IN VIVO OXIDATION IN TKA COMPONENTS:  
A SPECTROSCOPIC AND NANOINDENTATION STUDY

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INTRODUCTION

• *In vivo* oxidation confirmed for traceable THA polyethylene components. This phenomenon may be more relevant in TKA.

• FTIR is commonly used to characterize oxidation in medical polyethylene.

• Raman spectroscopy and Nanoindentation provide microstructure and mechanical information, respectively.
OBJECTIVE AND HYPOTHESIS

• Global
  – Compare the utility of FTIR, Raman spc., and nanoindentation to characterize mechanical and microstructure changes due to in vivo oxidation of historical TKA polyethylene tibial inserts.

• Secondary
  – These techniques would allow us to detect regional differences in the physical, chemical, and mechanical properties.
Knee Retrievals Information (n = 8)

- Processing route & resin:
  - Molded 1900H/Extruded GUR 415

- Implant designs:
  - Miller-Gallante I and II, Insall-Burstein II, AGC

- **Gamma-air sterilization**

- **Average Shelf Life:** 0.6 years (0.2-1.0 y)

- **Average Implantation Time:** 11.5 years (8.3-13.0 y)

Clinical information

- Gender: 6F/2M

- Age at revision: 54-84 years

- Diagnosis at revision:
  - Loosening, PE Wear, Instability, Failed Patella, Metallosis
FTIR spectroscopy

• Method
  - 200 mm thick sections:
    • Medial Condyle
    • Unloaded central spine
  - Boiled in heptane for 6 hours
  - Scanned at 0.1 mm increments
  - Max OI (ASTM F2102-01)
  - Max TVI (ASTM F2381)

\[
\% C = \frac{A_{1897}}{A_{1303}} + 1
\]
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  - **Max OI (ASTM F2102-01)**
  - **Max TVI (ASTM F2381)**
    \[
    \%C = \frac{A_{1897}}{A_{1303}} + 1
    \]
    - AMORPHOUS \(1303 \text{ cm}^{-1}\)
    - CRystalline \(1897 \text{ cm}^{-1}\)
Raman spectroscopy

- **Method**
  - Regions probed:
    - Surface, Subsurface and Bulk
  - Green laser line (514 nm)
    - Initial power 25 mW
  - 1800 mm\(^{-1}\) gratings.
    - 2 cm\(^{-1}\) spectral resolution
  - Integration time (\(~ 420 \) s)
  - Properties measured
    - Orthorhombic Crystallinity
    - Amorphous fraction
    - Intermediate fraction
    - Overall Crystallinity
Raman spectroscopy

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\[
\alpha_c = \frac{I_{1415}}{\left( I_{1295} + I_{1305} + I_{1269} \right) \times 0.45}
\]
Raman spectroscopy

• Method
  - Regions probed:
    • Surface, Subsurface and Bulk
  - Green laser line (514 nm)
    Initial power 25 mW
  - 1800 mm\(^{-1}\) gratings.
    2 cm\(^{-1}\) spectral resolution
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    • Orthorhombic Crystallinity
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    • Intermediate fraction
    • Overall Crystallinity

\[ \alpha_a = \frac{I_{1305}}{I_{1295+1305+1269}} \]
Raman spectroscopy

• **Method**

  - **Regions probed:**
    - Surface, Subsurface and Bulk
  - Green laser line (514 nm)
    - Initial power 25 mW
  - 1800 mm\(^{-1}\) gratings.
    - 2 cm\(^{-1}\) spectral resolution
  - Integration time (~ 420 s)
  - Properties measured
    - Orthorhombic Crystallinity
    - Amorphous fraction
    - Intermediate fraction
    - Overall Crystallinity

\[
\alpha_d = \frac{I_{1295}}{I_{1295+1305+1269}}
\]
Raman spectroscopy

- **Method**
  
  - **Regions probed:**
    - Surface, Subsurface and Bulk
  
  - **Green laser line (514 nm)**
    - Initial power 25 mW
  
  - **1800 mm\(^{-1}\) gratings.**
    - 2 cm\(^{-1}\) spectral resolution
  
  - **Integration time (~ 420 s)**
  
  - **Properties measured**
    - Orthorhombic Crystallinity
    - Amorphous fraction
    - Intermediate fraction
    - Overall Crystallinity

\[
\alpha_a = \frac{I_{1080}}{(I_{1295} + I_{1305} + I_{1269}) \times 0.80}
\]
Raman spectroscopy

