Oxidation in Ultrahigh Molecular Weight Polyethylene and Cross-Linked Polyethylene Acetabular Cups Tested against Roughened Femoral Heads in a Hip Joint Simulator

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This study was aimed at comparing the oxidative degradation of commercial acetabular cups made of cross-linked polyethylene (XLPE) and conventional ultrahigh molecular weight polyethylene (UHMWPE). After testing against deliberately scratched CoCrMo femoral heads in a hip joint simulator, the cups, microtomed parallel to the articulating surface, were analyzed by IR spectroscopy. Due to the potential for artifacts caused by absorbed contaminants, the IR spectra were compared only after hexane extraction; actually, XLPE was found to absorb more serum than UHMWPE. The two sets of unworn acetabular cups showed different oxidation patterns with consequently different distributions of carbonyl species; unworn XLPE was characterized by lower contents of carbonyl species and hydrogen-bonded alcohols and higher contents of trans-vinylene species than unworn UHMWPE. Upon simulator testing, UHMWPE showed more significant changes in oxidation indexes and distribution of carbonyl compounds than XLPE, confirming a better wear behavior for XLPE under the adopted testing conditions.

1. Introduction

Total hip arthroplasty is one of the most successful and cost-effective surgical interventions in medicine[1] and represents the most effective treatment for osteoarthritis of the hip joint. Due to its excellent combination of properties, ultrahigh molecular weight polyethylene (UHMWPE) has been the most commonly used bearing material for acetabular cups in total joint replacement.[2,3] However, in some cases, wear, failure, and delamination have been observed, and it is well-known that UHMWPE debris elicit osteolysis and foreign-body reaction.[4−6]

New formulations of UHMWPE components have been developed in the past, with the goal of reducing creep and wear rates. In recent years, a new approach using physicochemical methods has been adopted to improve the wear performance of UHMWPE and increase its mechanical properties, such as yield stress and Young's modulus. Cross-linking of UHMWPE has been performed using chemical agents such as peroxides,[7] variable-dose ionizing radiation,[8,9] or electron-beam irradiation. Cross-linking occurs when free radicals, located in the amorphous regions of PE molecules, react to form a covalent bond between adjacent polyethylene molecules.

Highly cross-linked polyethylene (XLPE) is now widely used in acetabular components for total hip replacements.[10,11] Actually, cross-linking has been reported to improve the wear characteristics with respect to non-cross-linked PE in clinical studies[12,13] and laboratory tests using hip joint simulators.[14−17] However, current XLPE has not yet gained widespread acceptance for joint replacement, partly due to concerns about the reduced fatigue and fracture resistance relative to conventional UHMWPE.[18−20] Moreover, most of the laboratory studies have been done under clean conditions (i.e., using high-quality prostheses and highly polished counterfaces); therefore, there is concern regarding how well an XLPE acetabular cup will resist abrasion by a femoral head that has been damaged by third-body abrasion in vivo.

Various studies have compared the wear behavior of UHMWPE and XLPE against roughened counterfaces;[21−25] however, the reported results appear contradictory, reflecting the fact that different testing conditions have been used and differently processed materials have been tested. Some authors[21−24] have reported a better wear resistance for XLPE relative to conventional UHMWPE, while others[25] have found the opposite wear behavior. Apparently, not all methods of cross-linking are beneficial for wear resistance. On the contrary, some may be downright deleterious, which should be remembered when XLPEs are discussed as a group of orthopedic bearing materials.

To gain more insight into this subject, clinically available acetabular liners made of electron beam XLPE and conventional UHMWPE were tested against deliberately scratched CoCrMo femoral heads in a hip joint wear simulator run for three million cycles with bovine calf serum as lubricant.[26] Gravimetric measurements revealed significant differences between the wear behaviors of the two sets of acetabular cups: XLPE exhibited a wear rate about 40 times lower than that of conventional UHMWPE.[26] Accordingly, Raman spectroscopy showed more pronounced crystallinity changes in the latter than in the former.[26]

The present paper was aimed at evaluating by IR spectroscopy the oxidative degradation of the above-mentioned acetabular cups. Actually, oxidative degradation has been identified as a prevalent factor in the breakdown of PE components,[27] being linked to changes in crystallinity (due to chain scission) and

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thus in the mechanical properties of the material, such as decreased fatigue strength,[28] and the production of wear particles around the site of the implant.[29−33]

2. Materials and Methods

2.1. Materials and Simulator Test Details. Three 28 × 44 mm conventional UHMWPE and three 28 × 44 mm highly XLPE acetabular cups were tested in conjunction with six 28 mm CoCrMo femoral heads in a hip joint simulator. Another six acetabular cups (three for each type of material used) were stored (nonloaded) in bovine calf serum as control specimens.

All specimens tested were commercial components for surgical implants (ISO 5834-2), manufactured and supplied by Zimmer, Inc., Warsaw, Indiana. Both types of PE cups were compression molded with no added calcium stearate (GUR 1050). According to the information brochure, the XLPE cups (Longevity) were cross-linked by electron-beam irradiation at 40 °C to an absorbed dose of 9.5 Mrad, treated to a post-cross-linking heat treatment to quench free radicals, followed by gas plasma sterilization. During the post-cross-linking heat treatment, the PE was heated above the melting temperature (150 °C) for 6 h to break up crystals and mobilize free radicals.[34] The conventional UHMWPE acetabular cups were sterilized by γ-irradiation (4 Mrad) in nitrogen.

Wear tests were carried out one month after sterilization using a 12-station hip joint simulator (Shore Western, U.S.A.), with bovine calf serum as lubricant. The simulator setup and the followed procedure are described in detail elsewhere.[26] A frequency of 1 Hz, according to the rotation test frequency, was applied with a sinusoidal load having a peak magnitude of about 2 kN under room-temperature conditions (23 ± 1 °C).

The tests were performed with the cups mounted 45° with respect to the load axis. Severe testing conditions were achieved by roughening the femoral heads, as previously described.[26]

The total length of the wear test was set to three million cycles, consistently with previous studies.[35−39] At intervals of 0.5 million cycles, the specimens were removed from the simulator for weight measurements. Tests were restarted with new lubricant.

