1th Dec 2021

AGING OF ELASTOMER O-RINGS AND PE NEUTRON SHIELDING MATERIALS FOR RADIOACTIVE WASTE CONTAINERS

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Background / Motivation

Role of BAM

- BAM is involved in the current licensing procedures for storage (and transport) casks
- Extending interim storage of radioactive waste containers will be necessary due to delays in the final repository projects in Germany (Konrad for LLW/ILW starting 2027; spent fuel and HLW repository after 2050)
- Safety of casks will have to be evaluated with regard to extended storage periods – can the components retain their functionality for several more decades?

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Current research activities at BAM in the area of radioactive waste container safety

- BAM has started several test programs for
  - ➢ evaluating long-term safety of components
  - ➢ developing suitable methods for accelerated aging, lifetime prediction and modelling
- With focus on
  - ➢ metal and elastomer seals
  - ➢ polyethylene neutron shielding materials
  - ➢ brittle failure of spent fuel claddings

- BAM is also involved in many other research activities dealing with long-term storage safety:
  - ✓ European Joint Programme on Radioactive Waste Management (EURAD)
  - ✓ Extended Storage Collaboration Program (ESCP)
  - ✓ Concepts and Requirements for HLW/SNF final disposal containers (KoBrA)
  - ✓ IAEA coordinated research projects (e.g. Ageing management, SPAR IV, Demo)

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  - metal and **elastomer seals**
  - **polyethylene neutron shielding materials**
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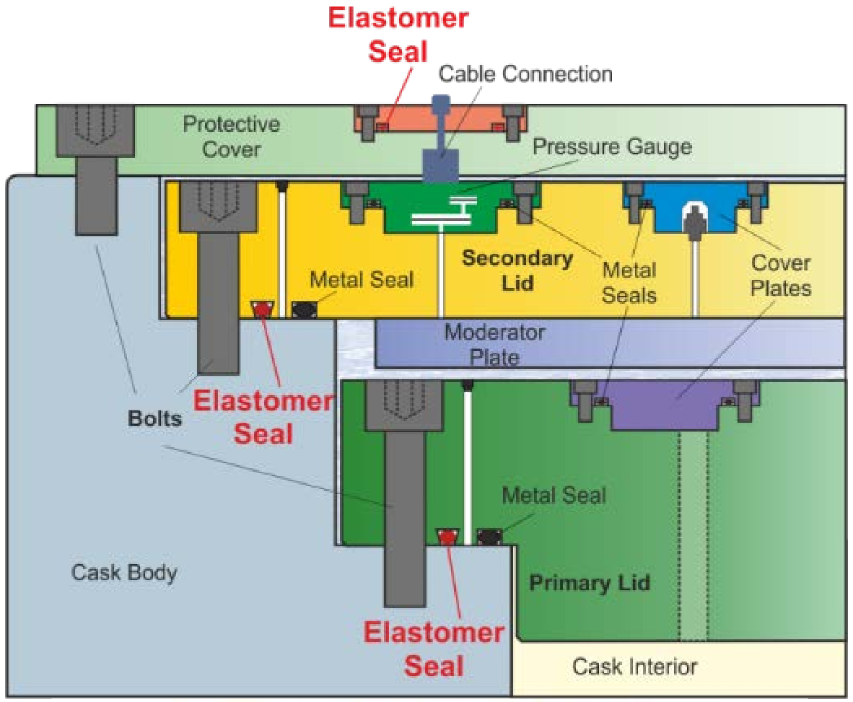
Elastomer Seals

Background

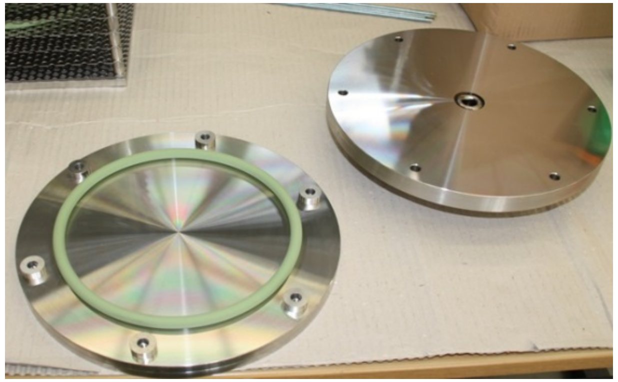
- Elastomer seals are used as auxiliary seals in casks for HLW/SNF and as primary seals in LLW/ILW containers
- Different materials are used, e.g. FKM and VMQ (in other countries EPDM as well)
- Under the influence of time and temperature, the sealability decreases
- BAM is working on developing suitable methods for accelerated aging and lifetime predictions
- Extensive test programme was initiated

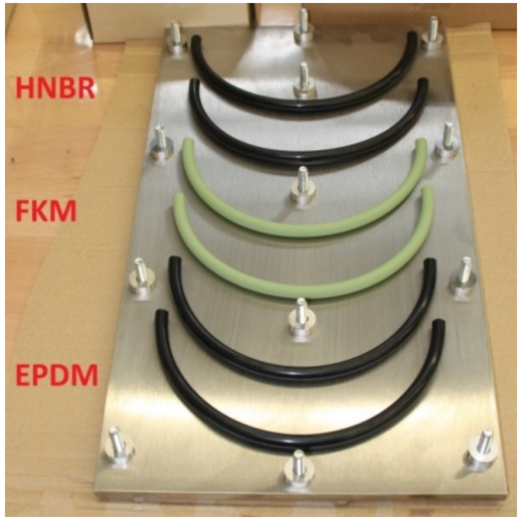


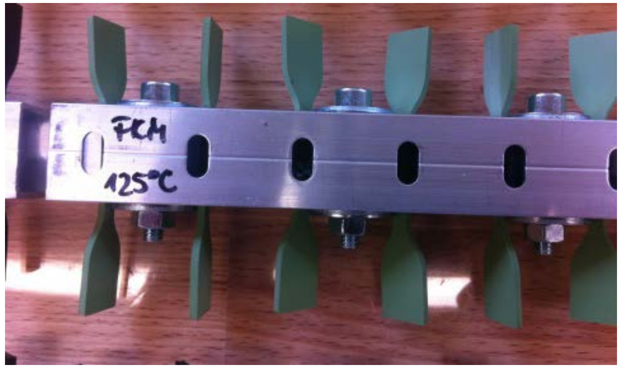
Source: www.gns.de, 01.03.2017

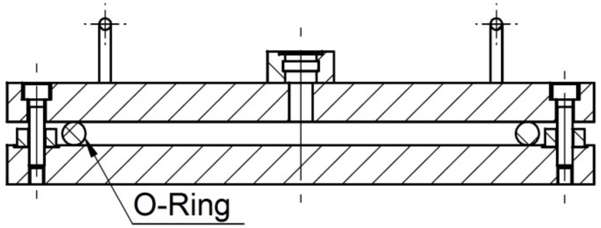
Elastomer Seals
Aging investigations

- Aging of four materials: FKM, VMQ, EPDM, HNBR
- Aging at several temperatures: 150°C, 125°C, 100°C, 75°C (60°C, RT)
- Aging periods from several days up to 5 years
- Aging of different samples: O-rings compressed/uncompressed, component tests (O-ring in flanges for leakage rate measurements), thin sheets, standard specimen for tension and compression tests





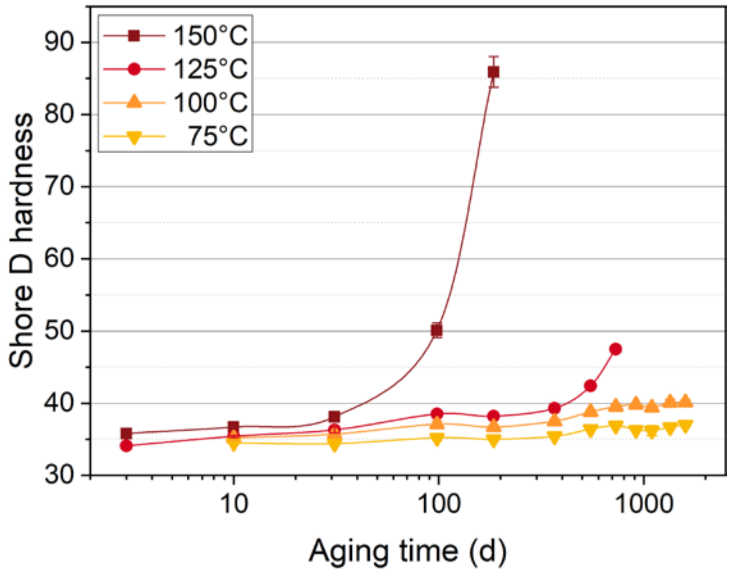




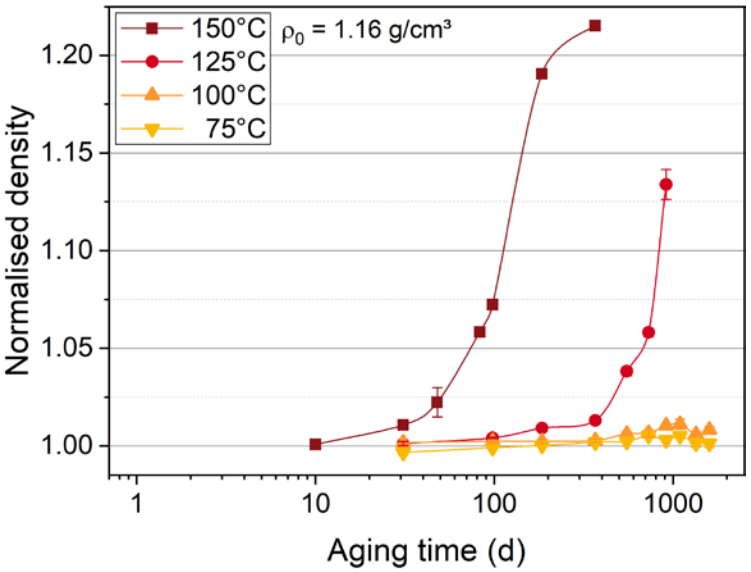
Results

EPDM (sheets)

