The Impact of Aging Environment on the Oxidation of Stabilized and Unstabilized Crosslinked Polyethylenes

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Polyethylene as a bearing surface

• UHMWPE has become the standard counterface for total joint replacements
  – Modern materials give 20+ year wear
  – Biologically inert
  – Easily handled

• Potential oxidation is one of the few weaknesses
  – Excessive wear
  – Particle generation
  – Osteolysis and implant loosening

• New materials and formulations require validation
Oxidation in Polyethylene

- Modern highly crosslinked polyethylene has potential for oxidation if care is not taken
  - Residual free radicals from the crosslinking process remain active
  - Often described by the Bolland cycle
  - Can drive oxidation and degradation

Currier et al. JBJS 2007

Costa et al. Biomaterials 1998
**Stabilized polyethylene**

- Recent advances have begun to utilize oxidatively stabilized polyethylenes
  - Help reduce risk of oxidation
- Usually result from additional component added to system
  - $\alpha$-tocopherol

- The addition of secondary species raises questions about how accelerated aging occurs and if physiological fluids interact with the materials differently
The importance of environment

- Costa reported in 2001 that the absorption of media species may also play a role
  - Synovial fluid a complex mixture
    - Cholesterol, proteins, fatty acids
  - Post-implant
    - Surface adsorbed proteins
    - Apolar materials diffused in to bulk
      - Cholesterol and esters, with fatty acids and squalene
  - Crosslinking does not prevent absorption
In vitro testing for oxidative stability

• Ambient, or “real-time” conditions
  – “shelf aging”
    • Room temperature and pressure
  – “fish tank”
    • Water, often at physiological temperatures, non-standard

• Accelerated
  – F 1980
    • Ambient atmosphere, 80 °C
    • “Q10”, 1 week is considered to be 1 year equivalent
  – F 2003
    • Five atmospheres, oxygen at 70 °C
**Materials and environments**

- **Materials**
  - Consolidated GUR 1050
    - $\gamma$-sterilized (25-37 kGy) “UHMWPE”
    - Vitamin E blended, consolidated and e-beam crosslinked “VE-PE”
  - 1 cm cubes cut from each consolidated puck

- **Environments**
  - ASTM F1980-99 (ambient atmosphere, 80 °C)
  - ASTM F2003-02 (5 atmospheres oxygen, 70 °C)
    - Oxygen 99.994% ultra high purity, Air Gas
  - Bovine Synovial Fluid (5 atmospheres oxygen, 60 °C)
    - BSF Animal Technologies Inc.
    - Oxygen 99.994% ultra high purity, Air Gas
    - Dissolved oxygen $\sim$4.41 mmol O$_2$/L H$_2$O (c.f. 1.07 mmol O$_2$/L H$_2$O)

- **Samples in BSF were refluxed against hexane for three days**
  - Verify that FTIR spectra due to immobile species
Bulk Oxidation

- UHMWPE BSF
- VE-HXPE BSF
- UHMWPE F1980
- VE-HXPE F1980
- UHMWPE F2003
- VE-HXPE F2003

Oxidation Index [ ]

Accelerated Aging Time [weeks]
Antioxidant potential of VE-PE (OIT)

Oxidation Induction Time [min]

Aging Time [weeks]

- **ASTM F1980**
- **ASTM F2003**
- **BSF**
F1980 (ambient air)
F2003 (Oxygen Bomb)
Synovial Fluid

Oxidation Index, ASTM []

Depth [μm]

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Surface Oxidation Spectra (UHMWPE)

Extraction: 3 days in hexane
BSF at 8 weeks, F2003 at 5 weeks, F1980 at 6 weeks
Bulk Oxidation Spectra (UHMWPE)

Extraction: 3 days in hexane
BSF at 8 weeks, F2003 at 5 weeks, F1980 at 6 weeks
Conclusions

• VE-PE exhibits excellent long-term stability in these accelerated environments
  – Evenly in highly demanding oxygen bomb, OI is negligible out to 24 weeks
• OIT suggests that stability is not lost as VE-PE is aged, even out to 24 weeks
  – However, very different measure of stability
• BSF is less demanding than oxygen bomb
  – Lower temperature
• BSF has different OI distribution in uncrosslinked materials
  – Bulk OI is higher – unique profile inconsistent with retrievals
    • Higher than F1980 (air) but lower than F2003 (bomb)
  – Surface OI falls off rapidly near surface
    • Possible indicator of protective effect of BSF constituents?
  – Oxidation profile still present after hexane extraction