pre-heated to 130°C for 2 hours. The gravimetric swell ratio was converted to a volumetric swell ratio using the density of polyethylene as 0.94 g/cc and the density of xylene at 130°C as 0.75 g/cc. The crosslink density was calculated as previously described [2]. Pin-on-disc (POD) wear testing was performed on cylindrical pins (dia. 9 mm, height 13 mm) as previously described [4] at 2 Hz for 1.2 million-cycles (MC). Wear was determined gravimetrically every ~0.16 MC and the wear rate was determined by the weight change from 0.5 to 1.2 MC. The Izod impact strength was determined by double notching and testing of the samples (6.35 x 12.7 x 63.5 mm, n=5) according to ASTM F-648. It is reported as (kJ/m²). The oxidation induction time (OIT) was determined using a differential scanning calorimeter. The samples (~5mg) were heated from 20 to 200°C at a rate of 20°C/min under nitrogen. After 5 minutes at 200°C the gas was switched to oxygen and the onset of oxidation was recorded as the OIT and determined as the intercept

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of the extended baseline and the steepest tangent drawn to the exotherm. Statistical significance was calculated using student’s t-test and the significance was attributed to p<0.05.

**Results:** DCP emulsion without vitamin E: The surface cross-link density of 0.1wt% vitamin E blended UHMWPE was similar at diffusion times of 4 and 8 hours after being decomposed at 150°C for 4 hours. For 0.3 and 0.8wt% vitamin E blended UHMWPE, the surface cross-link density was highest for 8 and 16 hours diffusion time, respectively, when decomposed at 150°C for 4 hours (Figure 1). The OIT calculated on the surface of the 0.1, 0.3 and 0.8 wt% diffused, vitamin E blended UHMWPEs was 4.1, 6.6 and 10.1 minutes, respectively.

DCP emulsion containing vitamin E: The surface cross-link density of the 0.1 and 0.3wt% vitamin E blended UHMWPEs after diffusion in emulsified DCP containing vitamin E was comparable to the samples diffused with DCP without vitamin E (p= 0.89 and 0.96 for 0.1 and 0.3wt% vitamin E respectively). The diffusion and decomposition temperatures and times were the same for both types of emulsions (Figure 2). The OIT on the surface of the 0.1 and 0.3wt% vitamin E blended UHMWPEs after diffusion in vitamin E-containing DCP emulsion was 13.6 and 19.5 minutes respectively, which was significantly higher than the samples diffused with the DCP emulsion without vitamin E (p<0.05).

Large scale processing: The surface cross-link density and wear rate of the large scale 0.3wt% vitamin E blended UHMWPE diffused in vitamin E-containing DCP emulsion were comparable to control E1 and CISM-100 while its impact strength was significantly higher (p<0.05, Table 1).

**Discussion:** Our goal was to develop a surface cross-linked, highly wear and oxidation resistant vitamin E blended UHMWPE with improved toughness. We aimed at obtaining the cross-link density of 100-kGy irradiated and melted virgin UHMWPE (245-260 mol/m3) on the surface of this material. Our approach was to diffuse the organic peroxide DCP in an emulsified form and cross-link the material during a subsequent decomposition step above the decomposition temperature of this peroxide (137°C), where free radicals are generated abundantly.

Our objective in using vitamin E blends of UHMWPE was to ensure oxidation resistance especially on the surface of the material. Since vitamin E can restrict cross-linking in UHMWPE with increasing concentration [5], we studied diffusion durations of DCP for each vitamin E concentration to achieve the highest possible surface cross-link density. We determined that the optimal diffusion durations for 0.1 and 0.3 wt% blends were 4 and 8 hours, respectively, which may be feasible in a manufacturing setting. The OIT of UHMWPEs surface cross-linked by diffusing just emulsified peroxide was lower than 10 minutes, corresponding to low oxidation resistance as defined by ISO11357-6:2002. This was presumably due to vitamin E extraction from the surface during the diffusion of the peroxide. We showed that incorporating additional vitamin E into the DCP emulsion improved the oxidation resistance substantially without compromising the wear resistance (Figure 2).

A large scale sample of 0.3wt% vitamin E blended UHMWPE was surface cross-linked using optimized parameters. The wear rate of this surface cross-linked UHMWPE was comparable to two clinically relevant, highly cross-linked UHMWPEs (Table 1). There was a substantial improvement (75 and 44% respectively) in the impact strength due to the restriction of cross-linking to the surface.

**Significance:** Surface cross-linking of vitamin E-blended UHMWPE by diffusion of emulsified DCP containing vitamin E achieved high wear and oxidation resistance with superior impact strength compared to clinically available highly cross-linked joint implant materials.
Figure 1: Crosslink density for DCP-doped (emulsion: 30mg DCP/mL) (a) 0.1wt%, (b) 0.3wt% and (c) 0.8wt% Vitamin E blended GUR 1020 decomposed at 150°C for 4 hours.

Figure 2: Crosslink density for DCP-doped (emulsion: 30mg DCP/mL, 15mg Vit E/mL) (a) 0.1 wt% and (b) 0.3wt% Vitamin E blended GUR 1020. The diffusion of DCP was performed at 100°C for 4 and 8 hours respectively. Decomposition was performed at 150°C for 4 hours.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Crosslink density (mol/m²)</th>
<th>Impact Strength (kJ/m²)</th>
<th>Wear (mg/MC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test Sample</td>
<td>287 ± 15</td>
<td>113.6 ± 2.0</td>
<td>0.86 ± 0.06</td>
</tr>
<tr>
<td>E1™</td>
<td>220 ± 6</td>
<td>65.0 ± 0.6</td>
<td>0.64 ± 0.08</td>
</tr>
<tr>
<td>CISM-100</td>
<td>229 ± 16</td>
<td>78.7 ± 3.6</td>
<td>0.93 ± 0.23</td>
</tr>
</tbody>
</table>

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