Evaluation of Oxidation in Virgin UHMWPE Knee Components after Retrieval and Shelf Aging

Mark Morrison
Research
Smith & Nephew Orthopaedics
Memphis, TN USA

Introduction

- Recent reports of oxidation in highly crosslinked, re-melted UHMWPE
- Surprising for two reasons:
  - Undetectable level of free radicals
  - Excellent in-vitro oxidation resistance
- Virgin, EtO-sterilized poly uniquely represents a similar material
  - Undetectable level of free radicals
  - Excellent in-vitro oxidation resistance
  - Longer clinical history

Introduction

- Previous studies of virgin UHMWPE
  - Costa et al., Biomaterials, 1998;19:1371.
    - Knee (n=1) and hip (n=10) components
    - No oxidation reported
  - Bracco et al., JBJS-B, 2009;91:274.
    - “Large number” of components over 15 years
    - No oxidation reported
  - Currier et al., JBJS-A, 2010;92:2409
    - Hip component (n=1, 8.2 years in vivo, 0.3 years shelf aging)
    - No oxidation
  - MacDonald et al., CORR, 2011;469:2278.
    - Hip components (n=24, 1.4 – 12.8 years in vivo, 0.1 – 11.3 years shelf aging)
    - “EtO sterilized liners showed undetectable oxidation…”
- Lack of well-defined studies of virgin knee components

Objectives

- Characterize distribution and amounts of lipids
- Characterize oxidation behavior of virgin, EtO-sterilized tibial inserts
  - Where is oxidation located?
  - When did oxidation occur?

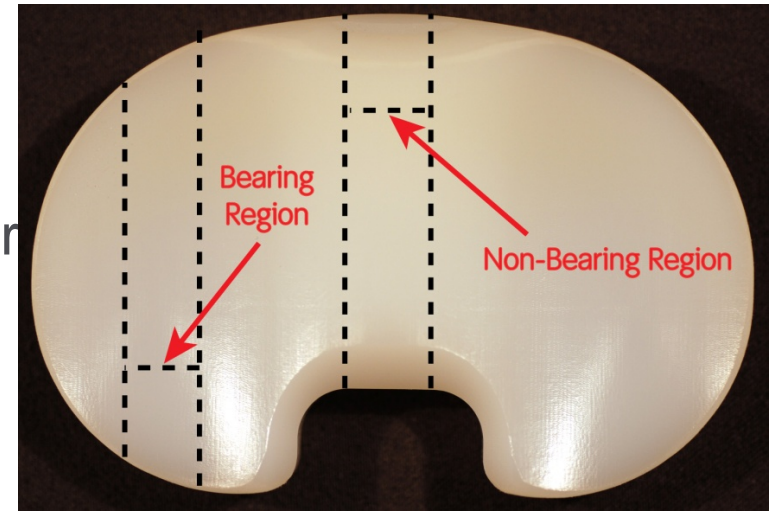
Materials

- Twelve knee retrievals
- Virgin, EtO-sterilized UHMWPE

Component	Material	In-Vivo Time (years)	Ex-Vivo Time (year)
TI-1	GUR1050 RE	0.4	14
TI-2	GUR1050 RE	0.8	9.1
TI-3	GUR1050 RE	0.5	8.3
TI-4	GUR1050 RE	2.6	8.2
TI-5	GUR1050 RE	0.8	8.5
TI-6	GUR1050 RE	5.5	8.2
TI-7	GUR1020 CM	2.8	3.4
TI-8	GUR1050 RE	0.3	3.3
TI-9	GUR1020 CM	3.5	3.3
TI-10	GUR1020 CM	1.2	3.2
TI-11	GUR1020 CM	0.1	3.1
TI-12	GUR1020 CM	0.6	3.1
Mean (± SD)		**1.6 ± 1.7**	**6.3 ± 3.6**

Experimental Methods

- One sample removed from each of two regions:
  - Bearing region
  - Non-bearing region
- Thin films (~200 μm) produced with microtome
- Transmission FTIR
  - Three profiles per film
  - 200 × 200 μm aperture
- Extraction in boiling hexanes for 16 hr

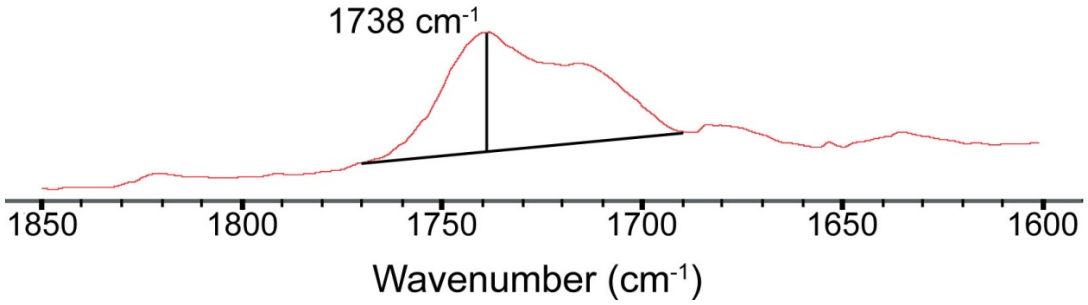


Derived FTIR Metrics

Peak-Area Oxidation Index = PA-OI = $\frac{A_{1718}}{A_{1396-1330}}$ (ASTM F2102-06)

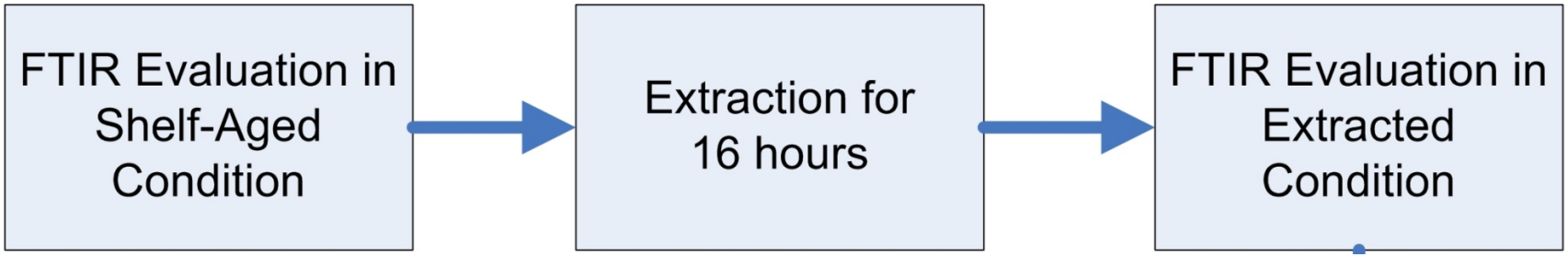
Peak-Height Oxidation Index = PH-OI = $\frac{H_{1718}}{H_{1368}}$

