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ON THE ASSESSMENT OF OXIDATIVE AND MICROSTRUCTURE CHANGES AFTER IN VIVO DEGRADATION OF HISTORICAL UHMWPE KNEE COMPONENTS BY MEANS OF VIBRATIONAL SPECTROSCOPIES AND NANOINDENTATION

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Abstract

This study reports on the suitability of different experimental techniques to evaluate chemical, microstructural and mechanical changes associated with *in vivo* oxidation encountered in historical polyethylene components. To accomplish this aim, eight traceable tibial inserts were analyzed after revision surgery. The knee bearings were gamma sterilized in air and implanted for an average of 11.5 years after a shelf life no longer than one year. Characterization of oxidation and transvinylene indexes, crystallinity, amorphous and intermediate phase fractions, along with hardness and surface modulus, were performed in transverse sections of each bearing using Fourier transform infrared spectroscopy, Raman spectroscopy, and nanoindentation, respectively. Generally, subsurface maxima in the crystallinity, oxidation index, and hardness were observed at a depth of about 1 mm in all of the bearings. The superior surfaces and anterior-posterior faces of the inserts exhibited significantly higher oxidation and greater crystallinity than the inferior side. These observations suggest that the metallic tray may limit the access of molecular oxygen to the backside of the tibial inserts. We conclude that chemical, physical, and mechanical property data confirm the occurrence of *in vivo* degradation in the long-term implanted knee components following gamma irradiation in air. Furthermore, infrared spectroscopy alone appeared to provide excellent insight into the oxidation and crystallization state of the *in vivo* oxidized polyethylene.

Keywords

ultra; high molecular weight polyethylene; *in vivo* oxidation; FTIR and Raman spectroscopies; nanoindentation; knee arthroplasty

INTRODUCTION

Since the 1980s, post-irradiation oxidation was recognized to alter the crystallinity and mechanical properties of medical grade ultra-high molecular weight polyethylene (hereafter,

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polyethylene) following gamma irradiation in air and prolonged storage in air prior to implantation^{1–5}. However, the relevance of *in vivo* oxidation was not fully appreciated at that time⁶, and mechanical embrittlement was attributed primarily to oxidation during long-term shelf storage^{7–9}. More recently, different formulations of polyethylene materials used for hip replacements have been shown to oxidize *in vivo* after gamma irradiation at different doses and in diverse environments^{10–12}. In these studies, the development of significant subsurface oxidation due to post-irradiation aging on the shelf was ruled out by collecting traceable retrieved liners implanted after a shelf life no longer than one year. Thus, *in vivo* oxidation was demonstrated to occur, resulting in regional mechanical degradation of the retrieved liners, with the greatest evidence of changes evident in unloaded regions of the bearing, such as the rim. Loaded regions of acetabular liners appeared to be afforded a certain degree of protection from oxidation, suggesting that *in vivo* degradation is not relevant to clinical performance of acetabular bearings in the first decade of implantation. Comparatively little is known about *in vivo* oxidation in total knee replacements. *In vivo* degradation may be more relevant for unicondylar and total knee replacements, as oxidative embrittlement after long shelf life has been considered a negative factor for their clinical performance^{9,13,14}.

Fourier transform Infrared spectroscopy (FTIR) is the technique of choice for the quantification of polyethylene oxidation after shelf aging, accelerated aging, or *in vivo* exposure^{15–18}. In addition to the assessment of oxidation, FTIR may provide additional information about the polymer's crystalline content, since some of the absorption peaks present in the infrared spectrum of polyethylene are sensitive to crystallinity, monoclinic content, amorphous regions, chain branching and unsaturations^{19,20}. However, some limitations have been noted about crystallinity assessments using FTIR, because the corresponding absorption peaks require complex analysis (doublets at 720/731 cm⁻¹ and 1464/1474 cm⁻¹) or may be affected by chain branching (band at 1897 cm⁻¹). On the other hand, differential scanning calorimetry (DSC) is routinely performed to analyze thermal, thermoxidative and structural properties (e.g., crystallinity) of medical polyethylene^{21–25}. However, DSC also presents certain disadvantages, as it involves the destruction of the sample, and the degree of crystallinity calculated by DSC may vary with sample weight by up to 5%²⁶.

