Sicherheit in Technik und Chemie

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Aging of elastomer seals for nuclear waste containers – Methods and lifetime prediction

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www.bam.de

Background / Motivation
Role of BAM

- BAM is involved in the current licensing procedures for storage (and transport) casks for nuclear waste
- Extending interim storage of radioactive waste containers will be necessary due to delays in the final repository projects in Germany
- Safety of casks will have to be evaluated with regard to extended storage periods – can the components retain their functionality for several more decades?
- 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

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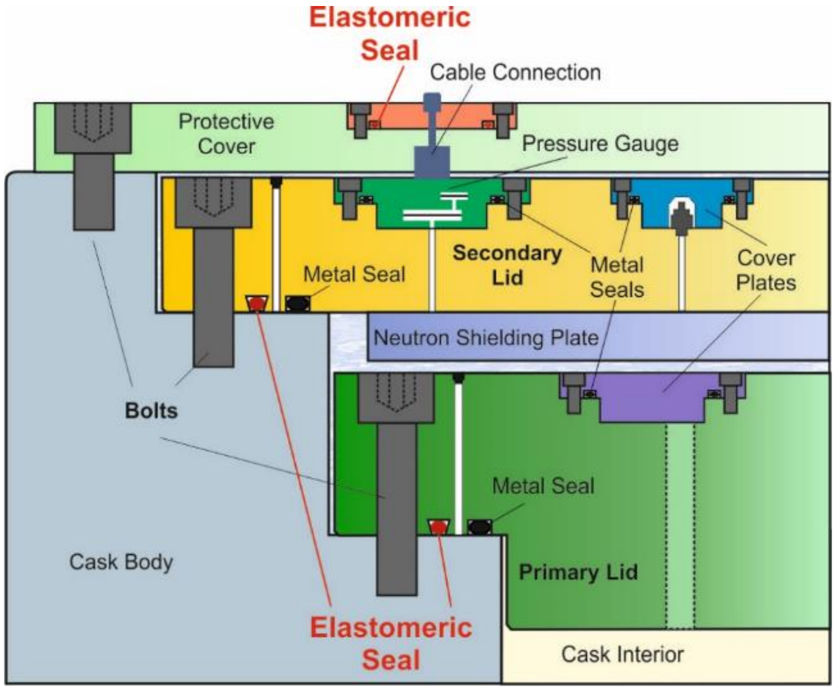
Function of elastomer seals
for safety of casks for radioactive waste



Lid system of a CASTOR® cask for spent fuel

- Elastomer seals are used as main seals or auxiliary seals depending on the cask type
- Complex lid system of the casks
- Risk of exposure when opened

➢ Seals cannot be exchanged easily

➢ They need to maintain leak tightness for extended storage periods (will be more than 40 years in Germany)

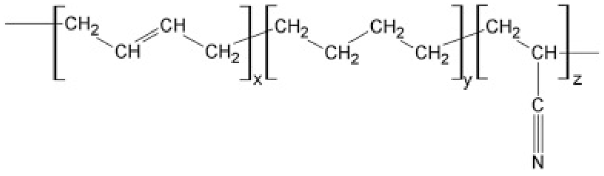
➢ **Aging investigations and lifetime predictions are needed**

Aging program

Materials – Elastomers for sealing applications

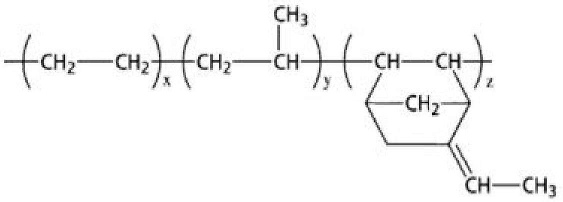
HNBR

- Hydrogenated Acrylonitrile Butadiene rubber
- Oil resistant



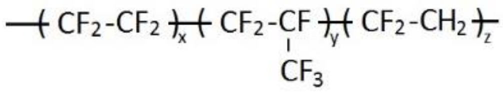
EPDM

- Ethylene Propylene Diene rubber
- Low Tg, water resistant



FKM

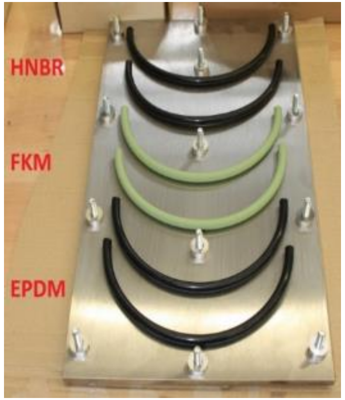
- Fluorocarbon rubber
- High chemical and heat resistance

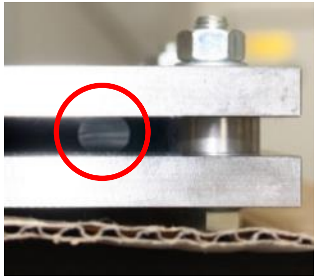


Aging program – O-rings
uncompressed – compressed – in flanges

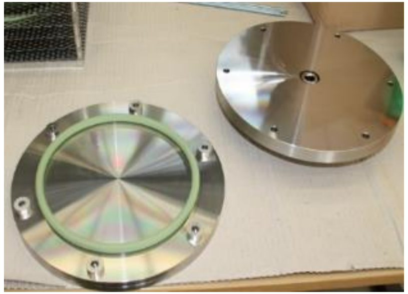
Uncompressed on punched sheets on a rack