Ester Index = EI = $\frac{H_{1738}}{H_{1368}}$ or $\frac{H_{1748}}{H_{1368}}$



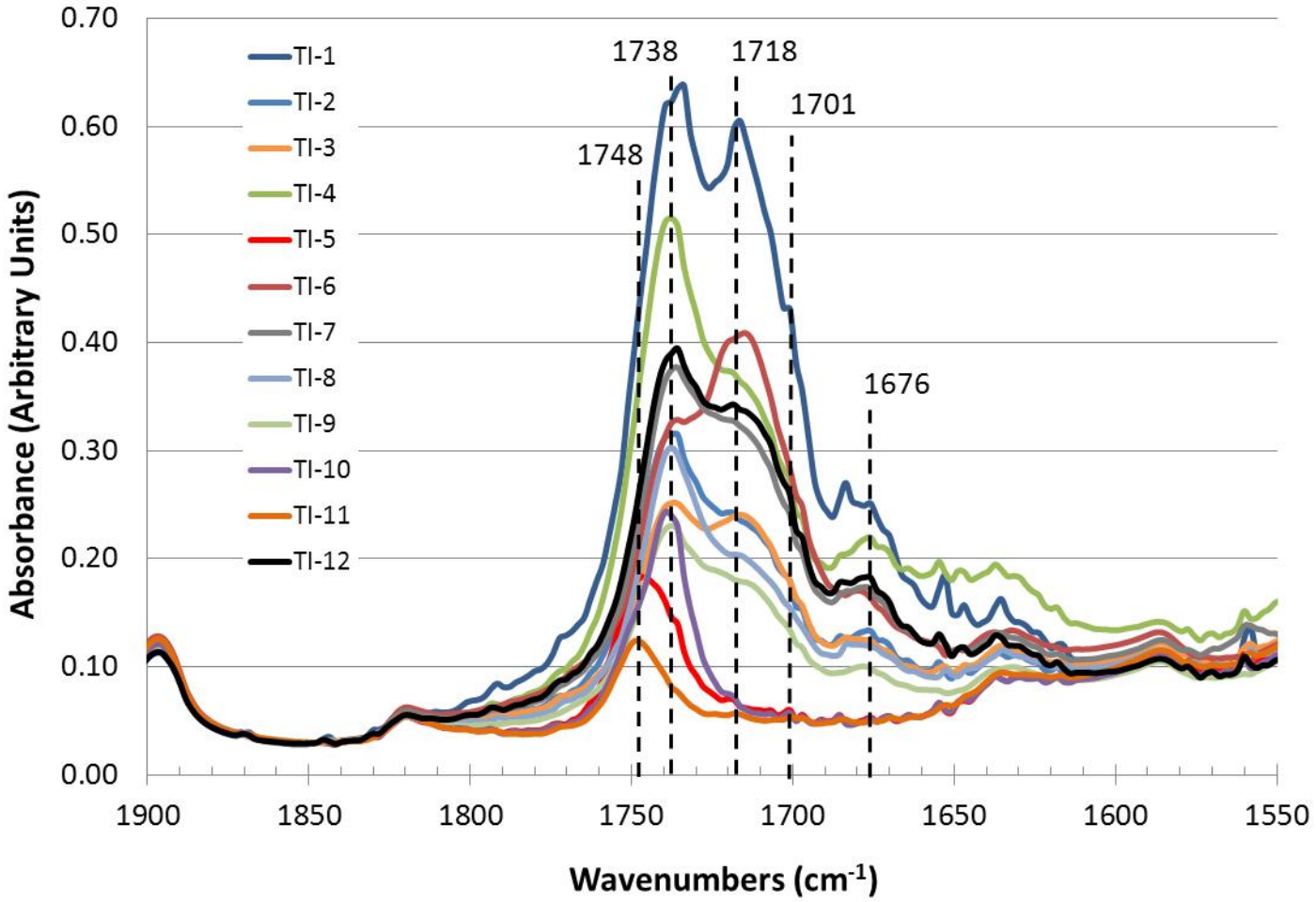
Baselines and integration limits
Adjusted to fit peak in numerator
Always 1396-1330 cm^{-1} in denominator

