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DOES CYCLIC STRESS AND ACCELERATED AGEING INFLUENCE THE WEAR BEHAVIOR OF HIGHLY CROSSLINKED POLYETHYLENE?

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ABSTRACT

First-generation (irradiated and remelted or annealed) and second-generation (irradiated and vitamin E blended or doped) highly crosslinked polyethylenes were introduced in the last decade to solve the problems of wear and osteolysis.

In this study, the influence of the Vitamin-E addition on crosslinked polyethylene (XLPE_VE) was evaluated by comparing the in vitro wear behavior of crosslinked polyethylene (XLPE) versus Vitamin-E blended polyethylene XLPE and conventional ultra-high molecular weight polyethylene (STD_PE) acetabular cups, after accelerated ageing according to ASTM F2003–02 (70.0 ± 0.1°C, pure oxygen at 5 bar for 14 days). The test was performed using a hip joint simulator run for two millions cycles, under bovine calf serum as lubricant.

Mass loss was found to decrease along the series XLPE_VE > STD_PE > XLPE, although no statistically significant differences were found between the mass losses of the three sets of cups. Micro-Raman spectroscopy was used to investigate at a molecular level the morphology changes induced by wear. The spectroscopic analyses showed that the accelerated ageing determined different wear mechanisms and molecular rearrangements during testing with regards to the changes in both the chain orientation and the distribution of the all-trans sequences within the orthorhombic, amorphous and third phases. The results of the present study showed that the addition of vitamin E was not effective to improve the gravimetric wear of PE after accelerated ageing. However, from a molecular point of view, the XLPE_VE acetabular cups tested after accelerated ageing appeared definitely less damaged than the STD_PE ones and comparable to XLPE samples.

Keywords: Accelerated ageing; Vitamin E; Crosslinked PE; Hip simulator; Raman spectroscopy.

1. INTRODUCTION

It is well established that the oxidative degradation of ultra-high molecular weight polyethylene (UHMWPE) decreases its mechanical properties and represents one of the main causes of its failure [1–3]. Efforts were faithful to improve UHMWPE and to extend the lifetime of orthopaedic implants [4]. Currently, highly crosslinked polyethylene (XLPE) used in total hip arthroplasty (THA), is clinically accepted as the material for acetabular liners articulated with metallic or ceramic femoral heads [1,5]. Annealed or remelted XLPE substantially reduces the residual free radicals, but also crystallinity and mechanical properties of the polymer [1,6,7]. Other strategies were approached to reduce or retard oxidation by adding suitable additives capable of interrupting the oxidation cycle, by decreasing the reactivity of the radical species; thus, stabilizers 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 [8,9]. Vitamin E seems to be the ideal candidate, being already employed as a natural antioxidant in the physiological processes of the human body [10].

The evolution of in vivo oxidation is complex, depending not only on the type of UHMWPE material, but also on the duration of implantation and the local availability of oxygen in body fluids and/or tissues [11]. To this regard, it is important not only to characterize the actual orthopaedic components from a tribological point of view, but also to expose these components to an accelerated ageing in order to compare their behavior with that observed following long-term exposure to natural ageing during shelf storage and/or in vivo exposure in human patients [11]. Hopefully, a procedure of accelerated ageing should simultaneously reproduce the chemical changes in materials, as well as the depth profiles of these changes, including oxidation [12].

Protocols and standards for accelerated ageing of UHMWPE usually involve heating for 21 days at 80 °C in air or heating for 14 days at 70 °C under 5 bar oxygen [12–15]. However, there are no ageing protocols that have been adequately validated to replicate real-time shelf and in vivo ageing of XLPE or conventional UHMWPE [16,17].

The present study was aimed at investigating the effects of the accelerated ageing on the wear behavior of vitamin E-stabilized XLPE acetabular cups in comparison to standard UHMWPE and remelted XLPE acetabular cups. To this purpose, in a first test, the wear behavior of the three sets of samples was investigated against CoCrMo femoral heads in a hip joint simulator for five million cycles [18]. After the test, the cups underwent an accelerated ageing treatment according to ASTM F2003-02 and subsequently were newly tested in the hip joint simulator for another two million cycles. The wear behavior of the three sets of acetabular cups was evaluated by gravimetric measurements. To gain more insights into the role of vitamin E in the wear mechanism of the aged acetabular cups, the samples were analysed by micro-Raman spectroscopy before the second test (i.e. after accelerated ageing) and after it. This technique proved suitable to investigate at a molecular level the morphology changes (i.e. in crystallinity, phases distribution and chain orientation) induced by wear. Micro-Raman spectroscopy was chosen due to its non destructive character, in view of continuing the tests under more severe conditions (i.e. in presence of third-body wear particles).

2. Materials and methods

The wear behavior of three different batches of polyethylene acetabular cups (28-mm inner × 44-mm outer dimensions; four specimens for each batch) coupled with 28-mm cobalt-chromium-molybdenum (CoCrMo) femoral heads was investigated using a hip joint simulator; three specimens of each test were tested, the fourth was used as control check (see below). All the components (acetabular cups and femoral heads) were produced through the same manufacturing procedures and supplied by the same manufacturer as finished-products. Standard UHMWPE acetabular cups (hereinafter called STD_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 XLPE 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). Further details are available in previous reports [18]. Following a standardized procedure, three control check acetabular cups (one 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 [18,19].

2.1 Accelerated aging

In the first wear test the specimens were run for five million cycles [18]. Then, all the acetabular cups (worn specimens and soak controls) underwent an accelerated ageing treatment, which was performed in a stainless steel pressure vessel, under 503 ± 7 kPa of oxygen pressure at 70.0 ± 0.1°C for 14 days, according to ASTM F2003-02. After accelerated ageing, the cups were newly mounted on the hip joint simulator and were run for two million cycles against the CoCrMo femoral heads (second wear test).

2.2 Wear test details

Wear test was performed using a 12-station hip joint simulator (IORSynthe, Bologna, Italy). Each channel has the ability to run an independent load profile under closed-loop control up to 2Hz. In this test, for each station an axial load up to 2600 N was applied, as recommended by the ISO 14242-3 international guideline, according to the rotation test frequency. Flexion/Extension and Adduction/Abduction translations are programmed using a 23° biaxial rocking motion common to all channels. Typically, in an in vivo situation, the surgeon fixes the acetabular cup with an abduction of about 45° and this scenario is reproduced in vitro by considering an inclination of 23° with respect to a horizontal plane as observed in a previous study [20]. The acetabular cup orientation was set in up-side-down (inverted anatomical) position with the aim of reproducing worst-case scenarios, i.e. the

entrapment of polyethylene wear debris, generated during the test, at the interface head-cup. The lubricant used was 25% (v/v) new born calf serum balanced with distilled water, with 0.2% sodium azide in order to retard bacterial growth and 20 mM EDTA (ethylenediaminetetracetic acid) to minimize precipitation of calcium phosphates. The mass loss of the cups was determined every 0.4 million cycles using a microbalance (Sartorius Cubis MSE 225, Goettingën, Germany) with a sensitivity of 0.01 mg and an uncertainty of 0.01 mg. Each mass measurement was repeated three times and the average mass was used for calculations.

Wear trend was determined from the mass loss of each acetabular cup, corrected by acetabular soak control; the wear rates, calculated from the steady-state slopes of the mass loss versus number of cycles lines, were obtained using least squares linear regression. The mass loss data were analysed using a non-parametric Kruskall-Wallis (K-W) test. Statistical significance was set at $P < 0.05$.