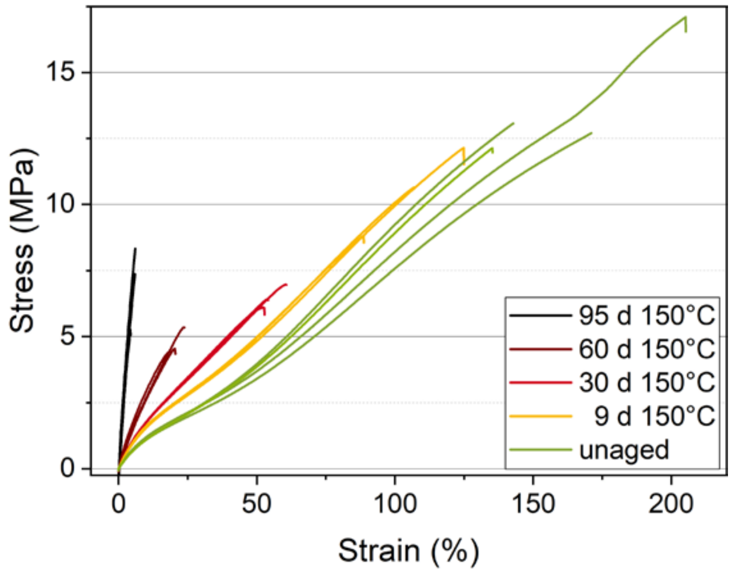
Hardness



Density



Tensile tests



- Hardness and density increase → crosslinking and/or oxygen insertion through chain scission (increase of polarity and intermolecular attraction, heavy O-atoms)
- Decrease of both elongation at break and tensile strength
- ➢ Both crosslinking and chain scissions are relevant degradation processes

Method

Compression Set (CS)

- Samples are aged compressed by 25%
- After release, some time is allowed for recovery
- CS is calculated from remaining deformation

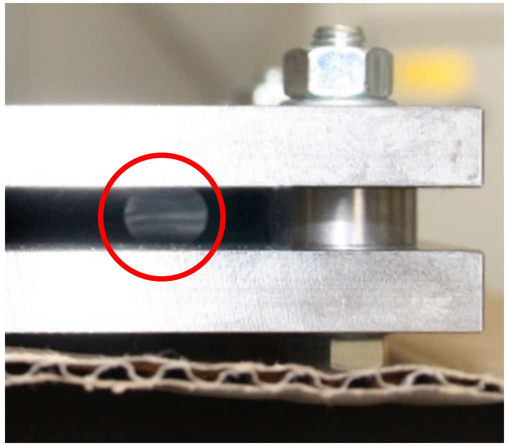
initial height ↘ ↙ recovered height

$$CS = 100\% \frac{(h_0 - h_2)}{(h_0 - h_1)}$$

← compressed height

CS = 100% ⇒ no recovery

CS = 0% ⇒ full recovery



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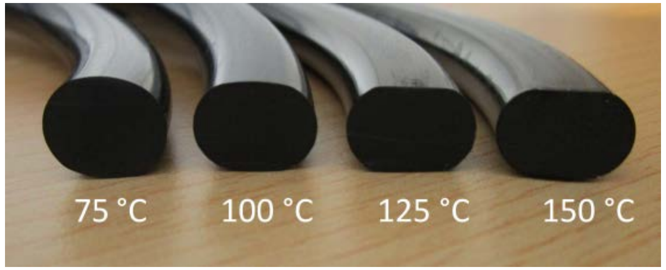
compressed height

CS = 100% ⇨ no recovery

CS = 0% ⇨ full recovery

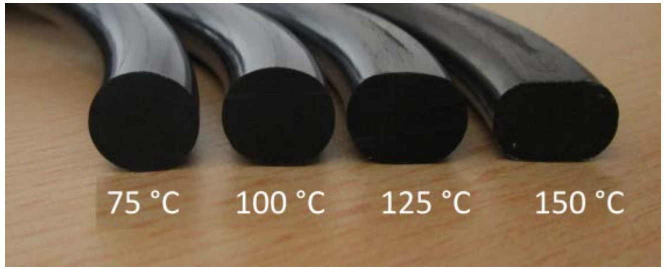
Compression set after 101 days of ageing