Experimental Methods

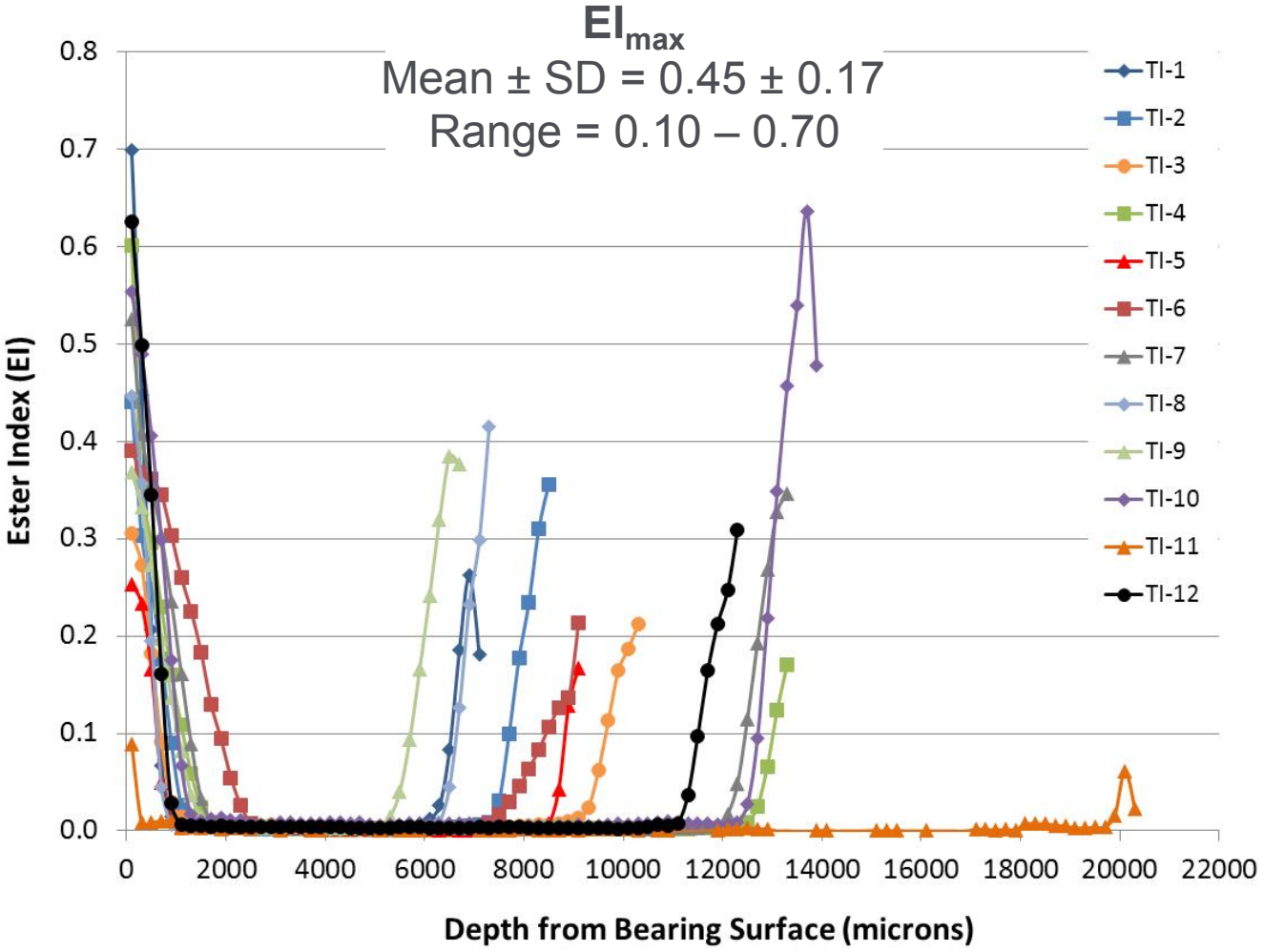


Pre-Extraction

Pre-Extraction Spectra

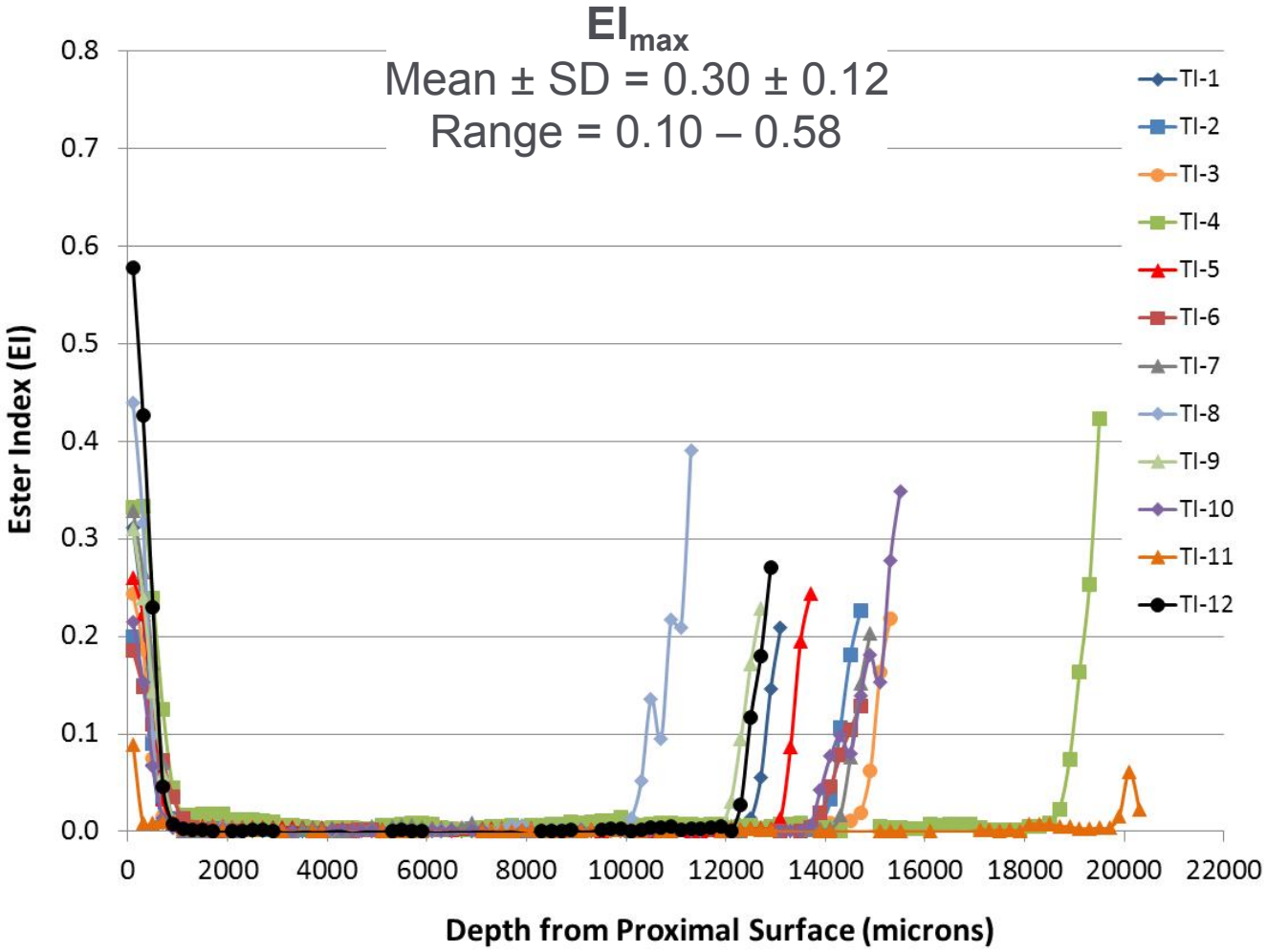


Ester Indices in Shelf-Aged Condition



Bearing Region

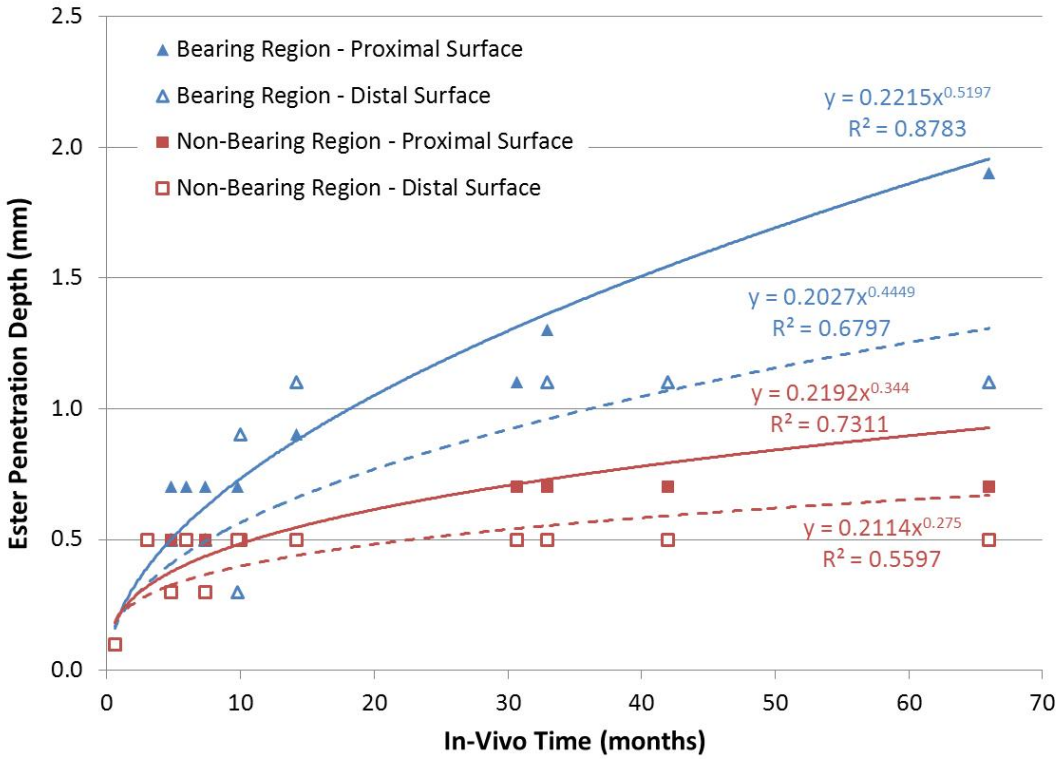
Ester Indices in Shelf-Aged Condition



Non-Bearing Region