2.3 Roughness measurements

The surface roughness of all the CoCrMo femoral heads was measured at the beginning and at the end of the second test using contact profilometer Hommel Tester T8000 (Hommel Werke, Koeln, Germany). Scanning operations were performed on ten point for each femoral head: one point on the pole and three random points on three different planes identified according to a previously standardized protocol [21]. Sampling lengths were taken using a cut-off of 0.08 mm. Three parameters (Ra, Rt, and Rsk), in agreement with a previous study [21], were taken into consideration to qualify the variation of surface roughness during the test.

2.4 Micro-Raman analyses

The PE components were analysed by micro-Raman spectroscopy before (i.e. after ageing) and after the second wear test. Micro-Raman spectra were obtained using a Jasco NRS-2000C instrument with a microscope of 50× magnification. All the spectra were recorded in back-scattering conditions with 5 cm^{-1} spectral resolution using the 532 nm Green Diode Pumped Solid State (DPSS) Laser Driver (RgBLase LLC, USA) with a power of ca. 20 mW. A 160 K cooled digital CCD (Spec-

10: 100B, Roper Scientific Inc.) was used as detector. A confocal pinhole with an aperture diameter of 200 μm was placed in the optical circuit to obtain signals from a limited in-depth region. All the Raman measurements were made in a fully non-destructive way, without any sample manipulation.

The worn components were analysed near the center of the articulating surface, which appeared the most damaged area according to previously reported data [22,23]; twelve spectra at least were recorded. At a first approximation, PE can be considered a composite of three different phases [24]: a crystalline phase, a melt-like amorphous one and an anisotropic disordered phase (i.e. a "third phase" with a prevailing trans conformation of the chains, which have lost their lateral order). The crystalline phase contains chains folded into highly oriented lamellae, with the crystals being primarily orthorhombic in structure, although monoclinic structures may coexist in particular stress conditions [25,26]. To evaluate the effects of wear testing on the PE structure, several spectroscopic markers were calculated according to the literature [24,27]; the bands used to this purpose are shown in Figure 1 together with their assignments [24,28].

The fraction of orthorhombic (α_o), amorphous (α_a) and intermediate anisotropic disordered (α_b) phases were calculated from the relative intensities of selected Raman bands, according to Strobl and Hagedorn [24]:

$$\alpha_o = \frac{A_{1414}}{0.46 \times A_{1295+1305}} \qquad (1)$$

$$\alpha_a = \frac{A_{1080}}{0.79 \times A_{1295+1305}} \qquad (2)$$

$$\alpha_b = 1 - (\alpha_o + \alpha_a) \qquad (3)$$

where A_{1414} and A_{1080} are the areas of the Raman bands at 1414 and 1080 cm^{-1}, respectively; $A_{1295+1305}$ is the area of the internal conventional (i.e. independent of chain conformation) band group. The A_{1080} band area was determined after a curve fitting analysis of the 1040-1109 cm^{-1} range by

means of a commercial software (Opus 5.0 from Bruker Optik GmbH, Germany). Curve fitting was performed on the original spectra after baseline correction, using the Levenberg-Marquardt algorithm. The Raman components were described as linear combinations of Gaussian and Lorentzian functions. According to a method proposed by Lagaron et al. [27], the fraction of all-trans sequences was evaluated through the following ratio:

$$\text{all} - \text{trans} = \frac{A_{1130}}{0.80 \times A_{1295+1305}} \qquad (4)$$

where A_{1130} is the area of the Raman band at about 1130 cm^{-1}, which has been associated with all-trans C-C bonds located both in the crystalline and amorphous phases. The fraction of all-trans sequences in an orthorhombic environment (namely ortho-trans) was calculated as:

$$\text{ortho} - \text{trans} = \frac{1.78 \times A_{1414}}{A_{1130}} \qquad (5)$$

The area of the above mentioned bands was determined by means of a commercial software (Spectra Analysis, Jasco Corporation, Japan). The occurrence of orientation upon wear tests was assessed by evaluating the A_{1130}/A_{1060} area ratio. The 1060 cm^{-1} band area was calculated by the curve fitting analysis of the 1040-1109 cm^{-1} range by means of a commercial software (OPUS 6.0 from Bruker Optik GmbH, Germany). Curve fitting was performed on the original spectra after baseline correction, using the Levenberg-Marquardt algorithm. The Raman bands were described as linear combination of Gaussian and Lorentzian functions.

3. Results

All the prosthetic acetabular cups completed the planned two Mc. As shown in Figure 2, mass loss constantly increased during the whole test and the XLPE_VE acetabular cups wore more than the XLPE ones. In particular, mass loss was found to decrease along the series XLPE_VE > STD_PE >

XLPE, although the results of the Post hoc test (Table 1) did not disclose any significant difference between the three sets of cups at any number of cycles.

The surface analysis of the metallic heads showed a general worsening of the three roughness parameters in comparison with the values measured at the end of the first test and before it [18] (Table 2). In particular, upon the second test, an appreciable increase of Ra is observed for the heads that articulated against both XLPE and XLPE_VE cups. Moreover, a significant increase of Rt was observed for all the sets of specimens. Upon the second test, the surface of the heads that articulated against STD_PE and XLPE cups became less negatively skewed, while an opposite behavior happened for those coupled with XLPE_VE samples, indicating the generation of diminishing peaks. This roughness trend is emphasized in Figure 3, which shows the topography of the three most worn samples obtained in particularly scratched areas.

Figure 4 reports the average values of α_o, α_a and α_b, calculated from the micro-Raman spectra recorded on the aged cups before and after testing. As can be easily seen from Figure 4, the α_o orthorhombic content underwent a general decrease upon testing, while a parallel increase in the α_b third phase content occurred; less noticeable changes occurred in the α_a amorphous content. The most significant changes in α_o and α_b were observed for the STD_PE acetabular cups, although were detected also for XLPE_VE 2 and XLPE_1.

The changes in the fraction of all-trans sequences (all-trans content) reflected these trends: the most significant decreases were revealed in the STD_PE acetabular cups (Figure 5), followed by the XLPE_VE samples; actually, these specimens underwent the highest weight losses. The ortho-trans content and the A_{1130}/A_{1030} ratio had different trends in the three sets of acetabular cups (Figure 5). Upon testing, the fraction of all-trans sequences in an orthorhombic environment (i.e. ortho-trans) overall increased in the STD_PE samples (and this change was significant in STD_PE 3), remained nearly constant in XLPE_VE, while generally decreased in XLPE (and this change was significant in XLPE 1). The A_{1130}/A_{1030} ratio, sensitive to changes in orientation, decreased in the STD_PE samples,

while increased in the XLPE and XLPE_VE acetabular cups, in agreement with a trend previously observed [4].

