IN-VITRO WEAR PERFORMANCE OF STANDARD, CROSSLINKED, AND VITAMIN-E BLENDED UHMWPE

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ABSTRACT

Cross-linked vitamin-E-stabilized polyethylene acetabular cups were compared with both commercially available conventional and custom cross-linked polyethylene acetabular cups in terms of wear behaviour, in a hip joint simulator for five millions cycles, using bovine calf serum as lubricant.

We correlated the wear experiments results with the chemical characterization of the investigated materials: FTIR analyses, DSC and cross-link density measurements were used to assess the chemical characteristics of the pristine materials. In addition, further FTIR analyses and cyclohexane extraction were carried out after the simulator experiments.

Lipids absorption was observed in all tested specimens and it has been shown to strongly affect the results of the wear test. The chemical analyses showed that the addition of vitamin E reduced the crosslinking efficiency.

Key words: Vitamin-E doped PE; Cross-liked PE; Standard PE; Hip simulator; FTIR analysis.
1. INTRODUCTION

It is well known that the oxidative degradation of ultra-high-molecular-weight-polyethylene (UHMWPE) decreases its mechanical properties, leads to the formation of wear debris and consequently may induce biological responses that cause osteolysis and implant loosening. The goal is to develop improved materials in order to extend the lifetime of orthopaedic implants up to 30 years. Several new and pending products aim to address this issue. Scientists have proposed alternative varieties of UHMWPE to improve the wear resistance of the polymer. In particular, attention has been focused on the development of polymer composite (i.e. UHMWPE through the inclusion of carbon fibre) and methods that increase the level of cross-linking in PE.

Currently, highly crosslinked, wear resistant UHMWPE, for clinical use, is prepared by irradiation and subsequent thermal treatment in order to decrease or eliminate the residual free radicals. Melting, subsequent to radiation cross-linking, decreases the concentration of residual free radicals to undetectable levels and prevents long-term oxidation. However, melting also reduces crystallinity and mechanical properties of the irradiated polymer. The complete elimination of free radicals is difficult due to the limited mobility of these radicals within the crystalline structure of the polymer.

Some studies focused the attention on delayed oxidation phenomena with the addiction of suitable stabilizing additives capable to decrease the reactivity of the radical species and so interrupt the oxidation cycle. Stabilisers are compounds added to the polymer in order to slow the oxidation processes and to preserve its chemical, physical and mechanical properties, i.e. to prolong its lifetime.

Considering that a stabiliser must be biocompatible, Vitamin E seems to be the ideal candidate: it is a compound already present in the human body as natural antioxidant in the physiological processes.

The aim of this study was to investigate the wear performance of vitamin E-stabilised cross-linked polyethylene in comparison with those of standard and cross-linked polyethylene.
2. Materials and methods

Specimens tested

The wear behaviour of three different batches of polyethylene acetabular cups (28-mm inner x 44-mm outer dimensions; 5 specimens for each batch) coupled with 28-mm cobalt-chromium-molybdenum (CoCrMo) femoral heads were investigated using a hip joint simulator. Standard UHMWPE acetabular cups (hereinafter called ST_PE) were machined from polymer bars made of GUR 1020 (Orthoplastics Ltd, Lancashire, UK). Crosslinked acetabular cups (hereinafter called XLPE) were obtained from a cylindrical bar, firstly electron beam-irradiated to 70 kGy, then thermally treated at 135°C, in order to remove free radicals formed during irradiation. After these treatments, the cups were machined to their final shape. Similarly, Vitamin E-containing, crosslinked acetabular cups (hereinafter called XLPE-VE) were machined from a Vitamin E-blended UHMWPE bar (0.1% w/w; Orthoplastics Ltd, Lancashire, UK), after electron beam irradiation to 70 kGy followed by a thermal treatment at 160°C under nitrogen for 12 hours.

All the cups were then subjected to Ethylene Oxide Sterilization (ETO).

Following a standardized procedure, another six acetabular cups (two for each type of material used) were stored (non-loaded) in bovine calf serum to compensate for weight changes due to fluid absorption. All polyethylene acetabular cups were pre-soaked for four weeks prior the wear tests.