HNBR



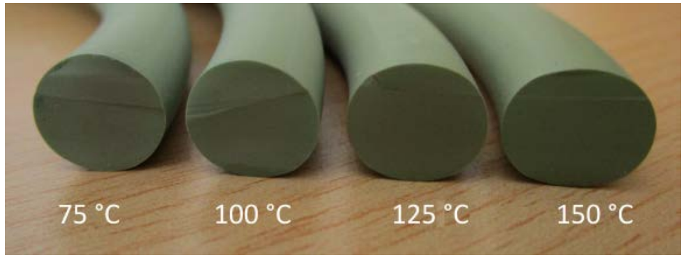
33% 59% 82% 80%

EPDM



13% 23% 56% 94%

FKM

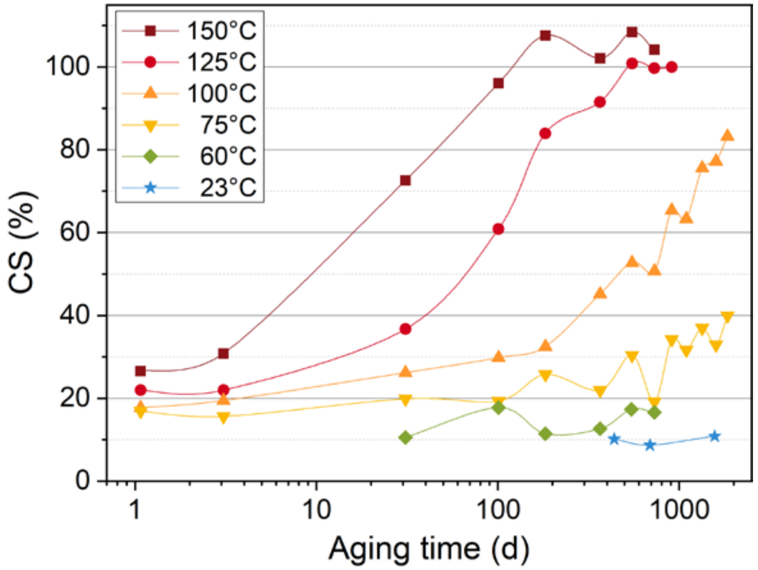


10% 10% 19% 29%

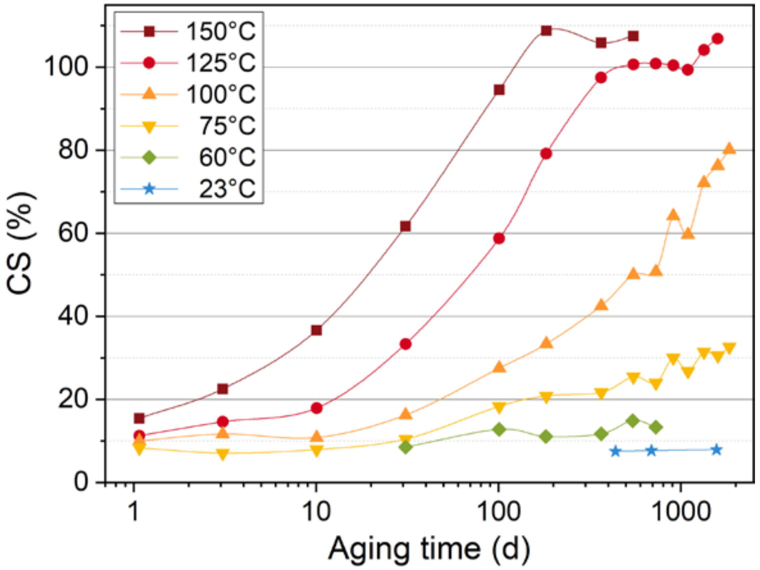
Results

EPDM – CS

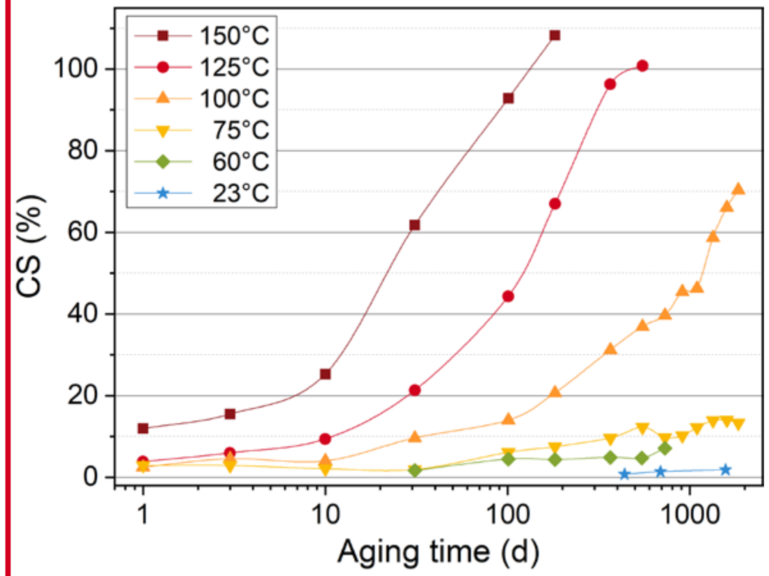
after 30 min



after 5 days



after tempering



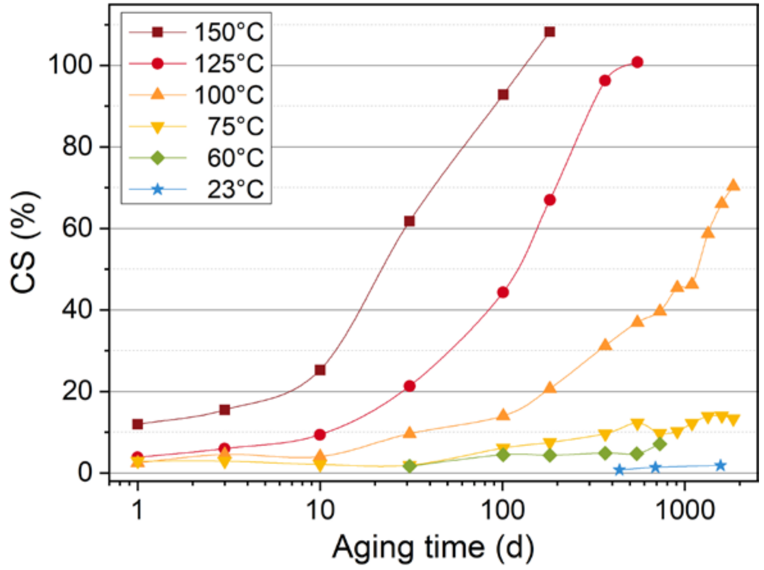
- According to standards ASTM D395 and DIN ISO 815-1
- High measurement time error

- Time dependency has decreased, smoother curves

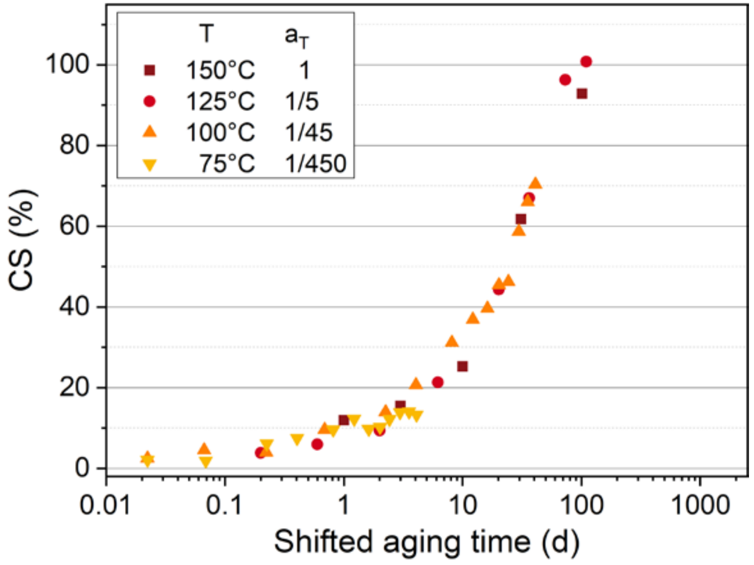
- Tempering (1 d at 100°C) yields lower values basically at equilibrium
- No time-dependence
- More reliable data

Results
EPDM – CS – TTS

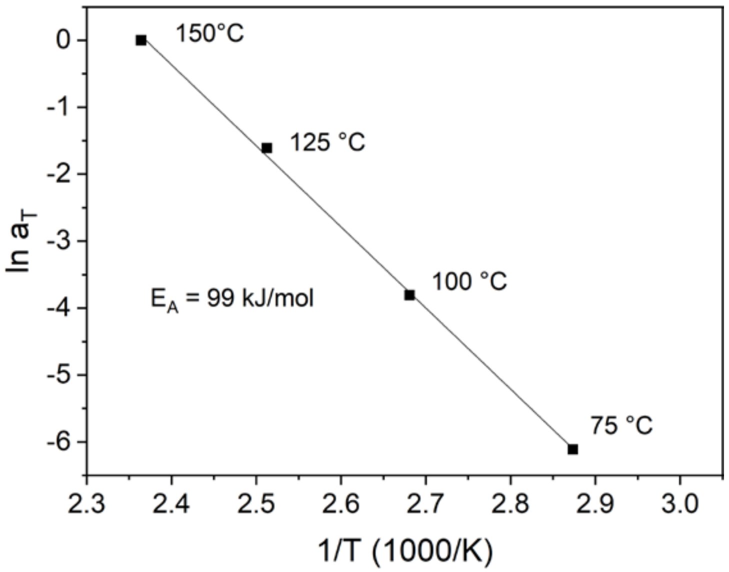
CS after tempering



CS - TTS



Arrhenius plot



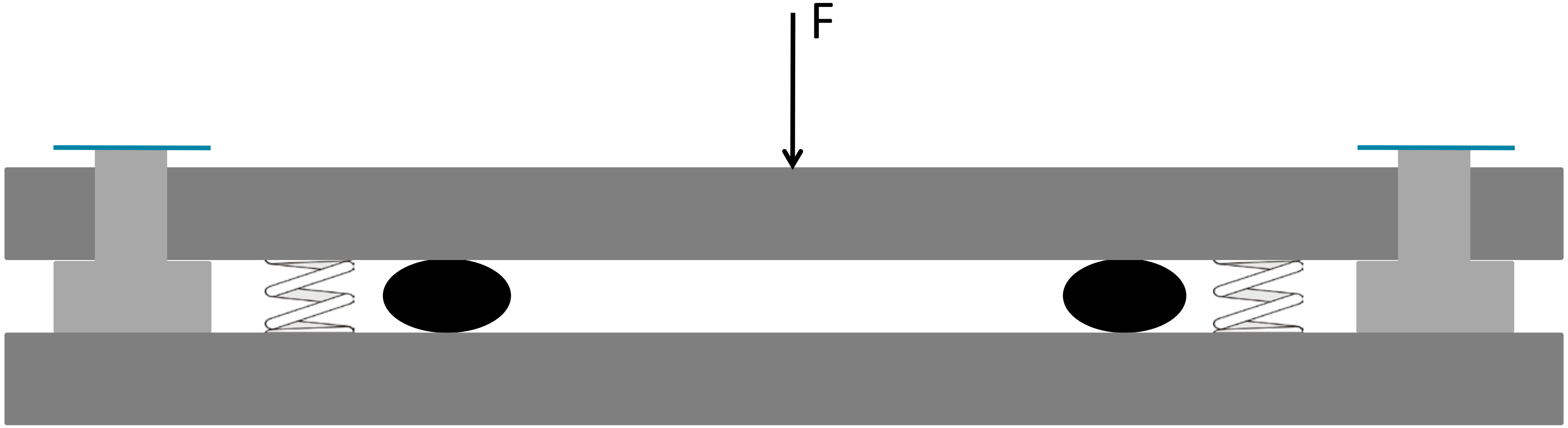
- As compression set is sensitive to degradation and related to the sealing function, it is chosen as the property for lifetime prediction using TTS
- TTS allows shifting data measured at higher temperatures to lower temperatures
- Lifetime at 75°C is 450 times longer than at 150°C
- For lifetime predictions, we need an end-of-lifetime criterion

Results

Determination of end-of-lifetime criterion

- End of the lifetime should be correlated to leakage as the point of seal failure
- Under static conditions, the leakage rate hardly changes and O-rings can remain leak tight down to almost zero sealing force

➢ A modified, more demanding leakage test involving a fast small partial decompression of the seal was developed



25% compression

Results

Determination of end-of-lifetime criterion

- End of the lifetime should be correlated to leakage as the point of seal failure
- Under static conditions, the leakage rate hardly changes and O-rings can remain leak tight down to almost zero sealing force

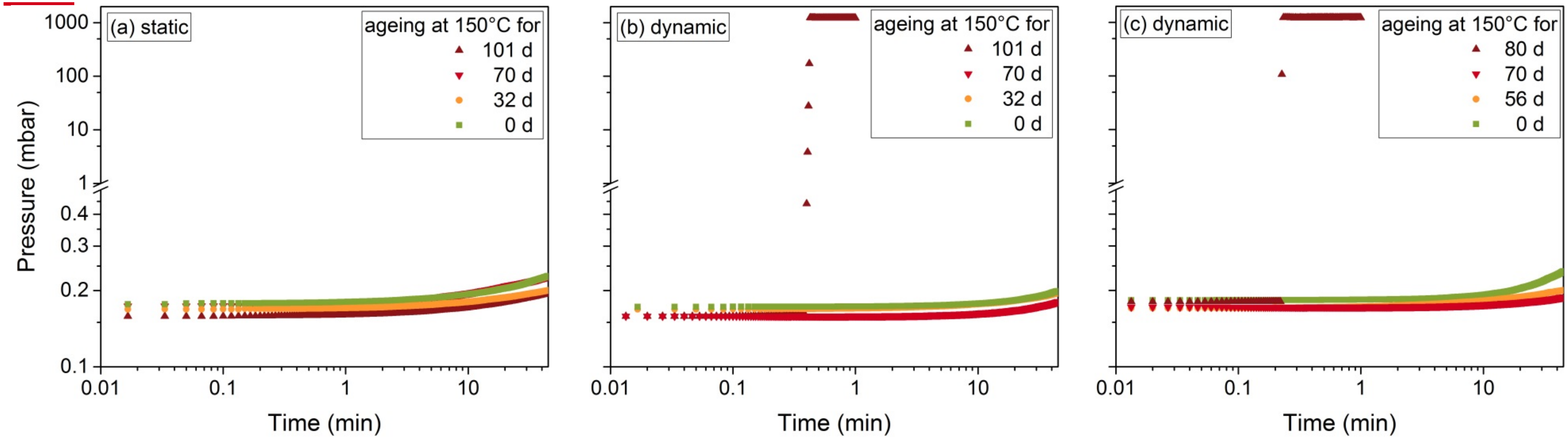
➢ A modified, more demanding leakage test involving a fast small partial decompression of the seal was developed

