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In-Depth Oxidation and Strain Profiles in UHMWPE Acetabular Cups Non-Destructively Studied by Confocal Raman Microprobe Spectroscopy

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Abstract

Raman spectroscopy is used for the characterization of the two main mechanisms responsible for the degradation of acetabular cups in hip joints: creep deformation and oxidation. The term creep refers to the permanent deformation that occurs under the effect of body weight and does not completely recover after load release. This mechanism involves no mass loss from the sample, but packing and adjustment of the polyethylene molecules in their reciprocal positions under pressure. Conversely, oxidation triggers wear, which is accompanied by irreversible mass loss from the material: surface molecules of the polyethylene body oxidize, delaminate and are progressively peeled off, involving volumetric changes and resulting in debris formation. Both degradation mechanisms negatively interact and converge toward cup loosening, which requires revision surgery. In this paper, we show that confocal Raman spectroscopy can be used to separate the contributions to the dimensional change observed in acetabular cups arising from creep and from wear. Raman measurements are completely non-destructive and contactless, and can guide surgeons and materials technologists to optimize surface treatments and molecular structure of polyethylene cups, thus maximizing their *in vivo* lifetime.

Keywords

UHMWPE, Raman spectroscopy, hip joint, acetabular cup, strain, oxidation

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1. Introduction

The polyethylene part of a hip prosthesis, usually referred to as acetabular cup or liner, is responsible for absorbing the impacts experienced by the implant during its lifetime [1]. It may eventually become subjected to extensive wear (i.e., resulting in the release of foreign debris into the patient body [2–4]), as well as to creep deformation under the effect of body weight [5–7]. Concurrently, *in vivo* oxidation of the polyethylene structure unavoidably takes place and greatly affects the structural integrity of the acetabular component [8–10]. The detrimental effect of local deformation is additive to structural degradation, such as oxidation, the latter progressing with long-term clinical use, leading to debris formation and, ultimately, to joint loosening [11]. Extensive wear and/or creep of the acetabular cup will necessarily result in the need for a revision surgery.

Modern acetabular cups are manufactured from ultra-high-molecular-weight polyethylene (UHMWPE), a material with extreme durability in its non-oxidized state [12]. Polymer scientists have long studied methods to concurrently improve wear resistance, deformation/fracture resistance and oxidative stability of UHMWPE by varying manufacturing methods, consolidation techniques and resin recipes. In particular, surface treatments of UHMWPE have been the object of intensive research [13–15]. Nowadays, orthopaedic implant industries usually employ a sterilization method involving the exposure of the liner to γ-irradiation. In applying such a treatment, extreme care should be taken in optimizing the dose of exposure. Insufficient irradiation doses lead to a poor deformation resistance of the liner, while high doses of irradiation may improve the creep resistance of the material, but also induce a tangible embrittlement effect [16]. In addition, when the γ-irradiation method is applied in air or in a non-completely controlled inert atmosphere, it may cause severe oxidation of the polyethylene structure, with the liner becoming highly brittle, defective and with a surface highly prone to wear [17]. These negative effects may be strongly amplified when irradiation in presence of air is coupled with an extended shelf life before implantation in a body.

In previous reports [18–20], we have shown that confocal Raman spectroscopic techniques allow visualizing in a fully non-destructive manner and with microscopic spatial resolution the salient structural and micromechanical characteristics of biomedical UHMWPE grades.

As compared to Fourier transform infrared spectroscopy, which can be used to characterize the hydroperoxide concentration and distribution in UHMWPE biomedical samples (but requires thin slicing of the sample) [21, 22], confocal Raman spectroscopy enables similar quantitative assessments of UHMWPE molecular mesostructures, but in a fully non-destructive manner. Raman spectra can identify crystalline and amorphous phase fractions [23, 24], oxidation state [18] and residual (plastic) strain [25] in the material. In other words, through in-depth confocal Raman experiments, it is possible not only to verify the structural changes that occurred in the as-received UHMWPE liners during sterilization by γ-irradiation, but also, to non-destructively scrutinize UHMWPE components after *in vivo* implanta-

tion. In this paper, we build upon our previous findings and show the possibility to concurrently examine in-depth profiles of oxidation and strain in unexposed, short-term and long-term *in vivo* exposed acetabular cups. According to this practice, a new possibility is opened to rationalize the origin of joint loosening and to link it to the molecular structure of UHMWPE. The confocal Raman method is used in this paper to rationalize the micromechanical and microstructural state of retrieved polyethylene liners in their main-wear zones. This study also opens the possibility to perform advanced procedures of quality control in biomedical implants, thus eliminating the inherent inability of randomized controlled trials to detect infrequent events and unexpected side-effects.