Experimental wear details

Wear tests were performed using a 12-station hip joint simulator (Shore Western, Monrovia, Los Angeles, USA). The simulator set-up followed is described in details elsewhere. Each articulating station was subjected to a sinusoidal loading with a peak up to of 2 kN and a frequency of 1.1 Hz, according to the rotation test frequency. The weight loss of the cups was determined every 0.5 million cycles (Mc) using a Sartorius analytical balance (Sartorius AG, Goettingen, Germany) with a precision of ±0.1 mg. Wear trend was determined by dividing the progressive weight loss by the number of
cycles during the whole test. The effects of the wear considering different polyethylenes were
evaluated using Kruskall-Wallis non-parametric statistical test.

Roughness measurements

The surface roughness of all the femoral heads was measured using a contact profilometer Hommel
Tester T8000 (Hommel Werke, Koeln, Germany). Scanning operations were performed identifying
three planes according to previous standardized protocol\textsuperscript{15}. Sampling lengths were taken using a cut-off of 0.08 mm. Three parameters (Ra, Rt, and Rsk), in agreement to previous study\textsuperscript{15}, were taken
into consideration to qualify the surface roughness and if this surface profile parameters could predict
the variance observed in the weight loss measurements. The measurements were acquired at the
beginning and at the end of the test.

FTIR spectroscopy

A Fourier Transformed Infra Red Spectroscopy (FTIR) Microscope (Spectrum Spotlight 300, Perkin-
Elmer, Shelton, Connecticut, USA) was used to monitor possible chemical changes across the cups
section. One control sample and the most worn acetabular cup from each batch were cut
perpendicularly to the articulating surface. From the cross section, a series of 180 µm thick slices was
obtained using a PolyCuts Microtome (Reichert-Jung, NuBlock, Germany) at 10 mm/s in air at room
temperature. Line-scan spectra were collected by setting the area of analysis at 100 x 100 µm\textsuperscript{2}; the
spectra were recorded every 100 µm along the mapping direction, starting from the articulating surface
towards the bulk. In the case of the worn cups, each line scan was collected starting from the worn
area of the bearing surface. All spectra were run in the transmission mode with a 4 cm\textsuperscript{-1} resolution
and 16 scans per spectrum and were normalised at 2020 cm\textsuperscript{-1} at an absorption of 0.05, corresponding
to a film thickness of ca. 100 µm. The peak at 2020 cm\textsuperscript{-1}, a combination band associated with the
twisting of CH\textsubscript{2}, was used as an internal standard, since it can be regarded as unaffected by minor
changes in the polymer structure\textsuperscript{16}. 
The molar concentration of vinyl (909 cm$^{-1}$) and trans-vinylene (965 cm$^{-1}$) double bonds was calculated from the respective absorption bands, using the molar absorptivity proposed by De Kock and Hol$^{17}$. The degree of oxidation of the samples was determined by the ketones absorption at 1718 cm$^{-1}$, while lipids absorption was assessed by the esters absorption at 1740 cm$^{-1}$.$^{18}$

**Cyclohexane extraction**

Three thin sections (approx. 65 mg each) per each polyethylene group were cut from a worn sample and soaked for six hours in boiling cyclohexane to extract adsorbed lipids. The specimens were weighted on an analytical balance before and after soaking and the weight difference was calculated to determine the amount of diffused lipids. The three thin sections were assumed to be representative of the whole cup and the total amount of lipids diffused in each cup was estimated by assuming the average weight fraction of lipids absorbed in a single section to be equal to that absorbed into the whole cup.

