COMRADE

Workshop December 4-5 2018

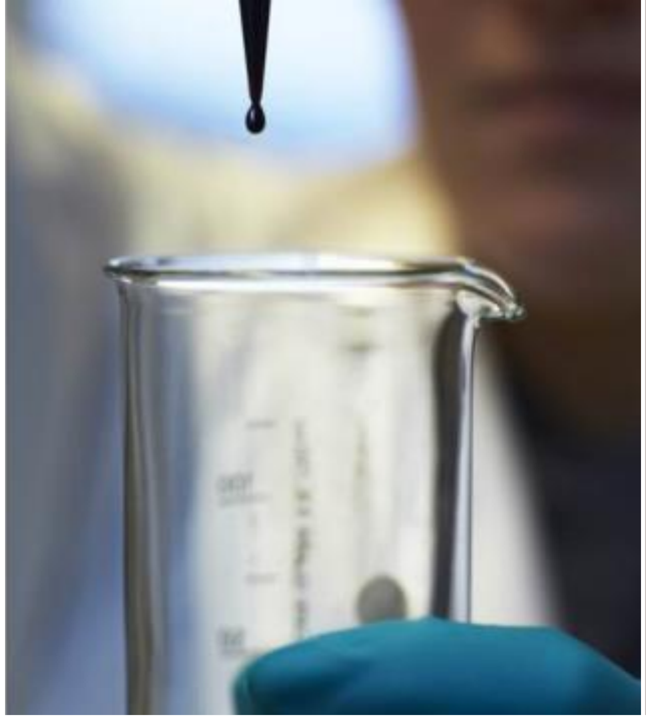
WP 1 and 2

Anna Jansson, Marcus Molander

Johan Sandström, Anna Bondeson

RISE Research Institutes of Sweden

Biovetenskap och Material
Kemi och Material



Aim

- Aim
  - To gain knowledge about polymeric components regarding
    - Degradation
    - Test methods for verification of properties and functions
    - Influence of heat and irradiation
    - Focus on End of Life criteria
    - Target group for using this knowledge are technicians on power plants, supervising authorities and manufacturer of polymers.

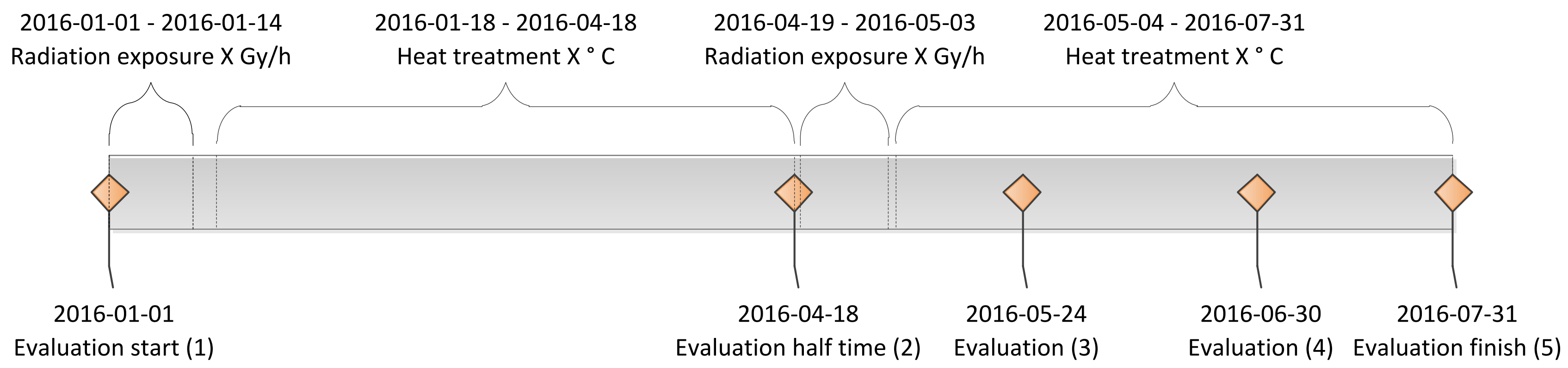
- 3 steps are taken to achieve the aim
  - **WP 1: Focus on method development for evaluation of functional properties connected to material properties.**
  - WP 2: Study how materials aged in reality can be used to verify the model in step 1.
  - WP 3: Study on a macro and molecular level how the degradation of polymers occur. Effect from oxidation, irradiation and reverse temperature effect taken into consideration.

Work package 1

- First the polymers were selected based on usage on power plants
  1. EPDM
  2. VITON
  3. NITRILE
- Then the function was decided
  1. Sealing in a connection by a o-ring
- Different environmental aspects were detailed
  1. Irradiation – Yes, ca 0.1 Gy/h
  2. Heat – Yes, ca 50°C
  3. Humidity - Pipe with nitrogen, limited
  4. Available oxygen – Oxygen, limited
  5. Pressure – Approximately 50 bar
- Available and well known evaluation methods for material properties were chosen
- Suitable ageing temperatures were chosen based on the polymer
- Irradiation 21 or 52 Gy/h until total dose 14-18 kGy. Gammacell.