2. Materials and Methods

2.1. Materials

One new and four retrieved cross-linked UHMWPE acetabular cups have been investigated. The four retrieved acetabular cups were obtained at the time of the respective hip arthroplasty revision surgeries. All acetabular components (ArCom®, Biomet) were made from 1900H bar stock by isostatically direct-compression molding and surface irradiated by a γ-ray dose of 33 kGy. One of the retrieved acetabular cups belonged to a 53-year-old female patient for which the cause of revision was infection dislocation with a follow-up period of 2 years and 10 months. In the remainder of this paper, this cup will be referred to as the 'short-term' or cup No. 1. The additional retrievals were all long-term exposed *in vivo* and belonged to female patients (61, 77 and 60 years old, for retrieval Nos 2–4, respectively). For all the long-term retrievals, the cause of revision was aseptic loosening after a follow-up period of 10 years and 1 month, 10 years and 11 months, and 12 years and 2 months for retrieval Nos 2–4, respectively. All four retrievals were from left hip joints, thus showing a main wear zone on the cup surface between the superior and the posterior poles. The non-wear zone of the cups could be also found on the surface portion between the interior and the anterior poles of the cups. All the acetabular cups analyzed in this paper were employed against CoCr femoral heads of the same type. It should be emphasized, since of relevance to the remainder of this paper, that the four retrievals examined were not defective; in other words, they performed according to standard and expected *in vivo* trends, both in terms of wear and oxidation, for UHMWPE liners.

2.2. Confocal Raman Analysis

Raman spectra were collected at room temperature by a triple-monochromator (T-64000, Jovin-Ivon/Horiba Group) equipped with a charge-coupled device (CCD) detector, and analyzed by using commercially available software (Labspec, Horiba/Jobin-Yvon). For calibration of the dependence of selected Raman bands on applied strain under the Raman microprobe, an uniaxial compression jig was

employed to *in situ* apply a controlled strain state to a calibration UHMWPE sample of 3 × 3 × 6 mm, purposely prepared by cutting a virgin cup. The sample was obtained from the core part of an unused acetabular cup of the same type as those investigated after retrieval. The outcomes of the calibration were then used to analyze the retrievals. Raman measurements on retrievals were made without any destructive sample manipulation by focusing the confocal probe on the respective wear zones. Figure 1a shows a draft of the *in situ* calibration performed using the uniaxial compression jig set under the Raman microprobe. In bandwidth/strain calibrations, the Raman probe was located at approximately the center of the sample and, taking advantage of the high transparency of polyethylene, translated by 50 μm below the surface in order to minimize both shear strain and surface roughness effects. In the experimental analysis of acetabular cups, a confocal pinhole with an aperture diameter of 100 μm was placed in the optical circuit to exclude photons scattered from out-of-focus regions of the probe. Accordingly, only signals from a limited in-depth region close to the selected abscissa of the focal plane were

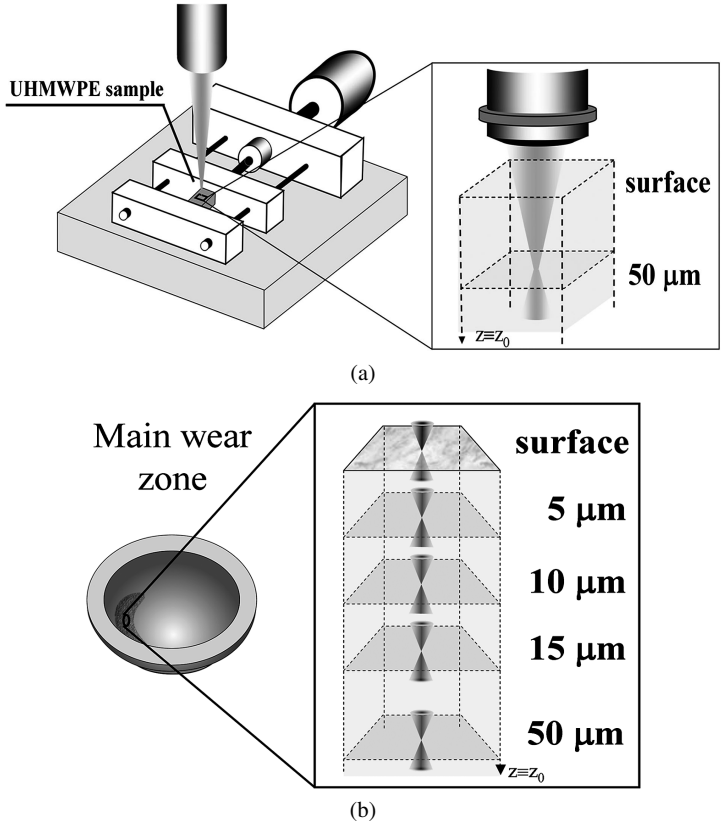

Figure 1. (a) A schematic draft of the uniaxial compression jig used for the calibration of UHMWPE samples obtained from the core of the hip cups. (b) The main wear zone of the hip cup in which the mapping procedure was performed at different depths, from surface to 50 μm inside.