Recent studies have highlighted the potential utility of Raman spectroscopy for characterization of polyethylene used in total joint replacements^{27–33}. The identification of polyethylene wear particles²⁷, assessment of crystallinity after sterilization and oxidation²⁸ or wear testing^{29,30}, and detection of different crystalline phases have been accomplished³¹. Pezzotti et al.³² have recently applied confocal Raman spectroscopy to medical grade polyethylene, and have developed methods to calculate an oxidation index and residual or applied strain from specific features of the polyethylene Raman spectrum^{32,33}. Despite the remarkable contributions of Raman spectroscopy, FTIR remains as the main technique to quantify oxidation, since the oxidation products show extremely weak bands in the Raman spectrum of low oxidized UHMWPE^{28,34}.

Nanoindentation has also recently been pioneered by Gilbert et al. as a characterization technique for polyethylene components^{35–37}. Gilbert and colleagues studied the effect of oxidation on mechanical properties in both one shelf-aged and one retrieved knee components³⁷. Increases in elastic modulus and hardness were confirmed to occur in both components, and, furthermore, differences between the oxidation and mechanical patterns of shelf and *in vivo* aging were noted. However, the shelf life of the knee retrieval was not reported, and oxidation of the component prior to implantation could not be ruled out.

The objective of the present study was to compare the utility of FTIR, Raman spectroscopy, and nanoindentation to characterize changes in the mechanical properties and crystallinity due to *in vivo* oxidation of polyethylene in gamma air-sterilized tibial inserts. We hypothesized

that FTIR, Raman spectroscopy, and nanoindentation would allow us to detect regional differences in the physical, chemical, and mechanical properties of the tibial inserts produced by *in vivo* oxidation. We also focused attention on microstructural characteristics, such as the degree of crystallinity, amorphous content and intermediate phase fractions, extracted from FTIR and Raman spectra of *in vivo* oxidized polyethylene.

MATERIALS AND METHODS

Knee retrievals

Eight total knee components were retrieved from revision surgery at two orthopedic institutions located in the Northeastern and Midwestern regions of the United States. Production and clinical history were traced in all cases, so that information concerning resin, processing route, shelf life, implantation time, patient gender and age, and reason for revision was available (see Table I). The tibial inserts were originally gamma sterilized in air prior to implantation and had an average shelf life of 0.6 years (range: 0.2 to 1.0 years). The inserts were implanted for, on average, 11.5 years (range: 8.3 to 14.3 years). The polyethylene components were stored in a subzero freezer (-80°C) after retrieval to minimize *ex vivo* changes before analysis.

FTIR measurements

200 micron-thick sections were microtomed transverse to the medial condyle and center of the knee retrievals (Figure 1). The sections were soaked for six hours in boiling heptane to extract adsorbed lipids, which would otherwise interfere with the FTIR analysis. Once extracted, the polyethylene sections were scanned in 0.1 mm-deep increments from the surface to a depth of 3 mm in the antero-posterior direction, or through the whole thickness in the medial condyle, central ridge and post areas using a Nicolet 6700 Fourier Transform Infrared Spectrometer with a microscope attachment (Thermo Fisher Scientific Inc., Waltham, MA). At each location, FTIR spectra were the average of 32 independent scans with a wave number resolution of 4 cm^{-1} . Oxidation Index (OI) was calculated from the carbonyl peak at 1715 cm^{-1} according to ASTM F2102. The vibrational peak at 965 cm^{-1} was used to calculate the Trans Vinylene Index (TVI) in accordance with ASTM F2381 to quantify the unsaturations (trans structures) in the polyethylene. The degree of crystallinity, %C, was also calculated from the FTIR spectra using equation (1), based on the crystalline and amorphous bands centered at 1897 cm^{-1} and 1303 cm^{-1} , respectively:

$$\%C = \frac{\frac{A_{1897}}{A_{1303}}}{\frac{A_{1897}}{A_{1303}} + 1} * 100 \quad (\text{eq. 1})$$

where A_{1897} and A_{1303} represent the intensity of the corresponding crystalline and amorphous peaks in the infrared spectra (see figure 9 in reference ³⁸).