Ester Penetration Rates

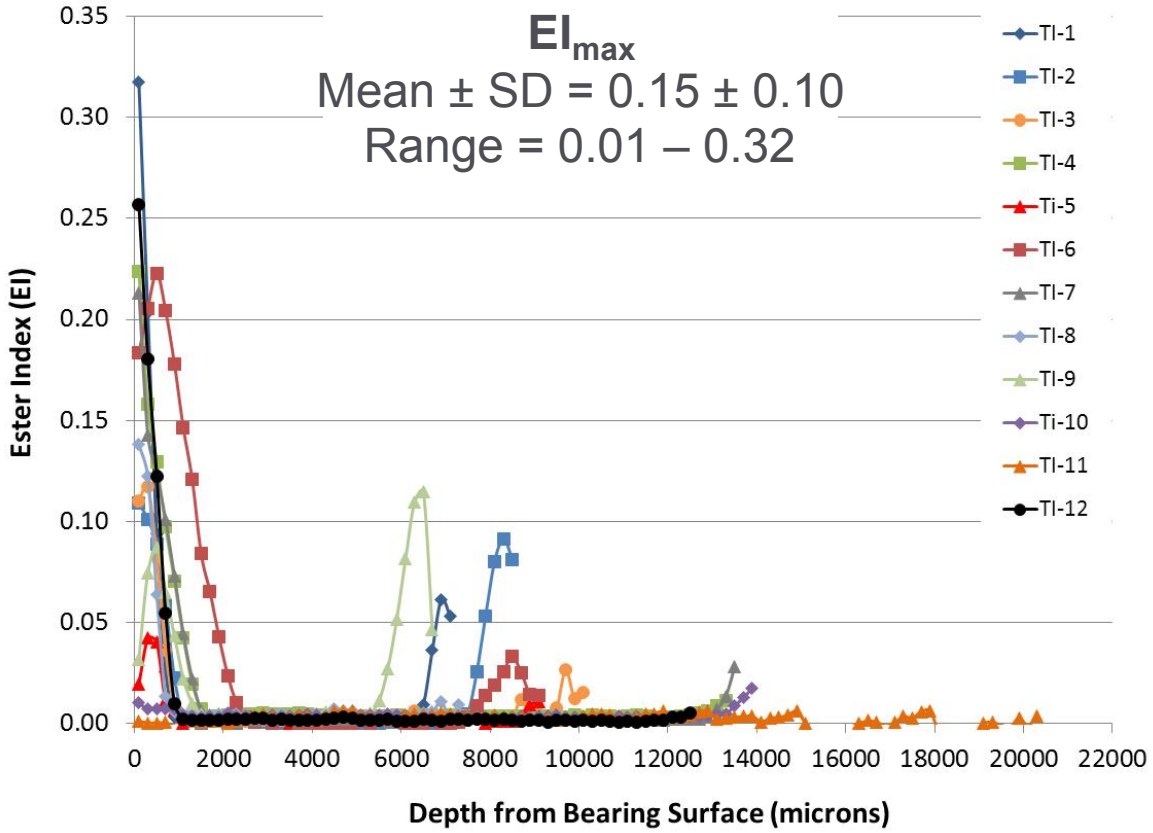
- Penetration depths correlated with:
  - Time
  - Region
  - Side
- Diffusion increases penetration depth with time
- Mechanical loading pushes esters into component
- Availability of synovial fluid affects quantities