2.2. IR Spectroscopy. After wear tests, one unworn control and two worn cups of each type of polyethylene were sectioned using a Reichert-Jung microtome. The cutting depth was set to produce slices with a thickness of about 100 μm. The microtomed sections, taken parallel to the articulating surface, were analyzed by IR spectroscopy eight months after sterilization. IR spectra were recorded in transmission mode using a Nicolet 5700 Fourier Transform spectrophotometer (Thermo Electron Corporation). The spectral resolution was 4 cm^{-1}. To assess the effect of potential contaminants on the apparent oxidation levels, the spectra were measured before and after soaking of the thin sections in hexane at room temperature for 10 days. The actual thickness of each section was evaluated by measuring the absorbance at 2022 cm^{-1},[40] based on the assumptions that the reference absorbance was approximately proportional to the thickness of the sample (an absorbance of 0.05 corresponds to a thickness of 100 μm) and independent of the level of oxidation.

Several indexes were used to characterize the oxidative degradation of the sections. In general, peak areas were used to estimate oxidation as the content of multiple oxidized species, while peak heights were used to estimate oxidation as the content of a single oxidized species.

The oxidation degree as carbonyl compounds was evaluated by two different indexes. The $I_{\nu C=O}$ ketones/I_{2022} absorbance ratio (calculated as peak heights) between the C=O stretching (νC=O) component of ketones (at 1718 and 1714 cm^{-1} in UHMWPE and XLPE, respectively) and the band at 2022 cm^{-1} (internal standard, CH_2 vibration in both crystalline and amorphous PE[41]) was used in agreement with other authors[42−46] to estimate the oxidation degree as ketone compounds. The A_{ox}/A_{1300} absorbance ratio (calculated as peak areas) between the 1785−1680 cm^{-1} and 1330−1395 cm^{-1} (internal standard, CH_2 bending) spectral regions was used similarly to ISO/FDIS 5834−4 (2005) to estimate the oxidation degree as total carbonyl compounds.

Table 1. Assignments (according to the literature[47−54]) of the Components Obtained from the Second-Derivative Spectra in the 1785−1680 cm^{-1} Region

band frequency (cm^{-1})	assignment
1687	unsaturated ketones[47,48]
1700	carboxylic acids[49,50]
1714	dialkyl ketones[51,52]
1720	alkyl methyl ketones[51,52]
1730	aldehydes[48−50]
1740	esters[48,51,52]
1749	other carbonyl species[53]
1755	
1770	
1778	γ-lactones[50,54]

The A_{3400}/A_{1300} absorbance ratio (calculated as peak areas) between the 3505−3290 cm^{-1} and 1330−1395 cm^{-1} spectral regions was used to evaluate the hydrogen-bonded hydroperoxide and alcohol contents. The I_{3370}/I_{2022} absorbance ratio (calculated as peak heights) was used to quantify the contribution of the alcoholic component to the A_{3400}/A_{1300} ratio. The I_{3605}/I_{2022} and I_{965}/I_{2022} absorbance ratios (calculated as peak heights) were used to evaluate the non-hydrogen-bonded alcohol and trans-vinylene contents, respectively.

Since in the articulating area the cups had a thickness of about 4 mm, the surface indexes were defined as the average of their values from the sample articulating surface to a depth of 1-mm subsurface; the bulk indexes were defined as the average of their values corresponding to the center 2-mm of material (i.e., obtained from a depth of 1 mm to a depth of 3 mm).

The IR spectra of unworn and worn UHMWPE acetabular cups were fitted in the 1785−1680 cm^{-1} range to detect the contribution of the various carbonyl species to the total absorption. For component analysis, the second-derivative spectra of the 1785−1680 cm^{-1} region were smoothed with a nine-point smoothing function, and the found band frequencies (at about 1687, 1700, 1714, 1720, 1730, 1740, 1749, 1757, 1770, and 1778 cm^{-1}) were used as starting parameters for curve-fitting analysis. It was performed by means of a commercial software (Opus 5.0 from Bruker Optik GmbH, Germany), on the original spectra after baseline correction, using the Levenberg−Marquardt algorithm. The IR components were described as Gaussian functions. The content of each carbonyl species was calculated from the area of the individually assigned band (according to Table 1[47−54]) and expressed as fraction of the total area of the carbonyl bands.

3. Results

Figure 1 reports the IR spectra corresponding to the unworn control UHMWPE and XLPE acetabular cups before and after hexane extraction. As can be easily seen from the spectra of Figure 1A, the hexane treatment of the UHMWPE acetabular cups did not cause any significant decrease in absorbance of the carbonyl νC=O stretching bands in the 1780−1680 cm^{-1} range. This was not the case for the XLPE cup (Figure 1B): Upon hexane treatment, the νC=O esteric component at 1738 cm^{-1} underwent the highest weakening and shifted to about 1740 cm^{-1}. To quantitatively evaluate the effect of hexane extraction, the A_{ox}/A_{1300} and $I_{\nu C=O}$ ketones/I_{2022} indexes were calculated. The trend of these oxidation indexes in the first millimeter (i.e., the most superficial) of the unworn control UHMWPE and XLPE acetabular cups before and after hexane extraction is reported in Figure 2.

