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Wear effects in retrieved acetabular UHMW-PE cups

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There is an increasing awareness of the clinical problems associated with ultra-high-molecular-weight polyethylene (UHMW-PE) wear and failure in orthopaedics. This disadvantage is certainly promoted from the various oxidation process that can occur during prosthesis life. Scanning electron microscopy, IR-spectroscopy, and X-ray-photoelectron spectroscopy were employed to investigate the mechanism of polymer degradation. In particular, comparison among the spectra of starting and retrieved UHMW-PE components shows that the polymer oxidizes mainly *in vivo*. The data indicate that hydroxyl radicals are likely to be a major factor in degradation of the surface of this polymer, these groups are produced *in vivo* during the implantation time. Several other chemical groups, produced in the different steps of the prosthesis life, are contained in the material.

1. Introduction

In total joint arthroplasty, various endoprosthesis components are fabricated in ultra-high-molecular-weight polyethylene (UHMW-PE). The components for which UHMW-PE has more successfully been utilized are hip joint cups and the gliding parts for knee, ankle, shoulder, and elbow joint replacements. This polymer is generally recognized as an adequate low-friction, low-wear material with sufficient biological performance (i.e. biocompatibility) for total joint replacement. In its recent formulation, with a molecular weight exceeding 1.5×10^6, it has been extensively used in the fabrication of acetabular components of total hip prostheses. In recent years, many authors have provided the impetus for its use in conjunction with a metal component and now a typical joint consists of a smooth hard metal or ceramic counterface which articulates on a softer UHMW-PE component. The counterface should have a very smooth surface, because it has been shown that the wear rate of UHMW-PE is dependent on the surface roughness of the hard metal/ceramic component. Experience has encouraged many surgeons to use this kind of design in the replacement of diseased joints.

The wear of UHMW-PE components remains a major cause of failure in long-term joint replacement. More than half a million diseased or damaged joints are replaced annually in the world, and the number of patients at risk from prosthesis failure is continually increasing. Reasons for failure and increased wear of polymer materials can be found in the property changes which occur in the biological environment.

In recent years, several clinical problems relating to degradation have become apparent and therefore polymer degradation is of increasing importance in the production and use of medical devices. However, the wear of the UHMW-PE cup creates two problems: (1) as the head of the femoral component bores into the cup its angular movements are restricted, which results in impingement of the neck of the stem on the cup rim, shock loading, and socket loosening in a proportion of patients over time; (2) it gives rise to the formation of particulate debris. Debris resulting from damage to the surface of polyethylene components of total joint arthroplasties has been shown to contribute to long-term problems such as loosening and infection [1–4]. For example, the biological response that is elicited in the surrounding tissue by particles of polyethylene can cause endosteal bone resorption and deterioration of the bone–implant interface [2, 4].

Recently, quantitative measurements of surface damage on retrieved total knee and total hip-joint components have shown that the severity of the damage to the surface increases with the length of time that the component has been implanted and the weight of the patient. This is consistent with experimental and theoretical studies that have shown that contact stresses increase with applied load (the weight of the patient). Surface damage is related to the contact stresses on the polyethylene and may be caused by a fatigue mechanism.

This process is certainly promoted from the various oxidation process that can occur in the bulk and on the surface during the prosthesis life. The modes of

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surface damage occurring on polyethylene joint components that can produce changes in the physical properties of the polyethylene can be related to the fabrication techniques, sterilization, and *in vivo* degradation. UHMW-PE components were subjected to hot pressing during fabrication, and this technique has been shown to influence the physical properties of the polyethylene material near the articulating surface [5].

The hypothesis of the formation of an oxidation layer (of low degree) on new cups, which presumably results from the high temperature compression sintering of the as-synthesized draw UHMW-PE powder [5], or produced from a subsequent gamma radiation sterilization in the presence of oxygen [6], has also been proposed.

The γ-radiation sterilization process is a promising method for sterilizing biomaterials: 2.5 Mrad is sufficient to kill most micro-organisms. However, radiation sterilization can significantly affect the physicochemical and toxicological properties of devices. The primary active species created by this irradiation are radicals and ions. Most of the radicals formed during irradiation remain trapped in the material and they can be converted in peroxidic radicals that further recombine, inducing crosslinks and material degradation.

Besides, when implants are inserted into living tissue an inflammatory response caused by the surgical trauma follows. Clinical experience shows that the response is different at different locations in the body and for different materials. One of the features of an inflammatory response is the release of superoxide and hydrogen peroxide from inflammatory cells into the extracellular space and an interaction between these chemical species and the foreign body is expected [4].