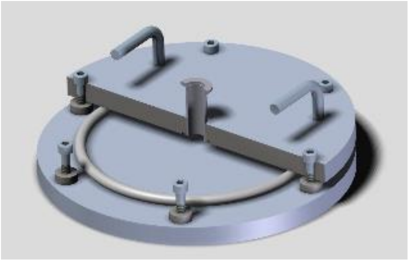
Compressed by 25% between plates





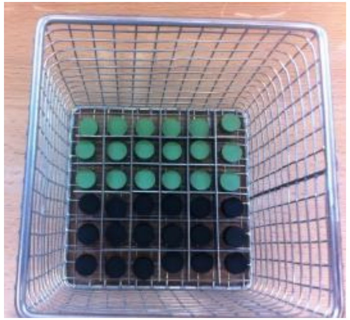
Compressed in flanges for leakage rate measurements





Aging program

Sheets (2 mm) and standard specimen



Aging program
Times & Temperatures

Start: May 2014

Ageing times:

1 d | 3 d | 10 d | 30 d | 100 d | 0.5 a | 1 a | 1.5 a | 2 a | 2.5 a | 3 a | 3.7 a | 4.3 a | 5 a

Ageing temperatures:

150°C, 125°C, 100°C, 75° C (additionally for compression set: 60°C, 23°C)

EPDM O-Ring after ageing for 1 year at 150°C

Aging program
Analysis

Material properties

- Tensile Tests
- Hardness
- Density
- DMA
- Mass loss
- TGA
- Relaxation and Recovery behaviour
- IR spectroscopy
- Kinetic analysis
- ...

Seal properties

- Compression Set
- Compression Stress Relaxation
- Leakage rate

Aging program

Relevant questions/aims

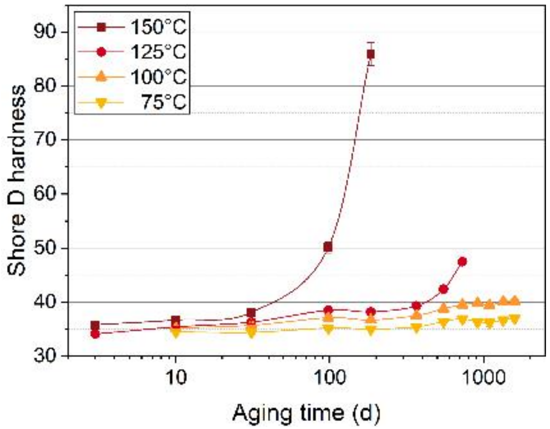
- Analysis of material property changes during aging and investigation of the respective degradation processes
- Determination of a suitable end-of-lifetime criterion for seals
- Reliable lifetime prediction

HNBR O-ring
after 1 year
at 150°C

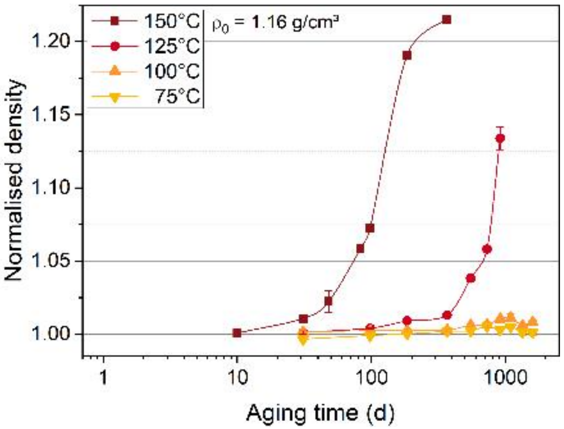
Results

EPDM (sheets)