Post-Extraction

Ester Indices After Extraction

- EIs reduced by 43-97%
- Ester peaks did not disappear in all profiles



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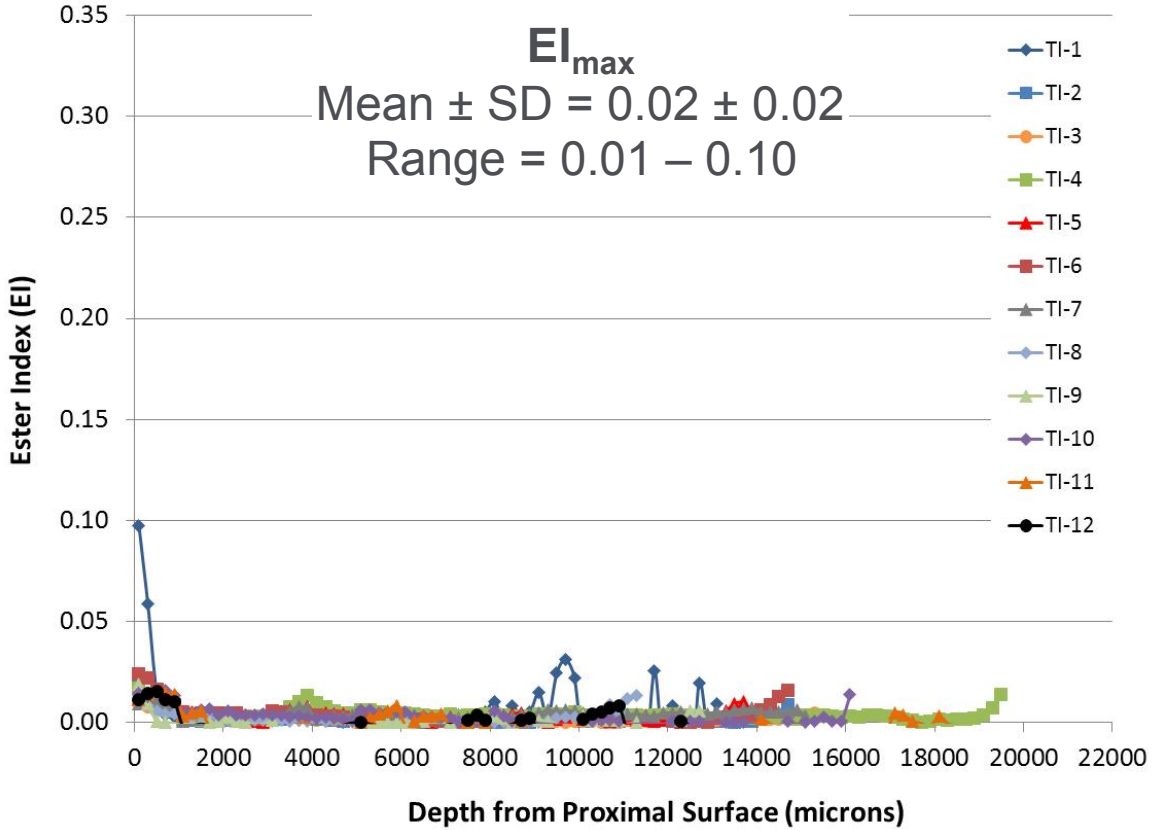
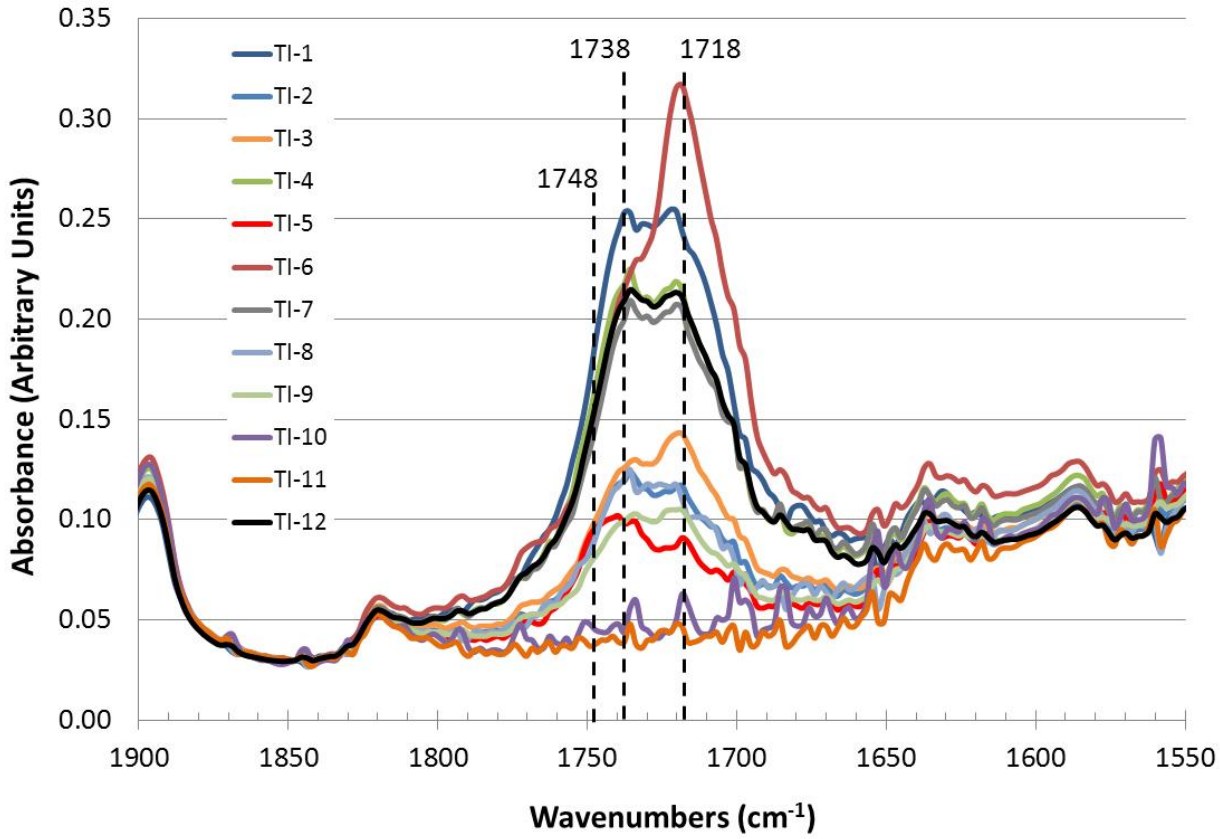


Non-Bearing Region

Post-Extraction Spectra

- Significant ester peaks remained in spectra
- Is extraction complete?