The aim of this study was to determine which mechanisms of degradation are mainly operative in the UHMW-PE prosthesis life and what are the consequences of these processes. The surfaces and the bulk of acetabular components retrieved during revision surgery were characterized by FT-IR spectroscopy, scanning electron microscopy (SEM), and X-ray-photoelectron spectroscopy (XPS). The results were compatible with virgin materials.

2. Materials and methods

The five hip joint cups endoprotheses used in this study were retrieved at re-operation because of loosening. All explanted hip cups were sterilized with gamma irradiation. After retrieval, the specimens were stored in the laboratory (room temperature, normal humidity, protected against UV-irradiation) for 1–3 months before tests were performed. As-sintered, γ-sterilized, and UHMW polyethylene powder, delivered from HIMONT Italia, were also investigated.

Scanning electron microscopy (SEM) (Hitachi S-2300 microscope) was used to study the morphology of the specimen surfaces. The samples were mounted and sputter-coated with gold, using an SC500 EM scope sputter coater. The entire surface from the edge to the bottom, and the cross section of the degraded specimens were prepared and analysed using secondary electron scanning mode (SE).

An infrared spectrometer (FT-IR) (Nicolet 5-PC spectrophotometer) was used to examine various areas on the surface of the acetabular cups. Thin microtomed sections of about 1 mm were obtained and mounted on a solid sample holder. The articulating surfaces, on both severely worn and fairly unworn areas, and the back (non-articulating, convex side) of every acetabular component were analysed. The reported results are selected from 10 similar tests.

X-ray-photoelectron spectra were obtained using an AXIS-HS instrument. The excitative source was magnesium with an excitation energy of 1253.6 eV. The gun voltage was 15 kV and the gun current 0.005 A. Wide spectra and elemental peaks were obtained.

3. Results and discussion

The macroscopic analysis conducted on the surface of explanted acetabular cups (9 years in a human body) showed the presence of a brown film on the surface involved in articulation. The explanted cups displayed two distinct regions and the transition between these two areas was often marked by a clear line. These two parts were a high-wear region and a low-wear region. The high-wear region of the cup was the articulating surface during the normal walking activity. The low-wear areas were associated with less-frequent activity during articulation life, and therefore displayed evidence of some pitting, small residual shear strains, and little deformation. The high-wear region is smooth, yellowish, highly polished and worn, the creep traces were evident that had caused the formation of thin lips along the perimeter of the cup concavity. Occasional yellow areas existed within the white region of the low-wear part too, indicating shear strain and deformation.

The surface texture of the explanted acetabular cup was studied using SEM, and a micrograph of a specimen is shown in Fig. 1. Several kinds of damage were observable by microscopical investigation of the

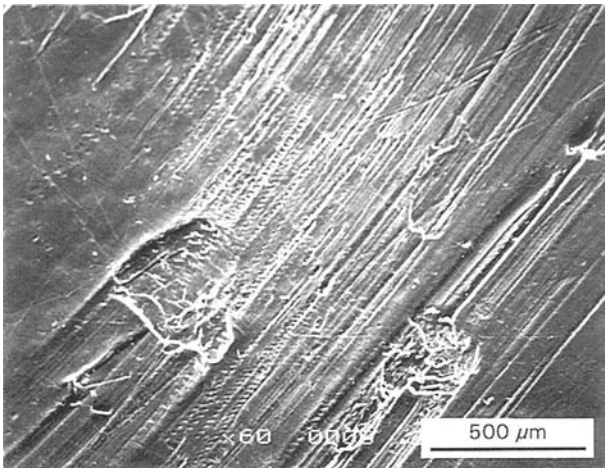

Figure 1 Scanning electron micrograph of the explanted UHMW-PE surface.

surface topography. The medial plateaus gave the impression of having more wear damage than the lateral plateaus; the subjective damage scores for the medial and lateral sections were not significantly different. Microscopic examination of the articulating surfaces revealed burnishing, scratching, pitting, and delamination as the most common modes of surface damage. Large areas of delamination formed by subsurface cracks propagating parallel to the articulating surface and a significant surface deformation were most notably in the medial and lateral edges of the articulating surface. Scanning electron microscopy examination of a surface that had suffered delamination showed a relatively smooth, featureless surface, consistent with continued loading and subsequent burnishing of the delaminated areas. The fracture surfaces of cracks propagating into the component from the medial and lateral walls showed uniformly spaced lines perpendicular to the direction of crack growth, and extensive local buckling. These are probably the result of the combination of compression and shear forces that act on the specimen surface in service. A ductile material such as polyethylene is highly resistant to crack initiation. Surface flaws caused by scratches, machining marks, or defects within the material itself can act as sites of stress concentration and thus enhance the possibility of crack initiation. As surface cracks propagate, they can result in pitting and delamination of the articulating surface.