4. Discussion

Although the long-term survival of hip prostheses is affected by multiple factors, a UHMWPE hip component articulating against a metallic or ceramic counterface remains the most commonly used bearing biomaterial in total joint arthroplasty [29,30]. Unfortunately, the limitless material does not exist and PE fails during hip implantation. The main concern about the failure of THA has been the biological response to particulate PE debris generated by conventional metal on polyethylene bearing surfaces leading to osteolysis and aseptic loosening of the prosthesis [31]. The wear particles generated by metal on UHMWPE articulation cause a chronic inflammatory response to foreign body, which is mediated by macrophages with release of lytic enzymes, bone resorbing mediators and pro-inflammatory cytokines [31]. The problem of wear debris induced osteolysis may be overcome with the use of new generation metal-on-metal or ceramic-on-ceramic prostheses [32]. However, for metal-on-metal prostheses, the prospects of increasing the osteolysis- free life of the implant are good, but additional biological problems associated with the nanometer size and reactivity of the wear particles in vivo are emerging [33–35]. For the ceramic-on-ceramic prostheses, initial prospects were encouraging with a significantly decreased risk of osteolysis, aseptic loosening, dislocation and thus revision [36]. Currently, standard UHMWPE has been improved through crosslinking for enhanced wear resistance and, more recently, also with the addition of antioxidants (i.e. vitamin E) to address oxidation [6]. The latter process is a complex sequence of various cascade reactions, which is not fully predictable in the long-term [12]. Efforts have been performed in the scientific community to approach ageing methodologies able to simulate the in vivo ageing of UHMWPE and to reproduce the chemical changes occurring in PE due to oxidation. Although none of the existing protocols can fully reproduce the in vivo environment and service conditions of the implants, thereby limiting the clinical

significance of this as of any other in vitro study, accelerated ageing according to ASTM F2003-02, has demonstrated satisfactory results in differentiating the oxidation stability of different UHMWPE configurations [2], which in turn is known to influence the wear performance.

With this in mind, we asked if the wear behavior of XLPE_VE was influenced by accelerated ageing to a different extent with respect to STD_PE and XLPE. To this purpose, the wear performance of the three sets of PE acetabular cups coupled with CoCrMo femoral heads was evaluated for two million cycles, using a 12-station hip simulator, after accelerated ageing. The results of this investigation clearly showed a different wear behavior with respect to our previous work [18]. In that study, a decreasing wear was measured along the series STD_PE > XLPE_VE > XLPE. We have already shown [18] that lipids absorption significantly affects the absolute gravimetric wear measurement, even if it did not influence the overall trend, in that case. We have therefore assumed that the same applies to the present study. We have not measured the actual lipid absorption here, since we chose to perform only non-destructive analyses, in order to preserve the cups for a further, highly demanding test. After accelerated ageing, all the polyethylene acetabular cups showed a different wear performance with respect to the previous test [18]. In fact, in the present study, the XLPE_VE acetabular cups wore more than the STD_PE ones and even more than the XLPE samples, although no statistically significant differences were observed between the three sets of PE cups using the K-S statistical test. The lower wear rate observed for XLPE was not unexpected, since radiation crosslinking of PE results in a substantially higher wear resistance as compared to uncrosslinked PE [26,37,38]. The addition of vitamin E has been found to protect PE from oxidative degradation resulting in improved mechanical and wear properties [39,40]; on the contrary, Bladen et al. have reported that the wear rates of UHMWPE with or without vitamin E were not significantly different [41] and also in our previous test XLPE_VE did not exhibit a lower wear rate than XLPE [18]. These apparent discrepancies must be explained in relation to the different methods utilized to incorporate vitamin E as well as to the differences in the PE processing conditions. With regards to vitamin E incorporation, this antioxidant may be added before irradiation (during moulding or extrusion) or by diffusion after irradiation. Both methods have some drawbacks. In the former, the crosslinking

efficiency is decreased due to the ability of vitamin E to scavenge free radicals during irradiation [42] even if it is difficult to control the concentration and the distribution of the antioxidant. In the present study, vitamin E was incorporated into PE before irradiation; actually, XLPE_VE displayed a lower crosslink density than XLPE [18]. Therefore, the higher wear rate measured for XLPE_VE compared to XLPE may be ascribed to the lower crosslinking extent of the former.

In association with a bad wear performance, a worsening of the surface roughness of the CoCrMo femoral heads was observed. An "ideal surface finish" should have low Ra and Rt values and a negative Rsk value [43,44]. The presence of depressions or holes (rather than scratches) with smooth (rather than sharp) edges seems to improve the lubrication and wettability properties. Smoother surfaces (Rsk < 0) are less detrimental than surfaces with a positive Rsk. In this test, an overall increase of Ra and Rt values was observed. Counterface roughness has been indicated as an important variable controlling the contribution of each wear process [45]. A significant change in the morphological features of the bearing surfaces, as happened in this case, could strongly affect the lubricating phenomena (boundary, mixed, hydrodynamic, squeeze) [46] and modify the fluid dynamic behaviour of the synovial fluid [47] favouring a fluid film rupture and causing localized contacts of the prostheses surfaces.

To gain insights into this subject at a molecular level, micro-Raman analyses were carried out. From a general point of view, spectroscopic investigations confirmed a bad wear behavior for the three sets of cups, definitely worst than that observed in a previous test comparing unaged STD_PE, XLPE_VE and XLPE [4]; the XLPE and XLPE_VE acetabular cups appeared to overall exhibit slightly lower differences in the evaluated spectral markers than the STD_PE samples. The spectroscopic analyses showed that upon ageing a different wear mechanism occurred: for the STD_PE, the α_o content decreased and the α_b content increased (Figure 4), while these parameters were found to have an opposite trend by testing unaged samples [4]. Moreover, the orthorhombic and third-phase contents were found to significantly change also in some crosslinked samples (XLPE_VE 2 and XLPE 1), while remained constant in our previous test on unaged samples [4], confirming the worse wear behavior after accelerated ageing. It must be stressed that, as observed for unaged

samples, also after accelerated ageing the three sets of acetabular cups underwent different structural rearrangements upon wear. Actually, the ortho-trans content overall increased in the STD_PE samples, remained nearly constant in XLPE_VE, while generally decreased in XLPE (Figure 5). These trends revealed a different rearrangement of the polymeric chains in the three sets of samples upon wear, with different changes in the distribution of the all-trans sequences within the orthorhombic, amorphous and third phases. The A_{1130}/A_{1060} ratio, sensitive to changes in orientation, decreased in the STD_PE samples, while increased in the XLPE and XLPE_VE acetabular cups, in agreement with a trend previously observed for unaged samples [4]. At this purpose, it must be recalled that the bands at 1130 and 1060 cm^{-1} have different vibrational symmetries; if the molecules are oriented in a preferred direction, the 1130 cm^{-1} band has been reported to become stronger with respect to the 1060 cm^{-1} band [48].

According to some studies, a decrease in crystallinity may represent a worsening of the mechanical properties; actually, Simis et al. [49] have reported that a decrease in crystallinity results in decreases in elastic modulus, yield strength and micro-hardness. Karuppiah et al. [50] have found that an increase in crystallinity results in a lower friction force, lower wear depth and width as well as increases in hardness and scratch resistance at a microscale and nanoscale. Figure 6 allows to gain more insights into the effects of accelerated ageing on the wear behavior of the acetabular cups at the molecular level; the reported graphs show that a correlation exists between the difference % observed upon the test in the α_o, α_a, α_b and all-trans contents and the value of these spectral markers measured before the test (i.e. after ageing). In other words, the acetabular cups that showed after ageing the highest α_o and all-trans values and the lowest α_a and α_b values underwent upon the test the most significant decrease in the orthorhombic and all-trans contents (Figure 6A and 6D) and the highest increase in the amorphous and third phases contents (Figure 6B and 6C), i.e. were the most affected by the wear testing. These trends are not unexpected. Actually, it is well recognised that the mechanical properties and wear performance of PE depend on the distribution of crystalline and non-crystalline phases as well as molecular orientation, besides molecular weight and degree of crosslinking. The trends of Figure 6 are in agreement with the findings by Takahashi et al. [51], who have related a

lower content of the amorphous phase to a higher resistance to creep deformation, but to a lower capacity of shape recovery after removal of the applied load.