23% compression

(Δ = 0,2 mm)

Results

Determination of lifetime criterion for EPDM O-Ring



- Under static conditions, the seal remained leak tight for up to 101 d at 150°C
- During the fast partial decompression, the seal remained leaktight for up to 70 d, but became untight after 101 d aging time at 150°C during the partial decompression

➢ Seal lifetime lies somewhere between 70 und 101 d

- During a second experiment, this range could be narrowed to 70-80 d
- The lifetime is conservatively assumed as 70 d

Results

Lifetime of EPDM O-Ring and general criterion

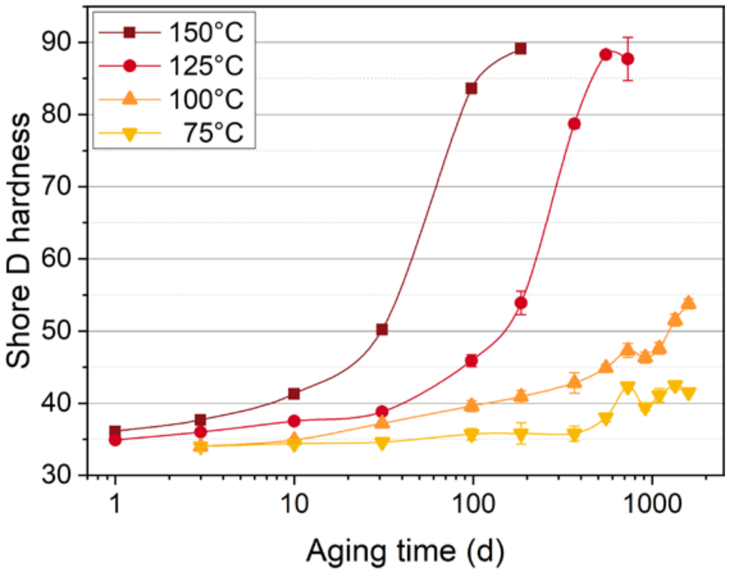
- Using the shift factors from TTS, the lifetime can be calculated for the other temperatures (± 20% confidence band)

- 70 d at 150°C corresponds to 84% CS (in equilibrium)
- EPDM O-rings aged at 125°C remained leaktight in the leakage test with the partial decompression for up to 278 d / 300 d
- This corresponds to 86% CS
- 80-85% CS could be a general end-of-lifetime criterion (also for lubricated seals), however, this has to be verified for other materials

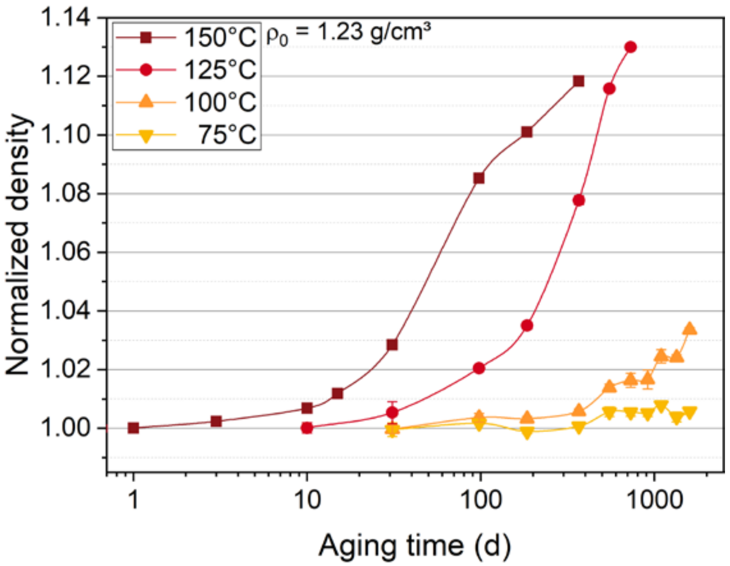
Temp.	a_T	Lifetime
150°C	1	70 d
125°C	5	350 d
100°C	45	8.6 a
75°C	450	86 a

Results
HNBR (sheets)

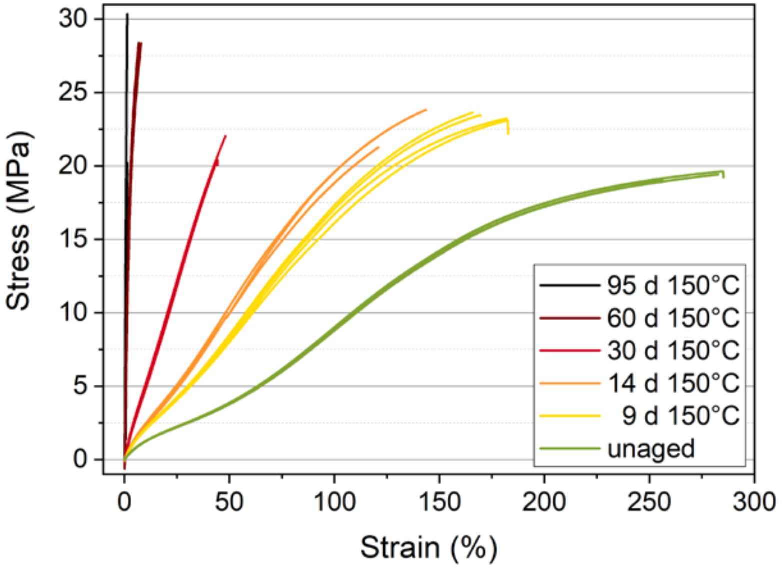
Hardness



Density



Tensile tests



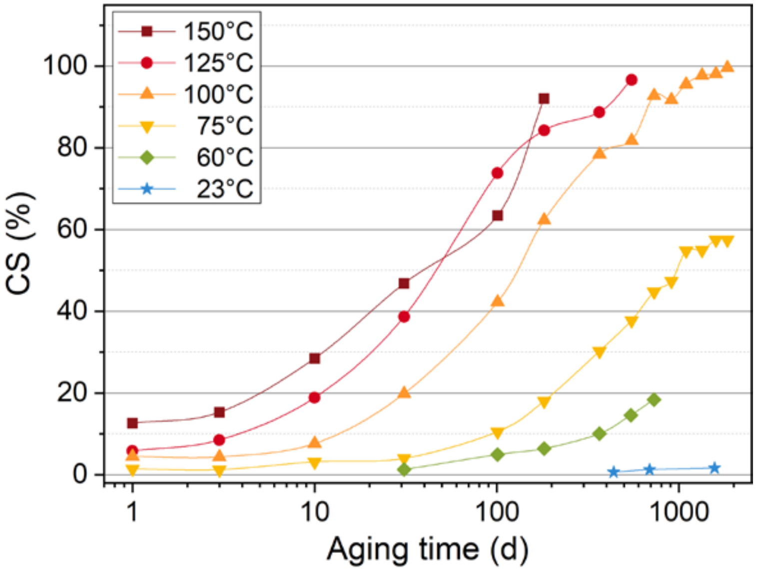
- Hardness and density increase
- Decrease of elongation at break, increase of tensile strength

➢ Embrittlement due to dominant crosslinking reactions

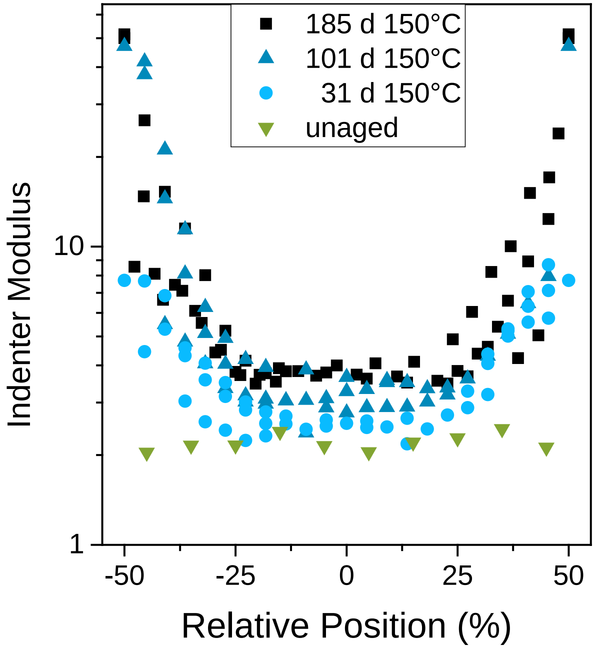
HNBR O-ring after 1 year at 150°C

Results
HNBR (O-rings)

CS (tempered)