Raman spectroscopy measurements

Raman spectroscopy was performed at room temperature using a Raman Microspectrometer (RM1000 VIS, Renishaw Inc., Chicago, IL). A short working distance objective (50x), and the green excitation line (514 nm) were used, while the initial laser power was adjusted to 25 mW to ensure no heating or degradation effects occurred on the surface sample. Working with this configuration, the laser spot size on the sample was approximately 2 microns. The backscattered light from the sample was dispersed with an 1800 mm^{-1} grating on the high sensitivity ultra-low noise RenCam CCD detector, providing a spectral resolution of 2 cm^{-1} . To achieve a signal-to-noise ratio as low as possible, integration times were relatively long ($\sim 420\text{ s}$), so that the final spectrum were the average of seven successive accumulations.

Moreover, some of the most highly oxidized regions required a preliminary bleaching 3 min long, to overcome a considerably high background (fluorescence) and to provide an enhanced signal. As the experimental time needed to perform a whole in-depth profile of Raman spectra was considerably longer than in FTIR measurements, we probed only three regions, specifically surface, subsurface and bulk areas, for each of the retrieved implants. These areas were chosen based on the OI profiles, so that the region where the OI maximum appeared was included in one of the Raman probed regions. At least two different measurements were performed on points 50 microns away from each other in every region.

The so-called fingerprint region of the Raman spectra, between 900 cm^{-1} and 1600 cm^{-1} , is normally divided into three subregions^{39–44}: the C-C stretching bands between 1000 and 1200 cm^{-1} ; the $-\text{CH}_2-$ twisting vibrations centered at 1300 cm^{-1} ; and the $-\text{CH}_2-$ bending modes between 1400 and 1480 cm^{-1} . As Strobl and Hagedorn proposed³⁹, the 1415 cm^{-1} bending band is generally attributed to the orthorhombic crystallinity phase, and therefore its content can be calculated as the intensity of this band with respect the integral intensity of the twisting vibrations bands^{31,39}, which are the appropriate internal standard band group for polyethylene:

$$\alpha_c = \frac{I_{1415}}{(I_{1295+1305+1269}) \times 0.46} \quad (\text{eq. 2})$$

where α_c is the orthorhombic phase content, whereas I_{1415} and $I_{1295+1305+1269}$ represent the intensity of the band at 1415 cm^{-1} , and the integral intensity corresponding to the twisting vibrations in the Raman spectrum of polyethylene, respectively.

The broad bands at 1305 cm^{-1} and at 1080 cm^{-1} in the twisting and stretching regions respectively are associated with the presence of the amorphous phase and its content, α_a , is likewise given by the following expressions³⁹:

$$\alpha_a = \frac{I_{1080}}{(I_{1295+1305+1269}) \times 0.79} \quad (\text{eq. 3})$$

$$\alpha_a = \frac{I_{1305}}{(I_{1295+1305+1269})} \quad (\text{eq. 4})$$

where I_{1080} and I_{1305} are the intensities corresponding to the aforementioned bands of the Raman spectrum of polyethylene. Results obtained from equation 3 will not be presented due to reasons explained in the next sections.

