Increasing the X-ray contrast of polymers

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Outline

- Introduction to polyethylene
- Joint replacement implants
- Polyethylene manufacturing
- X-rays for implant monitoring
- Radiopaque polymer additives
- Radiopaque polyethylene
Introduction to polyethylene

- Semi-crystalline polymer
- Can be:
  - low density (LDPE),
  - linear low density (LLDPE)
  - high density (HDPE),
  - ultra-high molecular weight (UHMWPE)
- Molecular weight, and degree of branching main differences
- Radiation crosslinking can increase Mw further

Source: Oral 2008, J Arthroplasty
## Introduction to polyethylene

<table>
<thead>
<tr>
<th>Property</th>
<th>HDPE</th>
<th>UHMWPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight ($10^6$ g/mol)</td>
<td>0.05-0.25</td>
<td>2-6</td>
</tr>
<tr>
<td>Melting temperature ($^\circ$C)</td>
<td>130-137</td>
<td>125-138</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.40</td>
<td>0.46</td>
</tr>
<tr>
<td>Tensile modulus* (GPa)</td>
<td>0.4-4.0</td>
<td>0.8-1.6</td>
</tr>
<tr>
<td>Tensile yield* (MPa)</td>
<td>26-33</td>
<td>21-28</td>
</tr>
<tr>
<td>Tensile ultimate strength* (MPa)</td>
<td>22-31</td>
<td>39-48</td>
</tr>
<tr>
<td>Degree of crystallinity</td>
<td>60-80</td>
<td>39-75</td>
</tr>
</tbody>
</table>

* Testing conducted at 23$^\circ$C

Source: Kurtz 2009, UHMWPE Handbook

Molecular weight so high, it has to be determined from the intrinsic viscosity.
Joint replacement implants

- We have a problem
- The population is aging
- More joint replacements operations are being performed
- Joint replacements need to last longer

Material performance is one of the limiting factors
Joint replacement implants

Source: Yuhua 2014, Materials
Joint replacement implants

Total Knee Replacement

Source: Yuhua 2014, Materials
Level walking - knee

- Max load:
  - 3.1 x Body Weight

- Number of times an average person steps in a year after replacement:
  - 1-2 million (Silva 2002, Schmalzried 1998)
Joint replacement implants

- Fatigue resistant (for N<20 million cycles)
- Wear resistant and low friction
- Fracture resistant
- Biocompatible
- Corrosion resistant
- Modulus comparable to bone
- Easily manufacturability for complex shapes
- Adheres well to PMMA cement, or easy to coat

Not many materials meet these criteria
Polyethylene manufacturing

From resin to implant:

1. Create polyethylene resin

![Structure of ethylene](image)

Ziegler Natta polymerisation (Or metallocene polymerisation)

2. Consolidate resin into part

Punch
Powder
Resin
Die

(direct compression moulding)

3. Machining and cleaning

γ-irradiation

4. Irradiate resin in inert gas to promote cross-linking

5. Packaging and storage

(Or direct compression moulding)
Polyethylene manufacturing

- UHMWPE Resin
- Celanese (formerly Ticona) are the only manufacturer of medical grade, in the world!
- Zeigler natta process used (ethylene, hydrogen and titanium tetra chloride)
- Powder very pure for medical, no calcium stearate used
- GUR 1050 and GUR 1020 are main resin types
Polyethylene manufacturing

Different consolidation methods

Direct compression moulding
Polyethylene manufacturing

Different consolidation methods

Ram extrusion

Sheet moulding

Heat & pressure

Female mold half

SMC charge

Male mold half

Heat & pressure
Polyethylene manufacturing

Microstructural changes over time *in vivo*:

Moulded UHMWPE

UHMWPE after irradiation

UHMWPE after 7 years

amorphous

crystalline lamellae

lamellar thickening

lamellar alignment

crystallite formation

Polyethylene manufacturing

Microstructural changes over time *in vivo*:

- UHMWPE resistant to most chemicals, but will absorb oils and other hydrocarbons (Costa, 2001)
- Retrieved UHMWPE implants have been shown to contain absorbed components of synovial fluid
- Studies have shown these plasticise the surface and increase likelihood of oxidation (Oral, 2012)


X-rays for implant monitoring

- X-rays are used routinely for patient follow-up after surgery (radiographs, fluoroscopy, CT)

- Provides information on implant placement, function, and condition

- Polyethylene components are not currently visible
Heavy metals and metal salts

- Barium sulfate, bismuth trioxide, tungsten powder
- High electron density
- Commonly used
- Can reduce mechanical properties: tensile strength, fracture toughness, and fatigue
Radiopaque polymer additives

• Metallic coatings and markers
  • Useful for short-term medical applications
  • Do not reduce mechanical properties
  • Coating delamination can be an issue
  • Embedded metallic markers (such as tantalum balls) can be used for long-term applications
Radiopaque polymer additives

- Halogen based radiopaque polymers
  - E.g. bromide and iodine
  - Can be covalently bonded, or co-polymerised into a polymer
  - Several studies reported, used in PMMA and PU, but none used clinically

- Lipiodol
  - Derived from poppyseed oil
  - Clinical used contrast agent
  - Lipophilic
Radiopaque polyethylene

Iodised oil
24h 110 °C
Untreated

Increased radiopacity on X-ray

Noticeable colour change

100°C
110°C
120°C
130°C
Radiopaque polyethylene

Significant volume change
Radiopaque polyethylene

Crystallinity not significantly changed
Radiopaque polyethylene

Reduction in tensile modulus
Radiopaque polyethylene

Relationship between modulus and Lipiodol concentration
Radiopaque polyethylene

Slight reduction in UTS, but not significant
Radiopaque polyethylene

Elongation significantly increased beyond 105 °C
Future work

• Fatigue and wear testing of durability

• Modelling the diffusion of Lipiodol, to optimise treatment parameters

• Different lipophilic radiopaque agents

• TEM imaging of the UHMWPE before and after treatment

• Chemical stability and aging tests of treated UHMWPE
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And thank you for listening!