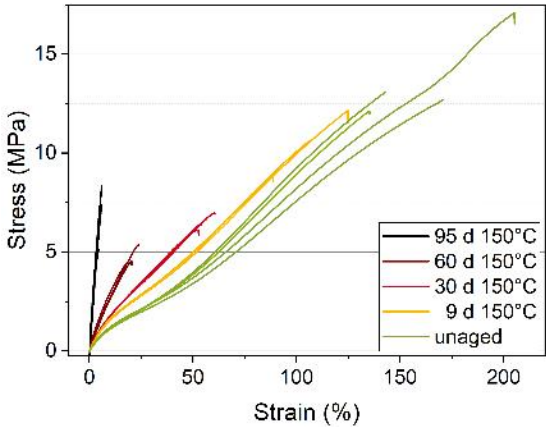
Hardness



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

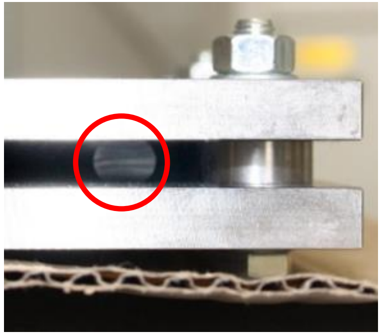
initial height, recovered height

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

compressed height

CS = 100% $\Rightarrow$ no recovery

CS = 0% $\Rightarrow$ full recovery



Method
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initial height

recovered height

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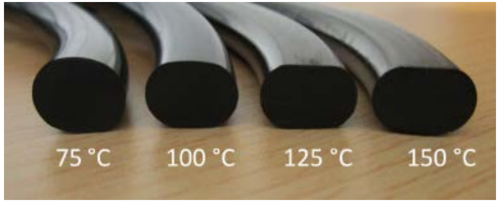
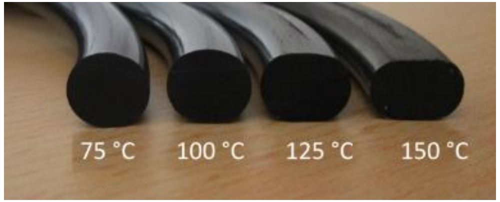
Compression set after 101 days of ageing

HNBR



33% 59% 82% 80%

EPDM



13% 23% 56% 94%

FKM

10% 10% 19% 29%

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% $\Rightarrow$ no recovery

CS = 0% $\Rightarrow$ full recovery

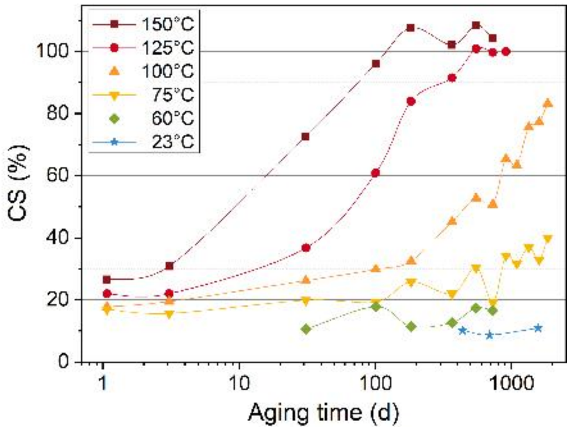
However, CS values depend on recovery time after release:

- 30 min according to standards ASTM D395 and DIN ISO 815-1
- ~ 5 days in previous experiments
- after tempering (1 d at 100°C) to be close to the equilibrium value

➢ For the application, short times after release are often more relevant, but for comparing material degradation, equilibrium values are more meaningful

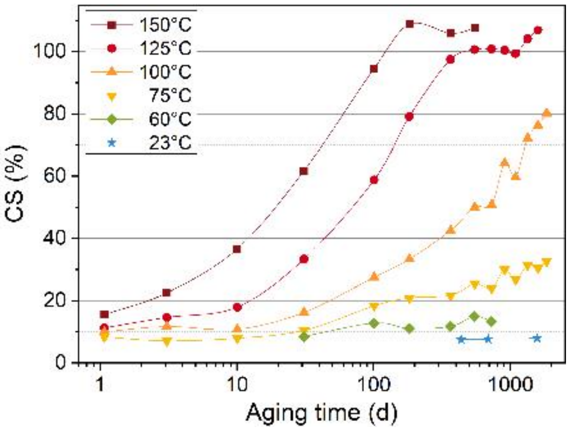
Results
EPDM – CS

after 30 min



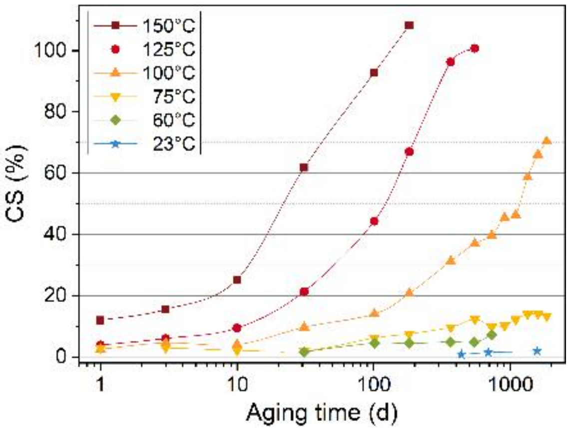
Bad data quality due to uncertainty of release time

