Correlation between crystallinity by Raman spectroscopy and oxidation index by Fourier-transform infrared spectroscopy in different types of unused polyethylene tibial inserts.

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INTRODUCTION: Raman spectroscopy is a non-destructive technique that provides structural information of materials and has been widely applied in polymer research [1]. Previous reports suggested a possible link between oxidative degradation and increased crystallinity in conventional ultra-high-molecular-weight polyethylene (UHMWPE) and first-generation highly cross-linked polyethylene (HXLPE), but this has not been experimentally verified [2, 3]. Oxidative degradation, which reduces the mechanical properties of polyethylene, has traditionally been assessed by Fourier-transform infrared spectroscopy (FT-IR). However, FT-IR requires sample sectioning and has limitations in retrieval analysis. Raman spectroscopy, in contrast, allows non-destructive measurement of crystallinity, which may reflect structural changes caused by oxidation. We hypothesized that crystallinity measured by Raman spectroscopy would strongly correlate with oxidation index obtained by FT-IR. The aim of this study was to experimentally clarify the relationship between crystallinity and oxidation index in three types of polyethylene with different processing methods.

METHODS: Three types of unused tibial inserts with different manufacturing processes were analyzed: conventional UHMWPE (GUR1050, gamma sterilized at 25–40 kGy), first-generation HXLPE (GUR1050, 65 kGy electron beam irradiated, remelted, gas plasma sterilized), and second-generation HXLPE (GUR1020, blended with 1000 ppm vitamin E, irradiated at >100 kGy under elevated temperature, EtO sterilized). From each material, slice samples (200 µm, 10 × 10 mm) were cut with a microtome. Five slices parallel to the articulating surface were obtained from each sample. Accelerated aging was performed in an air oven at 80 °C for 0, 3, 7, 14, and 21 days to induce progressive oxidative degradation [4]. Raman spectroscopy was performed using a 532 nm laser with adjustable power, a 10× objective lens, and an effective spot diameter of ~60 µm. The central 600 × 1000 µm region of each slice was scanned along 12 lines at 50 µm intervals. Spectra were analyzed by Gaussian fitting, and crystallinity was calculated from the intensity ratio of the 1296 and 1305 cm^{-1} bands [5, 6]. Mean values from each line were used as the representative crystallinity. FT-IR analysis was conducted with a imaging system using 200 × 200 µm spots across the same 600 × 1000 µm region, measured at 200 µm intervals along three lines. Oxidation index was calculated according to ASTM F2102 from the ratio of the carbonyl peak (1720 cm^{-1}) to the C–H bending peak (1370 cm^{-1}) [4]. The mean of three lines was taken as the representative oxidation index. This combined protocol enabled direct comparison of oxidation and crystallinity under controlled conditions, establishing the basis for correlation analysis.

RESULTS SECTION: In conventional UHMWPE, both crystallinity and oxidation index increased progressively with the duration of the accelerated aging test. After 21 days of aging, crystallinity reached a mean value of 95%, while the oxidation index rose to an average of 7.0. A significant positive correlation was observed between crystallinity and oxidation index ($R^2 = 0.998$, $p < 0.001$) (Figure 1). In first-generation HXLPE, no substantial increase in crystallinity or oxidation index was observed in the untreated, 3-day, or 7-day samples. However, both parameters increased in the 14-day samples, and after 21 days of aging, crystallinity reached a mean of 90% and the oxidation index increased to an average of 5.0. As with conventional UHMWPE, crystallinity and oxidation index were highly correlated ($R^2 = 0.999$, $p < 0.001$) (Figure 2). In second-generation HXLPE, no detectable increase in crystallinity or oxidation index was observed at any time point during the 21-day aging test, demonstrating superior oxidative stability compared with conventional UHMWPE and first-generation HXLPE (Figure 3).

DISCUSSION: The major finding of this study was the strong correlation between crystallinity measured by Raman spectroscopy and oxidation index evaluated by FT-IR. This is the first experimental evidence suggesting that crystallinity can serve as an alternative marker to the oxidation index, the current gold standard for assessing polyethylene degradation. The ability to evaluate crystallinity by Raman spectroscopy provides a non-contact and non-destructive approach for analyzing material degradation. While conventional UHMWPE and first-generation HXLPE showed progressive increases in both crystallinity and oxidation index with accelerated aging, second-generation HXLPE with vitamin E exhibited no detectable changes, confirming the antioxidative effect of vitamin E and supporting its clinical durability. This indicates that Raman spectroscopy may also be useful for evaluating the oxidative resistance of newly developed polyethylene materials. Furthermore, in retrieval analysis, crystallinity values could be used to estimate oxidation index based on the regression model derived from unused samples. This finding highlights the potential application of Raman spectroscopy for non-destructive evaluation of retrieved implants and long-term monitoring of clinical performance.

SIGNIFICANCE/CLINICAL RELEVANCE: Raman spectroscopy provides a non-destructive and clinically applicable method for evaluating oxidative degradation of polyethylene. Crystallinity, as measured by Raman analysis, may serve as an alternative marker for oxidation, enabling the monitoring of implant longevity and the evaluation of new antioxidant-stabilized materials. This technique has strong potential to complement or replace FT-IR in retrieval studies and implant research.

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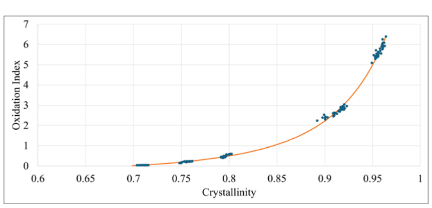

Figure 1. Correlation between crystallinity and oxidation index with regression curve obtained from accelerated aging samples of conventional UHMWPE evaluated up to 21 days of oxidative degradation testing (0, 3, 7, 14, and 21 days).

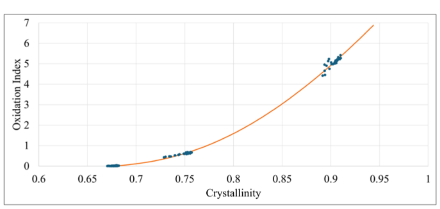

Figure 2. Correlation between crystallinity and oxidation index with regression curve obtained from accelerated aging samples of first-generation HXLPE evaluated up to 21 days of oxidative degradation testing (0, 3, 7, 14, and 21 days).

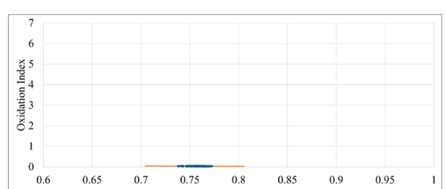

Figure 3. Correlation between crystallinity and oxidation index with regression curve obtained from accelerated aging samples of second-generation HXLPE evaluated up to 21 days of oxidative degradation testing (0, 3, 7, 14, and 21 days).