Finally, the fraction of the intermediate phase, α_b , which is thought to be in an anisotropic disordered state and is usually referred to as the third phase, can be expressed as³⁹:

$$\alpha_b = 1 - (\alpha_c + \alpha_a) \quad (\text{eq. 5})$$

Note that the intensity of the peak located at 1295 cm^{-1} , I_{1295} , can be used to estimate the overall degree of crystallinity in contrast to the orthorhombic or core crystallinity provided by equation 3. Thus, the overall crystallinity fraction, α_d , is calculated by means of the following equation^{31,32}:

$$\alpha_d = \frac{I_{1295}}{(I_{1295} + I_{1305} + I_{1269})} \quad (\text{eq. 6})$$

Bearing the previous expressions in mind, Raman spectra were processed using commercially available spectroscopy software GRAMS/AI 8.0 (Thermo Fisher Scientific; Woburn, MA), which after a curve fitting procedure provided the positions, widths, heights and intensities of the relevant vibrational bands. Following recommendations reported by Meier⁴⁵, the spectral envelope and the background were fit simultaneously, and Voigt band shapes (that is the convolution or product of a Gaussian and a Lorentzian profiles) were used to account for the instrumental broadening suffered by Raman spectra. The calculated intensities were brought into the corresponding equations to attain the different phase contents in the polymer. Mean values and standard deviations of these parameters were calculated for all probed regions.

Nanoindentation and mechanical properties

Nanoindentation experiments were performed with use of a XP Nanoindenter (MTS Corporation, Oak Ridge, TN). Experimental conditions similar to those reported by Gilbert et al.^{35–37} were chosen. Thus, a 13.5 micron-radius hemispherical indenter was displaced up to 4.5 microns into the microtomed cross-sections, while load and displacement data were collected. Sixteen to sixty indents, separated by 200 microns, were conducted depending on the region tested. Maximum load, $L_{\max}$, the maximum indentation depth, $h_{\max}$, and the residual indentation depth, h_r , were extracted from the raw load-displacement data, allowing the further calculation of mechanical parameters. Thus, hardness, H , and surface modulus, E , were obtained applying the method by Oliver and Pharr⁴⁶, and the Sneddon equation⁴⁷ respectively. The expressions used were:

$$H = \frac{L_{\max}}{A} = \frac{L_{\max}}{\pi \left(\frac{h_{\max} + h_r}{2} \right) \left[2R - \left(\frac{h_{\max} + h_r}{2} \right) \right]} \quad (\text{eq. 7})$$

$$E = \frac{(1 - \nu^2) \sqrt{\pi}}{2 \sqrt{A}} \frac{dl}{dx} = \frac{(1 - \nu^2) \sqrt{\pi}}{2 \sqrt{A}} \frac{2L_{\max}}{h_{\max} + h_r} \quad (\text{eq. 8})$$

where A is the projected contact area, R is the tip radius, and dl/dx is the unloading slope.

Statistical analysis

Regional differences in FTIR, Raman and nanoindentation results were evaluated with paired t tests. In addition, Student's t tests were used to assess differences between the average FTIR crystallinity, Raman orthorhombic content and Raman overall crystallinity maxima by region. All statistical tests ($p < 0.05$ for significance) were performed using JMP software (SAS Institute, Cary, NC).

RESULTS

Substantial oxidation, elevated transvinylene content, as well as increased crystallinity were generally observed, especially for the long-term implanted knee components. Typically, the property profiles exhibited a maximum below the surface at about 1 mm (Fig. 2). Furthermore, oxidation, unsaturations and crystallinity were also observed to be greater in the superior face than in the backside of the tibial inserts ($p = 0.02$, $p = 0.03$ and $p = 0.004$, respectively). As

shown in Table II, the maximum oxidation index was significantly greater in the medial anterior and medial posterior regions compared to the medial condyle ($p = 0.04$ and $p = 0.01$, respectively) and the central ridge ($p = 0.03$ and $p = 0.01$, respectively). Similarly, unsaturations levels were high in all the regions tested, and the medial condyle region had the lowest TVI maxima ($p < 0.05$). The medial anterior-posterior faces had significantly higher crystallinity than the medial condyle ($p = 0.02$ and $p = 0.01$ respectively) and the central ridge ($p = 0.03$, and $p = 0.02$).