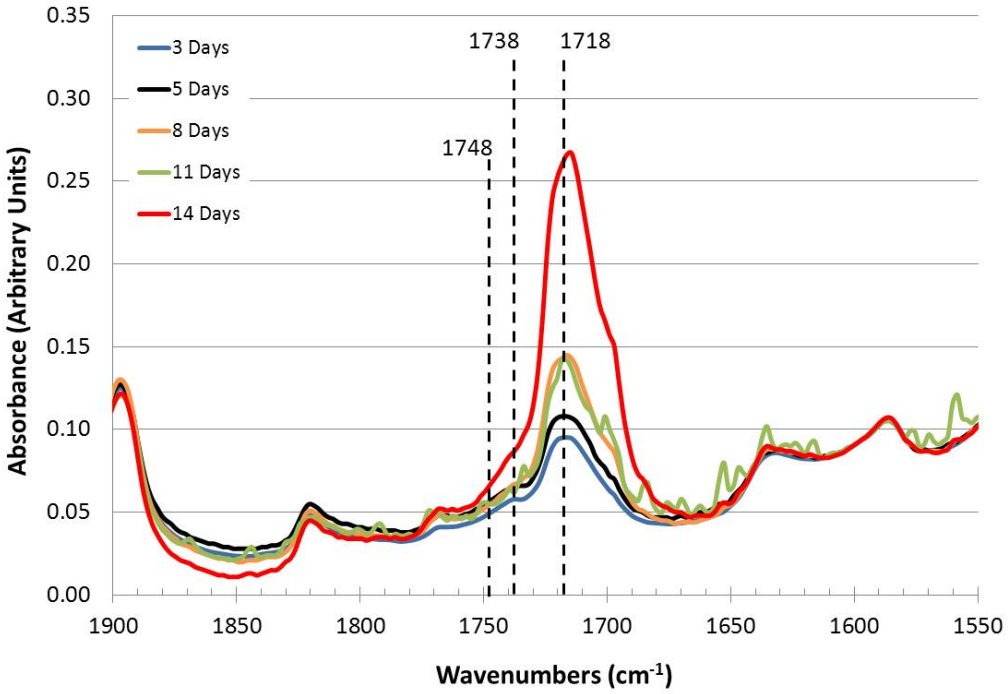
Ester Peak Formation

- Few studies in the literature
  - Directly quantified esters
  - Published spectra
- Accelerated aging studies without mechanical loading and lipids (i.e., oxygen bomb)
  - Ester peaks / shoulders
  - Small compared to ketone peak

$$\frac{PH-OI}{EI} = \frac{H_{1718}}{H_{1738}} = 6.1-6.6$$

Gamma-Inert

PH-OI / EI ≈ 6.5



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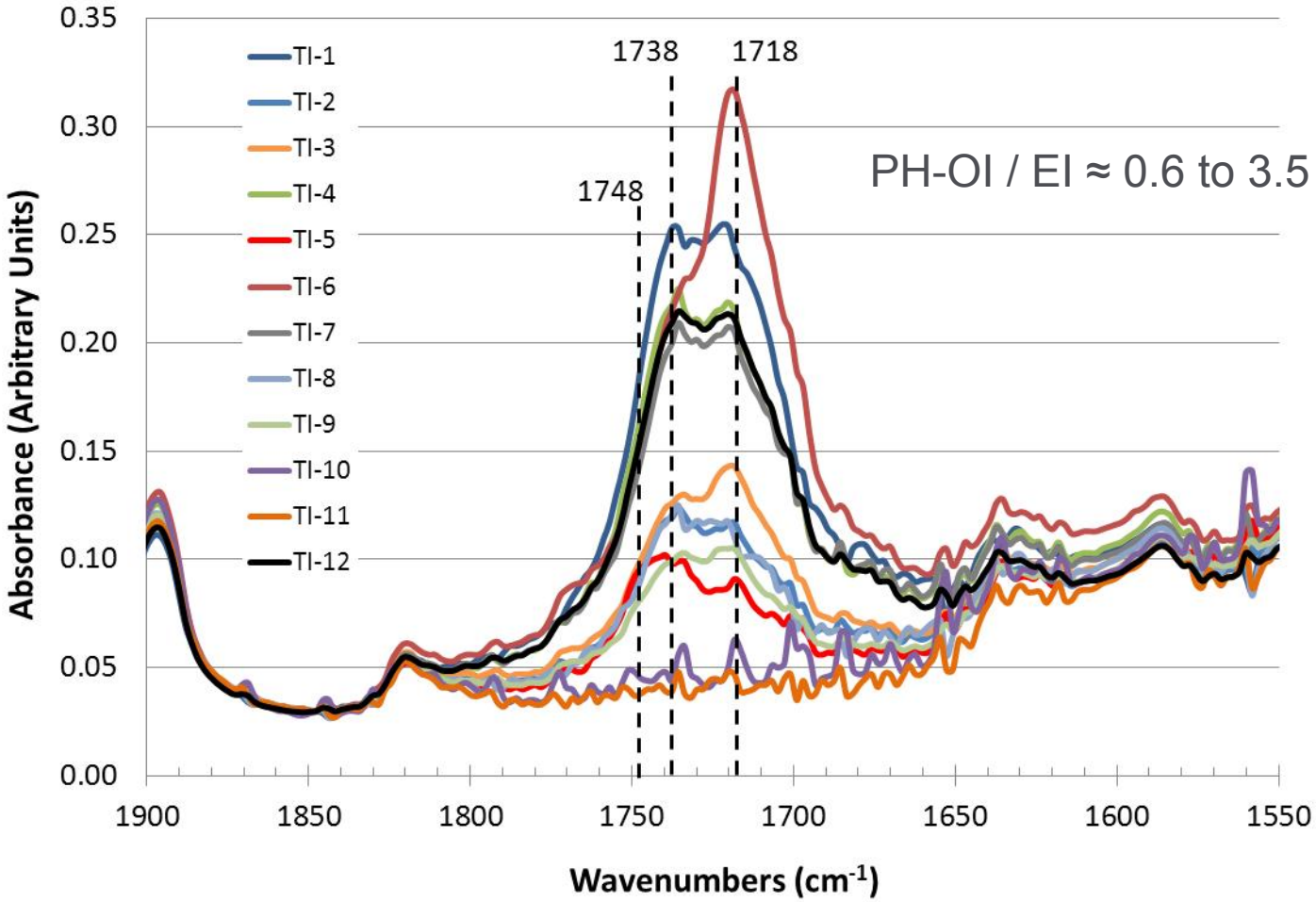
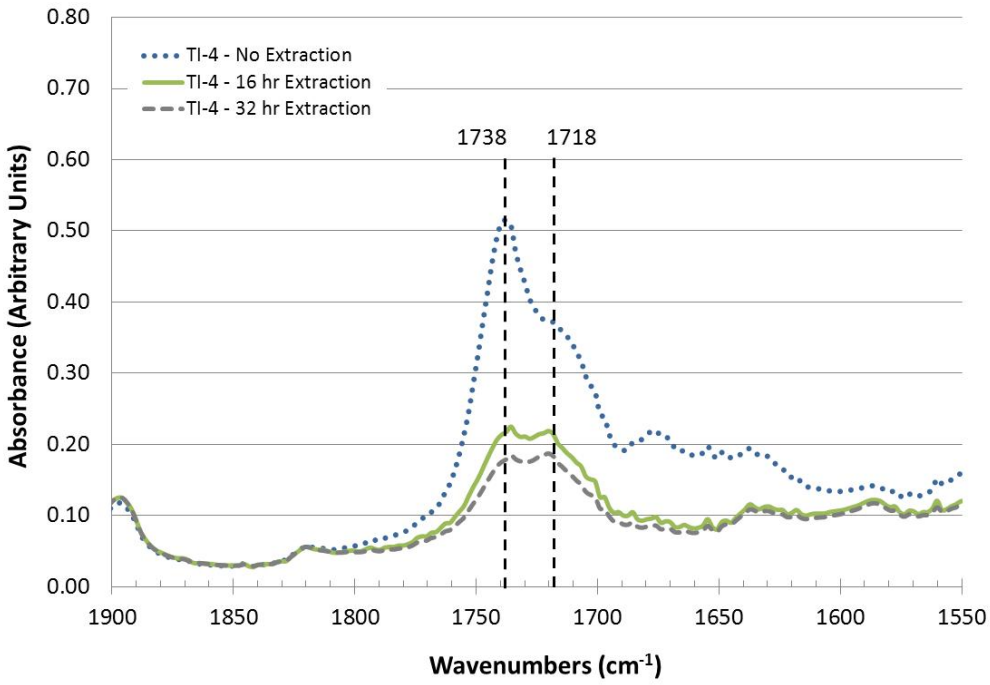