after 5 days



Regular data

after tempering

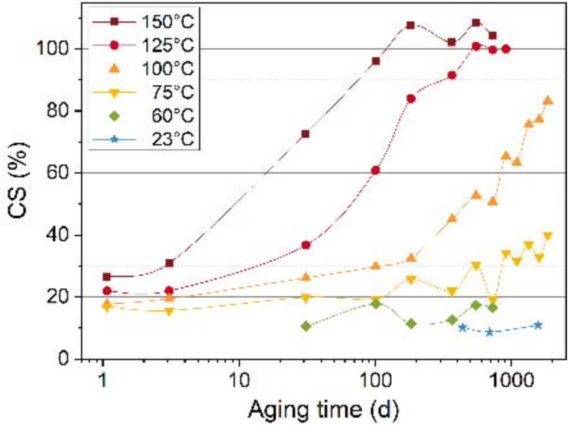


Lower values, especially for less-aged samples

Results

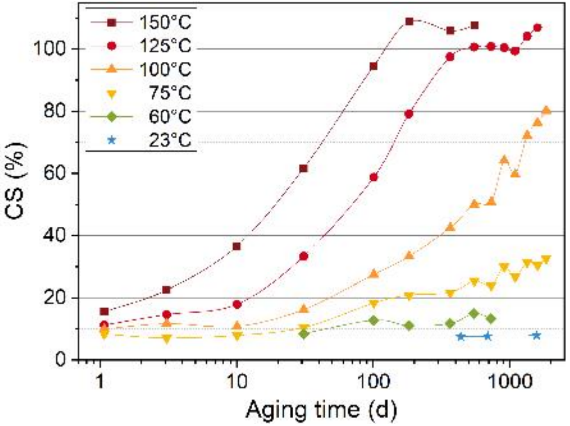
EPDM – CS

after 30 min



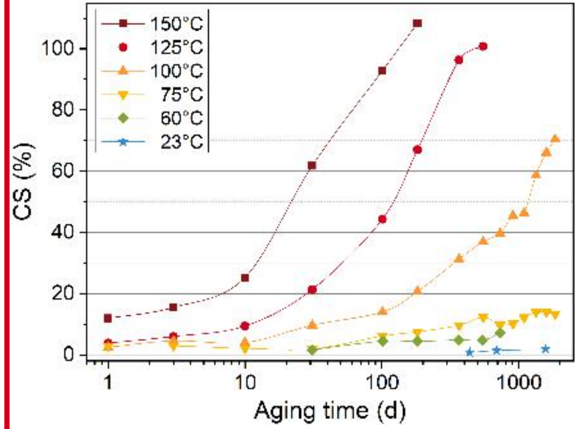
Bad data quality due to uncertainty of release time

after 5 days



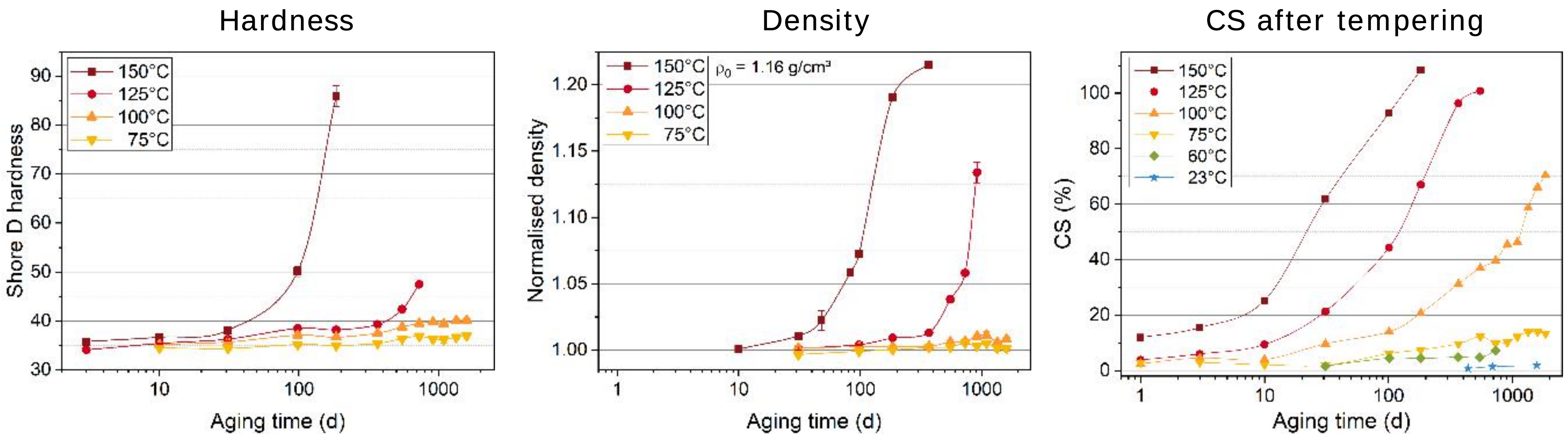
Regular data

after tempering



- **Equilibrium values**
- **No time-dependence**
- **More reliable data**

Results
EPDM



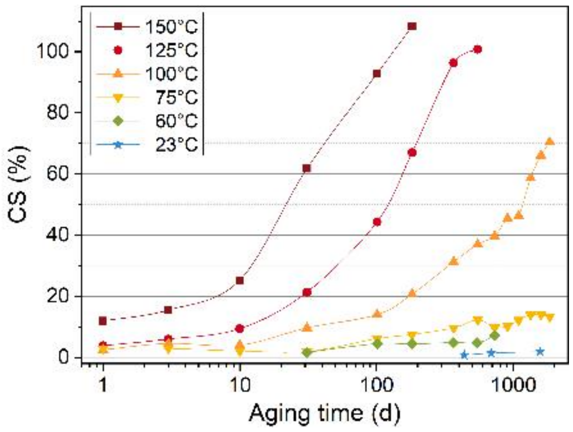
- CS increases much faster than e.g. hardness and density
- Explanation: Hardness/density shows only the net effect of the influence of crosslinking and chain scission, while CS increases additively through both reaction types