The infrared spectrum of the UHMW-PE synthesis powder is shown in Fig. 2. This spectrum can be interpreted in terms of vibrations of stretching and bending of C–H and C–C bonds. Not all the possible absorption frequencies are visible, e.g. the C–C bending vibration occurs at very low frequencies and therefore it does not appear in the spectrum. In addition, the bands assigned to C–C stretching vibrations are weak and they appear in the broad region of 1200–800 cm^{-1} (8.3–12.5 μm); they are generally of little value for identification. The most characteristic vibrations are those arising from C–H stretching and bending. Absorption arising from C–H stretching occurs in the general region of 3000–2840 cm^{-1} (3.3–3.5 μm). The four bending vibrations of the C–H bonds in the methylene group are referred to as scissoring ($\delta_s = 1465\ \text{cm}^{-1}$), rocking ($\rho = 720\ \text{cm}^{-1}$), wagging and twisting ($w, \tau = 1350$–$1150\ \text{cm}^{-1}$). The absorptions due to twisting and wagging vibrations are generally appreciably weaker than those resulting from methylene scissoring. The FT-IR spectrum of a sample of sintered UHMW-PE is similar to synthesis powder spectrum, and therefore the only resonances present in it are those characteristic of an aliphatic hydrocarbon. Neither synthesis or fabrication produce strong oxidization of the material.

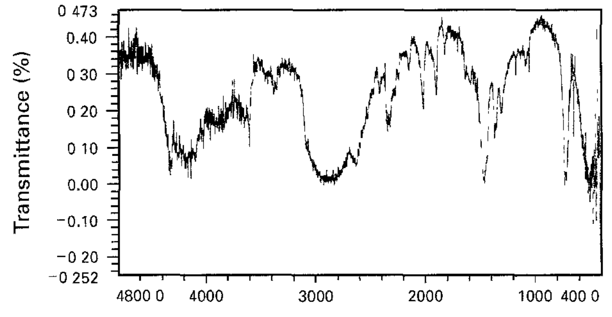

Figure 2 Infrared spectra from 4800 cm^{-1} to 400 cm^{-1} wave numbers of the UHMW-PE synthesis powder.

The infrared spectrum of the surface of a new sterilized UHMW-PE acetabular cup is shown in Fig. 3. Sterilization with γ-radiation produced a C=O stretching sharp peak at about 1735 cm^{-1}. Similar oxidization traces were also present in the bulk.

The analysis of the FT-IR spectra performed on a sample obtained from the bulk of an explanted acetabular cup shows, in addition to the expected CH_2 symmetric and asymmetric stretching vibrations, the presence of a small quantity of carbonyl resonances (Fig. 4). The frequency of this carbonyl function (about 1735 cm^{-1}) is that characteristic of esther groups. Probably, these chemical species are produced during the sterilization by γ-radiation in the presence of oxygen.

An FT-IR spectrum of a sample of UHMW-PE obtained by cutting the explanted acetabular cup near the articulating surface (i.e. the concave side) is shown in Fig. 5. New absorption bands are visible. The spectra indicate that the superficial PE have a high density of hydroxyl groups; their concentration changes significantly along the acetabular surface. The new bands observed in the spectra result from OH stretching and C–O stretching. The CO stretching vibrations produce a strong band in the 1260–1000 cm^{-1} region of the spectrum. The spectra

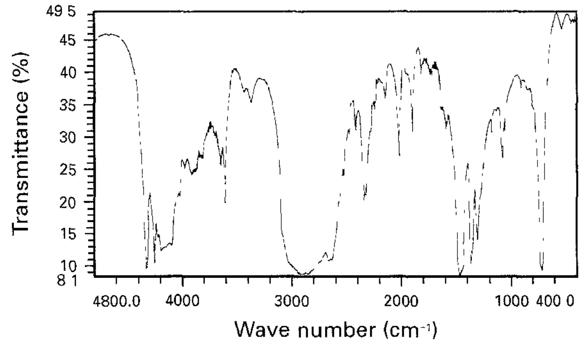

Figure 3 Infrared spectra from 4800 cm^{-1} to 400 cm^{-1} wave numbers of sintered and γ-sterilized UHMW-PE

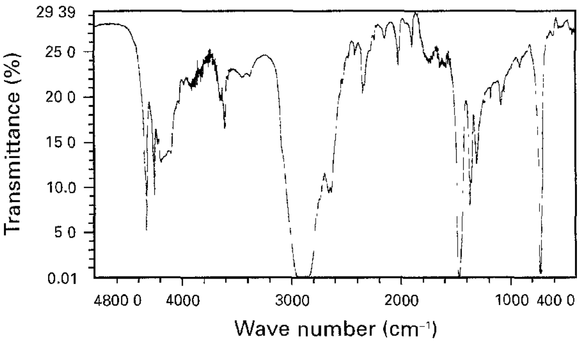

Figure 4 Infrared spectra from 4800 cm^{-1} to 400 cm^{-1} wave numbers of the bulk of an explanted acetabular cup (9 years in a human body).