brought to the detector. The confocal configuration of the probe adopted throughout the present experiments corresponded to a $\times 100$ objective lens; numerical objective aperture, confocal pinhole diameter, and focal length of the objective lens were fixed as: NA $= 0.9$, $\Phi = 100$ μm and $f = 0.3$ mm, respectively. Figure 1b shows a schematic draft of the sampling procedure adopted in a confocal Raman analysis of the wear zone of a UHMWPE acetabular cup. An automated sample stage with sub-micrometric step precision was employed, making it possible to record spectra at each depth with focusing below the sample surface, or to map spectra with lateral line scanning on the sample surface. In-depth oxidation and strain profiles were collected with translating the focal plane along the in-depth (sub-surface) direction.

3. Results

3.1. Assessments of In-Depth Creep Strain Profiles

In a previous study [25] we have shown the possibility to measure elasto-plastic strain in UHMWPE by using a proportionality relationship between strain and the increase in full-width at half maximum (FWHM) of the 1127 cm^{-1} Raman band (representing the symmetric C–C stretching of the PE structure). In that study, a calibration line was given for a (uniaxial) tensile strain configuration. Despite the novelty in measuring local strain in a biomedical grade PE, however, the shown Raman approach is not suitable for a direct analysis of the residual (compressive) strain state stored in retrieved acetabular cups (i.e., impinging against the femoral head during their *in vivo* lifetime). For this reason, we had to proceed first to a re-calibration procedure to make it explicit the dependence of FWHM of the 1127 cm^{-1} band on compressive strain. The results of this new calibration procedure are shown in Fig. 2. Broadening of the symmetric C–C stretching band under compressive strain is directly visible on the Raman spectrum and a rationalization

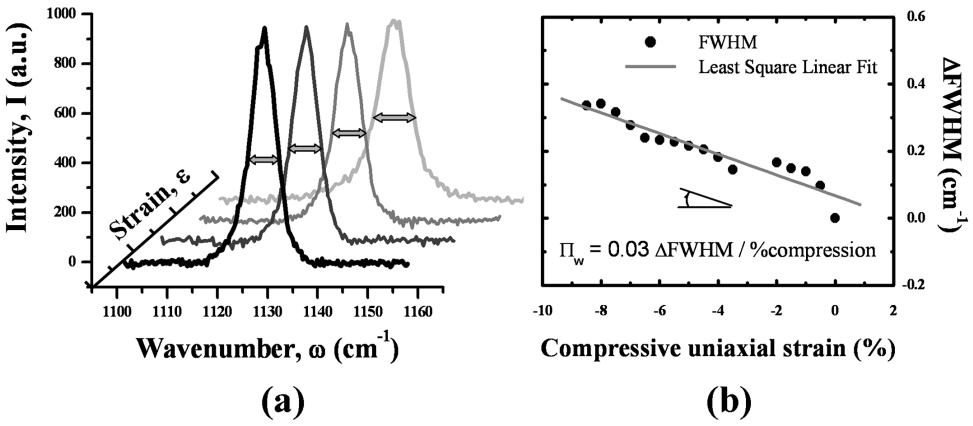

Figure 2. (a) Broadening of the symmetric C–C stretching band as a consequence of increasing compressive strain. (b) Compressive strain calibration line of UHMWPE and the Π_w coefficient.

of the trend is given in a linear plot as a function of externally applied strain percents (Fig. 2, inset). The relationship can be expressed as follows:

$$\Delta w = \Pi_w \varepsilon, \tag{1}$$

where Δw represents the variation in band width (Δ FWHM) of the symmetric C–C stretching band of UHMWPE, ε is the applied compressive strain and Π_w is a proportionality coefficient explicitly given in the inset of Fig. 2. By assuming as a standard bandwidth, w_0, the width of a band retrieved from the core of an unused (and unloaded) acetabular cup, profiles of strain stored in unused and retrieved cups could be measured in confocal configuration as a function of depth along the sub-surface. In Fig. 3, strain maps collected at increasing depths in the main wear zone of short-term No. 1 (Fig. 3f–3j) and long-term No. 4 (Fig. 3k–3o) retrievals