As can be easily seen from Figure 2A,B, the hexane treatment of UHMWPE did not cause significant changes of the oxidation

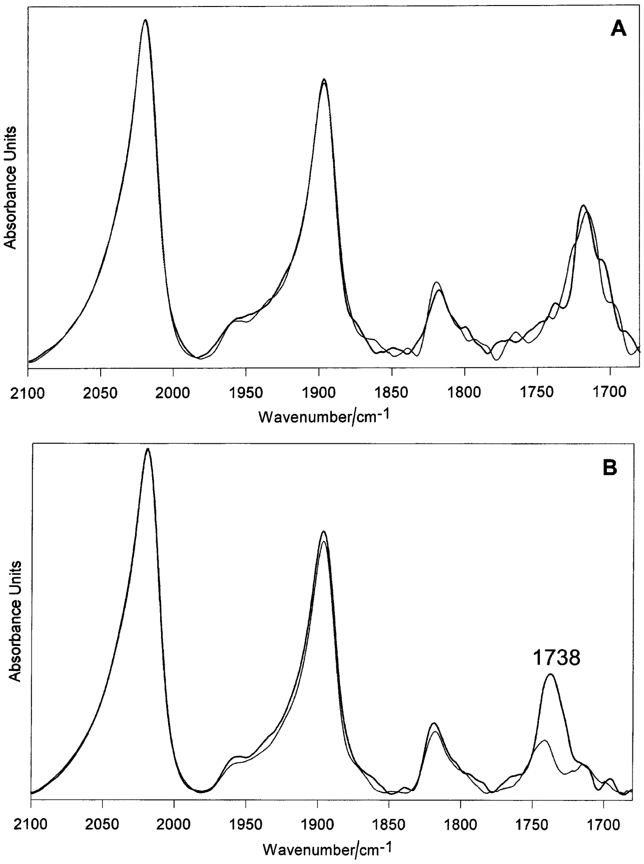


Figure 1. IR spectra recorded on two representative superficial sections (i.e., within 1 mm from the articulating surface) of unworn control UHMWPE (A) and XLPE (B) acetabular cups before (black) and after (gray) hexane extraction. The spectra are normalized to the absorbance of the 2022 cm^{-1} band.

indexes; in other words, the oxidation level of the cup remained unaltered in terms of both total carbonyl oxidation products (A_{ox}/A_{1300}) and ketones (I_{1718}/I_{2022}), i.e., the main oxidation product. This behavior perfectly resembles the trend of the spectra reported in Figure 1A. The same trend was observed also for the worn UHMWPE acetabular cups (data not shown).

Figure 2C shows that, upon hexane treatment of XLPE, the A_{ox}/A_{1300} oxidation index underwent a significant decrease, especially until a depth of about 700 μm from the articulating surface. An analogous result was observed also for the worn XLPE acetabular cups. However, the A_{ox}/A_{1300} decrease was less pronounced and was observed in a more limited area (i.e., until 400−500 μm from the articulating surface).

The decrease of the A_{ox}/A_{1300} oxidation index indicates that XLPE absorbed from calf serum contains a substantial amount of contaminants, which were removed by soaking in hexane. The trend of Figure 2D indicates that the main component extracted was not constituted by ketones. Actually, from the spectra of Figure 1B, it appears clear that the highest weakening was observed for the band at 1738 cm^{-1}, due to esters.

On the basis of the obtained results, it must be observed that, because of the potential for artifacts caused by absorbed contaminants, the oxidation levels have to be compared only after hexane extraction. Figure 3 reports the IR spectra of unworn UHMWPE (black) and XLPE (gray) acetabular cups after hexane extraction, and Table 2 reports the data obtained for all the analyzed specimens. No significant changes were observed between the surface and bulk values of each index.

Both spectra of Figure 3 show various bands due to oxidation products, in some cases with different relative intensities. With regard to the νC=O region, the spectrum of the unworn UHMWPE acetabular cup showed as the main component the ketone band at 1718 cm^{-1}. It appeared shifted to 1714 cm^{-1} in the spectrum of the unworn XLPE cup, which showed as the main component that at about 1740 cm^{-1}, due to esters. Other

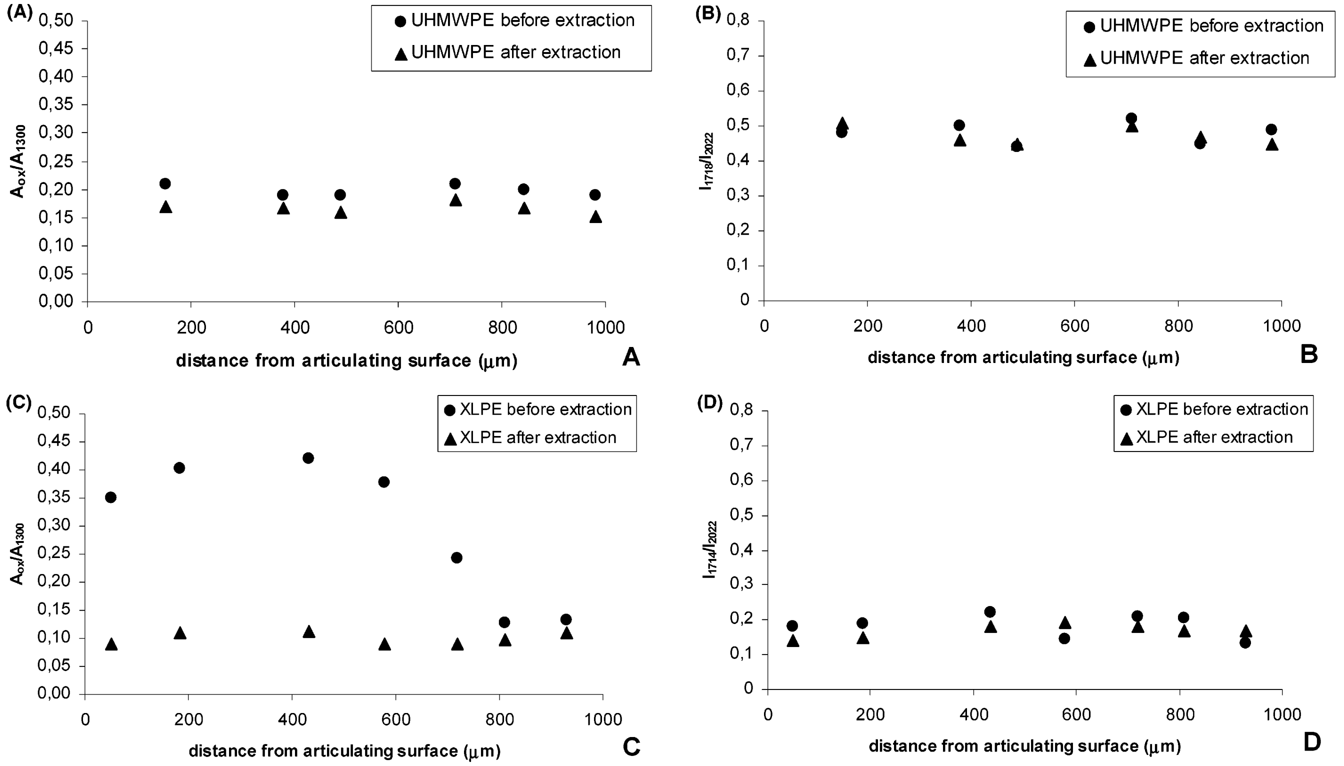


Figure 2. A_{ox}/A_{1300} (A) and I_{1718}/I_{2022} (B) vs distance from the articulating surface for an unworn UHMWPE acetabular cup before (●) and after (▲) hexane extraction; A_{ox}/A_{1300} (C) and I_{1714}/I_{2022} (D) vs distance from the articulating surface for an unworn XLPE acetabular cup before (●) and after (▲) hexane extraction.