**Determination of crosslink density.**

The crosslink density of each sample was quantified by gravimetric measurements. Small cylinders with diameter of 5 mm and approximate weight of 30 mg were cut out of the control cups and immersed in xylene at 135°C for 3 hours. The swell ratio ($\rho$) was calculated as:

$$\rho = \frac{(V_s + V_x)}{V_s}$$  \hspace{1cm} (1)

where $V_s$ is the initial volume of the sample, calculated by dividing the initial weight of the sample by the density of UHMWPE (assumed to be 0.93 g/cm$^3$) and $V_x$ is the volume of the absorbed xylene, calculated by subtracting the initial weight of the sample from its final, xylene-swollen weight and dividing the result by the density of xylene (0.75 g/cm$^3$).
The measured $\rho$ values were used to determine the crosslink density, $\nu_d$, and the molecular weight between crosslinks, $M_c$, using the equations reported by Muratoglu\textsuperscript{19}.

**Crystallinity.**

The crystallinity of the test samples was determined using a Differential Scanning Calorimetry (DSC 6- Perkin-Elmer, Waltham, Massachusetts, USA) at a heating rate of 10°C/min. The sample weights varied around 5 mg. The heat of fusion was calculated by integrating the DSC endotherm from 60 to 160°C. The crystallinity was calculated by normalizing the heat of fusion to the heat of fusion of 100% crystalline polyethylene (293 J/g)\textsuperscript{20}. 
3. Results

The physical-chemical characteristics of the control samples, resulting from FTIR, DSC and cross-link density measurements, are summarized in Table 1. Trans-vinylene groups formation was observed in the irradiated samples, their concentration being constant along the cup section. On the contrary, the concentration of vinyl groups, originally present in pristine UHMWPE, decreases by nearly 50% in XLPE-VE and of one order of magnitude in XLPE.

No significant differences were observed in the crystallinity of the tested samples.

The cross-link density \( (\nu_d) \) increases in the irradiated samples compared to ST_PE, though the increase was much more relevant for XLPE than for XLPE-VE. Accordingly, the molecular mass between cross-linking \( (M_c) \) shows the inverse trend.

All the prosthetic hip specimens completed the planned five Mc.

Compared to the different cups configurations, the XLPE-VE combination wore more than the XLPE but however, maintained a lower weight loss than the standard PE during the whole test (Figure 1).

Significant statistical differences \( (p < .01) \) were observed between all the polyethylene cups using the KS statistical test.

Table 2 shows the roughness values of the heads (± Standard Deviation) at 0 Mc and 5 Mc. A slight increase in Ra may be observed for the ST_PE and XLPE_VE combinations. Conversely, an appreciable increase in Rt is observed for all the configurations. The surface of all heads became more negatively skewed, indicating diminishing peaks. Smoother surfaces \( (Rsk < 0) \) allow higher contact between them and may be most suitable for lubricating sliding. The coefficient of correlation between the weight loss and the three roughness parameters was found to be 0.049 for the Ra, 0.186 for the Rt, and 0.001 for the Rsk.

Figure 2 shows the FTIR line-scan of one XLPE-VE sample analysed after the wear test, along with that of the XLPE-VE control, unloaded sample for comparison. The absorption band at 1740 cm\(^{-1}\) (Figure 2a) indicates the presence of lipids diffused into the polyethylene matrix \(^{21}\). The same absorption cannot be observed in the control-unloaded sample (Figure 2b).
Lipids absorption was observed at the articulating surface of all samples exposed to the wear test. On the contrary, none of the control-unloaded samples showed this phenomenon. No detectable oxidation was observed in any of the samples. The estimated average amount of absorbed lipids per each loaded polyethylene group is reported in Table 3, along with the corrected weight losses after 5 millions cycles. The raw value obtained gravimetrically for XLPE-VE was corrected taking in account that the cyclohexane soaking procedures is likely to remove vitamin E along with the lipids.
4. Discussion

The purpose to irradiate vitamin E-stabilized polyethylene is to obtain a cross-linked UHMWPE with enough cross-link density, in order to improve strength to resist cyclic stresses and long-term oxidative stability such that the wear and mechanical properties can be maintained in long term, and to obtain better wear performances. Using a 12-station hip simulator, the wear performance of three different polyethylenes coupled with CoCrMo femoral heads was evaluated for five million cycles. In particular, we asked how the addiction of vitamin E affects the wear properties, compared to conventional UHMWPE and cross-linked PE.