This study was approached to acquire further knowledge about the effects that the accelerated ageing protocol could elicit on the wear performance of these different polyethylenes. Further researches are needed to optimize this approach with the addition of third-body debris, in order to study the tribological behavior under more severe simulator conditions, as reported in a previous study by Zietz et al. [52]. Actually, third-body wear resistance of XLPE has not been extensively investigated yet and it has been supposed that this material, due to its micromorphology, could be less resistant than STD_PE to such wear [53].

CONCLUSIONS

All the acetabular cups studied in this work maintained an increased weight loss during the whole test. Lower weight losses (although not statistically significant) were exhibited by the XLPE acetabular cups, which have the potential for reduced wear and decreased osteolysis. The roughness of the CoCrMo femoral heads seemed to increase indiscriminately for all the analyzed configurations, not showing a predominant pattern correlated to weight loss.

The acetabular cups studied in this work showed a bad wear behavior, both at gravimetric and molecular levels. The micro-Raman analyses showed that accelerated ageing determined a worsening of the wear resistance, since the evaluated spectroscopic markers underwent more significant changes than for unaged acetabular cups [4]. The three sets of samples showed different wear mechanisms during testing with regards to the changes of both the molecular orientation and the distribution of the all-trans sequences within the orthorhombic, amorphous and third phases.

The results of the present study showed that the addition of vitamin E was not effective in improving the gravimetric wear behaviour of PE after accelerated ageing, differently from as reported by other authors [54,40]. However, from a molecular point of view, the XLPE_VE acetabular cups tested after accelerated ageing appeared definitely less damaged than the STD_PE ones and comparable to XLPE

samples. Further studies are in progress to assess the influence of vitamin E on the wear behaviour of PE under more severe conditions (i.e. in presence of third-body wear particles).

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Table 1 - Cumulative mass loss (mean ± standard deviation) for the three sets of PE acetabular cups tested. The p-values were obtained using a Kruskall-Wallis non-parametric test.

Table 2 - Mean roughness (± Standard Deviation) for the femoral heads coupled with the three sets of cups.

Figure 1 – Average micro-Raman spectrum of PE (STD_PE before the test, i.e. after accelerated ageing), in the CH_2 bending (δ), CH_2 twisting (τ) and C-C stretching (ν; s = symmetric; a = anti-symmetric) regions; the assignments to the amorphous (A) and crystalline (C) phases have been given according to the literature.

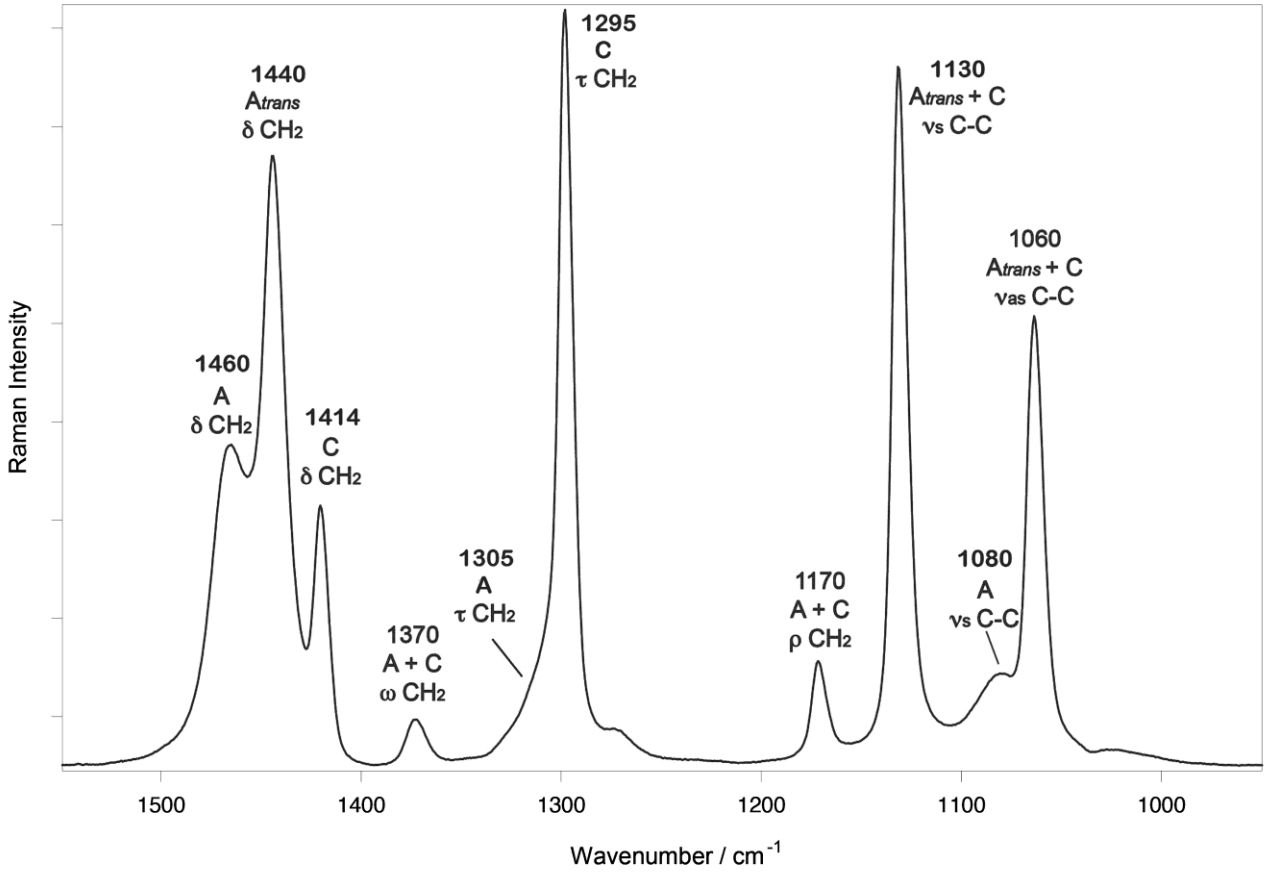
Figure 2 – Wear behavior and Regression coefficient for the different polyethylenes tested.