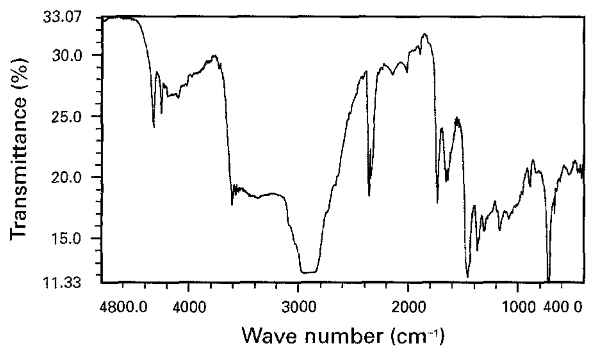

Figure 5 Infrared spectra from 4800 cm^{-1} to 400 cm^{-1} wave numbers of the surface of an explanted acetabular cup (9 years in a human body).

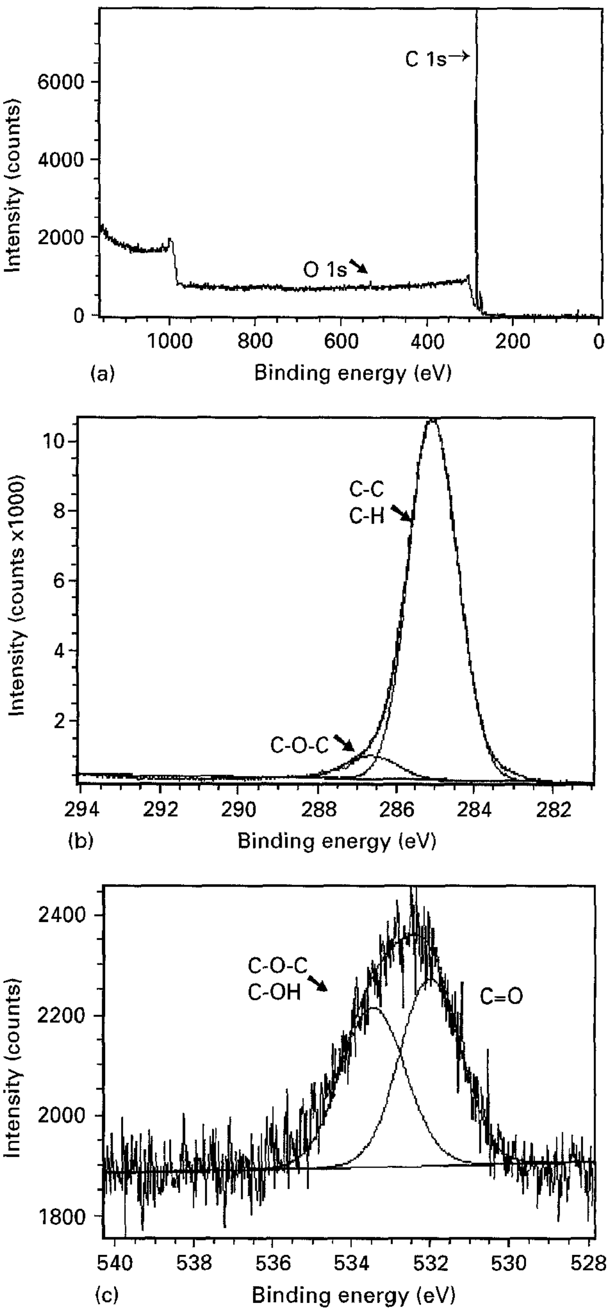

Figure 6 (a) XPS wide scan of a reference UHMW-PE surface; (b) C 1s peak of a reference UHMW-PE sample surface; (c) O 1 s peak of a reference UHMW-PE sample.

also reveals the presence of carbonyl groups. The carbonyl group shows a strong $C{=}O$ stretching absorption band at 1735 cm^{-1}, common to the polyethylene bulk infrared spectra, and a large band around 1715 cm^{-1}.