Raman spectra also confirmed regional variation in the crystalline and amorphous content of the retrieved knee components. Overall crystallinity and orthorhombic content maxima were typically located at the subsurface and matched oxidation index maxima, whereas amorphous and intermediate fractions were lower at these locations. Again, all phase fractions measured were significantly higher at the superior face respect to the backside of the components ($p = 0.04$, $p = 0.004$, $p = 0.002$ and $p = 0.005$ for orthorhombic, overall crystallinity, amorphous and intermediate phase contents, respectively). As an example, Figure 3 shows the orthorhombic, intermediate and amorphous phase fractions results obtained from Raman and FTIR spectra in the medial condyle region of knee CW184. Orthorhombic content maxima had higher mean values than mean crystallinity maxima obtained from FTIR in the medial condyle, central ridge and center posterior regions (see Table III). Regarding regional variation in the antero-posterior direction, average maxima orthorhombic contents were higher in the medial plane, and they were significantly greater at the medial posterior region compared to the remaining regions (p values within 0.01–0.03) except for the medial condyle. On the other hand, overall crystallinity maxima were significantly higher than maxima FTIR crystallinities in the bearing surface, central ridge and center posterior regions, but not than orthorhombic content maxima (Table III). In addition, there were no significant differences attending to regional variation in the antero-posterior direction. Minima amorphous contents were observed to vary by 50%, but the mean values were close to 0.2. Finally, mean minima intermediate phase contents usually ranged from 10 to 20%, but they were close to or even below zero in regions with high oxidation indexes (~ 7). These anomalous results will be discussed later, since they compromise the validity of the three-phase Raman model in the case of highly oxidized polyethylene. There were no significant regional variations in the antero-posterior direction in minima amorphous phase fractions, but the medial posterior region had minima intermediate phase fractions significantly lower than the medial anterior ($p = 0.002$) and center anterior ($p = 0.004$) regions.

Nanoindentation testing confirmed retrieved knee bearings underwent changes in elastic modulus and hardness *in vivo*. Generally, elastic modulus and hardness profiles exhibited subsurface maxima, consistent with results of vibrational spectroscopy (Fig. 4). However, we were unable to detect significant differences in the modulus or hardness between the superior face and the backside ($p = 0.3$). On the other hand, the modulus and hardness were lower and less variable in the medial condyle region particularly with respect to the antero-posterior faces in the medial plane ($p = 0.02$ and $p = 0.01$ for modulus and hardness respectively). The variability was higher in the central cross-section, but the mean maxima were close to each other and to the ones in the medial cross-section.

DISCUSSION

The results of this study support our hypothesis that historical, gamma air-sterilized polyethylene total knee replacement components undergo region-specific oxidative degradation *in vivo*. Furthermore, the results derived from infrared and Raman spectra suggest the antero-posterior and superior surfaces of the knee bearings were more severely degraded than the backside. This fact supports the additional hypothesis that the extent of *in vivo* degradation depends on the access to molecular oxygen (O_2) dissolved in body fluids. Recently,

our research group reported a similar result for acetabular liners^{10,12}, in which the femoral head appeared to limit the *in vivo* oxidation at the bearing surface. In this sense, the tibial tray may play a similar role, isolating the inferior surface of the tibial insert from oxygen. Moreover, some of the antero-posterior faces were significantly more degraded than the bearing surfaces, indicating that the femoral condyle may be protecting the superior surface from access of oxygen to some extent. These findings would also suggest that the femoral condyle is not as effective as the tibial tray in preventing oxygen dissolved in body fluids to reach the polyethylene surface, probably due to the characteristic lack of conformity at the articulating surface of knee components.