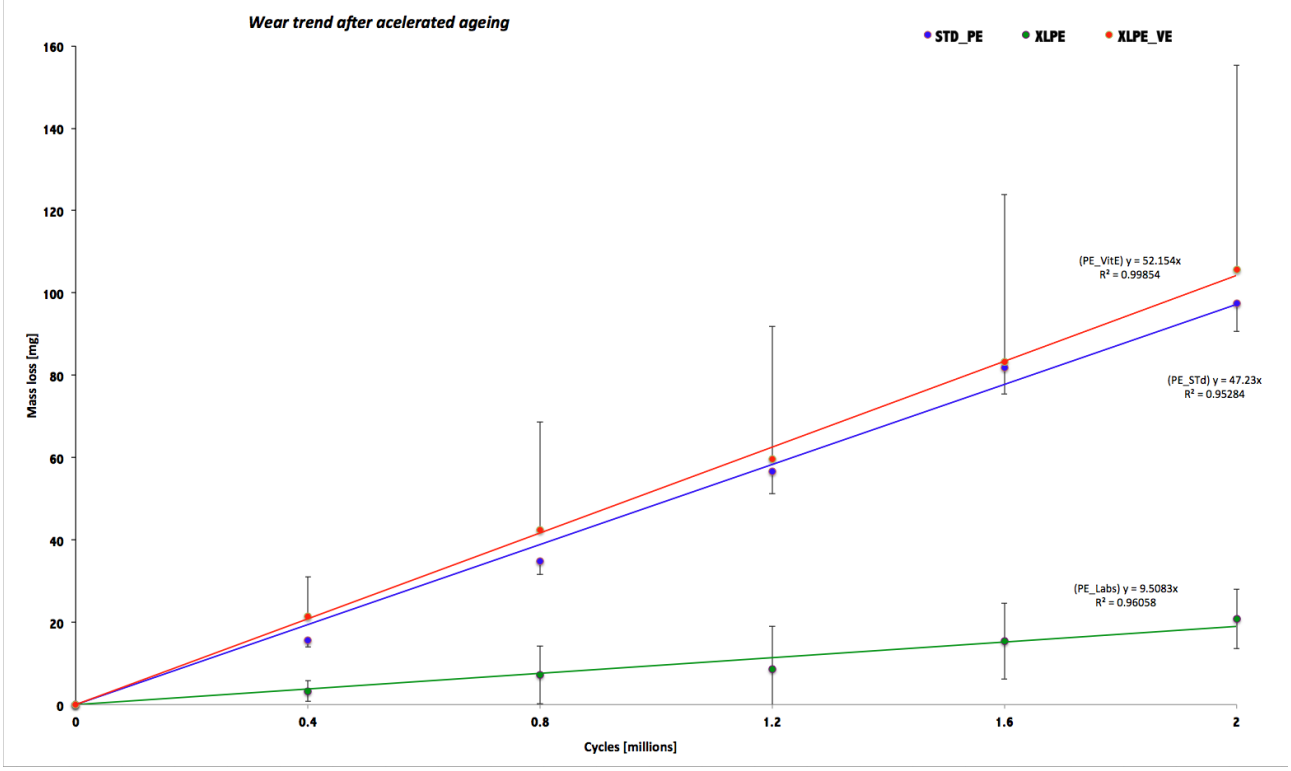
Figure 3 – Surface topography (a) and Abbott-Firestone curve (b) of the CoCrMo femoral heads coupled with the most worn PE specimens of each set.

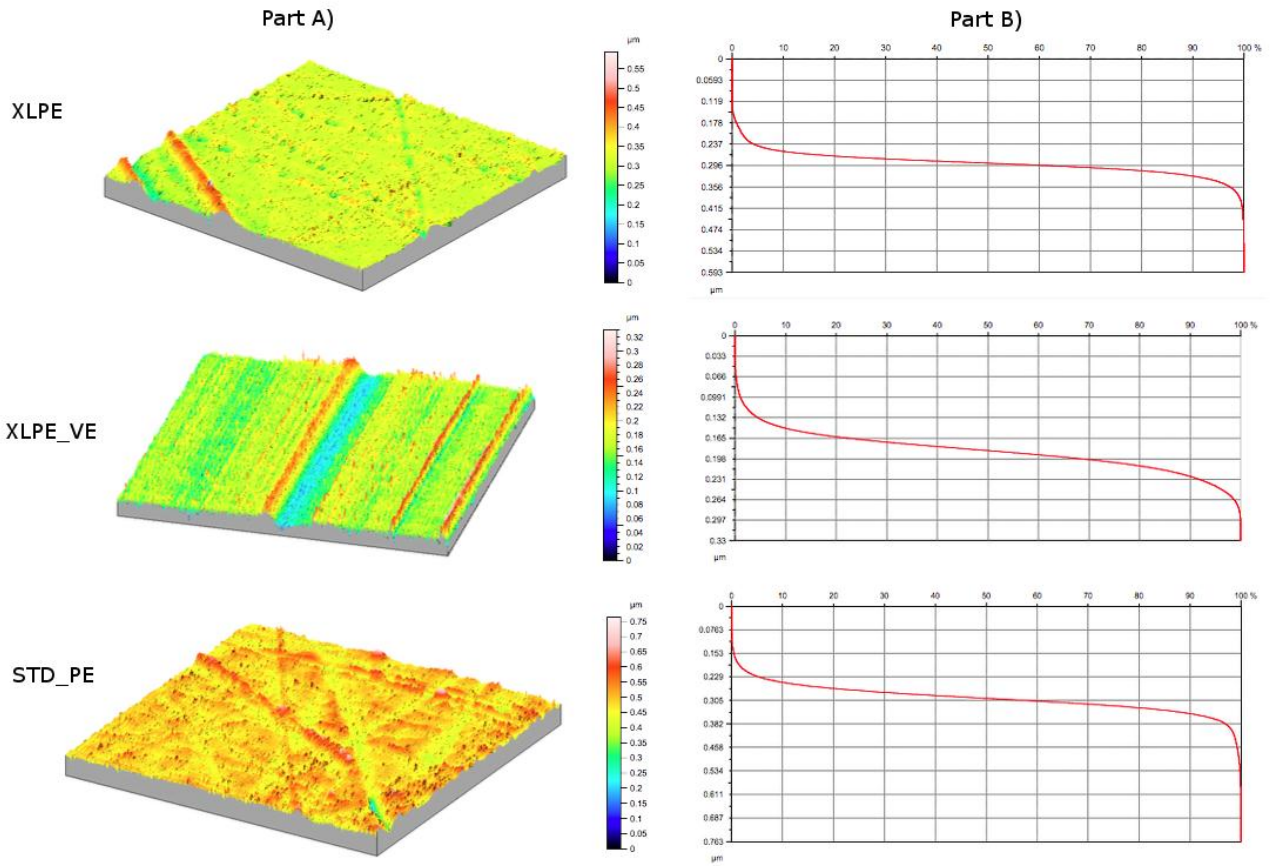
Figure 4 – Values (average ± standard deviation) of α_o, α_a and α_b contents as obtained from the spectra recorded before the test (i.e. after accelerated ageing) and after it on the STD_PE, XLPE_PE and XLPE acetabular cups.