The position in the infrared spectra of the $C{=}O$ stretching band is determined by the kind of functional group contained in the molecular structure. The fine structure of the carbonyl bands at ~1715 cm^{-1}, present on the surface of explanted UHMW-PE, consists of two superimposed carbonyl peaks. These bands are produced from two different carbonyl functions.

1715 cm^{-1}: $C{=}O$ (keto-carbonyl group)

1720 cm^{-1}: RCHO (aldehyde-carbonyl group)

These two infrared bands have been produced by an oxidative process different from that operative during gamma sterilization. The presence of aldehyde-carbonyl groups is indicative of an increase of chain terminals, and therefore a lowering of the molecular weight of the polymer on the surface follows. So the superficial layer of polymer can be easily removed during the joint work. The weight loss is produced only during long-term *in vivo* use.

The degree of superficial oxidation changed significantly along the concave surface of the acetabular cup. At some points the hydroxyls absorption band exceeded even the C–H stretching band, showing a strong degree of oxidation. In other areas only a low oxidation level was observed. The intensity behaviour of the carbonyl absorption was similar to that of hydroxylic bands. The intensity of the esther-carbonyl group band remains unchanged along the articulating surface.

XPS analysis of the surface and subsurface of an explanted acetabular cup was performed. In order to evaluate the extent of the compositional modifications in aged samples, bulk-like samples of UHMW-PE, obtained by freshly cutting a sintered sample, were used to characterize the level of chemical modification of the unaged polymer.

Fig. 6 shows the XPS wide scan as well as the two high resolution C 1s and the O 1s peaks for the reference bulk-like sintered sample. An O/C atomic ratio of 0.02 is derived from the C 1s and O 1s peak intensity ratios for the bulk-like material, i.e. the sampled layer contains, on average, one O atom for each 49 C atoms.

More detailed information about the composition of the surface layer of the explanted material can be obtained by analysing both the C 1s and O 1s peaks using a suitable peak fitting procedure [7]. In particular, such an analysis for the C 1s peak shows essentially two components, respectively assigned to the C–H and C–C linkage (at a binding energy (BE) of 285.0 eV) and to C–OH and C–O–C (at an average BE of 286.6 eV) [8, 9]. 94% of the C 1s peak is presented by the first component, and 6% is represented by the high BE component.

The analysis of the O 1s peakshape is more informative, as both the nature of the oxygen-containing groups and their relative weight can be derived. Thus, the O 1s peak is formed by two components, the first one, centred at about 532.0 eV and representing 60% of the peak, is assigned to carbonyl groups [8, 10], and the second one centred at about 533.5 eV and representing the remaining 40%, is due to –OH or C–O–C linkages [8, 10].

It has to be stressed that the observed carbonyl groups cannot be related to any component in the C 1s spectrum, as no evidence is found for the carboxylic component expected around 289.1–289.4 eV or for carbonyl groups expected in the range 287.6–288.0 eV [8, 9]. Furthermore, it is interesting to note that the atomic ratio between the C–C and the C–O components is higher than the measured elemental O/C ratio (0.02). This may be due to two factors: first is the fact that part of the oxygen atoms are evolved in an ether-like moiety, i.e. inducing the shift of two C atoms. The second factor involves the difference in the sampling depth for C 1s and O 1s photoelectrons, due to their different kinetic energy. In particular, the sampling depth of the O 1s photoelectrons is about 2.0 nm (for a KE of O 1s photoelectrons of ~710 eV, using the $MgK_{\alpha 1,2}$ line as exciting radiation), while it is 4.0 nm (for a KE of ~960 eV) for the C 1s ones [11]. According to such an intrinsic depth sensivity, we could argue that the carbonyl-related C 1s component is not detected due to its presence mainly on the top surface, where it is more effectively sampled by the O 1s band, while it is much lower at higher depth, where mainly carbon atoms singly bonded to one oxygen are present.

Such a low and "mild" level of oxidation for the PE surface is not surprising, as a number of very common processes may induce such an oxidation, including the reaction of atmospheric oxygen with defects present in the chain, the action of UV-activated oxygen, the interaction of dissolved oxygen with reactive defects induced by γ-ray irradiation used in sterilization processes or also to the formation of reactive sites due to mechanical and chemical events including cutting, wearing, scraping, etc. [12].

Fig. 7 shows the XPS wide scan spectrum for the same explanted acetabular cup discussed above. The XPS analysis has been performed in large area mode, i.e. by averaging the signals over a 5 × 5 mm wide surface.