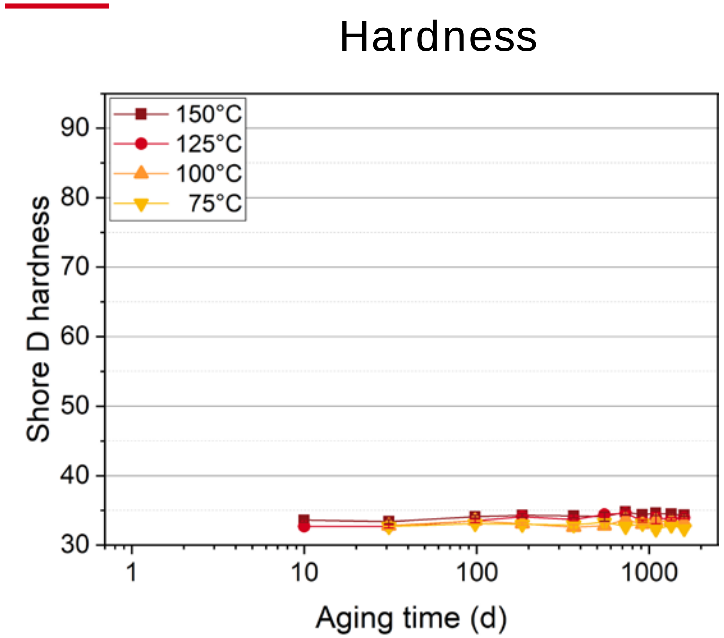


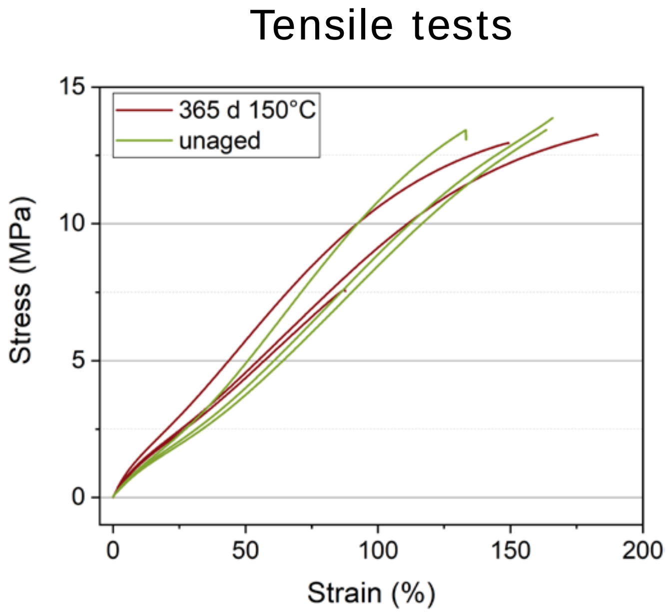
Cut cross-section of HNBR O-ring aged for 100 days at 150°C

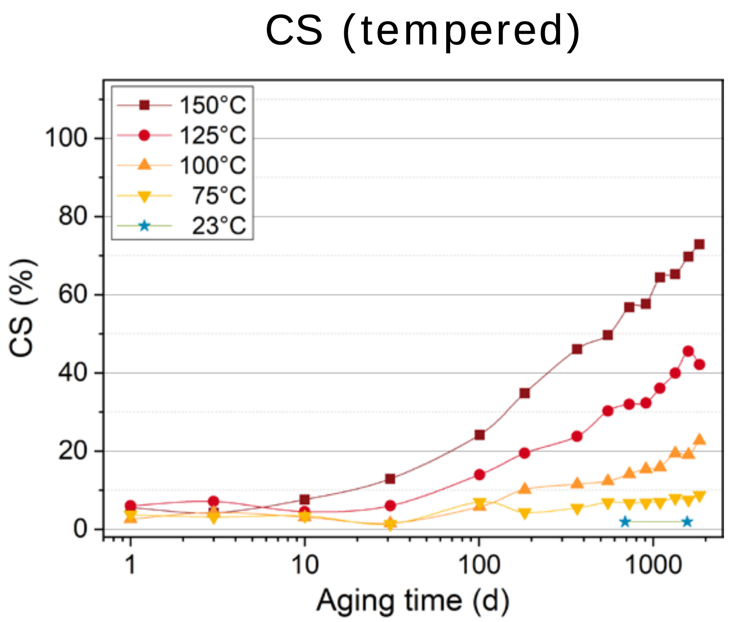


- Clearly distorted CS results for 150°C due to pronounced DLO effects

Results
FKM (sheets)





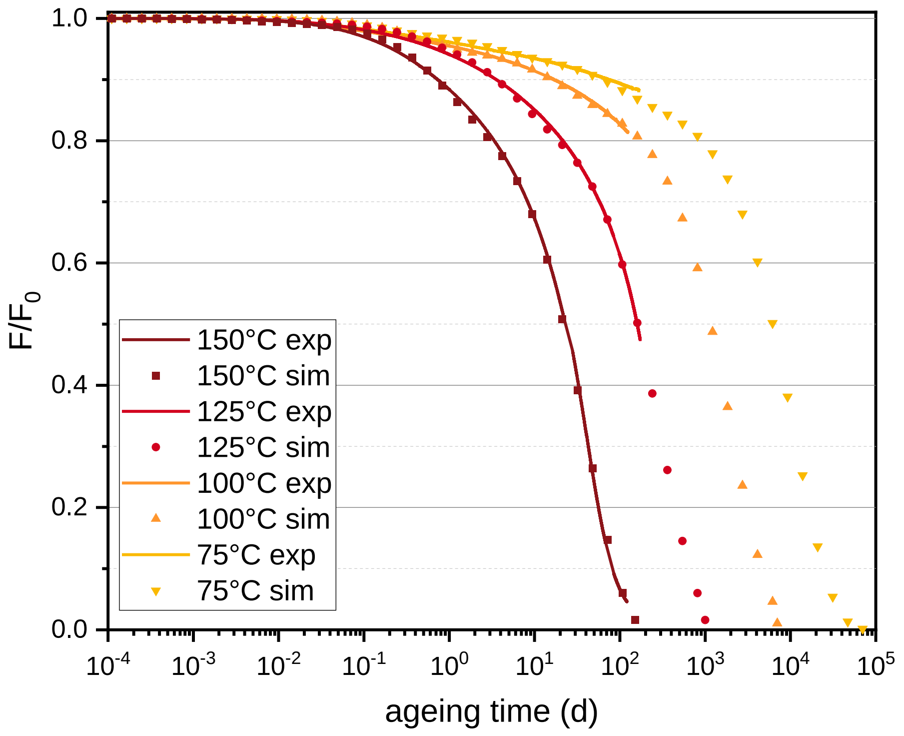


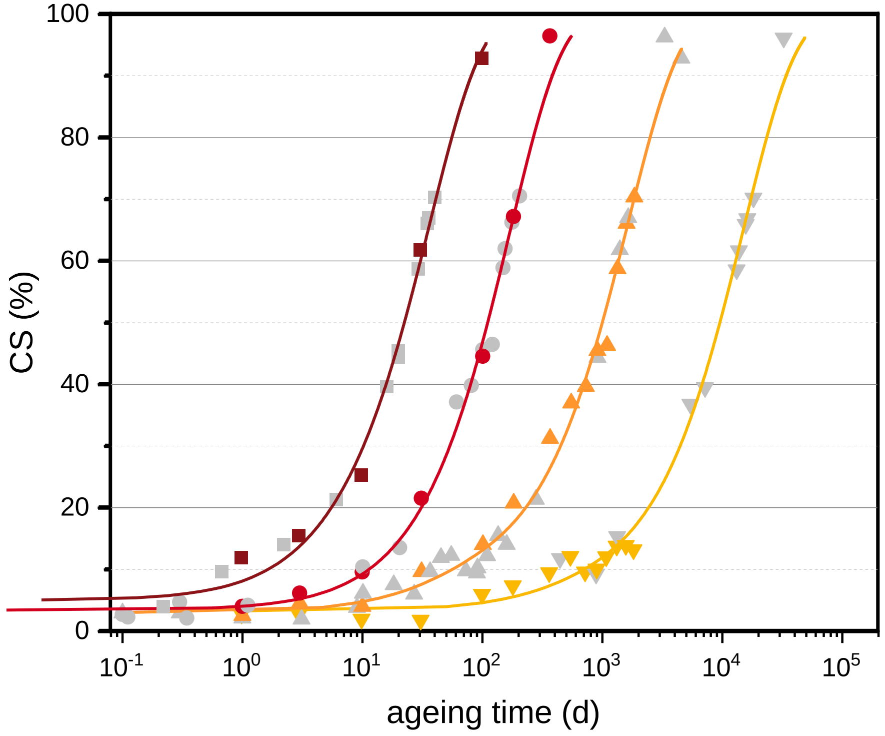
- Hardly any changes visible with these methods due to the high stability of FKM
- CS exhibits notable changes, but much smaller/slower compared to the other materials