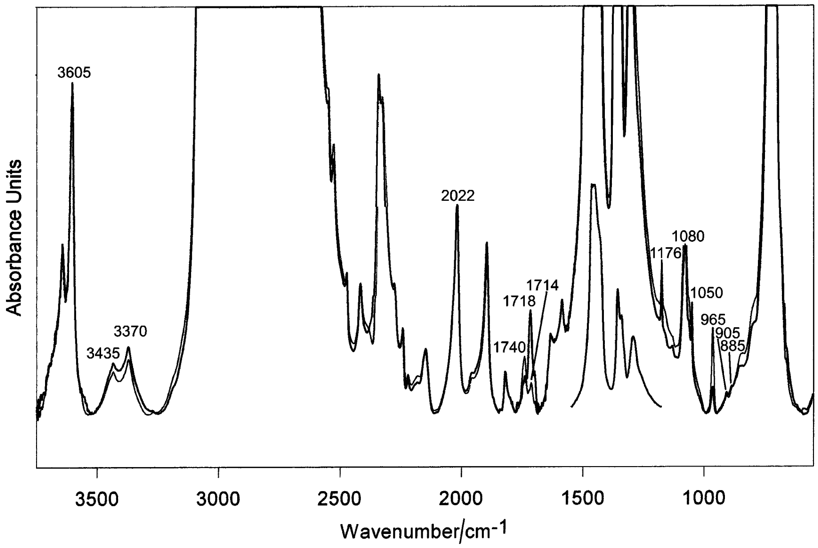


Figure 3. IR spectra of unworn UHMWPE (black) and XLPE (gray) acetabular cups after hexane extraction. The spectra are normalized to the absorbance of the 2022 cm^{-1} band.

Table 2. Data (index value ± standard deviation) Obtained from the IR Spectra of the Hexane-Soaked Unworn Control and Worn UHMWPE and XLPE Acetabular Cups[a]

sample	$I_{\nu C=O\ ketones}/I_{2022}$	A_{ox}/A_{1300}	A_{3400}/A_{1300}	I_{3370}/I_{2022}	I_{3605}/I_{2022}	I_{965}/I_{2022}
			UHMWPE			
unworn	**B** 0.47 ± 0.01	**B** 0.16 ± 0.01	**B** 0.28 ± 0.01	**B** 0.283 ± 0.005	**B** 1.60 ± 0.03	**B** 0.11 ± 0.02
	S 0.48 ± 0.03	**S** 0.17 ± 0.02	**S** 0.31 ± 0.03	**S** 0.287 ± 0.002	**S** 1.58 ± 0.05	**S** 0.11 ± 0.01
worn **1**	**B** 0.37 ± 0.03	**B** 0.13 ± 0.02	**B** 0.24 ± 0.01	**B** 0.26 ± 0.01	**B** 1.62 ± 0.05	**B** 0.11 ± 0.01
	S 0.40 ± 0.04	**S** 0.14 ± 0.03	**S** 0.26 ± 0.02	**S** 0.27 ± 0.01	**S** 1.60 ± 0.05	**S** 0.13 ± 0.02
worn **2**	**B** 0.23 ± 0.05	**B** 0.12 ± 0.02	**B** 0.23 ± 0.01	**B** 0.25 ± 0.01	**B** 1.64 ± 0.05	**B** 0.14 ± 0.02
	S 0.21 ± 0.02	**S** 0.10 ± 0.03	**S** 0.25 ± 0.02	**S** 0.26 ± 0.01	**S** 1.68 ± 0.05	**S** 0.12 ± 0.01
			XLPE			
unworn	**B** 0.16 ± 0.03	**B** 0.10 ± 0.02	**B** 0.23 ± 0.01	**B** 0.25 ± 0.01	**B** 1.57 ± 0.07	**B** 0.45 ± 0.03
	S 0.16 ± 0.04	**S** 0.10 ± 0.02	**S** 0.23 ± 0.01	**S** 0.25 ± 0.01	**S** 1.57 ± 0.06	**S** 0.42 ± 0.03
worn **4**	**B** 0.14 ± 0.03	**B** 0.07 ± 0.02	**B** 0.20 ± 0.01	**B** 0.249 ± 0.005	**B** 1.58 ± 0.05	**B** 0.44 ± 0.03
	S 0.10 ± 0.03	**S** 0.06 ± 0.01	**S** 0.21 ± 0.01	**S** 0.252 ± 0.002	**S** 1.59 ± 0.05	**S** 0.41 ± 0.03
worn **5**	**B** 0.11 ± 0.03	**B** 0.07 ± 0.01	**B** 0.20 ± 0.01	**B** 0.253 ± 0.002	**B** 1.63 ± 0.01	**B** 0.41 ± 0.03
	S 0.12 ± 0.03	**S** 0.06 ± 0.01	**S** 0.20 ± 0.01	**S** 0.252 ± 0.002	**S** 1.58 ± 0.02	**S** 0.40 ± 0.03

[a] The numbers used for indicating the cups were the same as in our previous paper.[26] *I* indicates that absorbance was calculated as peak height; *A* indicates peak area (see text for details). **B** = bulk; **S** = surface.