➢ **Property changes are measurable much faster**

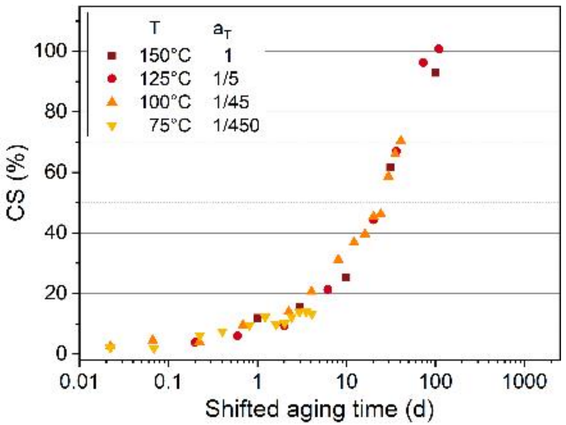
Results

EPDM – CS – TTS

CS after tempering



CS - TTS



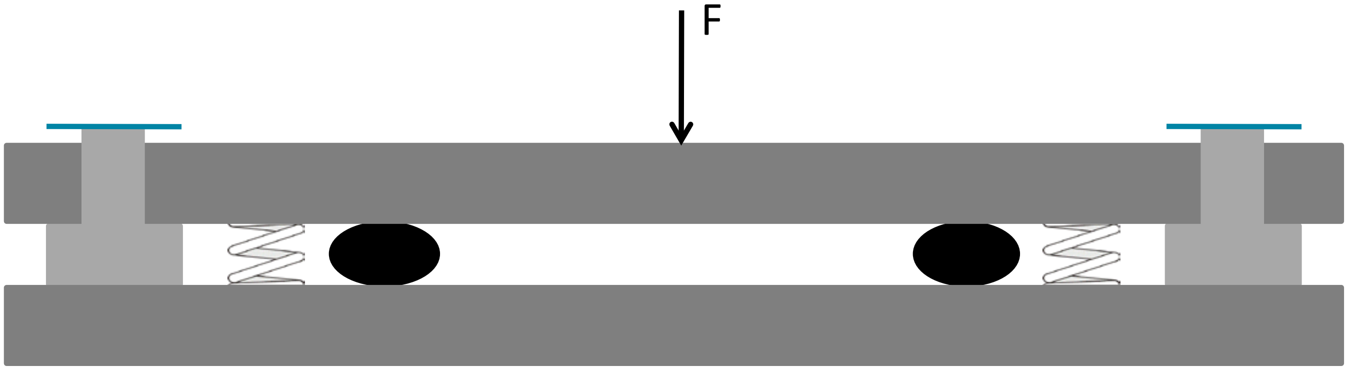
- As compression set is more sensitive to degradation and related to the sealing function, it is chosen as the property for lifetime prediction using TTS
- TTS allows shifting data measured at higher temperatures to lower temperatures
- Lifetime at 75°C is 450 times longer than at 150°C
- For lifetime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

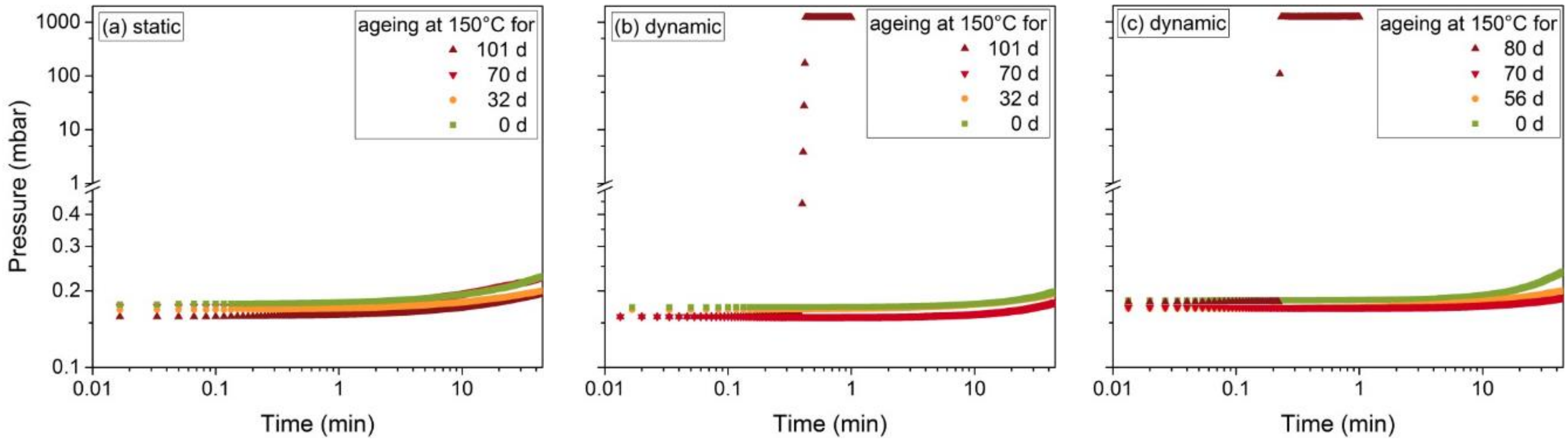
Determination of end-of-lifetime criterion

- 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 ageing 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