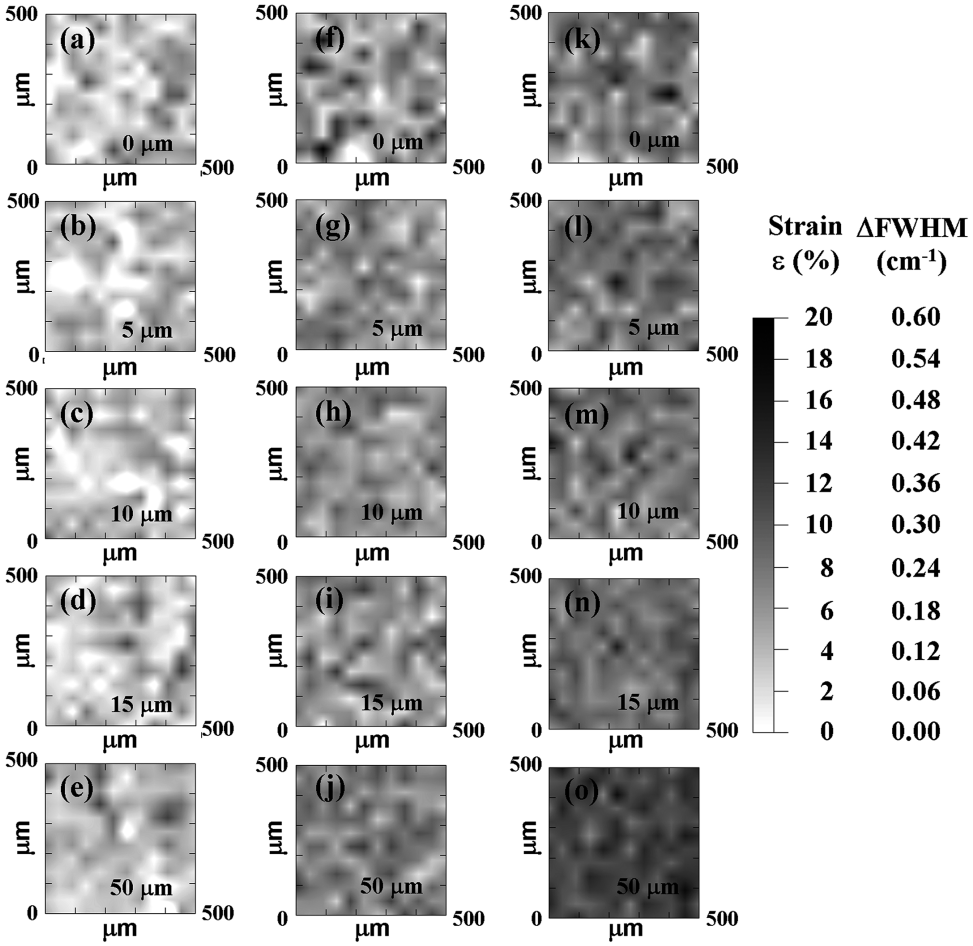

Figure 3. Maps of compressive strain collected focusing the laser on increasing depths. (a–e) Unused cup, (f–j) main wear zone of short-term retrieval (cup No. 1) and (k–o) main wear zone of long-term retrieval (cup No. 4).

as a function of probe depth are compared to strain maps collected at the corresponding locations in an unused cup (Fig. 3a–3e) from the same maker. A better quantification of the in-depth evolution of sub-surface strain fields for all the investigated cups is given in Fig. 4, which depicts the compressive residual strain profiles in the unused liner (Fig. 4a) and in the main wear zone of short-term cup No. 1 (Fig. 4b) and of all long-term retrieved acetabular cups (Fig. 4c–4e, for cups 2–4, respectively). Each data point in the plot represents the average value retrieved