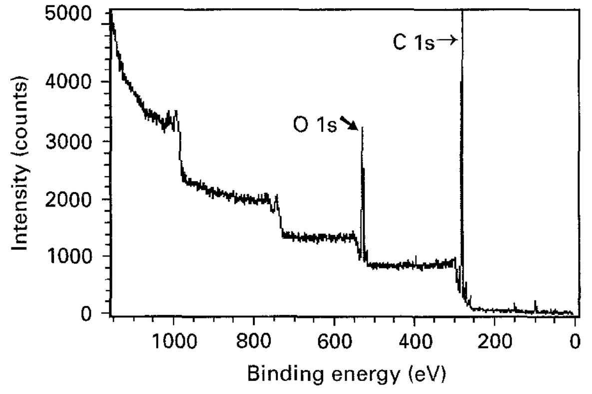

Figure 7 XPS wide scan of the surface of an explanted acetabular cup aged 9 years.

It is immediately evident that a massive oxidation process has occurred on the polymer surface. In fact, the O/C atomic ratio in this case is about 0.26, i.e. the sampled layer contains an O atom each 3.7 C atoms on average. It is interesting to note that also traces of N are found on the surface of the sample.

However, the surface of the explanted sample is not homogeneous, as it is formed by highly damaged regions, consisting of dark spots and large less damaged areas. This spotty-like aspect suggests that biological corrosion may proceed via a nucleation pattern. Thus, it is extremely interesting to analyse in detail the chemical structure of the highly damaged regions and that of the less damaged areas. This has been realized employing the small spot facility of the XPS apparatus [13], focusing onto an area of 200 × 200 μm within each type of region observed on the concave surface. The analysis has been repeated on different spots, representative of the two types of region, obtaining substantial reproducibility of the characteristic spectral features of the two types of areas.

XPS analysis of the high- and low-damage spots shows a dramatic difference in the oxidation level at the two different sites. In particular, the low-damage area has about 19% of O, with a C/O ratio of 0.23, while the high-damage area has as much as 27.5% of O, with an O/C ratio of 0.37. The comparison of this result with that obtained for the large area averaged value (20.9% of O) suggests that in fact most of the surface is in the low-damaged state.

Fig. 8 reports the C 1s peaks for the high- and low-damage regions. For the low-damage regions the

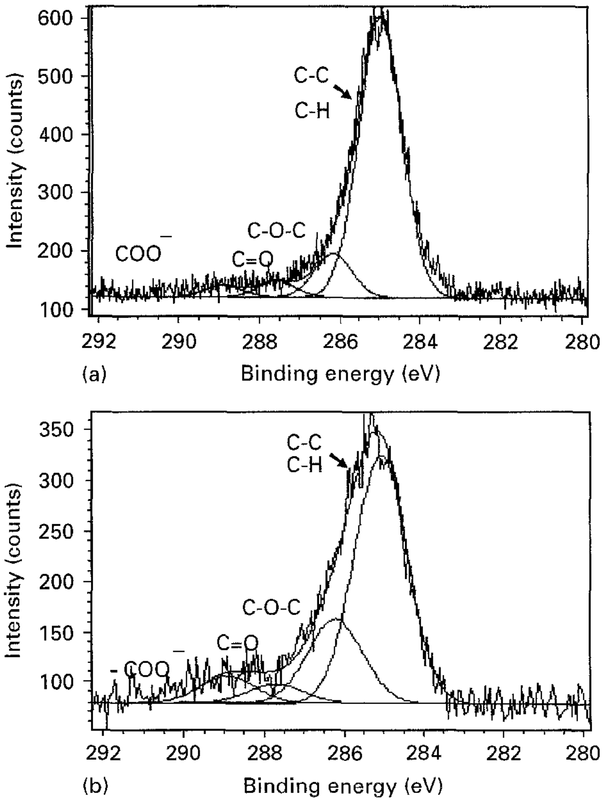

Figure 8 XPS C 1s peaks obtained in small spot mode on the surface of an explanted acetabular cup aged 9 years for: (a) low oxidation regions, (b) high oxidation regions.

C 1s peak (Fig. 3a) consists of a predominant component at a BE of 285 eV (about 78.0% of the total peak area), due to C–C and C–H bonding, with smaller components at 286.2 eV (13% of the total peak area), 287.6 eV (5.0% of the peak area) and 288.9 eV (4.0% of the peak area). The situation within the high oxidation spots is similar to that of low-damage spots in terms of position of the oxidation components, but different in terms of the extent of oxidation, as derived from the component intensity. In particular, the C–C and C–H component has an intensity of about 65% of the total area, while the intensity of the C–O–C and C–OH component is about 23%; that of the C=O and –COO– components are, respectively, 5% and 7%. Therefore, the overall effect of high biological corrosion is a dramatic increase of the C–O–C, C–OH groups and a smaller increase of the carboxylic groups.