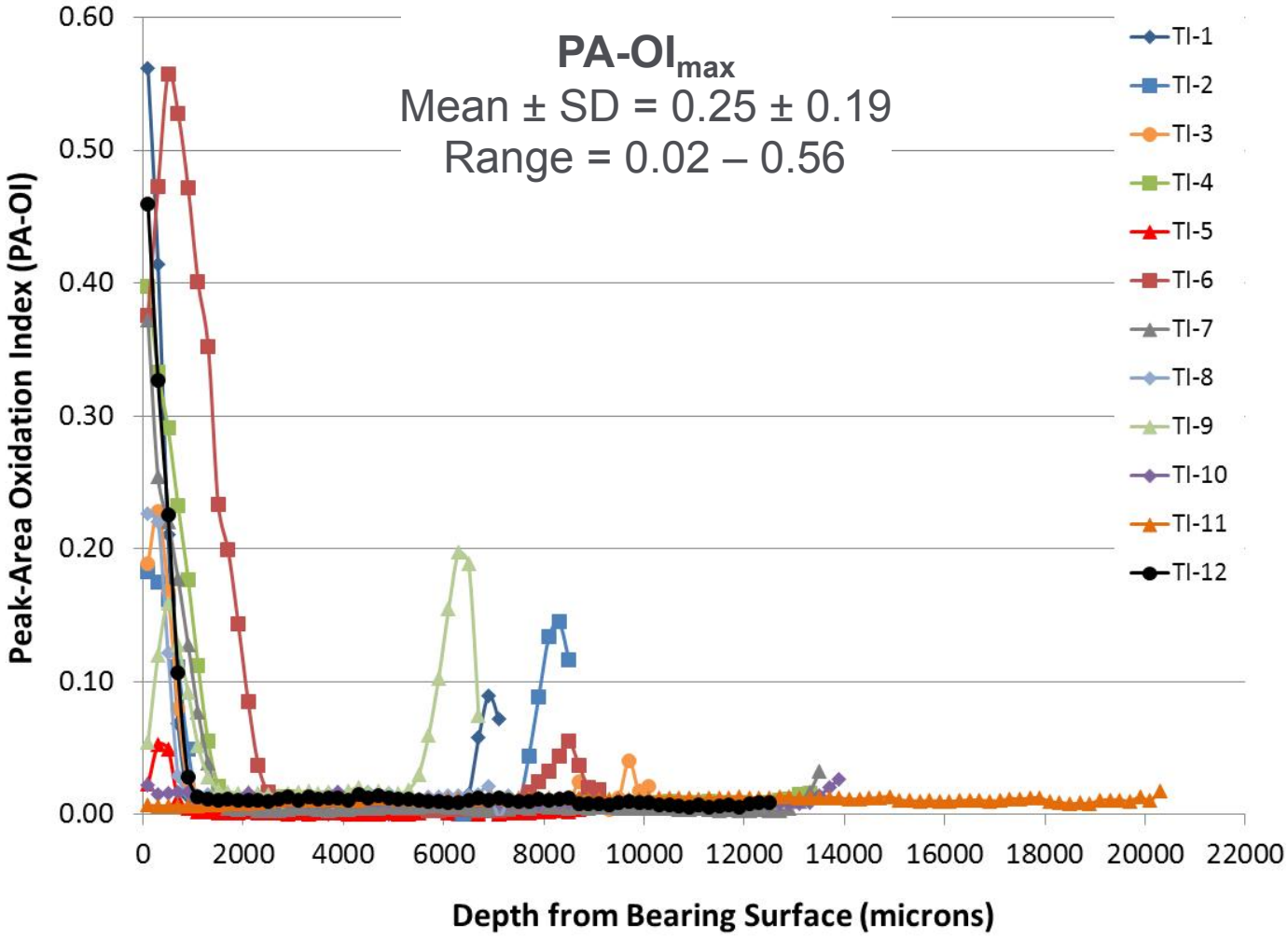
Extraction for 32 Hours

- Representative sample selected for extraction for an additional 16 hours
- FTIR metrics measured again and compared

Extraction Time (hrs)	PA-OI_{max}	PH-OI_{max}	EI_{max}
0	0.84	0.37	0.60
p	**0.275**	**0.275**	**0.383**