• Method
  - Regions probed:
    • Surface, Subsurface and Bulk
  - Green laser line (514 nm)
    Initial power 25 mW
  - 1800 mm\(^{-1}\) gratings.
    2 cm\(^{-1}\) spectral resolution
  - Integration time (~ 420 s)
  - Properties measured
    • Orthorhombic Crystallinity
    • Amorphous fraction
    • Intermediate fraction
    • Overall Crystallinity

\[ \alpha_b = 1 - (\alpha_c + \alpha_a) \]
Nanoindentation

• Method
  - Hemispherical tip (Ø 13.5 µm)
  - Indentation depth 4.5 µm
  - 0.2 mm steps
  - Hardness
    (Oliver and Pharr method)
  - Elastic Modulus
    (Sneddon equation)

\[
H = \frac{L_{\text{max}}}{A} = \frac{L_{\text{max}}}{\pi \left( \frac{h_{\text{max}} + h_r}{2} \right) \left[ 2R - \left( \frac{h_{\text{max}} + h_r}{2} \right) \right]}
\]
Nanoindentation

- **Method**
  - Hemispherical tip (ø 13.5 μm)
  - Indentation depth 4.5 μm
  - 0.2 mm steps

- **Hardness**
  (Oliver and Pharr method)

- **Elastic Modulus**
  (Sneddon equation)

\[ E = \frac{(1 - v^2)\sqrt{\pi}}{2\sqrt{A}} \frac{dl}{dx} = \frac{(1 - v^2)\sqrt{\pi}}{2\sqrt{A}} \frac{2L_{\text{max}}}{h_{\text{max}} - h_r} \]
RESULTS
OI, TVI and %C

- Property profiles showed subsurface maxima (~ 1 mm)

- Backside less degraded than the superior surface \((p \leq 0.03^*)\)

- Antero-posterior faces more degraded than bearing surfaces \((p < 0.05^*)\)

* Paired t-tests
RESULTS

Raman spectroscopy

• Subsurface extrema (~ 1 mm)
  ✓ Orthorhombic crystallinity ($\alpha_c$)
  ✓ Overall crystallinity ($\alpha_d$)
  ✓ Amorphous content ($\alpha_a$)
  ✓ Intermediate fraction ($\alpha_b$) (Anomalous)

• Phase fractions higher/lower at the superior surface ($p \leq 0.04^*$)

• Higher %C and $\alpha_c$ in the antero-posterior faces ($p < 0.03^*$)

• $\alpha_c$ and $\alpha_d$ higher than %C ($^\dagger$)

*Paired t-tests
†Student t-test
## RESULTS

### Crystallinity contents

<table>
<thead>
<tr>
<th>Region</th>
<th>Property</th>
<th>% C</th>
<th>$\alpha_c$</th>
<th>$\alpha_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M. Anterior</td>
<td>% C</td>
<td>0.64 ± 0.17*</td>
<td>0.68 ± 0.16</td>
<td>0.73 ± 0.07</td>
</tr>
<tr>
<td>M. Condyle</td>
<td>$\alpha_c$</td>
<td>0.55 ± 0.10</td>
<td>0.74 ± 0.14†</td>
<td>0.71 ± 0.07†</td>
</tr>
<tr>
<td>M. Posterior</td>
<td>$\alpha_d$</td>
<td>0.70 ± 0.20*</td>
<td>0.79 ± 0.07*</td>
<td>0.74 ± 0.06</td>
</tr>
<tr>
<td>C. Anterior</td>
<td>% C</td>
<td>0.62 ± 0.16</td>
<td>0.68 ± 0.16</td>
<td>0.73 ± 0.08</td>
</tr>
<tr>
<td>Ridge</td>
<td>$\alpha_c$</td>
<td>0.55 ± 0.09</td>
<td>0.67 ± 0.14†</td>
<td>0.71 ± 0.04†</td>
</tr>
<tr>
<td>Post</td>
<td>$\alpha_d$</td>
<td>0.53 ± 0.14</td>
<td>0.53 ± 0.08</td>
<td>0.71 ± 0.01</td>
</tr>
<tr>
<td>C. Posterior</td>
<td>% C</td>
<td>0.59 ± 0.11</td>
<td>0.69 ± 0.09†</td>
<td>0.73 ± 0.04†</td>
</tr>
</tbody>
</table>

Antero-posterior faces: **Higher %C and $\alpha_c$** (Paired t-tests; $p < 0.03^*$)

$\alpha_c$ and $\alpha_d$ higher than %C (Student t-test†)
RESULTS

Hardness and Modulus

- Harder and stiffer material: **subsurface maxima** (~ 1 mm)

- No significant differences between superior and inferior surfaces (p = 0.3*)

- Lower hardness and modulus at the **medial condyle** (p ≤ 0.02*)

* Paired t-tests
RESULTS

Nanoindentation

Defective Indentations

Normal Indentation

500 μm
RESULTS

Nanoindentation

Normal Indentation

勆 50 μm
RESULTS

Nanoindentation
DISCUSSION

• Historical TKA tibial inserts undergo oxidative, microstructural and mechanical degradation *in vivo*: access to body fluids is a key mechanism.

• FTIR and Raman spectroscopies confirm *in vivo* oxidation induces crystallinity changes
  – Qualitative estimations (dependence with density)
  – 3-Phase model not valid for highly oxidized PE

• Nanoindentation confirms evolution to a harder and stiffer PE, in spite of the high sensitivity to surface defects.
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