Fig. 9 shows the O 1s peaks for the high- and low-damage regions. For the low-damage regions, the peak is formed by the two components already found in the reference sample, i.e. the carbonyl-like group at 531.9 eV (53.0% of the O 1s peak) and the –OH and C–O–C groups overlapped at 533.4 eV (47.0% of the O 1 s peak). We can extract more precise quantitative information from a comparison of the relative intensities of the various C and O components. In particular, one can estimate the presence of, respectively, 6 carbonylic and 5 carbonylic carbons, i.e. 11 C=O groups per 100 C + O atoms, which is in good agreement with the estimate of 10 carbonyl-like oxygen determined from the ratio between the relevant O and C 1s components. The same evaluation can be performed for the C–OH and C–O–C related carbon and oxygen components. Thus, the related component in the C 1s band involves about 9 atoms, while the analogous component in the O 1s band involves about 4 atoms, in roughly good agreement with the fact that each ether-like oxygen is linked to two carbons.

The component analysis in the highly oxidized spots clearly reflects the marked increase in the C–O–C and C–OH groups already observed in the C 1s peak. In particular, the intensity of the C–O–C and C–OH components in the O 1s peak increases from the 25% observed for the low oxidation regions to 49% in the highly corroded spots. Such an increase obviously justifies the much higher content of O (27%) in the spots against the relatively lower content in the less-damaged regions (19%).

A final interesting observation may be made about the presence of N traces on the surface of the biologically aged sampled. Fig. 10 reports the N 1s peaks obtained for a wide area region (10a), for a low-damage region (10b) and for a high-damage region (10c). In particular, Fig. 10a, having a better statistic, makes easier the assignment of the main components of the peak, which consists of an amidic component at about 400.0 eV [14]. Comparison of Fig. 10b and

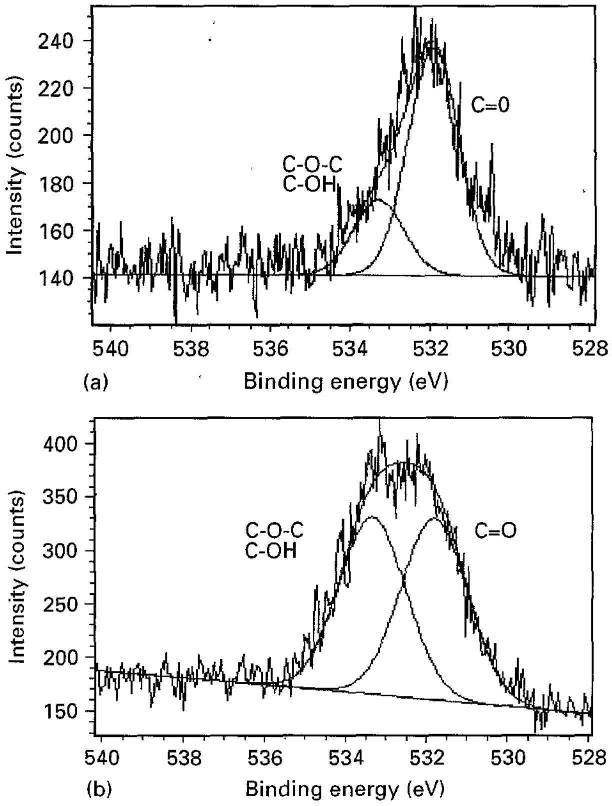

Figure 9 XPS O 1s peaks obtained in small spot mode on the surface of an explanted acetabular cup aged 9 years for· (a) low oxidation regions; (b) high oxidation regions.