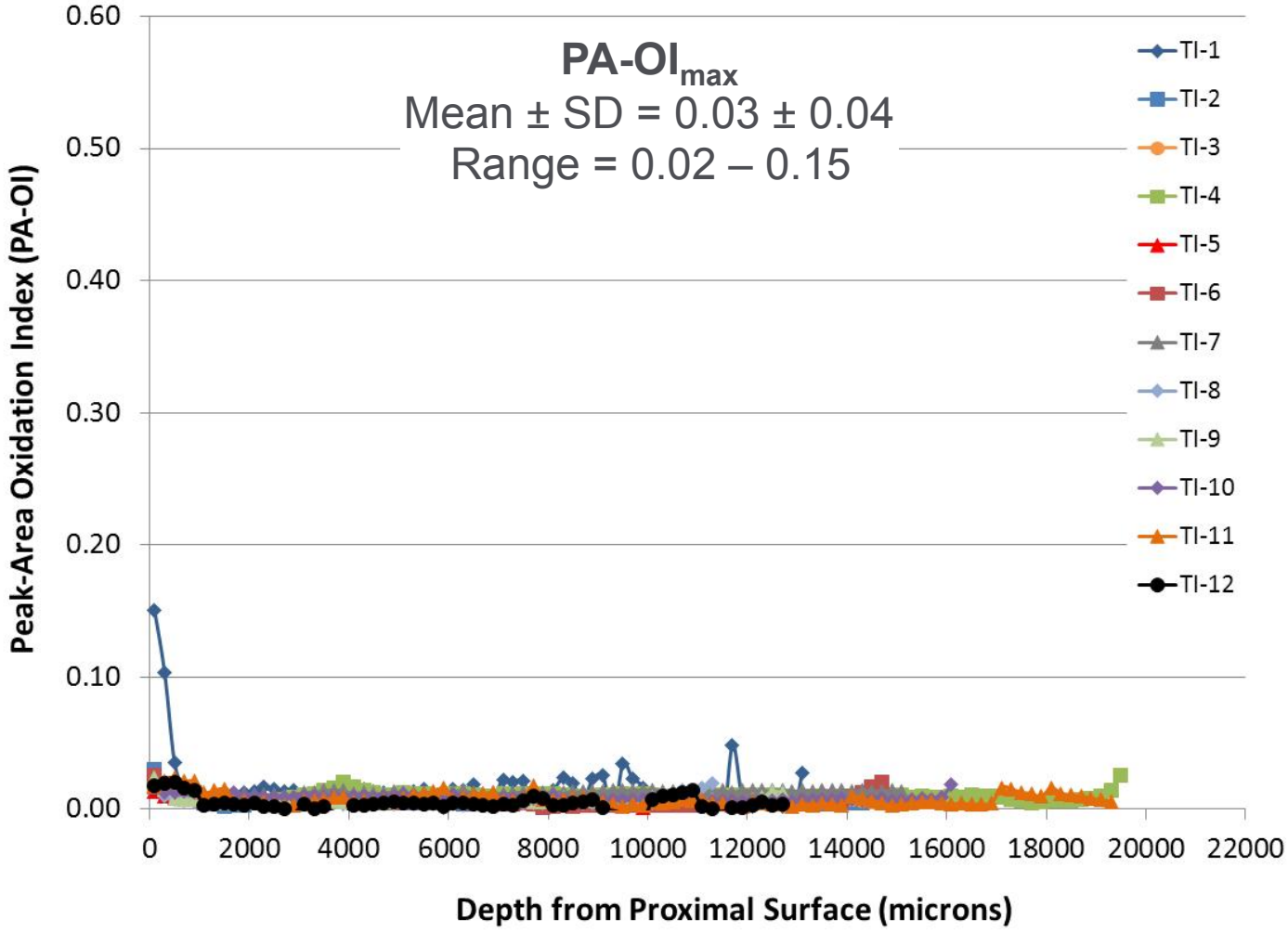


Peak-Area Oxidation Indices After Extraction



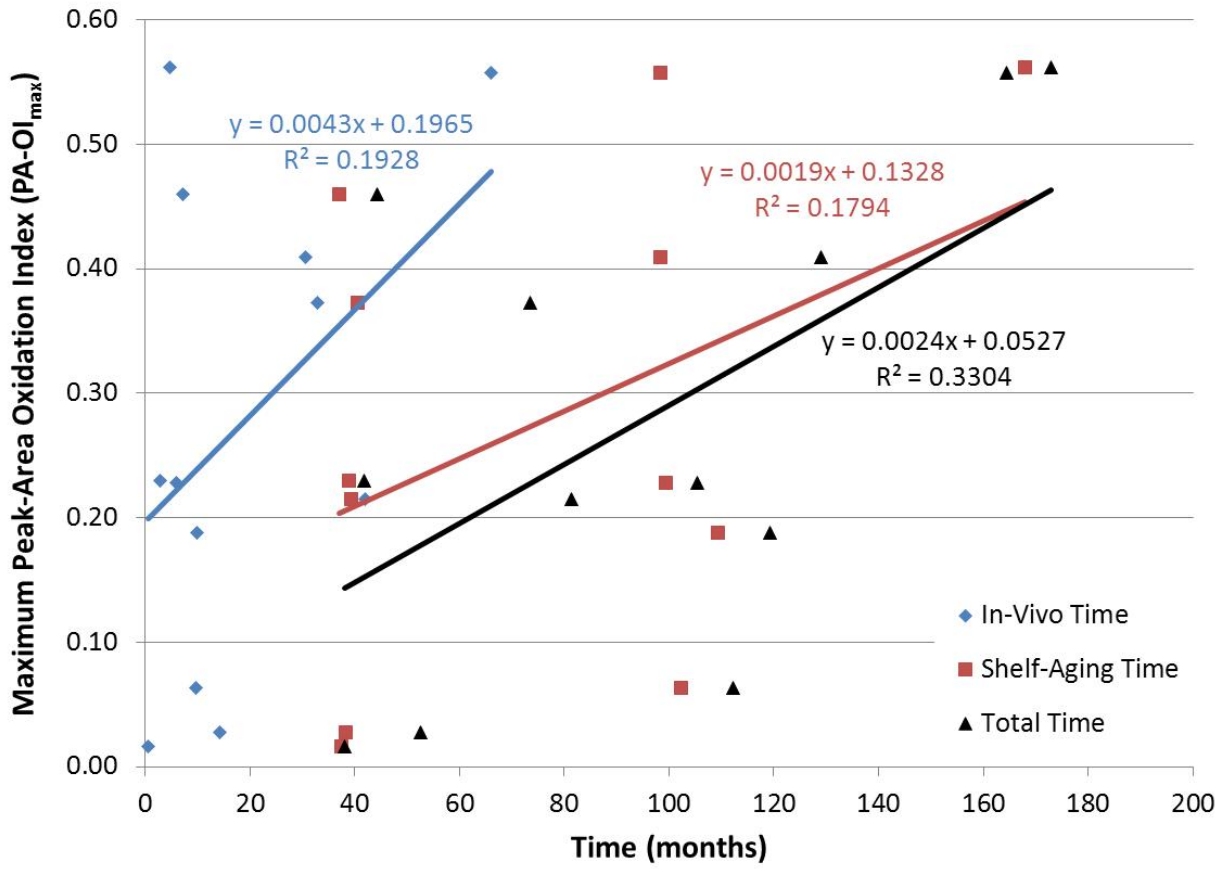
Bearing Region

Peak-Area Oxidation Indices After Extraction



Non-Bearing Region

Correlation Analyses



Time	Rho	p
In-Vivo	0.20	0.54
Shelf-Aging	0.24	0.46
Total	0.51	0.09

Limitations

- Small number of samples
- Short in-vivo times
- Long shelf-aging times

Conclusions

- Esters present on all surfaces
- Content and depth dependent upon
  - In-vivo time
  - Mechanical loading
  - Exposure to synovial fluid
- Large, residual ester peaks observed in bearing regions
- Low levels of oxidation observed in 10 of 12 tibial inserts
  - Concentrated at bearing surfaces
  - Present on distal sides within bearing region
  - Little measurable oxidation in non-bearing regions
- Oxidation likely occurred during shelf-aging