We found a reduced wear rate for the XLPE configurations in comparison to the standard PE. In particular, the results of this investigation clearly showed a reduced wear for the experimental XLPE and the XLPE-VE acetabular cups with respect to the conventional UHMWPE components.

It must be emphasized that the lipids absorption has been shown to strongly affect the measured weight losses (see Table 3), even if it do not influence the overall trend. In the case of XLPE, the measured weight loss after the wear test is equal to that of the extracted lipids. This can lead to an error in the absolute measurement of the wear volume of about 100%. This factor should be taken in account when evaluating absolute weight losses coming from wear tests. It has also been shown that the practice to keep a control, unloaded sample it is largely unsatisfactory in correcting this mistake, the diffusion rate being strongly influenced by the applied load (Figure 2).

Trans-vinylene groups are known to be formed in UHMWPE upon irradiation and can be used to assess the absorbed radiation dose [ASTM F2381 - 04]. A nearly identical concentration of vinylene double bonds measured in both our irradiated samples confirms that they received the same radiation dose. On the other hand, vinyl groups are consumed as a consequence of irradiation, being involved in the formation of Y-shaped cross-links. Although the radiation dose was the same for XLPE and XLPE-VE, the vinyl consumption was less efficient in the latter, suggesting a lower extent of cross-linking. The lower cross-link density measured in XLPE-VE, compared to XLPE, confirmed this assumption. However, it must be pointed out that XLPE-VE exhibits a much higher cross-link density,
when compared to ST_PE. It was already observed that the addition of vitamin E reduces the cross-linking efficiency, because of the establishment of a competition between the vitamin E itself and the vinyl double bonds, in the reaction with the radicals created by irradiation \(^\text{10}\). A precise quantification of this effect, along with its correlation with the vitamin E concentration and the dispensed radiation dose, is still under study \(^\text{23,24}\).

The surface analysis of all metallic heads clearly showed increased roughness for all three parameters measured for all different configurations of polyethylene tested in this study. An “ideal surface finish” should have a low Ra value and a negative Rsk value \(^\text{25,26}\). The presence of depressions or holes (rather than scratches) with smooth (rather than sharp) edges seems to improve the lubrication and wettability properties. The surface of all heads became more negatively skewed, indicating diminishing peaks. Smoother surfaces \((\text{Rsk} < 0)\) are less detrimental than surfaces with a positive Rsk; they allow higher contact between them and may be most suitable for lubricating sliding \(^\text{27}\).

However, it should be noted that the amount of weight loss after five million cycles in a hip joint wear simulator didn’t correlate with the three roughness parameters measured in these studies \((\text{Ra}, \text{Rt}, \text{Rsk})\). On the contrary, it is well known that the cross-link density is strongly correlated with the wear resistance of UHMWPE \(^\text{28}\). Therefore, the lower wear rates observed for both XLPE compared to ST_PE is a consequence of cross-linking induced by irradiation, but at the same time the higher wear rate measured for XLPE-VE, compared to XLPE can be attributed to the lower cross-linking extent of the former. An improvement in the cross-linking yield could have been obtained by increasing the radiation dose given to XLPE-VE.
5. CONCLUSIONS

All the acetabular cups studied in this work showed significant differences in respect to the wear behaviour. Lower weight loss was exhibited by the XLPE, which has potential for reduced wear and decreased osteolysis. The amount of weight loss after five million cycles in a hip joint wear simulator didn’t correlate with the roughness parameters while cross-link density is strongly correlated with the wear resistance of UHMWPE.

Two crucial aspects of this study must be taken into account:

- lipids absorption can affect gravimetric measurements of wear. This phenomenon is a potential source of misinterpretation of wear experiments. This observation is completely original and innovative and, in the authors' opinion, it is highly relevant for the interpretation of wear experiments results.

- Blending vitamin E with UHMWPE protects the polymer from long-term oxidation and deterioration of the mechanical properties, but it also decreases the cross-linking efficiency, with an adverse effect on the wear resistance. Although this observation has already been reported in the literature, there are very few studies presenting a complete correlation among vitamin E concentration, radiation dose, cross-link density and wear resistance.