Although the metal components may play a protective role for the polymeric component, the oxidation rate of irradiated polyethylene depends on the amount of free radicals, $[R^\bullet]$, present in the polymer, the concentration of available oxygen, $[O_2]$, and the temperature and time of exposure, according to the classic studies by Costa and coworkers^{5,48,49}. In addition, hydroperoxides take part in the oxidation cycle as well, leading to the final products of oxidation and potentially accelerating the kinetics of oxidation by thermal decomposition at temperatures close to 37 °C. The previous factors depend, in turn, on the irradiation conditions, namely, dose, dose rate, temperature, and environment, and the oxygen availability before, during and after irradiation^{50,51}. Thus, the oxidation products-depth distributions might vary depending on the characteristics of the irradiation process as reported by Bracco et al⁵⁰. In particular, high hydroperoxide and ketone concentrations in the subsurface of gamma sterilized polyethylene components have been attributed to large oxygen availability, high irradiation temperature (~ 50 °C) and low dose rates⁵⁰. Nevertheless, the typical subsurface oxidation maximum usually shown by shelf-aged implants had been explained before as a consequence of the subsurface peak in the absorbed dose originated by the Kerma effect⁵². Regardless of the mechanism, the fact that the main oxidation occurs below the surface in the current *in vivo* aged knee components supports that the mechanism is related to oxygen diffusion, as occurs in shelf aging and in real-time aging in an aqueous environment of gamma-irradiated polyethylene components⁵³. Other pre and post-implantation factors, such as resin type, additives, shelf life, implantation time and patient variables may influence the observed variability of the oxidative, microstructural and mechanical degradation. For example, 1900H resin has no added calcium stearate and lower molecular weight than GUR 415; these differences have been cited as reasons for why it may oxidize more slowly^{54,55}. In this study, we evaluated a small number of explanted knee components, and, therefore, further research is needed to support our hypothesis regarding oxidation and access to oxygen *in vivo*.

The FTIR results provided evidence of *in vivo* oxidation-induced crystallinity changes in the tibial components, as crystallinity profiles corresponded closely to the measured oxidation profiles (Fig. 2). However, the reliability of quantitative crystalline characterization from the infrared band at 1897 cm^{-1} has been considered to be questionable, as it is sensitive to the chemical structure of the polyethylene, specifically the presence of chain branching³⁸. In spite of this limitation, it is remarkable that the variation pattern seems to be well identified by the current FTIR spectra. An assessment of the chain branching and density would be needed to validate a quantitative estimation of crystallinity using infrared spectroscopy.

The information extracted from Raman spectra corroborates the trend found for crystallinity from infrared spectra. In addition, it provides a deeper insight into the microstructural evolution provoked by the *in vivo* oxidation process. In particular, the findings of this study support that the oxidation process of historical (gamma radiation sterilized in air) UHMWPE provokes a noticeable increase in overall crystallinity and orthorhombic contents, as well as a decrease in the amorphous and intermediate phase fractions of the polymer after long-term *in vivo* implantation. The cause of these changes lies again in the substantial chain scission induced by the high extent of oxidation, which allows secondary crystallization to start probably both

at the crystal interfaces and the amorphous regions^{22,56,57}. These phenomena would result in the thickening of the original crystals, and the creation of smaller crystallites or partial recrystallization in the amorphous region, with the concomitant changes in crystalline and amorphous regions. Other authors^{28–32} have reported increased crystalline content both in mechanically stressed (wear tested) and in long-term retrieved UHMWPE liners as measured by Raman spectroscopy. However, some of these studies assessed only surface locations of the acetabular cups^{28,31}, or they were limited to a few microns (50 microns) near the free surface³². It should be noted that the conventional Raman signal reaches its maximum intensity at a depth of about 3 microns in UHMWPE as measured by Zerbi⁵⁸, so the Raman spectrum corresponds to the very surface of the sample. This is the reason why sectioning of the implants is needed to characterize the through-thickness effects of *in vivo* oxidation on UHMWPE components.