bands due to oxidation products were observed at about 3605 cm^{-1} (νO—H of non-hydrogen-bonded alcohols[47,49]), 3435−3370 cm^{-1} (νO—H of hydrogen-bonded hydroperoxides and alcohols, respectively[48,51,54,55]), 1176 cm^{-1} (νC—O of lactones and long linear esters[51,55,56]), 1080−1050 cm^{-1} (νC—O of hydroperoxides[48,55]), 965 cm^{-1} (trans-vinylene, CH═CH[48,51,52]), 905 cm^{-1} (vinyl, CH═CH$_2$[48,51,52]), and 885 cm^{-1} (vinylidene, C═CH$_2$[48,51,52]). The most significant differences between the spectra of Figure 3 were observed for the band at 965 cm^{-1}, in the 1785−1680 cm^{-1}, and 3505−3290 cm^{-1} spectral ranges. From a more quantitative point of view, the data reported in Table 2 confirmed this qualitative result: The indexes which showed the most significant differences between unworn UHMWPE and XLPE acetabular cups were I_{965}/I_{2022}, $I_{\nu C=O\ ketones}/I_{2022}$, A_{ox}/A_{1300}, I_{3370}/I_{2022}, and A_{3400}/A_{1300}. The unworn XLPE cups showed significantly lower $I_{\nu C=O\ ketones}/I_{2022}$ and A_{ox}/A_{1300} ratios than unworn UHMWPE cups. Moreover, the νC═O spectral profile of the two sets of cups appeared significantly different; accordingly, the fitted spectra showed pronounced differences (Figure 4A,C) as well as the corresponding distributions of carbonyl compounds (Figure 5). In the unworn UHMWPE acetabular cups the mainly represented carbonyl species was constituted by ketones (methyl alkyl ketones and dialkyl ketones: 31 ± 3% and 7 ± 2% of the total carbonyl compounds, respectively; Figure 5A); accordingly, the original spectrum showed as the main component in this range the band at about 1718 cm^{-1} (see Table 1 for assignment). However, in addition, carboxylic acids, esters, and other carbonyl compounds were quite abundant (26 ± 4%, 14 ± 2%, and 14 ± 1% of the total carbonyl species, respectively).

In unworn XLPE cups, the distribution of the carbonyl species appeared significantly different; actually, as can be seen from Figure 5B, carbonyl compounds were definitely less differentiated than for unworn UHMWPE (Figure 5A). Esters constituted by far the most represented carbonyl compound (56 ± 3% of the total carbonyl species; Figure 5B). Dialkyl ketones (19 ± 2% of the total carbonyl species) were more abundant than methyl alkyl ketones (11 ± 2% of the total carbonyl species) and carboxylic acids (6 ± 2% of the total carbonyl species). Accordingly, the original spectrum of unworn XLPE showed as the main component the band at about 1740 cm^{-1} and the ketone band shifted to 1714 cm^{-1}, reflecting the fact that dialkyl ketones (band at 1712 cm^{-1}; see Table 1 for assignment) became more abundant than methyl alkyl ketones (band at 1722 cm^{-1};

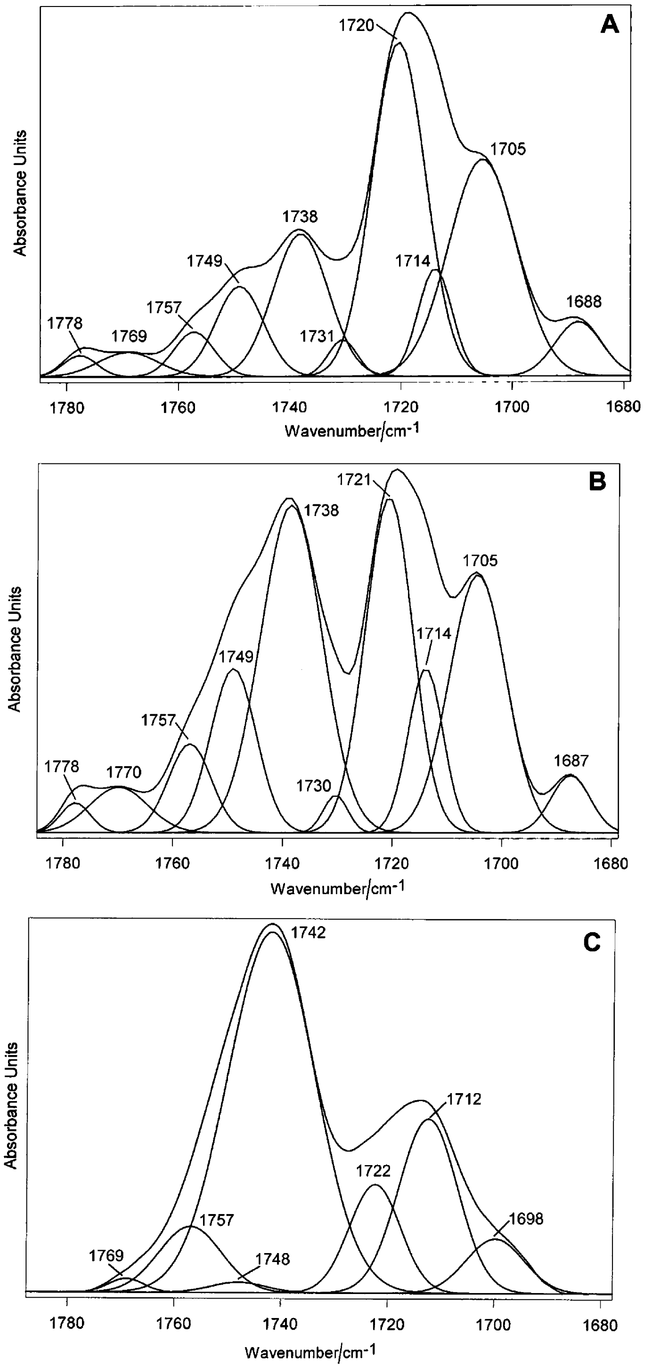


Figure 4. 1784−1679 cm^{-1} IR fitted spectra resolved into the different components recorded on the surfaces (i.e., within 1 mm from the articulating surface) of unworn UHMWPE (A), worn UHMWPE, cup 2 (B), and unworn XLPE (C), after hexane extraction.