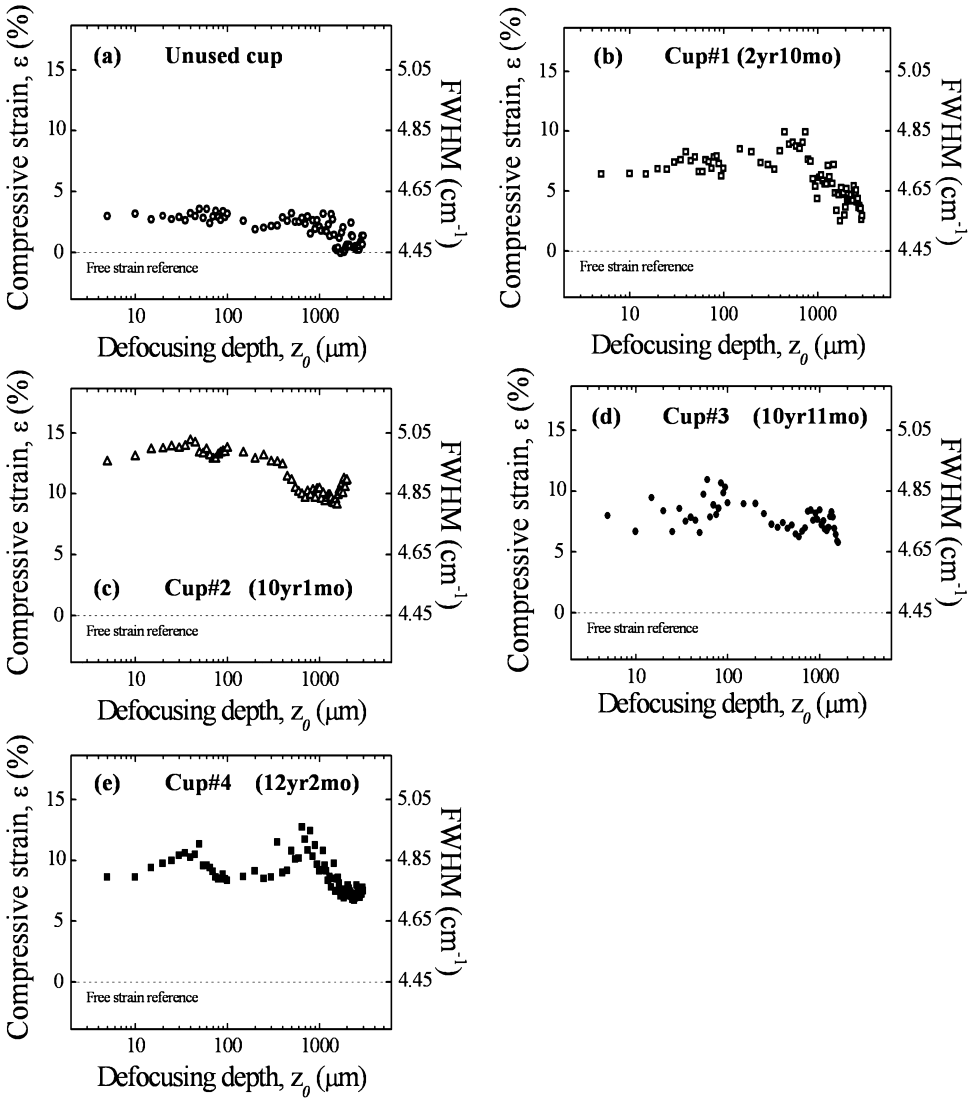

Figure 4. Profiles of compressive strain calculated along depth axis in the new cup and in the main wear zone of the 4 retrieved cups analyzed. The free strain level corresponds to the spectrum characterized by the shortest FWHM calculated in the new cup.

over an area of about 500 μm^2 at each sub-surface depth. Strain maps and profiles (from Figs 3 and 4, respectively) show that the compressive strain stored in the acetabular cup increases with increasing exposure time *in vivo*, although large differences could be found among long-term retrievals most likely depending on patient activity. Interestingly, besides the overall increase in strain level with increasing exposure time *in vivo*, two strain maxima were noticed at several tens of μm and at around 1 mm in depth. These results not only help visualizing the creep contribution to the *in vivo* penetration of femoral component into the UHMWPE liners, but also enable one to quantify the thickness reduction due to creep, thereby facilitating the measurement of true *in vivo* wear.

3.2. Assessment of In-Depth Oxidation Profiles

With concurrently performing Raman and infrared spectroscopy characterizations on a series of UHMWPE oxidized samples, we have previously shown the validity of a relationship between the oxidation index, OI, of UHMWPE and the relative intensity of selected Raman bands, as follows [18]:

$$\mathrm{OI} = \exp\left\{1.19 \times \tan\left[14.26\left(\frac{I_{1414}}{I_{1293} + I_{1305}} - 0.26\right)\right] - 0.13\right\}, \qquad (2)$$

where I_{1414}, I_{1293} and I_{1305} represent the intensities of the Raman bands of UHMWPE associated with –CH_2– bond wagging and –CH_2– twisting vibration. Explanations about the experimental procedure followed for validating equation (2) and details on the reliability of the Raman measurements of oxidation index have been given in the Appendix of Ref. [18]. It should be noted that Raman measurements of oxidized synthetic polymers might be very difficult due to the presence of a broad fluorescence background, which results from oxidative degradation. However, we have not only shown that equation (2) can be used to a degree of precision for OI assessments but also that this practice enables the determination of OI non-destructively from the same spectral records used for analyzing microstructural features in polyethylene [18].