Our findings should serve as a warning to the producers: it must be kept in mind that, when treating a vitamin E-blended UHMWPE, the usual radiation dose given to obtain a conventional “highly cross-linked” UHMWPE should be adjusted to higher values, in order to obtain the same cross-link density and thus the same wear resistance properties.

Little is known or understood about the relationship between PE wear particles debris and the biological response leading to osteolysis and less is known about the role of crosslinking in this process. The promise of improved clinical performance in respect to osteolysis is a matter to be determined by long-term (>10 years) clinical follow-up studies. An increased understanding of the
related biological processes and osteolysis is needed to provide the ability to better evaluate the PE, XLPE, and XLPE-VE performance \textit{in-vivo}.

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References


**Tables Captions**

**Table 1** - Physic-chemical characteristics of the control samples, resulting from FTIR, DSC and cross-link density measurements.

**Table 2** - Mean roughness (± Standard Deviation) for the femoral heads coupled with different polyethylenes.

**Table 3** - Weight losses after completion of the wear test, corrected for lipids absorption.
Figures Captions

**Figure 1** – Wear behaviour and Regression coefficient for the different configurations of polyethylene tested.

**Figure 2** – FTIR line-scan of a thin section cut from: A) XLPE-VE after five million cycles; B) control, unloaded XLPE-VE.
Tables Captions

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Table 1 - Physic-chemical characteristics of the control samples, resulting from FTIR, DSC and cross-link density measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Trans-vinylene groups concentration [mmol/l]</th>
<th>Vinyl groups concentration [mmol/l]</th>
<th>Crystallinity %</th>
<th>νt [g/m³]</th>
<th>M_c [g/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST_PE</td>
<td>0.0</td>
<td>4.5</td>
<td>52 ±2</td>
<td>10.0</td>
<td>93570</td>
</tr>
<tr>
<td>XLPE</td>
<td>12.1</td>
<td>0.4</td>
<td>49 ±2</td>
<td>176.8</td>
<td>5289</td>
</tr>
<tr>
<td>XLPE-VE</td>
<td>12.5</td>
<td>2.5</td>
<td>52 ±2</td>
<td>85.4</td>
<td>10944</td>
</tr>
</tbody>
</table>
Table 2- Mean roughness (± Standard Deviation) for the femoral heads coupled with different polyethylenes.

<table>
<thead>
<tr>
<th></th>
<th>0 Million cycles</th>
<th>5 Million cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ST_PE</td>
<td>XLPE</td>
</tr>
<tr>
<td>$Ra$</td>
<td>0.01 ± 0.01</td>
<td>0.01 ± 0.01</td>
</tr>
<tr>
<td>$R_t$</td>
<td>0.05 ± 0.01</td>
<td>0.05 ± 0.01</td>
</tr>
<tr>
<td>$R_{sk}$</td>
<td>0.053 ± 0.07</td>
<td>0.037 ± 0.05</td>
</tr>
</tbody>
</table>
**Table 3** - Weight losses after completion of the wear test, corrected for lipids absorption

<table>
<thead>
<tr>
<th></th>
<th>XLPE</th>
<th>XLPE_VE</th>
<th>ST_PE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Avg. Weight loss at 5 millions cycles [mg]</strong></td>
<td>32</td>
<td>87</td>
<td>142</td>
</tr>
<tr>
<td><strong>Extracted lipids [mg]</strong></td>
<td>36</td>
<td>42</td>
<td>21</td>
</tr>
<tr>
<td><strong>Corrected weight loss at 5 millions cycles [mg]</strong></td>
<td>68</td>
<td>129</td>
<td>163</td>
</tr>
</tbody>
</table>
Wear behaviour and Regression coefficient for the different configurations of olyethylene tested.

221x138mm (96 x 96 DPI)
FTIR line-scan of a thin section cut from: A) XLPE-VE after five million cycles; B) control, unloaded XLPE-VE.

221x244mm (96 x 96 DPI)