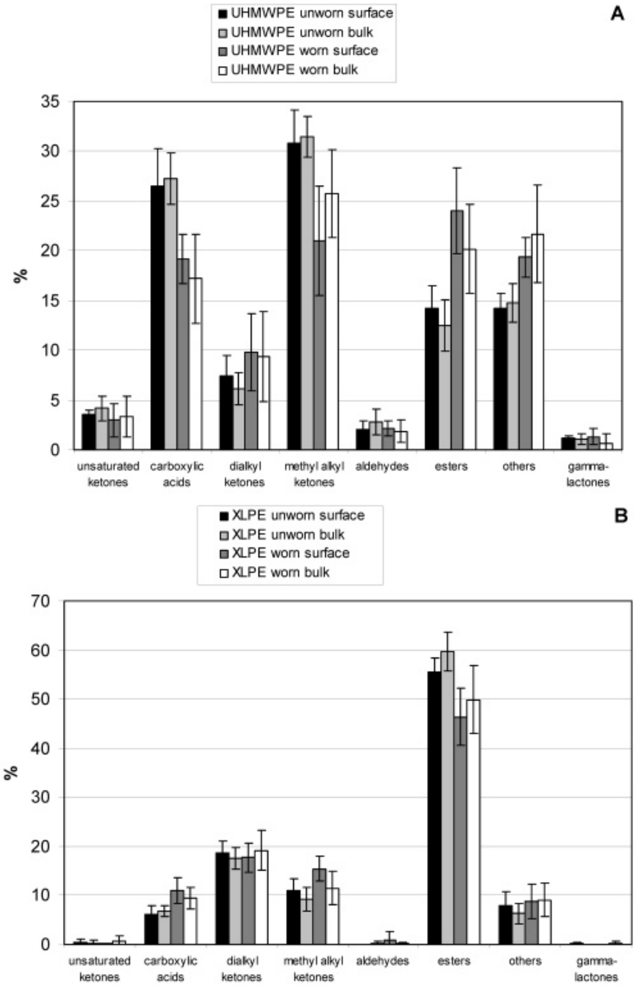


Figure 5. Percentages (±standard deviations) of the different carbonyl compounds detected in UHMWPE (A) and XLPE (B) unworn and worn acetabular cups (2 and 5), as determined from the curve fitting of the 1784−1679 cm^{-1} IR spectral range.

see Table 1 for assignment). Unsaturated ketones, aldehydes, and γ-lactones were less represented than in unworn UHMWPE cups.

As can be easily seen from Table 2, unworn XLPE acetabular cups also showed lower A_{3400}/A_{1300} and I_{3370}/I_{2022} values than unworn UHMWPE cups, suggesting the presence of lower amounts of hydrogen-bonded alcohols and similar contents of hydrogen-bonded hydroperoxides. On the other hand, unworn UHMWPE and XLPE showed similar I_{1080}/I_{2022} values (0.66 ± 0.03 and 0.70 ± 0.03, respectively), confirming similar amounts of hydroperoxides. Both sets of unworn specimens also showed similar contents of non-hydrogen-bonded alcohols, as revealed by the I_{3605}/I_{2022} values. On the contrary, the unworn XLPE acetabular cups contained significantly higher amounts of trans-vinylene species, as revealed by the I_{965}/I_{2022} ratio.

Upon simulator testing, UHMWPE acetabular cups showed more significant changes than XLPE acetabular cups. As can be seen from Table 2, the most significant changes involved cup 2 (i.e., that which showed the most significant weight and crystallinity changes[26]), mainly concerning the $I_{\nu\mathrm{C=O\ ketones}}/I_{2022}$ ratio and to lesser extents also the A_{ox}/A_{1300}, I_{3370}/I_{2022}, and A_{3400}/A_{1300} values.

Upon simulator testing, the νC═O spectral profile significantly changed for UHMWPE; accordingly, the fitted spectra showed pronounced changes (Figure 4B) as well as the corresponding distribution of carbonyl compounds (Figure 5A): The contents of esters and other carbonyl compounds increased (from 14 ± 2% to 24 ± 4% and from 14 ± 1% to 19 ± 2%, respectively). At the same time, the contents of carboxylic acids decreased either on the surface (from 26 ± 4% to 19 ± 2%) or into the bulk (from 27 ± 3% to 17 ± 5%); methyl alkyl ketones decreased only on the surface (from 31 ± 3% to 21 ± 5%).

Contrary to what was observed for UHMWPE, simulator testing did not induce any change in the νC═O spectral profile of XLPE (the fitted spectra were nearly coincident with those in Figure 4C) or in the distribution of carbonyl compounds (Figure 5B).

4. Discussion

The results reported in Figure 2 indicate that XLPE tended to absorb definitely more serum—namely, esteric compounds—than UHMWPE.

Actually, the affinity of PE for lipids has been widely described;[57−61] esters of fatty acids have been reported to absorb on the surface of PE components[57,61] and diffuse into them.[59−61] Apolar components of synovial fluid, such as cholesterol and fatty acid esters of cholesterol and squalene, have been reported to diffuse into UHMWPE during implant life.[61] Absorption and diffusion have been hypothesized to have a great diffusion on the mechanical properties: Absorbed and diffused species probably plasticize the material, causing a decrease of ultimate tensile strength and ultimate elongation and thus of the resistance to abrasion.[61] However, a systematic study on the effects of absorbed lipid species on the mechanical properties of PE is still lacking. On the other hand, an increased phospholipid concentration in protein-containing lubricants (up to 5% w/v phosphatidyl choline) has been reported to significantly reduce the wear rate of UHMWPE in hip joint wear simulators.[62]

Due to the potential for artifacts caused by absorbed contaminants, the oxidation indexes were compared only after hexane extraction and are reported in Table 2. For this purpose, it must be stressed that the data were presented as oxidation indexes corresponding to surface and bulk areas of each sample rather than as oxidation values versus distance from the articulating distance (i.e., as depth profiles). This choice was due to the fact that no index showed significant changes with depth for any of the cups analyzed; in other words, the depth profile of all the oxidation indexes in all the cups was similar to that reported in Figure 2 for hexane-soaked samples. Many studies have reported oxidation depth profiles for differently processed, sterilized, and aged UHMWPE specimens.[43,46,49,63−66] Upon γ-irradiation in air, right after irradiation or after short-term aging, oxidative changes have been reported to be maximal on the surface of UHMWPE.[43,64−66] Upon longer-term and accelerated aging, maximum oxidation has been found about 0.5−2 mm below the surface.[43,63−66] These depth profiles have been explained in terms of both oxygen diffusion into the polymer and concentration of free radicals (mainly hydroperoxides) produced by γ-irradiation.[63−66]

The oxidation data obtained in the present study appeared more comparable to those reported for UHMWPE specimens γ-sterilized in nitrogen after short-term aging;[65,66] for the latter samples, as for ours, no significant changes in oxidation indexes with depth have been found.