Figures 5 shows typical sub-surface oxidation profiles as measured in the UHMWPE acetabular cup in the unused state, after short-term (cup No. 1) and long-term (cups Nos 2–4) exposure *in vivo*, respectively. It should be noted that both the revised implants were used in successful surgeries from the viewpoint of the quite small amounts of volumetric wear detected. From a comparison among the five profiles shown in Fig. 5 it is clear that the overall amount of oxidation increases with increasing exposure time. In addition, two maxima of the OI can also be observed in the sub-surface profiles of the retrieved cups, which are roughly coincident with the depths at which maxima were observed in the profile of compressive strain. However, unlike strain, the difference in oxidation profiles between short-term and long-term exposed cups is more pronounced. A puzzling observation for *in vivo* exposed UHMWPE components is the occurrence of the most severe oxidation paths just below the exposed surface of the component. This in fact has been widely reported, in particular in the delamination of PE inserts in knee replacements [26].

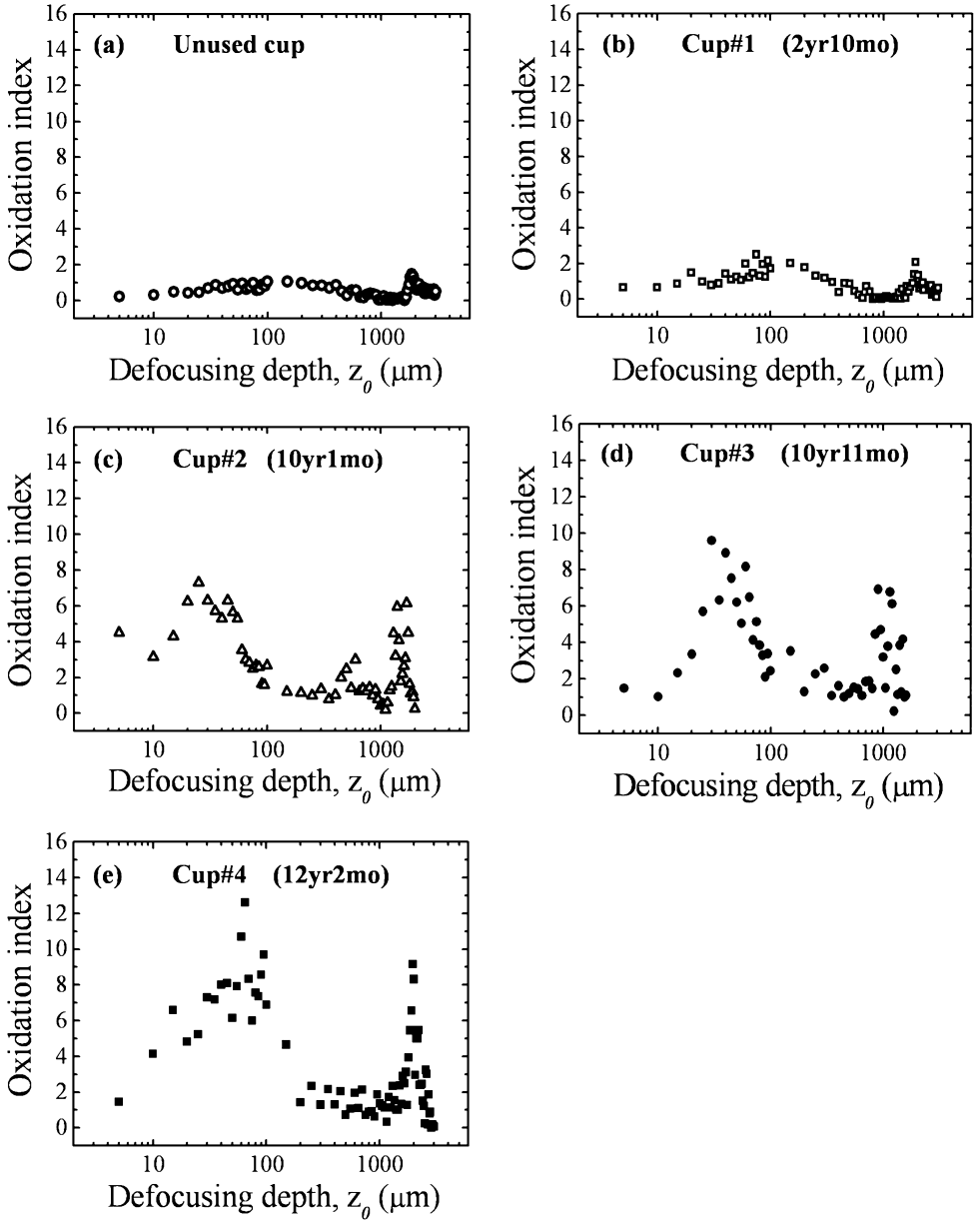

Figure 5. Sub-surface oxidation profiles calculated by means of Raman spectra collected in the main wear zone of the 4 retrievals and the new hip cup. Two maxima of oxidation appears at a depth of around 50–100 μm and 2000 μm.

A comparison between the strain and oxidation profiles plotted in Figs 4 and 5, respectively, might help to partly rationalize the peculiar in-depth property patterns observed in retrieved acetabular cups. This aspect will be the object of the discussion given in the next section.

4. Discussion

A considerable problem with the evaluation of the polyethylene performance *in vivo* resides in the determination of liner penetration kinetics; in other words, it is always difficult to understand when creep-dominated penetration slows and when wear-dominated penetration begins. On the other hand, it is important to establish the point at which this transition occurs since the degree of wear can only be determined accurately once the dominance of creep has decreased considerably. *In vitro* studies have suggested that significant creep deformation takes place up to approx. 2×10^6 loading cycles [27]; according to variations in the patients' activity, such a target may be reached at any point between three months and two years after surgery [28, 29]. On the other hand, *in vivo* studies suggest that there is great variability in the point at which creep-to-wear transition occurs [30, 31]. Consequently, in order to avoid overestimations [30, 32, 33], measurements of wear rate necessarily require that the amount of penetration in PE be systematically measured *in vivo* for at least three years using radiostereometric analyses [31].