Despite the good agreement between the current crystallinity results, Raman orthorhombic crystallinities should be considered cautiously. Changes in density were found to affect this parameter more in comparison to the crystallinity values characterized by DSC or WAXS⁴³. Furthermore, the anomalous intermediate phase contents raise questions regarding the three-phase Raman model. The characterization of a third phase in semicrystalline homopolymers by Raman spectroscopy has been controversial^{39,59,60}. In particular, Naylor et al.⁵⁹ questioned previous assessments of the amorphous region from the broad band at 1080 cm⁻¹, and therefore their associated intermediate contents, because they were based on excessively simplified curve fittings, but otherwise problematic. Moreover, they found that the assessment of the amorphous fraction from the band at 1305 cm⁻¹ gave rise to third phase fractions results zero or even negative in the case of HDPEs, and only significantly different from zero for low-density polyethylenes. As the present study confirms similar results for highly oxidized polyethylene, the three-phase Raman model may not be appropriate in that case. Nevertheless, the current intermediate content results may indicate the evolution from an initially mildly oxidized polyethylene with thicker interfaces (third phase contents ~ 20%) to a highly crystalline polyethylene free of interfacial material (third phase contents ≤ 0) via the aforementioned oxidative chain scission and recrystallization phenomena. After long-term oxidation, the region with the highest concentration of free radicals would presumably suffer the highest number of chain scissions events and develop this highly crystalline material similar to HDPE. Typically, this region is the subsurface of the implant, but its location will depend on the irradiation dose-depth profile, exposure to oxygen and irradiation conditions^{50,61}.

Nanoindentation testing confirmed the evolution of a higher-modulus and harder material after long-term *in vivo* oxidation, in agreement with previous findings for polyethylene aged in different conditions^{37,62}. The elastic modulus and hardness with depth profiles correlated quite well with the oxidation profiles, as Wernlé and Gilbert found previously using a microindentation apparatus³⁷. However, the nanoindentation technique appeared not to be sensitive enough to discriminate a difference in mechanical degradation between the superior and inferior faces of the components in this study. This may be due to the lack of correlation between mechanical properties and oxidation for samples thinner than 300 microns, as established by Wernlé and Gilbert³⁷. Also, the nanoindentation technique is more sensitive to defects on the surface of a sample than microindentation, and this may represent a limitation in the mechanical measurements. From a microstructural point of view, chain scission, recrystallization phenomena and incorporation of oxygen atoms into the molecular chains would be the underlying mechanisms that convert UHMWPE into a harder and stiffer material.

This study was limited to knee components made of either GUR 415 or 1900H and subjected to a 25–40 kGy dose of gamma sterilization in air. We did not have access to control or shortly implanted knee bearings fabricated with these resins following gamma irradiation in air, as this sterilization practice was discontinued in the United States during the 1990s. Thus, it was not

possible to assess oxidation, microstructure and mechanical degradation rates *in vivo*. Furthermore, the results found in this study may not necessarily be extrapolated to contemporary polyethylene resins sterilized in a gamma-inert environment or to highly crosslinked formulations processed with high gamma radiation doses. Finally, this study was not designed to investigate how *in vivo* degradation changes correlate with the mechanisms of fatigue wear prevalent in total knee replacements. Further research is needed to evaluate the potential influence of oxidative and microstructure degradation of historical and contemporary polyethylene components on clinical performance of knee prostheses.

CONCLUSIONS

In summary, this study demonstrates the complementary utility of infrared and Raman spectroscopies and nanoindentation to evaluate oxidative, microstructural and mechanical changes in historical polyethylene, with the advantage of preserving the sections obtained from the knee components. However, it was apparent that infrared spectroscopy alone is sufficient to provide key information about the degradation state, and its regional variations, in polyethylene tibial inserts following long-term implantation. We observed greater degradation at the anterior-posterior and the superior surfaces of the polyethylene tibial knee inserts as compared to the backside. These findings may indicate that the tibial tray may limit the access of molecular oxygen dissolved in body fluids to the inferior surface of the tibial inserts.

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Figure 1. Schematic of the locations tested in sagittal cross-sections of the medial condyle and the center of the retrieved tibial inserts.

Figure 2.