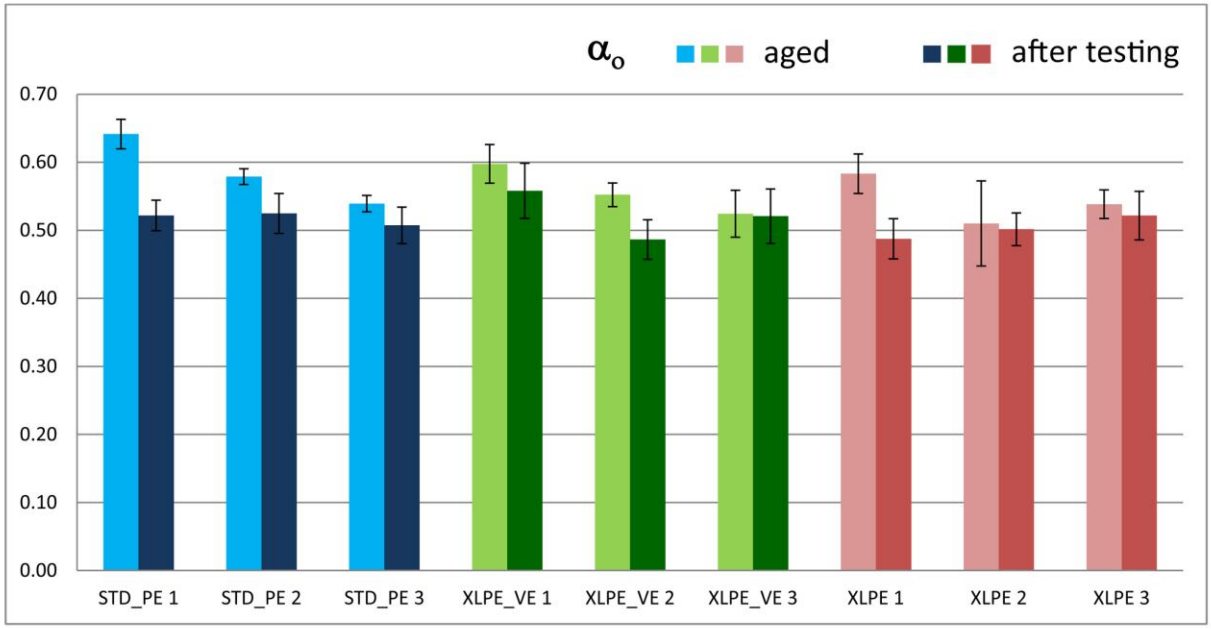
Figure 5 – Values (average ± standard deviation) of all-trans and ortho-trans contents, and A_{1130}/A_{1060} ratios as obtained from the spectra recorded before the test (i.e. after accelerated ageing) and after it on the STD_PE, XLPE_PE and XLPE acetabular cups.

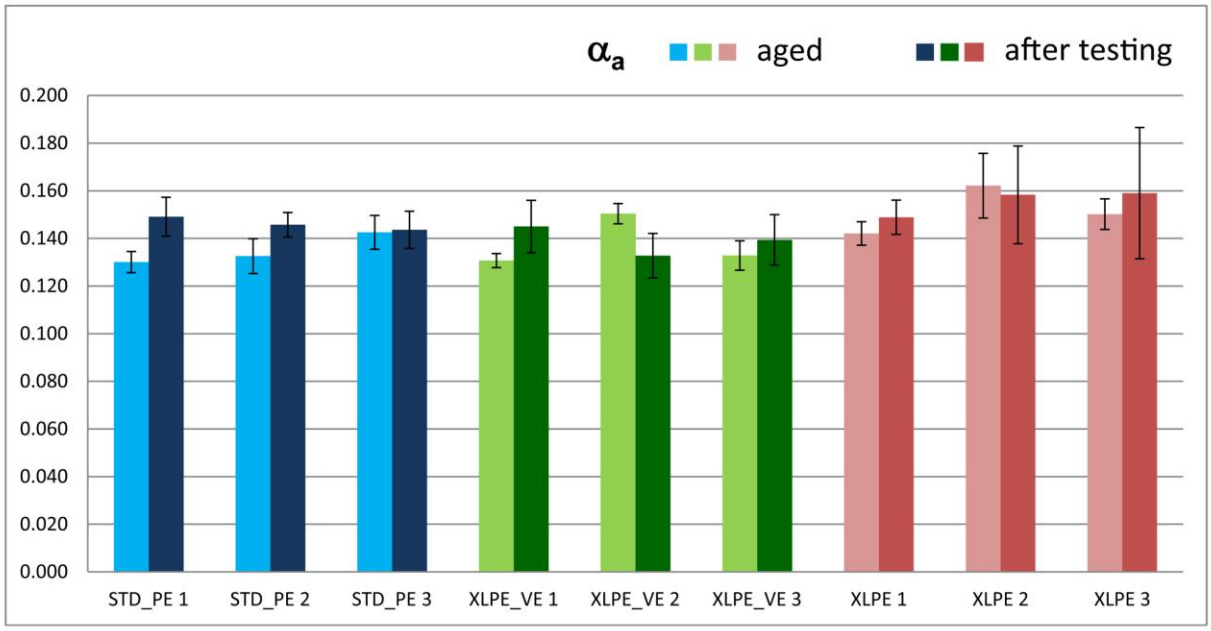
Figure 6 – Trend of the difference % observed upon the test in the α_o, α_a, α_b and all-trans contents of the analysed acetabular cups as a function of the value of these spectral markers measured before the test (i.e. after ageing).

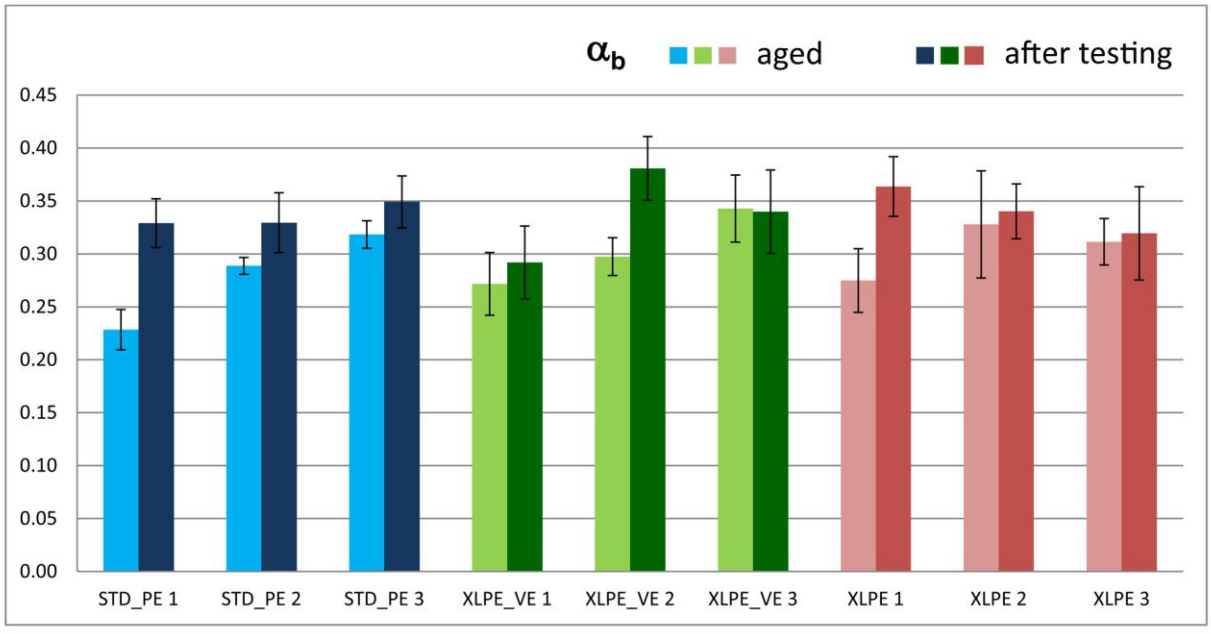

1440
Atrans
δ CH2
1460
A
δ CH2
1414
C
δ CH2
1370
A + C
ω CH2
1305
A
τ CH2
1295
C
τ CH2
1170
A + C
ρ CH2
1130
Atrans + C
νs C-C
1080
A
νs C-C
1060
Atrans + C
νas C-C
Raman Intensity
1500
1400
1300
1200
1100
1000
Wavenumber / cm-1