The Raman spectroscopic approach shown in this study may enable one to directly measure the creep displacement along the liner thickness, and thus to discriminate, within the loading history of the liner, between the amounts of penetration arising from creep deformation and that due to wear. The reduction in thickness, Δt, can be calculated from experimental residual strain profiles along the in-depth abscissa, z, according to the following equation:

$$\Delta t = \int_0^t [\varepsilon(z) - \varepsilon_0(z)]\,\mathrm{d}z \cong \sum_{j=1}^{n} [\bar{\varepsilon}_j(z) - \bar{\varepsilon}_{oj}(z)]\Delta z, \tag{3}$$

where n is the number of data points collected at increasing depths along the liner thickness, t is the thickness of the cup in the main wear zone, $\bar{\varepsilon}_j$ is the average strain value measured in the probe at each location, $\bar{\varepsilon}_{0j}$ is the average strain value measured in the unused cup depending on the position along the thickness and Δz is the in-depth size of the confocal probe (i.e., equal to about 8 μm for PE in the optical probe configuration from 0 to 100 μm in-depth and 25 μm in the optical probe configuration from 100 to 3000-μm in-depth [18]). Using the strain profiles shown in Fig. 4, we were able to calculate thickness reductions due to creep deformation of 160 μm (cup No. 1), 600 μm (cup No. 2), 300 μm (cup No. 3) and 350 μm (cup No. 4) (i.e., representing approx. 2.5, 16.2, 8.1 and 9.4% of the initial thickness) for short-term and long-term *in vivo* exposed acetabular cups, respectively. Our measurements of creep displacements are in line with the findings of other studies [32, 34]. In a recent article, Glyn-Jones *et al.* [34] have examined both creep and wear behaviors in highly cross-linked polyethylene liners on a large number of patients in order to determine and ultimately give a statistical prediction of three-dimensional penetration of the femoral head in the liner with elongating exposure time *in vivo*. These researchers were capable to discriminate creep from wear according to the pattern of penetration in the liner. The main outcomes of the

study showed that penetration was initially creep-dominated (i.e., 95% of creep deformation occurred within 6 months of implantation), but after one year virtually any additional penetration was due to wear. Our Raman characterizations partly agree with the study by Glyn-Jones *et al.* since we show here that a non-negligible amount of creep deformation is already present in the short-term exposed cup as compared with the long-term exposed one (*cf.*, also Fig. 4). In addition, our Raman experiments also show that while creep deformation is already remarkable in the short-term exposed liner, oxidation in the main-wear zone yet experiences a low profile. In other words, although sub-surface maxima of creep strain and oxidation ultimately occur at the same locations in depths, the PE structure creeps first and then oxidizes, and not *vice versa*.