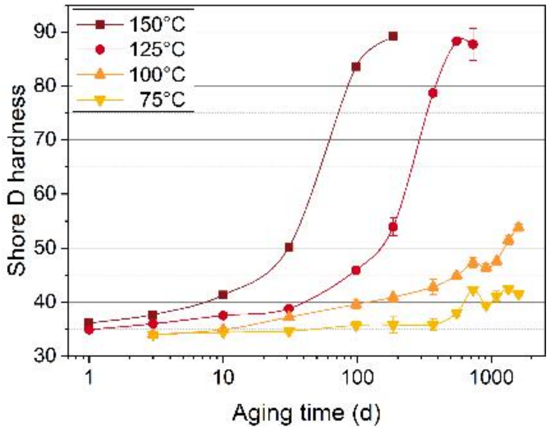
- Using the shift factors from TTS, the lifetime can be calculated for the other temperatures

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

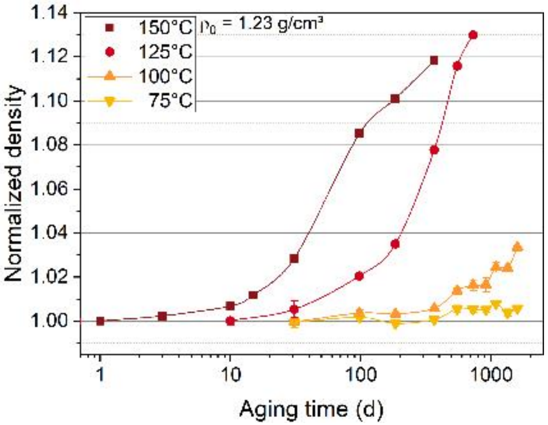
Temp.	a_T	Lifetime
150°C	1	70 d
125°C	5	350 d
100°C	45	8.6 a
75°C	450	86 a

Results
HNBR (sheets)

