UHMWPE Oxidation and Stabilisation during e-beam irradiation

L. Costa

University of Turin, Italy

Dipartimento di Chimica IFM

3rd UHMWPE INTERNATIONAL MEETING
“Polyethylene in total joint replacement systems: Concerns and solutions”
Plan of the presentation

• The e-beam irradiation reaction in vacuum

• The UHMWPE post-irradiation oxidation induced by e-beam

• The UHMWPE stabilisation against oxidation and post-irradiation oxidation.
Physical characteristic of orthopaedic UHMWPE

Molecular mass > 2,000,000
Crystallinity original powder > 75%
Bar and plate around 50%
Density 0.927-0.944 g/cm³
Glass Transition -70°C
Melting interval 90°-150°C
Very high viscosity of the melt
UHMWPE powder (more than 75% of crystallinity)

Compression molding or ram extrusion

Bar or sheet (crystallinity 50-52% and under stress)

Mechano-oxidative degradation
Ester and acids formation

Shaping and microtome materials

films

Treatment by electron beam

Degradation induced by electron beam under vacuum

Post irradiation oxidation
Materials: Gur 1020 or 1050 powder prepared by Ticona and machined by Orthoplastics Perplas or Poly Hi Solidur-MediTECH Division

The film are prepared by microtome in air. The thickness is around 160 micron

FTIR Perkin Elmer 2000, 16 scan. Spectra are normalised at 0.05 Å at 2020 cm⁻¹. We work with difference spectra. In this case we have good spectra with absorbance difference of 0.001

Irradiation with e-beam at Bioster was performed with a 10 MeV accelerator (Bioster, Seriate, Italy), operating at 25 kW power, with a dose rate of $6 \times 10^4$ kGy/h, at room temperature.
Identification of oxidised species by IR analysis

Alcohols and hydroperoxides were measured at 3630, 3550 and 3420 cm\(^{-1}\) and converted to nitrites and nitrates respectively, by reaction with gaseous NO in absence of oxygen.

\[
\text{RCH}_2\text{OH} + \text{NO} \rightarrow \text{RONO}
\]
\[
\text{RCOOH} + \text{NO} \rightarrow \text{RONO}_2 \ (1630 \text{ cm}^{-1})
\]

Carboxylic acids were estimated as acid fluorides after reaction with SF4.

\[
\text{RCOOH} + \text{SF4} \rightarrow \text{RC(O)F} \ (1848 \text{ cm}^{-1})
\]

After high energy treatment (gamma or e-beam) in vacuum in function of the dose:

- Presence of secondary macroradicals, free to move inside the UHMWPE amorphous phase, less free in the crystalline phase.
- Presence of allylic and probably tertiary macroradicals in amorphous phase
- Less vinyl double bonds and some polymeric chain are crosslinked
- New $trans$ and $cis$ vinylene double bonds
- Increase of the crystallinity, from 50% to 54% in function dose
Oxidation in polymer solid state.

$\text{R}^\circ$ macroradicals move to O2 and form $\text{ROO}^\circ$ fixed in the polymeric chain that can abstract the H and form $\text{ROOH}$ and new sec macroradicals free to move.
The rate of oxidation process is described as:

\[ V = K [R^\circ][O_2] \text{ at } T = \text{constant} \]

\[ [R^\circ] \text{ measurable only in radiation process} \]

\[ [O_2] \text{ depend on solubility of } O_2 \text{ in the polymer amorphous phase} \]

\[ K = A \ e^{-E_{\text{att}}/RT} \]

Which is the value of A?

Function of effective collision between the species (Oxygen and Radicals). Any problems in gas phase or in solution. Problems are in solid state.

This concept is valid for all the reactions that happen inside the polymers.
Irradiation conditions with gamma or e-beam

The rate and the behaviour of oxidation induced by high energy radiation depend on production of radiation:

- Absorbed dose and dose rate which govern the residence time in the sterilisation cell and the rate of radical generation
- Characteristics of the sterilisation plant
- Temperature of the sterilisation cell
- Sample thickness
- Oxygen concentration
The UHMWPE post-irradiation oxidation at RT induced by e-beam in control condition
Thermal decomposition of ROOH under vacuum

Decrease in hydroperoxide concentration as a function of the decomposition time in vacuum at 100 and 120°C.
Thermal decomposition of ROOH under vacuum at 120°C

(—) sample decomposed 0h in vacuum minus reference GUR 1050;

(---) sample decomposed 22h in vacuum minus reference GUR 1050;
Thermal decomposition of ROOH under vacuum

The thermal decomposition of ROOH happen at temperature > 70°C in partial melt state.

The main products of thermal decomposition are ketones and some α,β-unsaturated ketones

\[
\text{ROOH} \rightarrow \text{R}_2\text{C}=\text{O} + \text{H}_2\text{O}
\]

But ketones are formed also during the e-beam post-irradiation
Hydroperoxide total concentration after NO treatment as a function of radiation dose in air and of storage time in air at RT. Films 40 microns

(Curve A: 0h after irradiation; Curve B: 5h after irradiation; Curve C: 360h after irradiation)
Spectral subtraction of UHMWPE irradiated in vacuum 60 kGy and stored in air at RT minus reference GUR 1050

The post-irradiation oxidation at RT films irradiated with e-beam at 60 kGy in vacuum

Spectral subtraction of UHMWPE irradiated in vacuum 60 kGy and stored in air at RT minus reference GUR 1050
The post-irradiation oxidation at RT films irradiated with e-beam at 60 kGy in vacuum
Formation of acids