Results
Modelling/simulation

Modelling of CSR according to the two-networks theory

Modelling of CS with second order exponential functions based on TTS results





Results

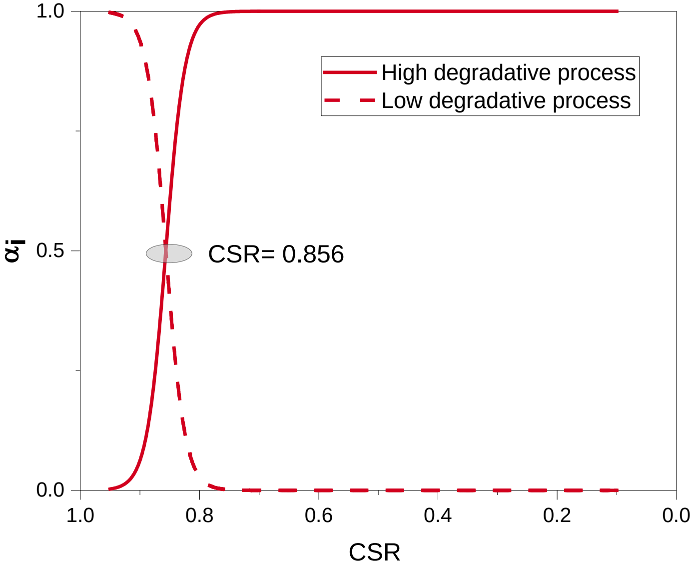
Modelling/Simulation

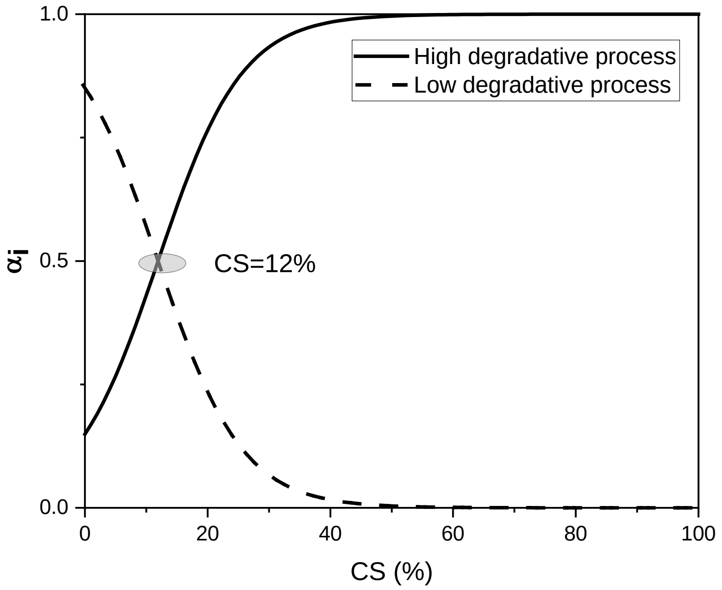
$$\begin{cases} E_a^{total} = \alpha_1 \cdot E_a^{\tau_1} + \alpha_2 \cdot E_a^{\tau_2} \\ \alpha_1 + \alpha_2 = 1 \\ \alpha_1, \alpha_1 \geq 0 \end{cases}$$

$E_a^{\tau_1}$ and $E_a^{\tau_2}$ are single-process energies for low and high degradative processes

$$\begin{cases} \alpha_1 = 0.5 \cdot \left[1 + \tanh\left(\frac{Y - x}{l}\right)\right] \\ \alpha_2 = 0.5 \cdot \left[1 + \tanh\left(\frac{x - \mathrm{Y}}{l}\right)\right] \end{cases}$$

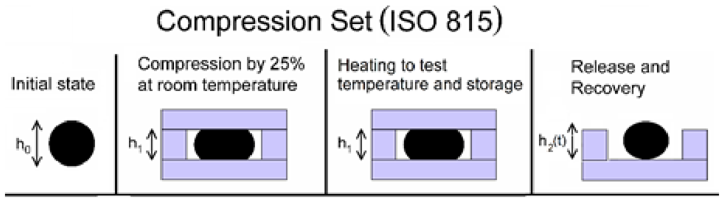
Y	property (as a fraction of initial value)
x	crossover point
l	scaling factor



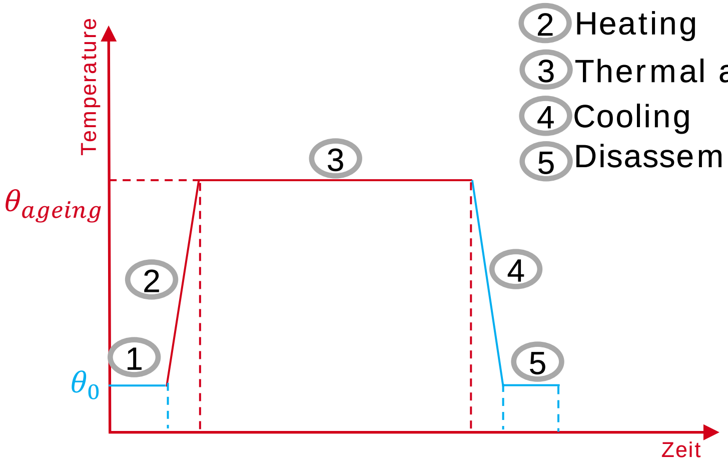


Results
Modelling/Simulation

Simulation with ABAQUS®

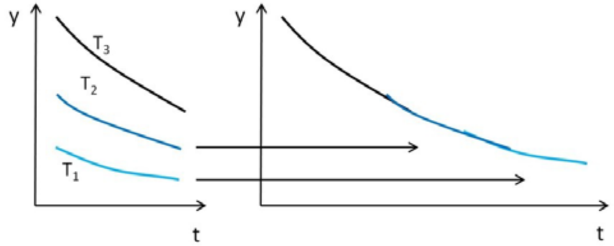


$$cs(\%) = \frac{h_0 - h_2(t)}{h_0 - h_1}$$

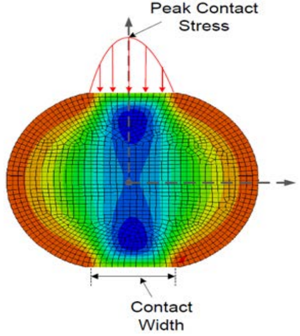


- ① Assembly
- ② Heating
- ③ Thermal ageing
- ④ Cooling
- ⑤ Disassembly

- **Thermo-rheological Temperature Effect**
  - WLF User-Subroutine UTRS



- **Correlation with tightness**



Elastomer Seals

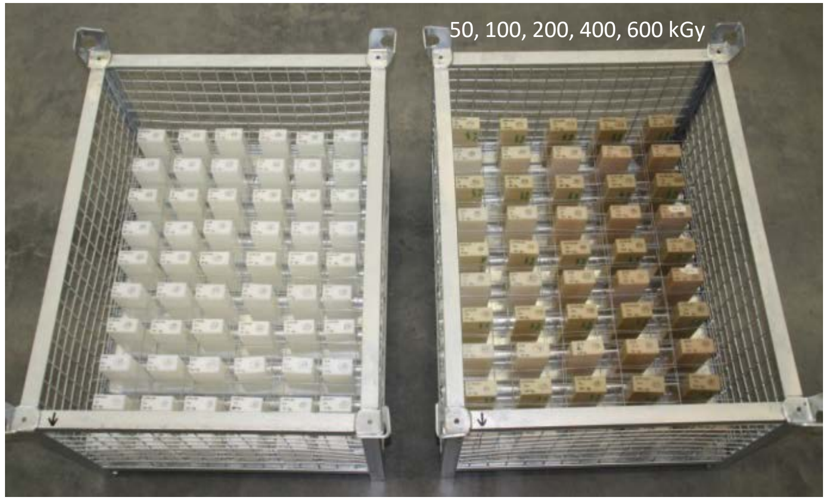
Publications

- Insights for lifetime predictions of O-ring seals from five-year long-term aging tests, A. Kömmling, M. Jaunich, M. Goral, D. Wolff, Polym. Degrad. Stab., 179 (2020) 109278
- Analysis of O-Ring Seal Failure under Static Conditions and Determination of End-of-Lifetime Criterion, A. Kömmling, M. Jaunich, P. Pourmand, D. Wolff, M. Hedenqvist, Polymers 11 (2019) p. 1251
- Erroneous or Arrhenius: A Degradation Rate-Based Model for EPDM during Homogeneous Ageing, M. Zaghdoudi, A. Kömmling, M. Jaunich, D. Wolff, Polymers (2020) 12(9) p. 2152
- Scission, Cross-Linking, and Physical Relaxation during Thermal Degradation of Elastomers, M. Zaghdoudi, A. Kömmling, M. Jaunich, D. Wolff, Polymers (2019) 11(8) p. 1280
- Effects of heterogeneous aging in compressed HNBR and EPDM O-ring seals, A. Kömmling, M. Jaunich, D. Wolff, Polym. Degrad. Stab., 126 (2016) 39-46

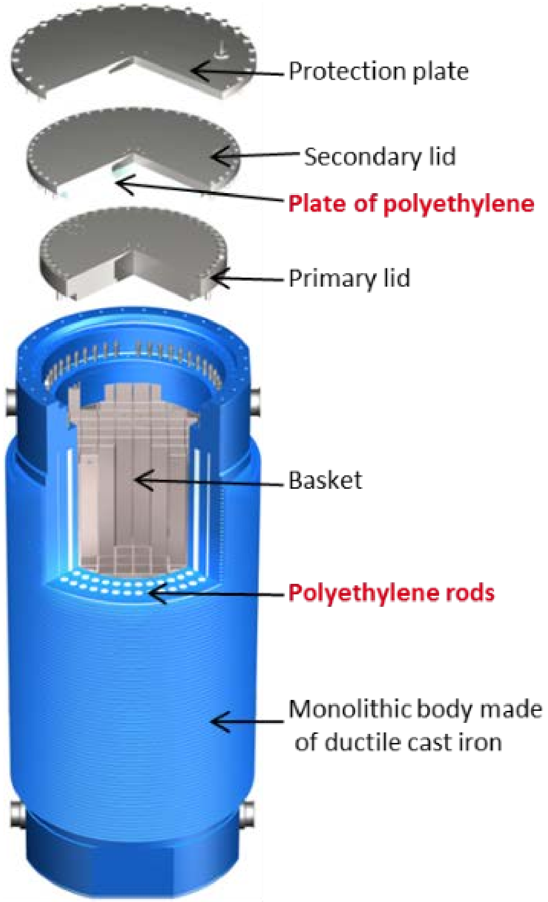
Polyethylene Neutron Shielding Materials