The present study indicates a trend, which differs from the prior art [35–37] in that the effect of a preliminary oxidation state on the deformation behavior of the UHMWPE does not represent a matter of concern in the investigated (non-defective) liners. Instead, it appears that it is the configuration of the plastically strained profile of the UHMWPE structure, which allows for an increased reaction with atmospheric oxygen in selected zones. As far as the more deeply located maximum in strain/oxidation is concerned (*cf.*, Figs 4 and 5), it has been reported that it originates from a delamination process [38–40]. Since the delamination of UHMWPE is a plastic-strain driven fatigue process [41], occurring in sub-surface portions of material continuously exposed to large cyclic stresses, it is possible to justify a time lag between the built-up event of internal strain and the formation of a highly oxidized internal slab of material, which is consistent with the findings of this study. It can also be thought that the initiation and growth of sub-surface microcracks in such a zone may potentially contribute to the locally enhanced oxidation profile. Of more difficult interpretation is the kinetics leading to the formation of the creep/oxidation peak located just below the liner surface (at about 2000 μm in depth; *cf.*, Figs 4 and 5). It has been reported [42] that the formation of a peak of oxidation just below the free surface of γ-irradiated UHMWPE is due to the combined effects of the distribution of residual free radicals and of oxygen diffusion gradients. The interactive relationship between oxidation and cross-linking has provided a fundamental basis for understanding the wear behavior of liner components in past clinical use. The information newly obtained from this study resides in the fact that the sub-surface structure immediately below the irradiated surface slab of the liner is prone to severe creep strain. Such a plastic deformation takes place in a relatively short time span since *in vivo* implantation, before any severe oxidation is yet observed. It can be reasonably expected that the highly structurally graded zone at the interface between the directly irradiated (highly cross-linked) surface and the sub-surface, in which the level of cross-linking achieved is lower, be strained due to a mismatch in hardness and elastic modulus. *In vivo* aging may then result in an increased density at or below the component surfaces, which is mainly due to changes in crystallinity within the UHMWPE and, to a smaller extent, to oxygen incorporation within the polymer structure. In other words, oxidation of UHMWPE may

lead to further development of a residual strain field near the liner (γ-irradiated) surface, which may in turn contribute to the wear mechanism of UHMWPE acetabular cups during service. Buchanan *et al.* [43] indeed reported that accelerated aging of UHMWPE in pressurized oxygen resulted in peaks of polymer density and degree of oxidation up to 500 μm below the polymer surface. Shelf and *in vivo* aging was also found leading to density increases (i.e., mainly arising from changes in crystallinity) below the sample surface. Formation of radial cracks may occur *in vivo* in regions of maximum crystallinity [44], assisted by the presence of high subsurface strain gradients. As oxidation proceeds, the microscopic elongation needed to locally break the UHMWPE structure decreases [45]. Therefore, at some point, the cumulative effect of applied and residual strain may result in the formation of cracks.

In Ref. [43], however, it was also reported that the application of compressive stress did not appear to directly influence the accelerated aging and the oxidation rate of UHMWPE. This finding is clearly in contrast with the theory of mechanico-oxidative degradation of polymers [46], but can be justified by the low level of applied load in that study. On the other hand, the mechanical loading impinged on the liner surface *in vivo* can be estimated for the present retrievals to be at least one order of magnitude larger than the load applied in the study of Buchanan *et al.* [43]. Therefore, a contribution to enhanced sub-surface oxidation due to mechanico-oxidative effects cannot be ruled out.

5. Conclusion

In conclusion, the present study has provided a direct method to quantitatively and non-destructively assess in-depth residual strain and oxidation profiles in UHMWPE acetabular cups, has clarified some peculiar aspects of the *in vivo* time dependence during the development of such profiles, but has not allowed us to provide a final answer as to the micromechanical origin of two maxima in strain and OI (almost coincident in their locations), as observed along the in-depth profile in the main-wear zone. The possibility to non-destructively and quantitatively measure strain and OI from confocal Raman spectra in polyethylene acetabular cups may also help materials technologists to put forward new guidelines for the development of polyethylene grades with improved resistance to oxidation and wear, with particular relevance to the estimation of the amount of cross-linking and crystallinity needed to potentially eliminate the clinical problem of osteolysis.

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