Aging of $\gamma$-sterilized UHMWPE: Influence of oxygen on the oxidation and the oxidative potential

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History

- $\gamma$- Sterilization of UHMWPE implants packaged in air
- Severe oxidation of the shelf
- Delamination / mechanical failure
History

- One of the alternatives: Packaging under inert atmosphere

Ionizing irradiation for sterilization and modification of high molecular weight polyethylenes*

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Abstract: UHMWPE and HMWPE were treated by electron beam and $^{60}$Co-irradiation to obtain an implant material with better mechanical properties, especially less plastic deformation, and improved wear resistance. The mechanical properties could be modified by irradiation, but the wear resistance is worse than for unirradiated UHMWPE.

UHMWPE irradiated to the minimum sterilization dose of 25 kGy showed a significant sensitivity to the environment during the treatment and storage. Post reaction of latent free radicals in UHMWPE created during the irradiation showed a change in the properties after sterilization depending on time and the storage environment. UHMWPE, which mainly crosslinks during irradiation, degrades by an oxidation process when stored in air or water. The use of nitrogen gas during the sterilization process and during storage for several weeks afterwards seems to be beneficial for UHMWPE used as a long-term biomaterial.

"the use of nitrogen gas during the sterilization process and during storage for several weeks afterwards seems to be beneficial for UHMWPE as a long-term biomaterial"
- Inert atmosphere and the quality of the packaging play a crucial role
Goal

- The influence of the oxygen concentration in the packaging on the oxidation (and oxidative potential) by selecting different diffusion rates for the oxygen

- Threefold peel polymeric pouches either with standard or barrier film
Experimental

- 4 packaging systems
- Barrier films with 70 fold reduction in oxygen transmission rate ($\text{cm}^3/\text{m}^2 \times \text{d} \times \text{P}$) compared to standard films
- Threefold peel pouches with
  - A -> 0 Barrier / 3 Standard
  - B -> 1 Barrier / 2 Standard
  - C -> 2 Barrier / 1 Standard
  - D -> 3 Barrier
- Packaged, flushed with nitrogen and gamma sterilized (3 Mrad)
Experimental

- 400 PE Rings, GUR 1020 CMS
- Diameter 36 mm, wall-thickness 3mm
- Accelerated + real time ageing
- Ageing after ASTM F1980:
  55°C / 50% RH (acceleration factor 9.3: 6wks ~ 1 yr)
Experimental

- Residual oxygen concentration (n = 5)
- Dimensions (n = 3)
  - Height / diameter / roundness
- Oxidation profiles (n = 2, FTIR, ASTM F2101)
Results: Oxygen concentration

- Week 0: 0 years acc.
- Week 5: 3 years acc.
- Week 15: 6 years acc.

Oxygen concentration [%]

Weeks at 55°C

Lines represent:
- A
- B
- C
- D
Results: Oxidation vs Depth

- System A / Yrs accelerated
Results: Max oxidation vs. time

![Graph showing the relationship between oxidation index and time for different categories A, B, C, and D. The y-axis represents the oxidation index, ranging from 0 to 0.35, and the x-axis represents years [accelerated], ranging from 0 to 7. Each category shows a different trend over time, with A and D showing a steady increase, B showing a peak around year 3, and C showing a fluctuating pattern.]
Results: Max oxidation vs. time

Oxidation Index [-]

A B C D

6 yr accelerated
Oxidative potential

Mild ageing in the packaging at 55°C (ASTM F1980)
Carbonyl groups / Hydroperoxides (3 + 6 yrs accelerated)

Remove from packaging

Ageing at 70°C/5atm O2 / 2wks after ASTM F2003
Carbonyl groups (~ 5 yrs shelfageing gamma-air)
Oxidative potential

![Graph showing oxidation index for different samples A, B, C, and D. The x-axis represents the samples, and the y-axis represents the oxidation index. The graph compares oxidation at 6 years (55°) and oxidative potential.]

- Oxidation @ 6 yrs (55°)
- Oxidative potential
Reaction with oxygen I: Linear

Premnath V. et al. Biomaterials 17, 1741, 1996

Oxidation Index

Ketones

Water

Oxygen
Reaction with oxygen II: Exponential

Hydroperoxides

OH

UHMWPE

Alkyl Radical

Alcohol

O₂
Oxidative potential

![Graph showing oxidative potential with concentration vs. time axes. The graph includes lines for Hydroperoxides and Oxidation index, marked with points at D, C, B, and A.]
Limitations

- Accelerated aging
  - Elevated temperatures (55°C /70°C)
  - Acceleration of chemical oxidation vs. decrease in radical content
  - Must be verified using real time ageing
- Oxidative potential /Hydroperoxides can also be measured using NO treatment
Conclusions

- Oxygen concentration important during gamma steri but also afterwards during storage
- Oxygen concentration can be controlled by selecting the packaging materials
- Oxygen has a strong influence on the oxidative potential
- Small differences in the oxidation index still can have huge differences in oxidative potential
Thank you!