As can be seen from Table 2, the unworn XLPE cups showed significantly lower $I_{\nu\mathrm{C=O\ ketones}}/I_{2022}$ and A_{ox}/A_{1300} ratios than unworn UHMWPE cups. This finding appears a direct consequence of the post-cross-linking heat treatment the XLPE cups underwent. This treatment was used to quench free radicals and actually led to the absence of detectable amounts of these species.[34] With regard to the UHMWPE acetabular cups, it must be recalled that they were γ-sterilized. It is well-known that γ-irradiation of UHMWPE leads to long-lived macroradicals which react with oxygen resulting in the formation of hydroperoxides. These species decompose rapidly, yielding highly reactive radicals which accelerate the oxidation process where different types of oxidation products are formed (carbonyl and C═C unsaturated species, alcohols).[67,68] However, it must be stressed that the UHMWPE cups under study were irradiated under nitrogen, and this environment has been reported to reduce—with respect to sterilization in air—oxidative degradation occurring during short-term and accelerated aging.[66,69] Companies in support of γ-irradiation such as Zimmer, Inc., claim that, by γ-sterilizing polyethylene in a reduced oxygen environment (nitrogen processing and packaging), free radicals are able to recombine rather than react with oxygen, leading to increased cross-linking.[69] Actually, there is no scientific evidence that packaging and γ-sterilization in a nitrogen environment instead of air really reduces oxidation significantly during long-term storage and implantation.[70] Researchers not in favor of γ-sterilization claim that sterilizing polyethylene in an inert environment will help to reduce the initial oxidation that occurs, but cannot eliminate oxidation due to the presence of dissolved oxygen in polyethylene. Thus, the oxidation of UHMWPE continues for long periods of time following γ-irradiation.

Besides having shown lower contents of carbonyl species, unworn XLPE acetabular cups also showed lower amounts of hydrogen-bonded alcohols. On the contrary, the unworn XLPE acetabular cups contained significantly higher amounts of trans-vinylene species, as revealed by the I_{965}/I_{2022} ratio. For this purpose, it must be observed that at room temperature the generation of free radicals and the reaction between them occur simultaneously. As a consequence, carbon−carbon double bonds have been reported to form as a result of the occurrence of two alkyl free radicals next to each other on the backbone.[68] Evidently, this situation occurs with higher probability for XLPE than for UHMWPE, and thus, a higher content of internal double bonds (i.e., trans-vinylene species) was observed in the former. On the other hand, in the latter, other reactions[68] occurred, which led to higher concentrations of oxidized species (primarily, carbonyl compounds).

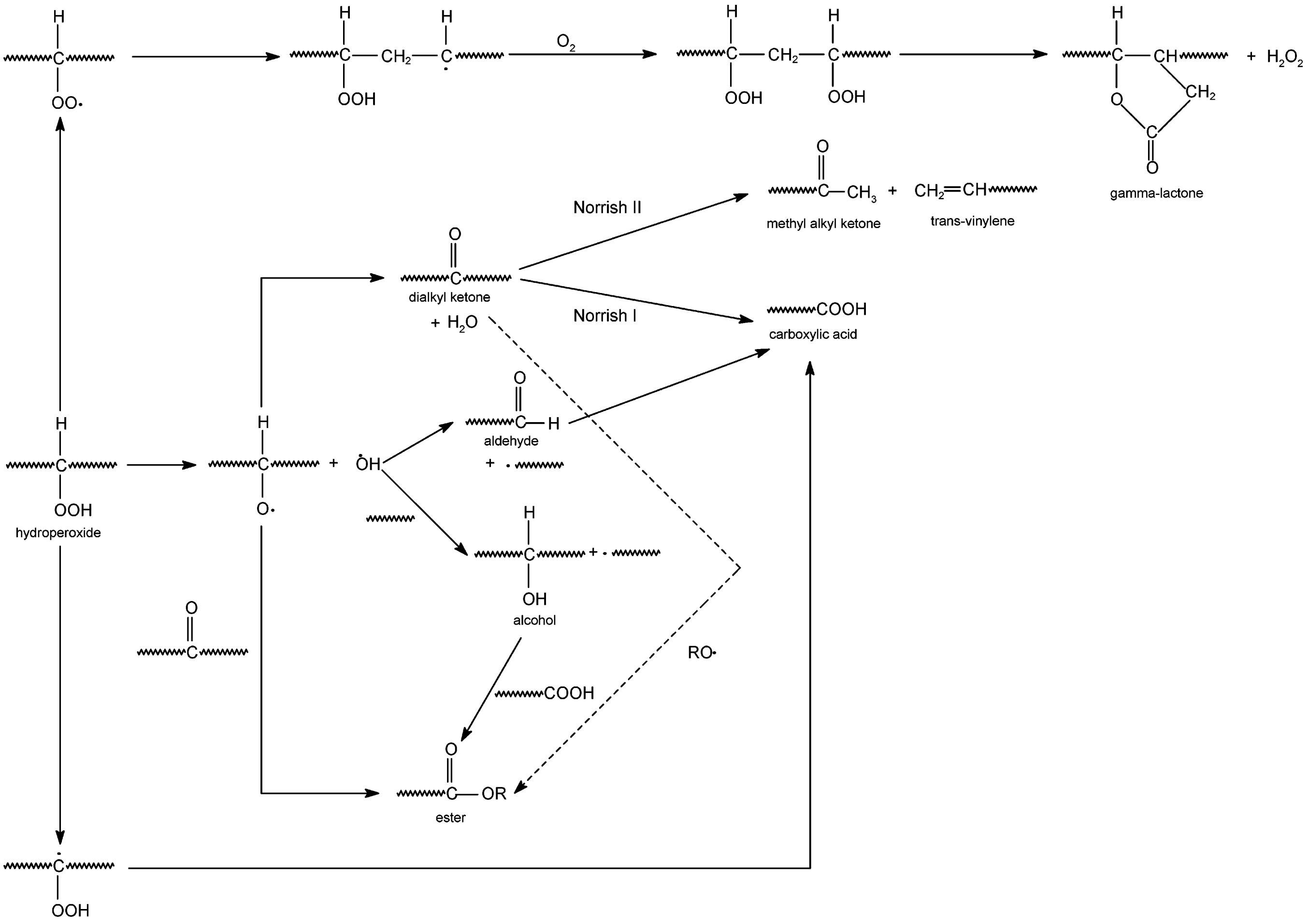
The obtained results indicate that UHMWPE and XLPE were characterized by different oxidation patterns with consequently different distributions of oxidation products. Actually, in the unworn UHMWPE acetabular cups, the mainly represented carbonyl species was constituted by ketones (Figure 5A); however, carboxylic acids, esters, and other carbonyl compounds were also quite abundant. In unworn XLPE cups, carbonyl compounds were definitely less differentiated (Figure 5B) than for unworn UHMWPE, and esters constituted by far the most represented carbonyl compound.