Typical oxidation (□), transvinyene index (●), and crystallinity percentage (▲) versus depth profiles for a retrieved knee bearing. Oxidation, TVI and crystallinity maxima are generally found at about 1 mm deep.

Figure 3.
 Orthorhombic, amorphous, and intermediate phase fractions as obtained from Raman spectra
 for the medial condyle region of knee CW184.

Figure 4.

Typical elastic modulus (●) versus depth profile as measured by nanoindentation. Peak oxidation coincides with peak mechanical properties for the retrieved knees.

Table 1
Summary of clinical data for eight retrieved knee components sterilized by gamma irradiation in air.

Knee Component	Gender	Age at revision(y)	Diagnosis at revision	Resin	Processing Route	Implant Design	Shelf-Life(y)	Implantation Time(y)
RI10	F	54	Aseptic Loosening	GUR 415	Ram Extruded	Miller-Gallante II	0.2	8.3
RI61	F	71	Aseptic Loosening	GUR 415	Ram Extruded	Insall-Burstein II	1.0	8.9
RI99	M	77	Polyethylene Wear, Instability	1900H	Molded Shape	AGC	0.9	14.3
RI156	F	73	Aseptic Loosening	GUR 415	Ram Extruded	Insall-Burstein II	0.4	11.0
CW184	F	60	Polyethylene Wear, Aseptic Loosening	GUR 415	Ram Extruded	Miller-Gallante II	0.7	10.1
CW281	M	84	Aseptic Loosening	1900H	Molded Shape	Miller-Gallante I	0.3	12.9
CW303	F	79	Failed patella, metallosis	1900H	Molded Shape	Miller-Gallante I	0.7	13.6
CW304	F	69	Infection	GUR 415	Ram Extruded	Miller-Gallante II	0.8	13.0

Table II
ASTM oxidation and transvinylene index maxima, average $\pm$ standard deviation, by region as obtained from FTIR spectroscopy for eight retrieved knee components.

	Medial Anterior	Medial Condyle	Medial Posterior	Center Anterior	Central Ridge	Post	Center Posterior
OI	3.5 $\pm$ 2.7 *	1.9 $\pm$ 1.3	4.0 $\pm$ 1.7 *	2.7 $\pm$ 2.6	2.1 $\pm$ 1.8	0.8 $\pm$ 0.7	3.0 $\pm$ 2.7
TVI	0.04 $\pm$ 0.02	0.02 $\pm$ 0.01 *	0.04 $\pm$ 0.03	0.03 $\pm$ 0.01	0.03 $\pm$ 0.02	0.03 $\pm$ 0.01	0.03 $\pm$ 0.02

* Significant difference with respect to the regions indicated in the text (Paired t-test)

Table III

Crystallinity maxima, average $\pm$ standard deviation, by region as obtained from FTIR and Raman spectra for eight retrieved knee components.

	Medial Anterior	Medial Condyle	Medial Posterior	Center Anterior	Central Ridge	Post	Center Posterior
FTIR Crystallinity	0.64 $\pm$ 0.17	0.55 $\pm$ 0.10	0.70 $\pm$ 0.20	0.62 $\pm$ 0.16	0.55 $\pm$ 0.09	0.53 $\pm$ 0.14	0.59 $\pm$ 0.11
Raman Orthorhombic Crystallinity	0.68 $\pm$ 0.16	0.74 $\pm$ 0.14*	0.79 $\pm$ 0.07	0.68 $\pm$ 0.16	0.67 $\pm$ 0.14*	0.53 $\pm$ 0.08	0.69 $\pm$ 0.09*
Raman Overall Crystallinity	0.73 $\pm$ 0.07	0.71 $\pm$ 0.07*	0.74 $\pm$ 0.06	0.73 $\pm$ 0.08	0.71 $\pm$ 0.04*	0.71 $\pm$ 0.01	0.73 $\pm$ 0.04*

* Significant difference with respect to FTIR crystallinity in the corresponding region (Student's t test).