A Novel Assessment of Ultra-high Molecular Weight Polyethylene Oxidation for Orthopedic Applications

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INTRODUCTION: Polyethylene oxidation has been a concern for the arthroplasty field. After iterative developments of polyethylene (PE) biomaterials to address wear and related osteolysis concerns, oxidation and resulting PE embrittlement-driven wear is seen in retrieved components[1]. Fourier-transform infrared (FTIR) spectroscopy is the standard technique used to measure polyethylene oxidation based on the carbonyl absorbances centered near 1720 - 1740 cm^{-1} ratio to the 1370 cm^{-1} polyethylene methyl absorbance, as demonstrated in previous studies[2,3]. FTIR as a technique is diffraction-limited and thus the maximum spatial resolution is wavelength dependent and on the order of ~ 6 µm. Further, sample preparation requires microtoming thin sections. Optical photothermal infrared (O-PTIR) spectroscopy is a recent development in the spectroscopy field that provides a higher spatial resolution of 500 nm, and with non-contact reflection-based detection mode, can accommodate thicker samples for assessment. As implants often oxidize very unevenly (e.g. along stress concentrations, nearer to the surfaces), sub-micron oxidation mapping could uncover localized regions of degradation that would yield insight into oxidation mechanisms. This study aims to assess O-PTIR as an alternative method to FTIR for ultra-high molecular weight PE (UHMWPE) oxidation evaluation based on the carbonyl peak ratio method.

METHODS: A retrieved compression-molded UHMWPE patellar component (PC) from our IRB-approved institutional implant retrieval system was used for this study. The sample was stored in a -4° freezer within 6 months of retrieval. Primary surgery date is not available. Two types of samples were prepared: a 5 mm thick section made using a razor blade, and a 200 µm thick microtomed section (termed "thin section") from the region adjacent to the thick section. Care was taken to select a component and a region on the component that did not exhibit delamination, which results from oxidative embrittlement[4]. Both samples were boiled in 500 mL n-heptane for 6 hours to dissolve any penetrating lipids, as is standard for these analyses[2]. FTIR spectral data were collected in transmittance mode as line scans ~ 6.5 – 7 mm in length from the PC thin section starting near the articular surface through to the backside at 6.25 micron pixel resolution with a Perkin Elmer Spotlight 400 imaging spectrometer equipped with a broadband source. O-PTIR data were collected as line scans on the same thin section from the same regions for comparison to FTIR data. The O-PTIR data were collected using a mIRage instrument (Photothermal Spectroscopy Corp.) at 500 nm spatial resolution equipped with quantum cascade lasers (QCL) infrared sources. O-PTIR line scan data were also collected from the thick 5mm section of the PC in regions that paralleled those collected on the thin section. It was not possible to collect FTIR transmittance data from the thick section. As the O-PTIR laser source is inherently polarized, data were also acquired from 500-micron line scans starting at the articular surface in the thin and thick samples in perpendicular orientations (along X and Y stage axes) to assess whether orientation impacts spectral parameters. Spectral data were processed in Isys spectral imaging software (Malvern Instruments). The line scans (N = 3 per section/technique) were processed with a smoothing filter and integration of the areas of the carbonyl absorbance centered near 1730 cm^{-1} and the methyl peak centered at 1370 cm^{-1} followed by ratioing of those peaks to obtain the oxidation index (OI). Data were compared based on trends in the OI values in the line scans.

RESULTS: The component was revised for right knee osteolysis confirmed. The overall trend in the oxidation index (OI) obtained from the thin section is qualitatively similar for the FTIR and O-PTIR data (Figure 1). The higher OI values are in the same location in both data sets, but the magnitude of the values differs. In the FTIR data, the OI values range from ~0.02 and ~0.32, with little scatter in the data. In the O-PTIR data, the OI values range from ~0.2 to over 2.0, with more scatter in the data. Nevertheless, a significant correlation was found for each data set (Figure 1). The O-PTIR data collected in two orientations from the thin and thick sections also demonstrate similar trends (Figure 2), indicating lack of a laser orientation effect.

DISCUSSION: These data demonstrate that O-PTIR can be used to assess oxidation information from UHMWPE implants, with values that parallel those using the FTIR approach. The additional scatter in the O-PTIR data compared to the FTIR data arises from the higher sub-micron resolution, showing a more granular view of the oxidation variation within the implant material, which is smoothed out in the FTIR data due to the larger data collection regions. The absolute values of the O-PTIR oxidation indices are ~ 10-fold higher than the FTIR OI values, a difference which arises largely from a larger oxidation peak absorbance as opposed to smaller methyl absorbance (data not shown). Obtaining a scaling parameter for the O-PTIR carbonyl absorbance to enable standardization to the FTIR carbonyl absorbance is feasible and would enable a standard implementation of this approach. Lastly, we demonstrated that for these samples, a polarized laser source does not impact the OI values.

SIGNIFICANCE/CLINICAL RELEVANCE: Support is provided for an alternate approach to FTIR, O-PTIR spectroscopy, for the assessment of oxidation index of UHMWPE implants at high spatial resolution. In combination with other approaches such as mechanical testing and material analysis, insight into oxidation initiation and spatial correlation with specific microstructural features could be elucidated.

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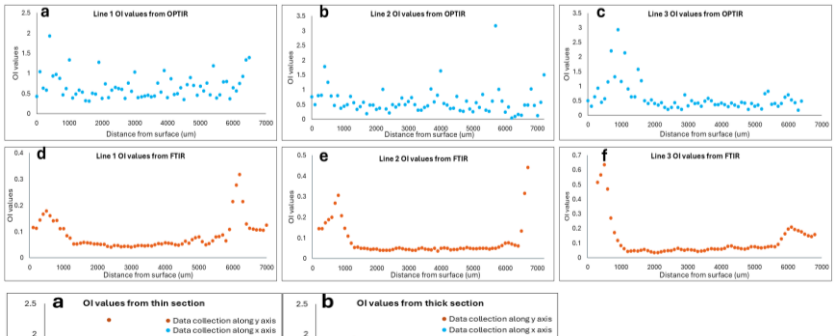

Figure 1: Oxidation index (OI) profiles from three-line scans of a thin section measured by O-PTIR (a-c) and FTIR (d-f), showing spatial variation with distance from the articular surface (0 microns).Some data is cut off in the FTIR scan in panel F as it did not align precisely with the O-PTIR scan of the same line in panel C.

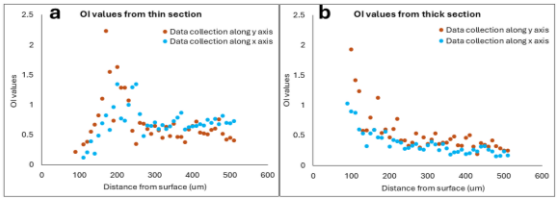

Figure 2: Oxidation index (OI) profiles from the a. thin section and b. thick section collected by O-PTIR, showing polarization effect on OI values variation with distance from the surface. Some data is cut off in the scan from the thick section in panel b as it did not align precisely with the scan of the thin section in panel a.