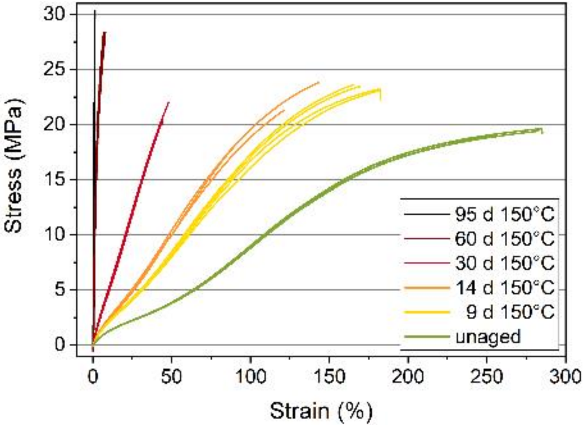
Hardness



Density



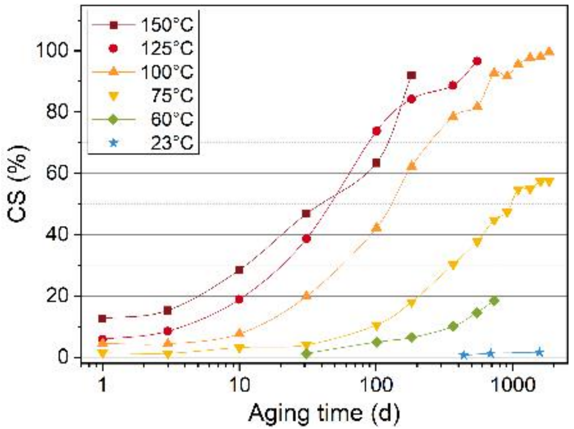
Tensile tests



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

➢ Embrittlement due to dominant crosslinking reactions

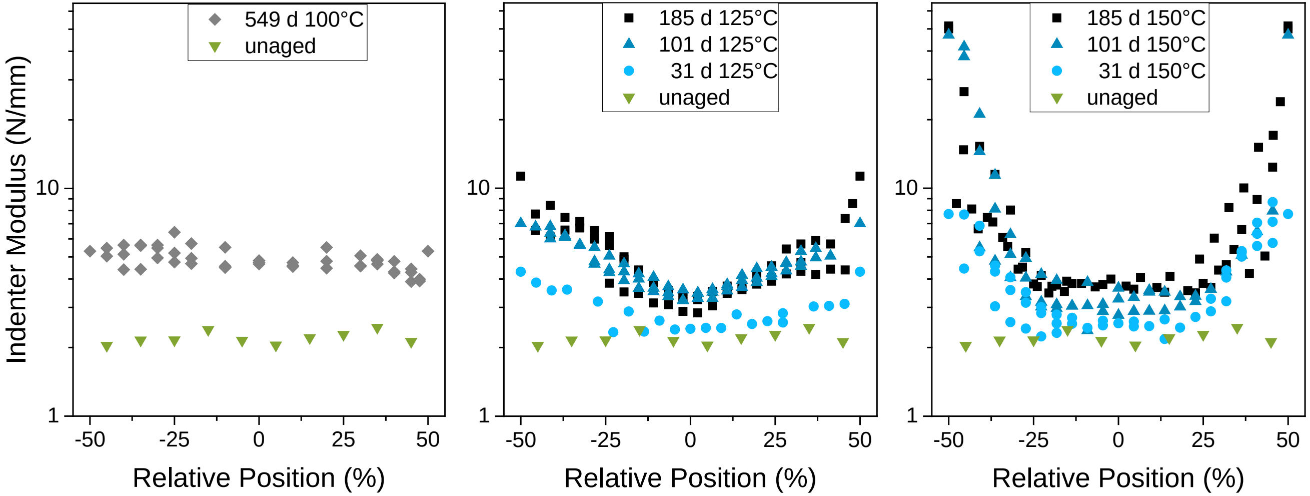
Results
HNBR (O-rings) – CS



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

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

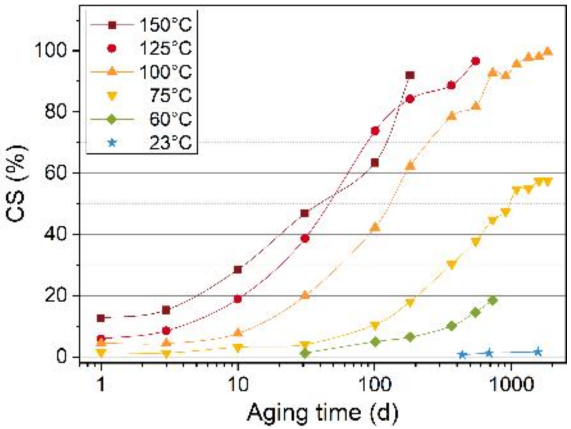
Results
HNBR (O-rings) – DLO effects



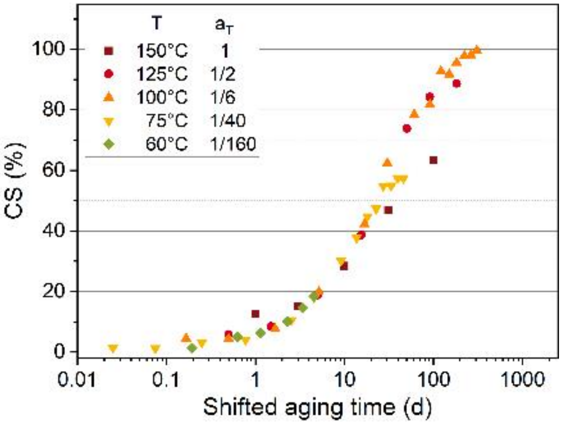
- Clearly distorted results for 150°C due to pronounced DLO effects
- Slight DLO effects at 125°C
- No DLO effects at 100°C (and below)

Results
HNBR (O-rings) – CS - TTS

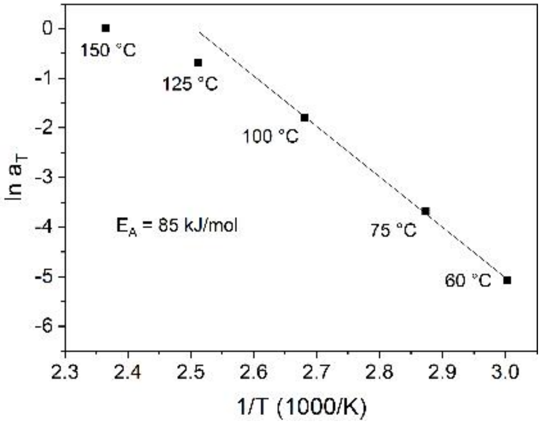
CS values



TTS



Arrhenius plot

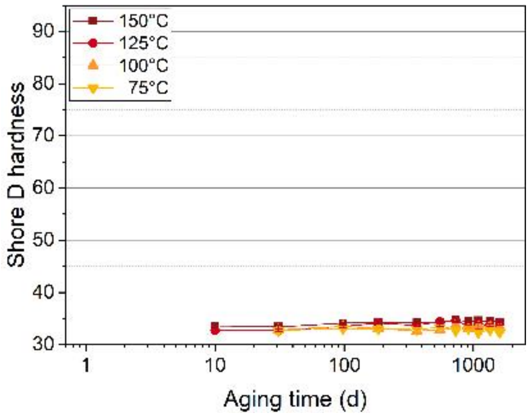


- No superposition for 150°C values with pronounced DLO effects
- Exclusion of 150°C and 125°C from fit for Arrhenius line
- 85% CS is reached after 585 d/1.6 a at 100°C
- Using the shift factors, this corresponds to 10.7 a and 42.7 a at 75°C and 60°C

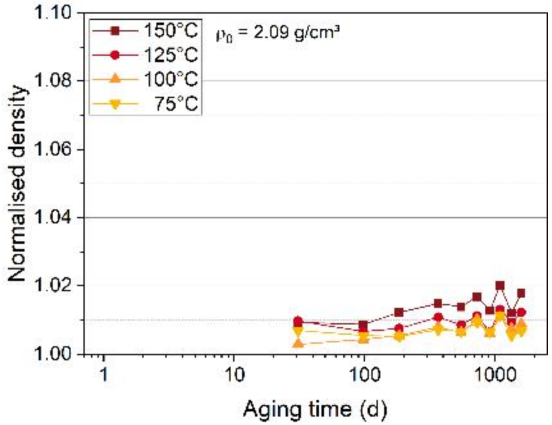
Results

FKM (sheets)