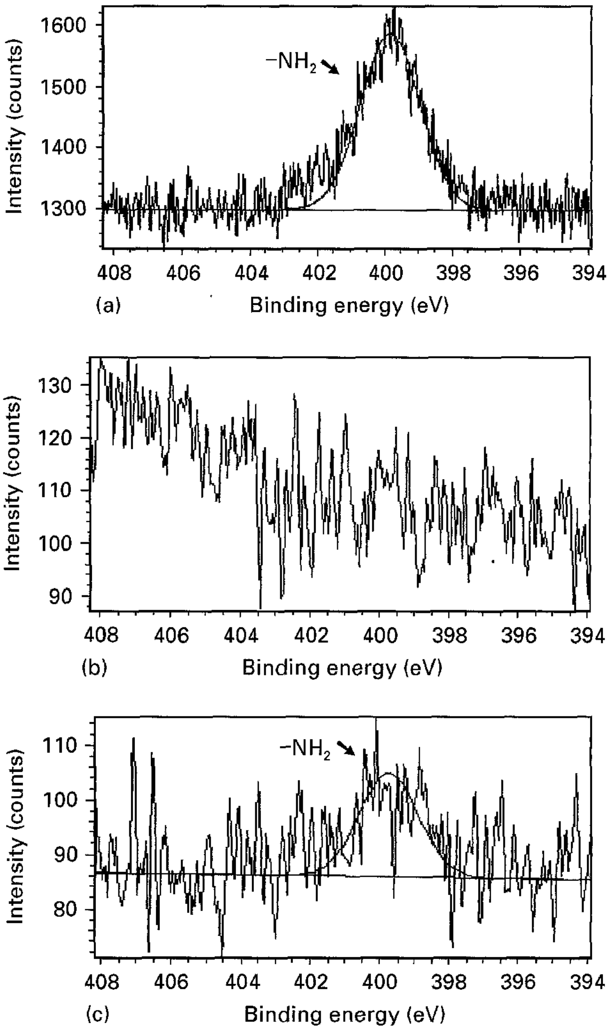

Figure 10 N 1s peaks obtained for. (a) wide area scan, (b) a high-damage region, and (c) a low-damage region.

10c make clear that the signal comes entirely from the less-damaged regions, while it is completely absent within the high oxidation spots.

The above reported results allow a few considerations. First, the qualitative results are complementary to those obtained by FT-IR for the bulk chemical composition. Indeed, the surface is the obvious site where the oxidative processes start. Thus, it is not surprising that traces of "environmental" oxidation are found by XPS within the first few nanometres. It is important to recall that such mild "environmental" oxidation mainly involves the formation of small amounts of C–OH and C–O–C groups, with a very small amount of carbonyl groups, overall oxidation remaining at the level of 1–2 at % of O.

On the other hand, the oxidation pattern at the initiating surface of biologically aged samples is very different to that of the "environmental" oxidation, being based on the simultaneous formation of substantial quantities of many different oxidation products, including C–O–C and C–OH groups, the C = O groups and the –COOH terminations. In particular, we note that these results confirm the detection by FT-IR of hydroxyl and carbonyl groups as oxidation products, but they clearly indicate that an important oxidation product is –COOH.

As to the presence of such carboxylic groups, we remark that it can occur only as an effect of an oxygen-induced chain scission event at an oxidation site, probably formed by a C–O–C linkage. Such a chain scission is clearly responsible for the lowering of the molecular weight of the UHMW-PE, in turn responsible for the weight loss of the joint. The characteristics of the observed oxidation pattern clearly indicate that such an oxidation is very drastic, as far as only a photo-oxidative process has been shown to be able to induce the formation of such highly oxidized groups as carboxyls.

Another very important observation concerns the fact that the oxidation process has a spot-like characteristic. In particular, the relative intensities of the oxidized groups and hence also of C–OH and –COOH groups drastically change along the surface of the joint, producing high-damage spots (–OH and C = O rich) and less-damaged regions, again supporting the FT-IR results.

Beyond the. relative oxidation level, the other interesting difference between the two kinds of oxidized regions consists in the presence of amidic nitrogen traces (not detected by FT-IR, due to its very small amount and very surfacial location) in the less-damage areas, suggesting that some proteic residue could be still adsorbed onto most of the investigated surfaces. This fact may suggest in turn that the presence of highly corroded spots is due to the random spot-like lack of a proteic protecting film, which acts as a starting point to promote massive degradation of the polymer. It is clear that such a hypothesis has to be tested by controlling the nature of the real interface produced in the biological medium as well as the nature of the adsorbed proteins. However, as such a test is very difficult to realize, we must rely on indirect experimental evidence such as that presented here.

4. Conclusions

Experimental observations showed that both chemical and physical changes take place in UHMW-PE during the implantation time. Microscopic examination of the articulating surfaces revealed burnishing, scratching, pitting, and delamination as the most common modes of surface damage; γ-irradiation does not produce a significant modification of the chemical composition of the polymer, only a low oxidation (predamage); the chemical modification of UHMW-polyethylene occurs principally during the implantation period and it consists of an oxidization of the prostheses surface; a large quantity of hydroxylic and carbonyl functions are produced during the *in vivo* oxidization of the exterior surface of the prosthesis; finally, aldehyde-groups occur in γ-irradiated samples only in very small quantities, however, they are distinctly measurable in retrieved cups after service *in vivo*. A reduction of the average molecular weight and the development of low-molecular-weight components in the area near the surface follows. These investigations show that further developments in the fabrication and sterilization of UHMW polyethylene are necessary.

Acknowledgement

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