Upon simulator testing of UHMWPE, the distribution of the carbonyl species significantly changed (Figure 5A): The contents of esters and other carbonyl compounds increased, while the contents of carboxylic acids and methyl alkyl ketones decreased. An analogous trend for the distribution of oxidized carbonyl species was observed by Brach del Prever et al.[59] These authors have found higher ester contents on the articulating worn surface of retrieved PE tibial components than on the same area of new ones. A similar distribution has been found also by Albertsson et al.[71,72] for biotic degradation of PE in nonsterile soil.

No significant changes were observed in aldehyde content upon simulator testing of UHMWPE, contrary to observations by other authors[48,73] after in vivo service and in vitro wear simulation. However, Imlach et al.[74] have observed that aldehyde content always remained negligibly small in retrieved UHMWPE acetabular components.

Some preferential oxidation pathways can be proposed to tentatively explain the distribution of oxidized products observed in our samples. For this purpose, it must be stressed that oxidation is a complex phenomenon, different oxidation reactions can occur, and every oxidation product can derive from more than one pathway.[67,68] As an example, from Scheme 1, it can be observed that carboxylic acids can derive from aldehydes, Norrish I reaction, or β-scission of peroxy radicals. Different

Scheme 1



mechanisms have been proposed also for ester formation; according to two possible pathways, they derive from dialkyl ketones (Scheme 1). However, recent papers[54,75,76] have claimed that the condensation reaction between carboxylic acids and alcohols significantly contributes to the overall ester group production.

Our results seem to confirm this latter hypothesis. Actually, the simulator testing of UHMWPE acetabular cups caused an increase of the ester content and a simultaneous decrease of the carboxylic acid and alcohol contents. In fact, as can be seen from Table 2, the A_{3400}/A_{1300} and I_{3370}/I_{2022} ratios decreased upon wear, suggesting the presence of lower amounts of hydrogen-bonded alcohols and similar amounts of hydrogen-bonded hydroperoxides. On the other hand, wear induced no significant changes in the I_{1080}/I_{2022} ratio of UHMWPE (0.66 ± 0.03 and 0.68 ± 0.02 in unworn and worn cups, respectively). On the basis of these results and of the constancy of the dialkyl ketone content (see Scheme 1), it can be affirmed that the formation of higher concentrations of esters in worn UHMWPE was due to the occurrence of a condensation reaction between carboxylic acids and alcohols, whose contents decreased upon simulator testing. The same reaction could also explain the different distributions of carbonyl products observed in unworn UHMWPE and XLPE acetabular cups. The latter were characterized, if compared with the former, by higher amounts of esters and lower amounts of carboxylic acids (Figure 5) and alcohols (see Table 2).

Contrary to the trend observed for UHMWPE, no significant changes were observed in the distribution of carbonyl species in the XLPE cups upon simulator testing (Figure 5B). Moreover, the latter cups definitely showed less significant change in oxidation indexes upon wear testing (Table 2). This finding appears in agreement with the previously reported gravimetric and Raman findings,[26] which showed a better wear behavior for XLPE, under the adopted testing conditions. Therefore, our findings seemed to confirm the results of McKellop et al.[21,22] and Saikko et al.[23,24] rather than those of Sakoda et al.:[25] Actually, gravimetric, Raman, and IR measurements disclosed a better wear resistance for XLPE relative to conventional UHMWPE. However, for this purpose, it must be stressed that a comparison is not completely allowed, since different testing conditions have been used and differently processed materials have been tested. In particular, it must be recalled that several different procedures can be used to obtain XLPE.

5. Conclusions

The present study investigated the oxidative degradation of conventional UHMWPE and XLPE acetabular cups, tested under conditions more similar to the in vivo occurrence.

Due to the potential for artifacts caused by absorbed contaminants, the oxidation indexes were compared only after hexane extraction. Actually, XLPE cups were found to absorb definitely more serum (especially esteric compounds) than UHMWPE.

The unworn XLPE cups were characterized by lower contents of carbonyl species and hydrogen-bonded alcohols and higher contents of trans-vinylene species than unworn UHMWPE cups. The two sets of unworn acetabular cups showed different oxidation patterns with consequently different distributions of oxidation products (carbonyl species in particular).

Upon simulator testing, UHMWPE showed more significant changes in oxidation indexes and distribution of carbonyl compounds than XLPE. In agreement with the previously reported gravimetric and Raman results,[26] these findings confirmed a better wear behavior for XLPE acetabular cups.

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