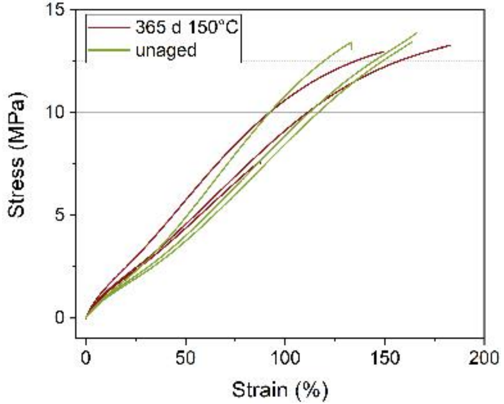
Hardness



Density



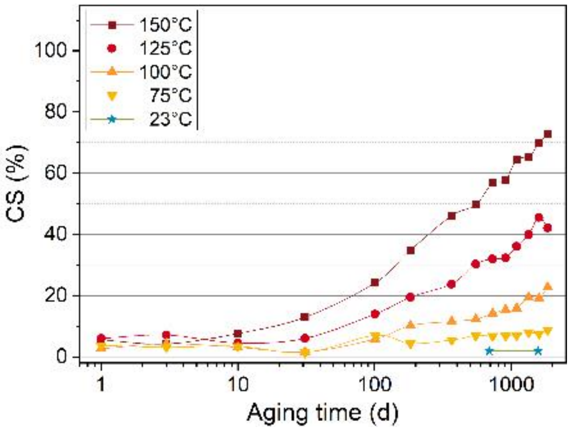
Tensile tests



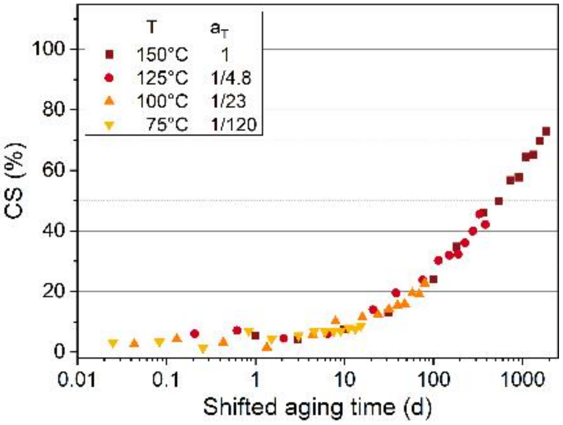
- Hardly any changes visible with these methods due to the high stability of FKM

Results
FKM (O-rings) – CS - TTS

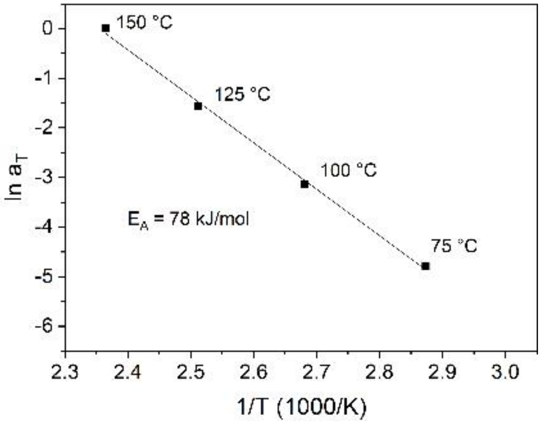
CS values



TTS



Arrhenius plot



- Stronger degradation visible for CS, perhaps due to cage effect
- Highest reached CS after 5 years is 72%
- Using TTS/shift factors, 72% would be reached after 600 years at 75°C
- Note: E_A of FKM is the lowest, but lifetime is the highest

➢ E_A is a measure for the spread between the temperatures, but not for stability

Conclusions

- Crosslinking and chain scission are relevant degradation mechanisms for EPDM, for HNBR it is mainly crosslinking
- DLO effects distort aging data of HNBR at 150°C and (less) at 125°C
- Compression set shows more pronounced degradation than other methods
- Additionally, CS is related to the sealing force/function
- ➢ Lifetime predictions should be performed using (equilibrium) CS data
- Time-temperature superposition is a suitable method for extrapolation
- ➢ End-of-lifetime criterion was determined using a modified leakage test involving a small fast partial decompression of the seal
- Using this test, EPDM seals remained fully functional for up to 70 d at 150°C and 278 d at 125°C (corresponds to 84% and 86% CS)
- Lifetime at 75°C was about 86 years (EPDM), 11 years (HNBR) and 600 years (FKM, for 72% CS)
- Activation energy is not a direct indicator of the oxidative stability

Publications

- 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(8) (**2019**) 1251
- Influence of Ageing on Sealability of Elastomeric O-rings, A. Kömmling, M. Jaunich, P. Pourmand, D. Wolff, U. Gedde, Macromolecular Symposia 373 (1) (**2017**)
- 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
- Revealing effects of chain scission during ageing of EPDM rubber using relaxation and recovery experiment, A. Kömmling, M. Jaunich, D. Wolff, Polymer Testing 56 (**2016**) p. 261-268.
- Scission, Cross-Linking, and Physical Relaxation during Thermal Degradation of Elastomers, M. Zaghdoudi, A. Kömmling, M. Jaunich, D. Wolff, Polymers 11(8) (**2019**) 1280

The End