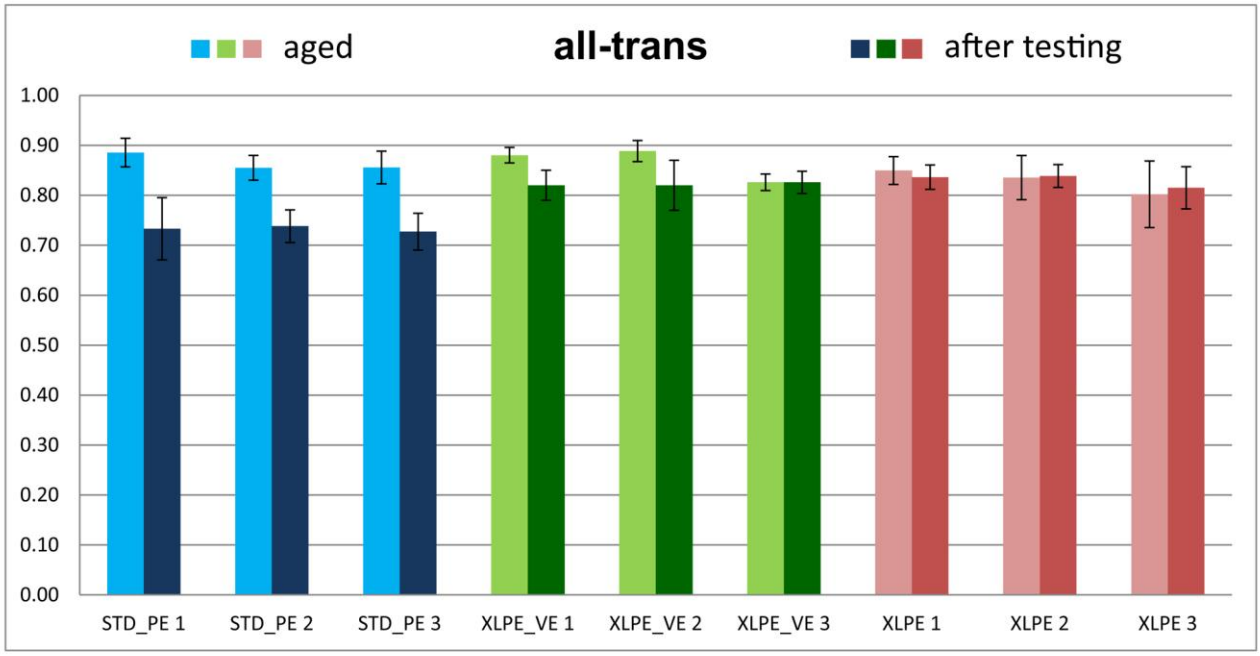

Wear trend after acelerated ageing
STD_PE
XLPE
XLPE_VE
(PE_VitE) y = 52.154x
R² = 0.99854
(PE_STd) y = 47.23x
R² = 0.95284
(PE_Labs) y = 9.5083x
R² = 0.96058
Mass loss [mg]
Cycles [millions]
0
20
40
60
80
100
120
140
160
0.4
0.8
1.2
1.6
2