Background and Testing

- Poleythylenes (PE) with very high molecular weight are used as neutron shielding materials in the cask body, lid system and bottom
- The influence of time, temperature and radiation leads to material changes/degradation of the PE materials
- Test program with two materials (HMWPE & (U)HMWPE) was started: radiological ageing with doses ranging from 50 to 600 kGy and subsequent thermal aging at 125°C up to 5 years



Left: untreated samples before aging at 125°C
Right: Samples irradiated with different doses before aging at 125°C



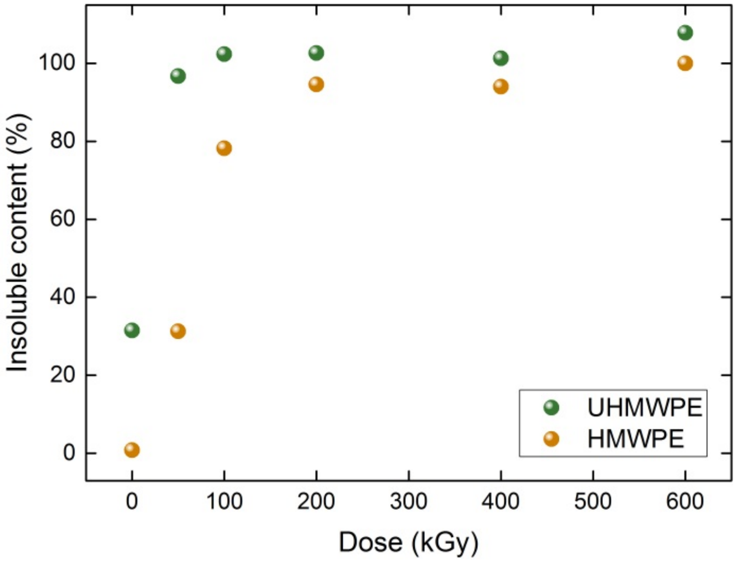
CASTOR® V cask design by GNS

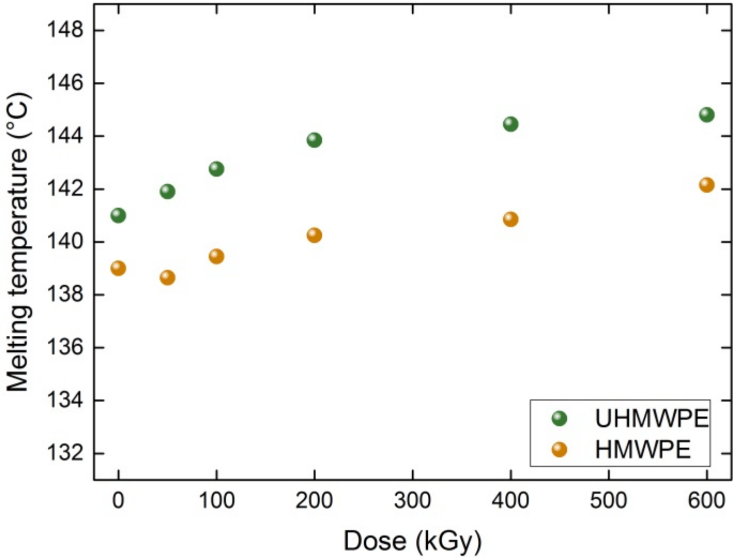
Polyethylene Neutron Shielding Materials

Results

– **UHMWPE** (GUR)
- Irradiation caused crosslinking and slight increase of melting temperature

– **HMWPE** (Lupolen) containing phenolic antioxidant
- Irradiation caused crosslinking and slight increase of melting temperature





Polyethylene Neutron Shielding Materials

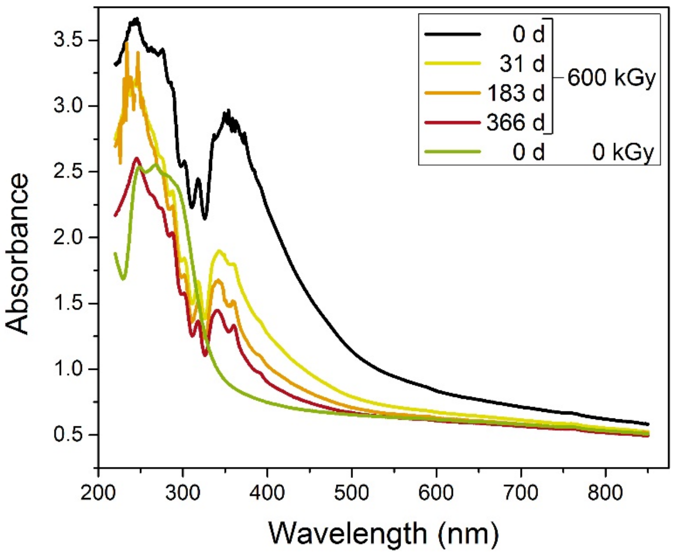
Results

– **UHMWPE** (GUR)

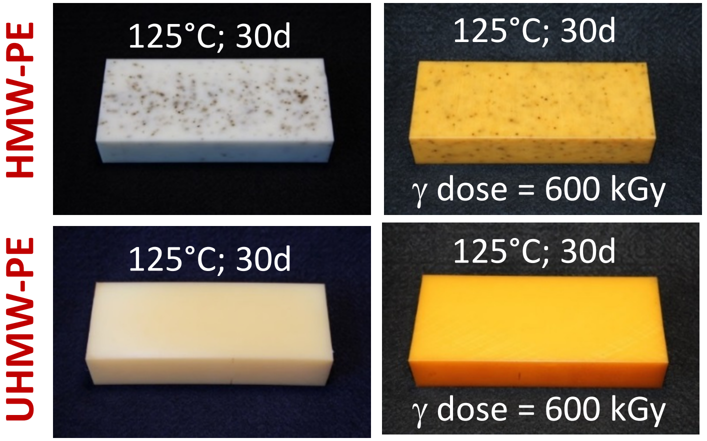
- Irradiation caused crosslinking, increase of T_M and yellowing
- Yellowing was reversed during thermal aging

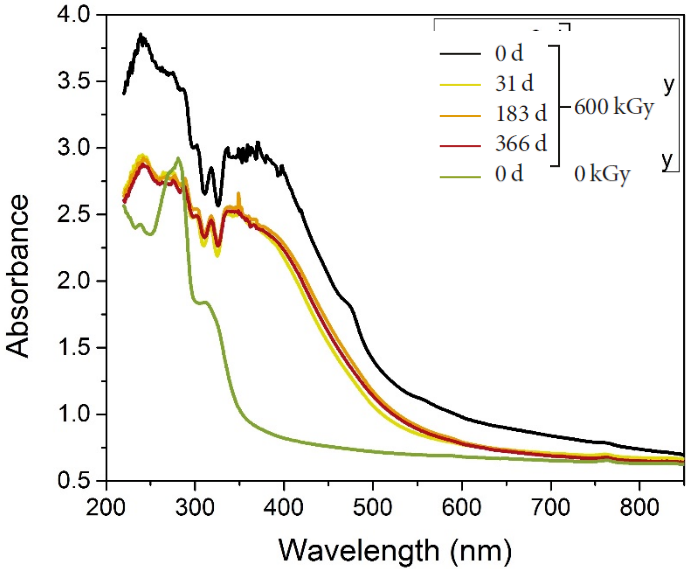
– **HMWPE** (Lupolen) containing phenolic antioxidant

- Irradiation caused crosslinking, increase of T_M and strong yellowing
- Yellowing was partly reversed during thermal aging, partly due to AO decomposition
- Thermal aging caused the formation of black spots



UV-Vis Spectra of UHMWPE after different irradiation and thermal aging steps





UV-Vis Spectra of HMWPE after different irradiation and thrmal aging steps

Polyethylene Neutron Shielding Materials

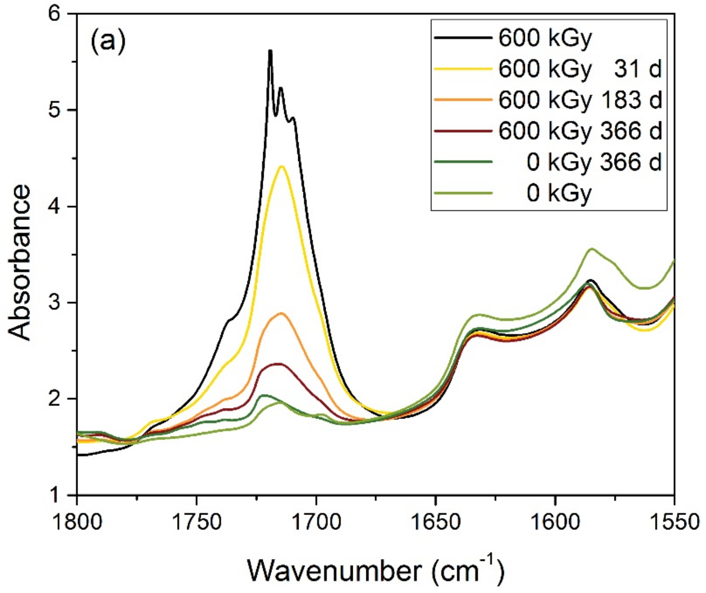
Results

– **UHMWPE** (GUR)