Spectra of UHMWPE after SF$_4$ treatment with: film irradiated 60 kGy in vacuum and stored in air at RT for about 2500 h
Oxidation products in function of the storage time in a film of UHMWPE irradiated in vacuum 60 kGy and ageing in air at RT;
Rate of formation of oxidation products in function of the storage time in a film of UHMWPE irradiated in vacuum 60 kGy and ageing in air at RT.
1. The ketones and ROOH are accumulated during the post-irradiation process
2. The rate of ketones formation is high when the concentration of ROOH is minimum
3. The ketones and ROOH formation rate are very similar.
4. Ketones and ROOH could form with same mechanism: direct reaction between macroalkyl radicals and oxygen
5. The first part of oxidation is due to the reaction of O₂ and the alkyl macroradicals produced by e-beam in amorphous phase. In the same time the macroradicals can decay.
6. The second part of oxidation could be due to the alkyl macroradicals present in crystalline phase that move to amorphous phase or O₂ move to crystalline-amorphous interphase.
Hydroperoxide formation

Ketones formation

$\Delta H$ for model reaction = -47 kJ/mole
The Bolland cycle

\[ \text{Alcohols} + \text{Carboxylic acids} \]

\[ \text{ROO}^- \]

\[ \text{UHMWPE} \]

\[ \text{ROOH} \]

\[ \text{-H}_2\text{O} \]

\[ \text{.OH} + \text{RC} \]

\[ \text{O}_2 \]
The UHMWPE stabilisation against oxidation and post-irradiation oxidation.
UHMWPE- Ultra High Molecular Weight Polyethylene for prosthetic utilisation

UHMWPE is controlled by ASTM F648-06 or ISO 5834

ASTM Designation F 648-06 “Standard specification for UHMWPE powder and fabricated form for surgical implant”

The standards states the minimum mechanical characteristics of the original UHMWPE powder and the absence of any stabiliser

5.1.1 “No stabilizers or processing aids are to be added to the virgin polymer powder during manufacture of a fabricated form.”
**BREVETTO PER INVENZIONE INDUSTRIALE**

**N. 01271590**

Il presente brevetto viene concesso per l'invenzione oggetto della demanda sotto specificata:

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**TITOLARE**
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- COSTA LUIGI
- CROVA MAURIZIO
- DALLERA ALESSANDRO
- GALLINARO PAOLO
- LUCA DI CORTESMILIA MARIA PAOLA
- A TORINO

**RAPP. TE**
- GERBINO ANGELO

**INDIRIZZO**
- JACOBIANI & PERANI SPA
- CORSO REGIO PARCO 27
- 10136 TORINO

**TITOLO**
- IMPIANTO PROTESICO COMPRENDEUNETTE UN COMPONENTE DI MATERIALE PLASTICO

**INVENTORE**
- BRACH DEL PREVER ELENA MARIA
- CAMINO GIOVANNI
- COSTA LUIGI
- DALLERA ALESSANDRO
- GALLINARO PAOLO
- LUCA DI CORTESMILIA MARIA PAOLA
- CROVA MAURIZIO

Roma, 4 GIUGNO 1997

IL DIRETTORE DELLA DIV. V
F.to GIOVANNA MORELLI

PER COPIA CONFORME DELL'ORIGINALE

Conseguito il 11 OTTO. 1997

SEGUE (sottofirmato dalla copia conforme)
VITAMIN E (α-tocopherol):

- Biocompatible
- Approved for food-packaging and orthopedic applications

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Item 1

Work Item Number: WK14943

Date: June 7, 2007

To: Members of ASTM F04.11 - Polymeric Materials

From: Jon Moseley

Subject: WK14943 Standard Specification for Ultra-High Molecular Weight Polyethylene Powder Blended With Alpha-Tocopherol (Vitamin E) and Fabricated Forms for Surgical Implant Applications
Sec alkyl macroradicals can react with:

1. Vinyl double bond to form crosslink

2. Residue of catalyst and macroradicals may be decay

3. Oxygen to form ROO° and ROOH, ketones and acids

4. Additive (H donator) to form PH and Additive°
   (stable radical; does not react with UHMWPE)

   0.05 % of Vit. E = 1.2 mmoli/l

   0.1% of Vit. E = 2.4 mmoli/l

   0.5% of Vit. E = 12 mmoli
Vinyl consumption:

Graph showing Vinyl consumption of UHMWPE and UHMWPE with Vitamin E at 2500 ppm and 1000 ppm, plotted against Dose (kGy) and Vinyl concentration [mmol/l].
Film of UHMWPE + 0.5% vitamin E: vitamin E consumption of OH species as a function of radiation dose.
Radicals evolution

EPR spectra of UHMWPE + Vit° irradiated at 60 kGy
Hydroperoxides concentration as a function of amount of vitamin E and of storage time in air at RT. The samples are irradiated to 60 kGy in air.
Ketone concentration as a function of amount of vitamin E and of storage time in air at RT. The samples are irradiated to 60 kGy in air.
Rate of formation of ketones as a function of amount of vitamin E and of storage time in air at RT.
Ketones and carboxylic acids

\[ \text{A} \xrightarrow{\text{O}_2} \text{B} \]

\[ \text{C} \xrightarrow{?} \text{B} \]

\[ \text{B} \xrightarrow{?} \text{C} \]
Acknowledgements

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Ponchione

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Thank you