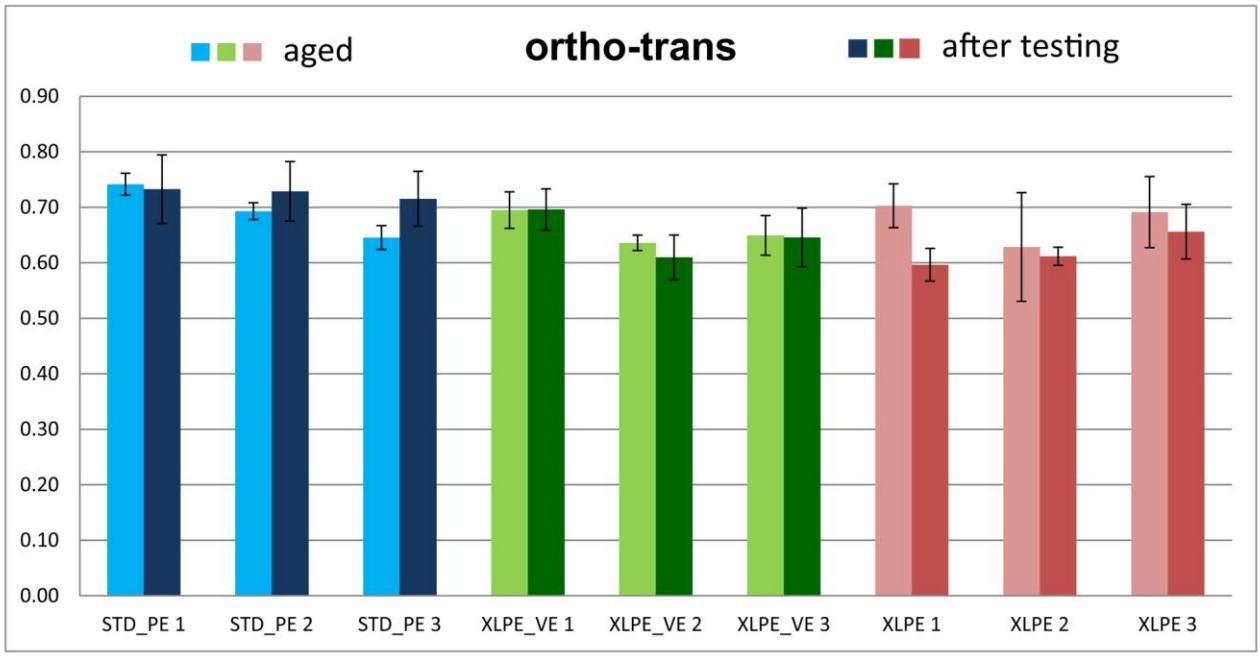


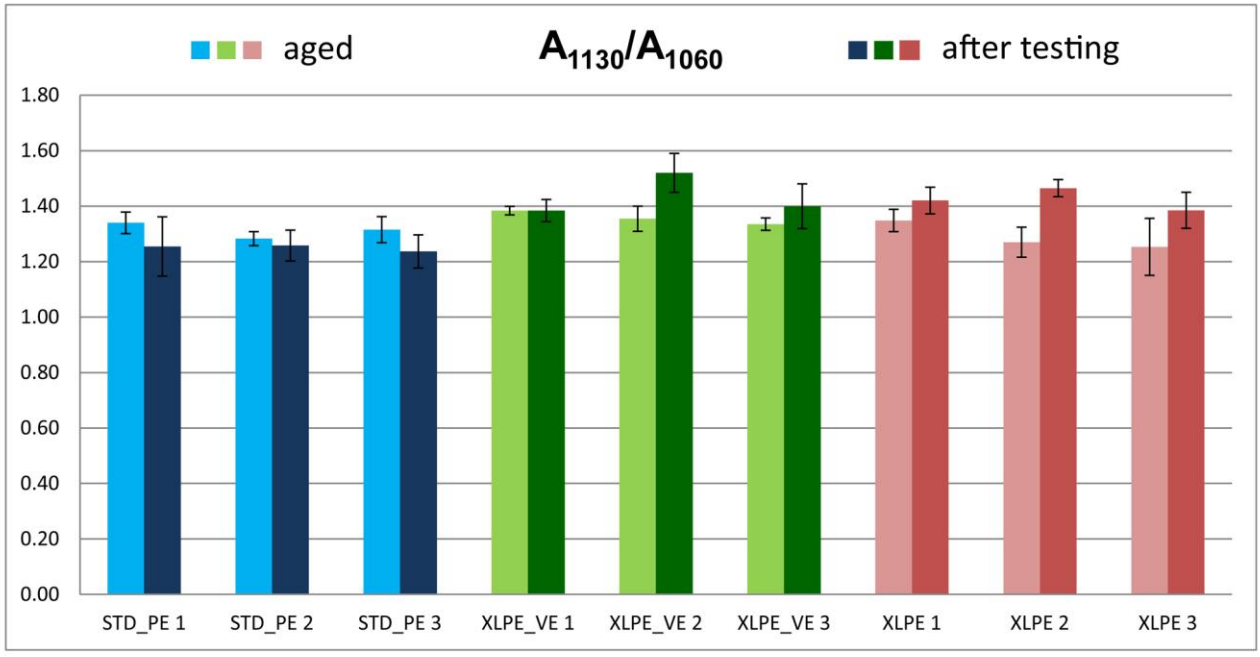

α_o
aged
after testing
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
STD_PE 1
STD_PE 2
STD_PE 3
XLPE_VE 1
XLPE_VE 2
XLPE_VE 3
XLPE 1
XLPE 2
XLPE 3


α_a
aged
after testing
0.200
0.180
0.160
0.140
0.120
0.100
0.080
0.060
0.040
0.020
0.000
STD_PE 1
STD_PE 2
STD_PE 3
XLPE_VE 1
XLPE_VE 2
XLPE_VE 3
XLPE 1
XLPE 2
XLPE 3


α_b
aged
after testing
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
STD_PE 1
STD_PE 2
STD_PE 3
XLPE_VE 1
XLPE_VE 2
XLPE_VE 3
XLPE 1
XLPE 2
XLPE 3


aged
all-trans
after testing
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
STD_PE 1
STD_PE 2
STD_PE 3
XLPE_VE 1
XLPE_VE 2
XLPE_VE 3
XLPE 1
XLPE 2
XLPE 3


aged
ortho-trans
after testing
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
STD_PE 1
STD_PE 2
STD_PE 3
XLPE_VE 1
XLPE_VE 2
XLPE_VE 3
XLPE 1
XLPE 2
XLPE 3


aged
A1130/A1060
after testing
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
STD_PE 1
STD_PE 2
STD_PE 3
XLPE_VE 1
XLPE_VE 2
XLPE_VE 3
XLPE 1
XLPE 2
XLPE 3

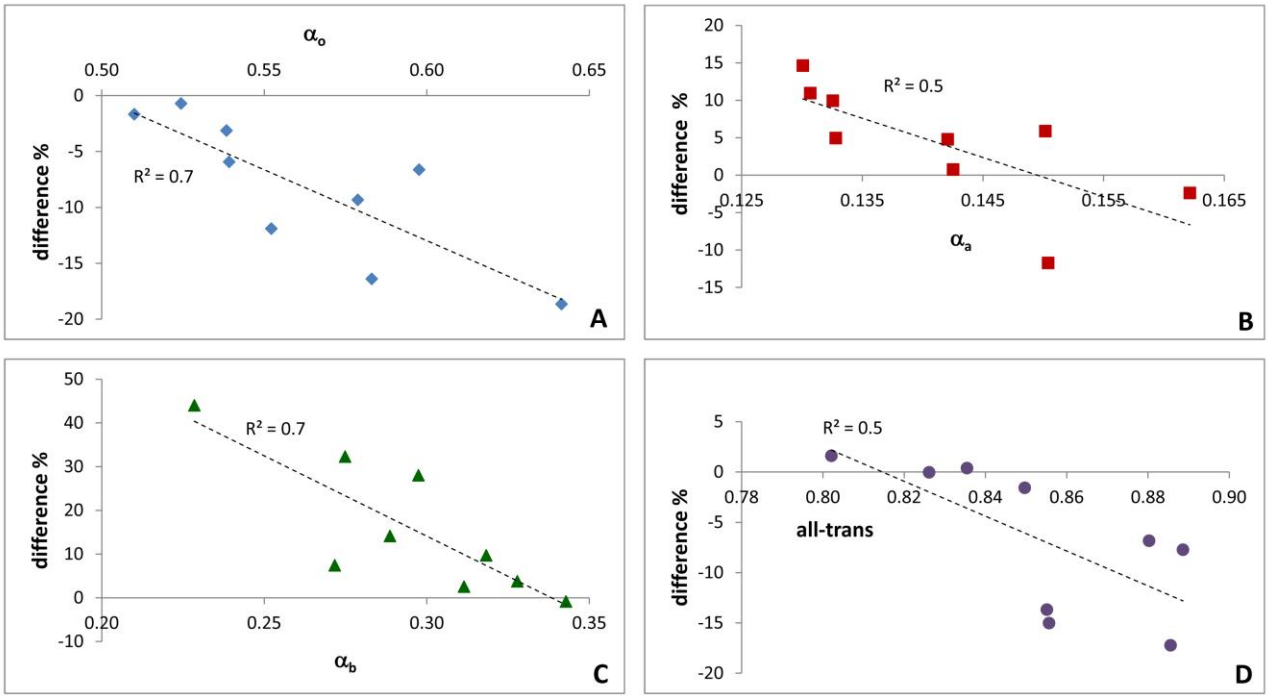


Table 1 - Cumulative mass loss (mean ± standard deviation) for the three sets of PE acetabular cups tested. The p-values were obtained using a Kruskall-Wallis non-parametric test.

	Mean ±Standard deviation			K-W test (p-value)
Cycles [Mc]	XLPE	STD_PE	XLPE_VE	
0.4	3.3 ±1.7	15.7 ±2.5	21.4 ±9.7	0.061
0.8	7.2 ±3.2	34.8 ±6.9	42.5 ±16.3	0.066
1.2	8.6 ±5.4	56.6 ±10.0	59.7 ±18.3	0.068
1.6	15.4 ±6.6	81.9 ±9.21	83.3 ±20.7	0.066
2	20.8 ±6.8	97.4 ±7.2	105.7 ±21.7	0.061

Not significant = p value > 0.05; K-W = Kruskall-Wallis; Mc = millions cycles.

Table 2 - Mean roughness (± Standard Deviation) for the CoCrMo femoral heads coupled with the three sets of cups.

	Before wear tests [18]			After the first wear test [at five million cycles] [18]			After the second wear test [at seven million cycles]			Difference % (second test – first test)		
	STD_PE	XLPE	XLPE_VE	STD_PE	XLPE	XLPE_VE	STD_PE	XLPE	XLPE_VE	STD_PE	XLPE	XLPE_VE
Ra	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.04 ± 0.01	0.01 ± 0.01	0.02 ± 0.01	0.04± 0.02	0.03 ± 0.01	0.04 ± 0.02	0	66.7	50.0
Rt	0.05 ± 0.01	0.05 ± 0.01	0.05 ± 0.01	0.11 ±0.09	0.11 ± 0.03	0.13 ± 0.03	0.41 ± 0.07	0.38 ± 0.17	0.37 ± 0.05	73.2	71.1	64.9
Rsk	0.053 ± 0.07	0.037 ± 0.05	0.001 ± 0.03	-0.56± 0.08	-0.64±0.60	-0.20±0.15	-0.35± 0.96	-0.36 ± 0.49	-0.46 ± 0.29	-60.0	-77.2	56.5