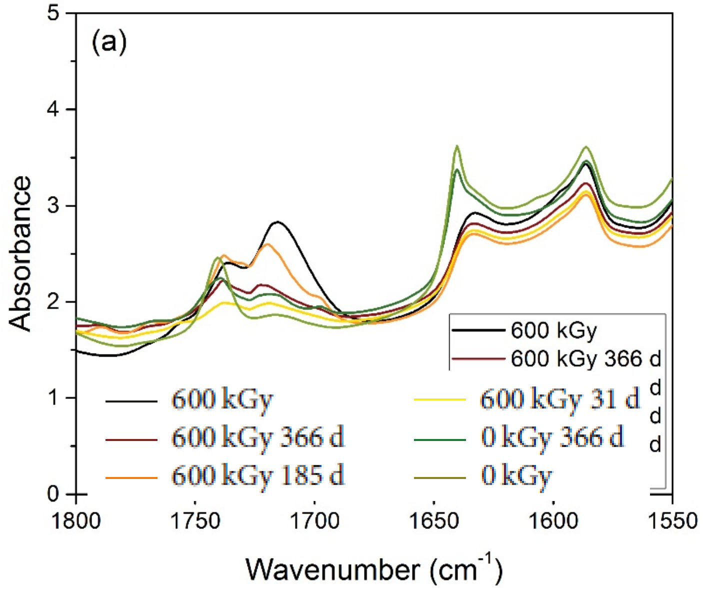
- Irradiation caused crosslinking, increase of T_M, yellowing and carbonyl group formation
- Yellowing and IR carbonyl peak were reversed during thermal aging

– **HMWPE** (Lupolen) containing phenolic antioxidant

- Irradiation caused crosslinking, increase of T_M, strong yellowing and small carbonyl peak
- Yellowing and carbonyl peak were partly reversed during thermal aging



IR Spectra of UHMWPE after different irradiation and thermal aging steps



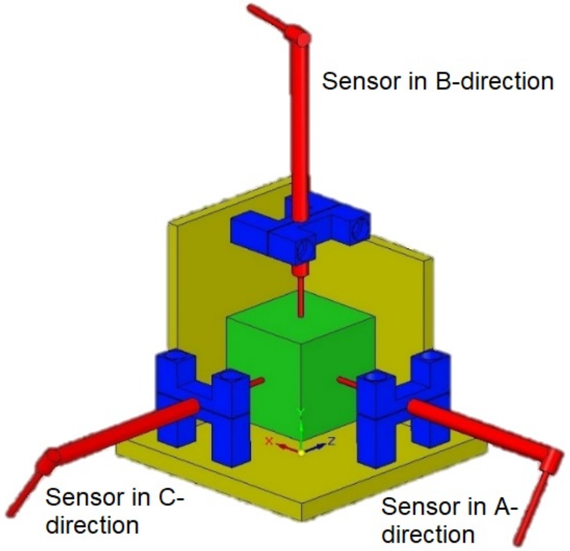
IR Spectra of HMWPE after different irradiation and thrmal aging steps

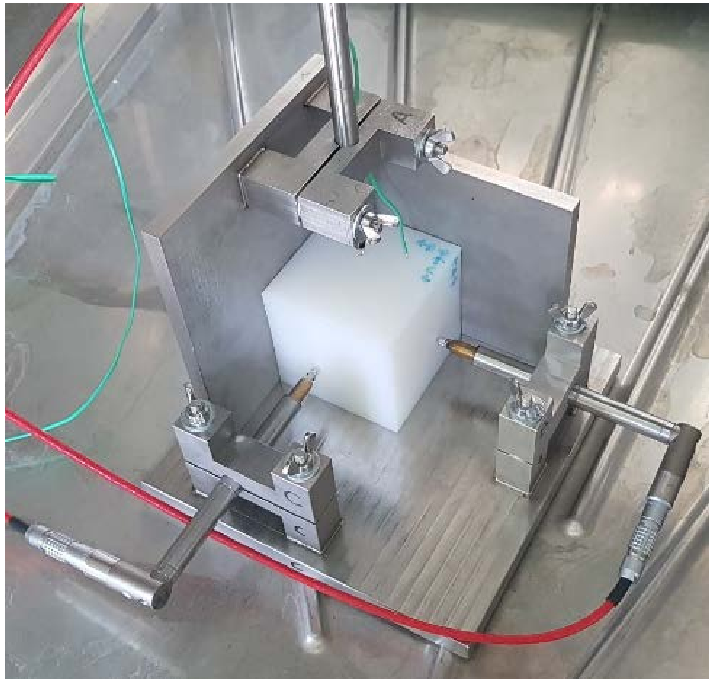
Polyethylene Neutron Shielding Materials

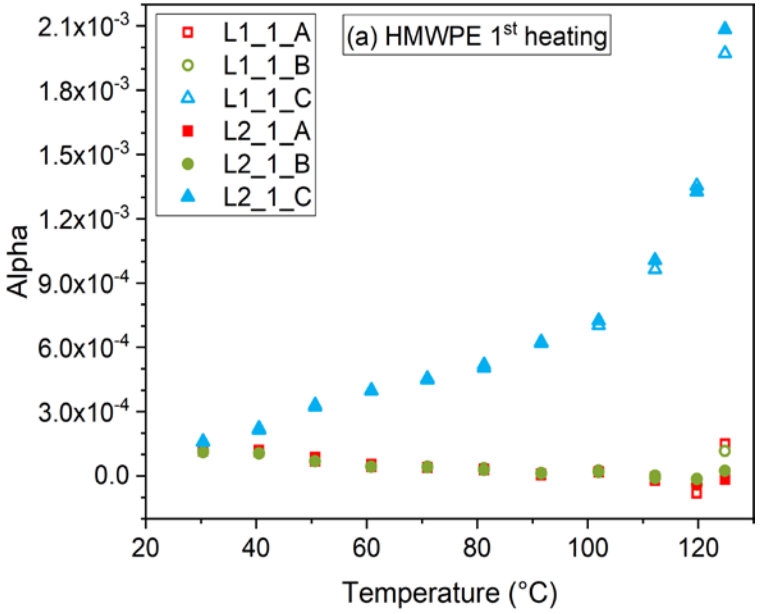
Thermal Expansion

– Second focus point: thermal expansion of PE due to decay heat can be an issue if there is not enough space

➢ Construction of devices for measuring both PE cubes, and rods to scale as in CASTOR® casks







Thermal expansion coefficients (alpha) measured in three different directions on two cube samples of HMWPE with ca. 8x8x8 cm³

Polyethylene Neutron Shielding Materials
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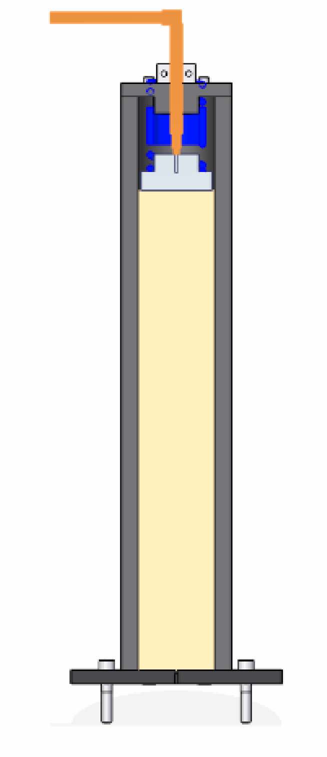

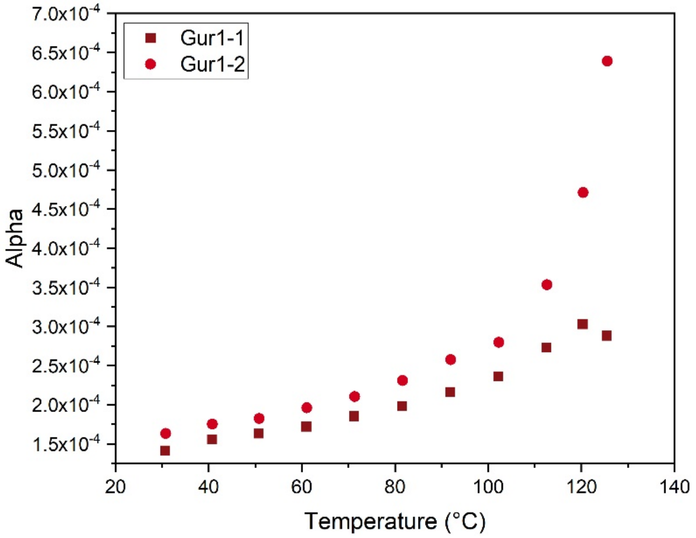

Thermal expansion coefficient during first and second heating run of UHMWPE (Gur) rod with 50 x 7,8 cm

Polyethylene Neutron Shielding Materials

Publications

- Discoloration Effects of High-Dose γ-Irradiation and Long-Term Thermal Aging of (U)HMW-PE, A. Kömmling, E. Chatzigiannakis, J. Beckmann, V. Wachtendorf, K. von der Ehe, U. Braun, M. Jaunich, U. Schade, D. Wolff, International Journal of Polymer Science (2017)
- Effect of high-dose gamma irradiation on (U)HMWPE neutron shielding materials, A. Kömmling, K. von der Ehe, D. Wolff, M. Jaunich, Radiat. Phys. Chem. (2018) 142 p.29
- Manuscript about thermal expansion of PE cubes in progress

Thank you for your attention!