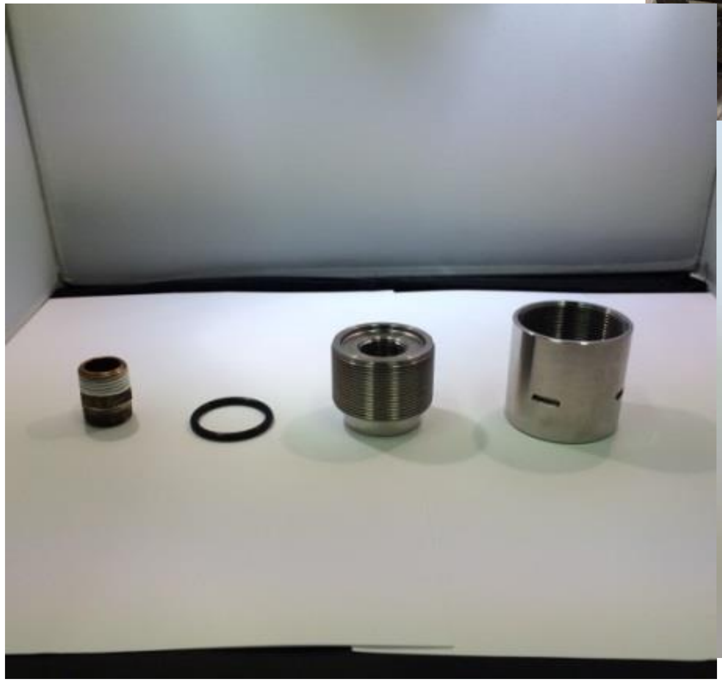
Work package 1:

- O-rings EPDM with 2 different sizes (finalised)
- O-rings Nitrile (finalised December 2018)
- O-rings Viton (finalised)
- All materials are exposed to dose rates 21-57 Gy/h, total dose 14-18 kGy and heat according to the scheme below.



End of Life O-ring

- Tightness – What water pressure causes leakage? Water pressure up to 110 bar. ”End of life criterium”.
- Modeling – Try to predict the behavior through a mathematic model that is built on real test data. Connect to ”end of life” criteria.



Evaluation methods

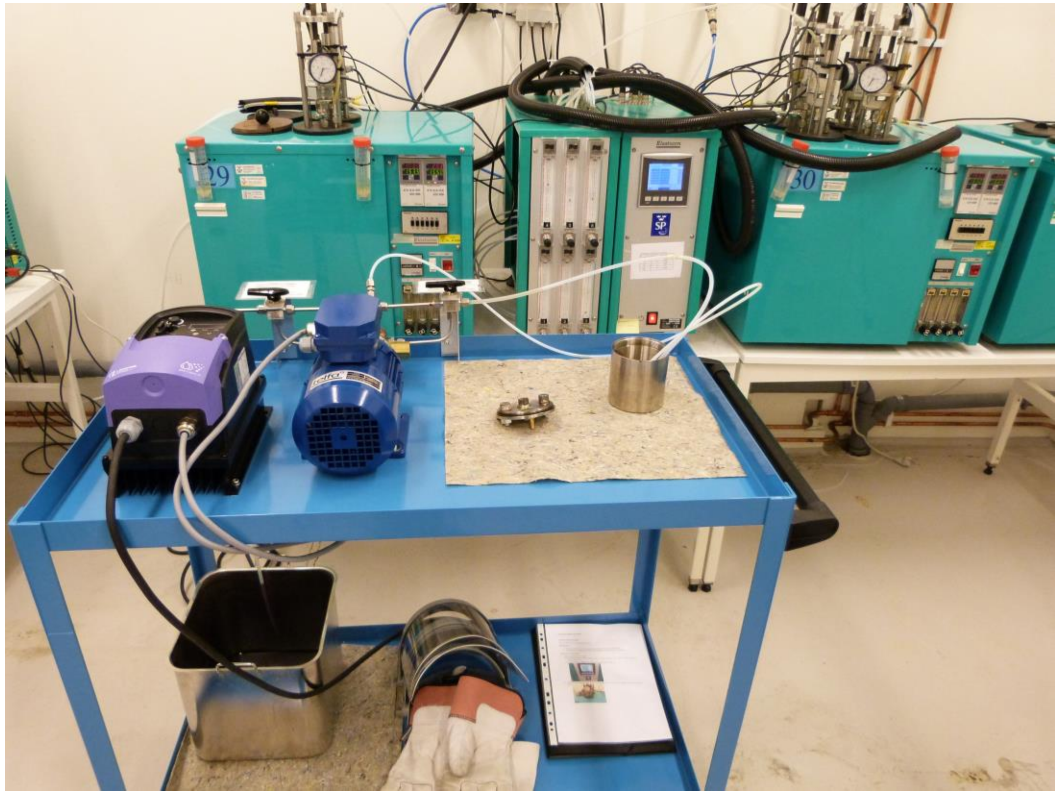
- Compression set (ISO 868, in leakage test rig)
- Tensile testing (ISO 37) on dumb bell test specimen
- Hardness (ISO 48) – The materials hardness. Crosslinking, chain scission or evaporation of softeners/plasticizers.
- Differential Scanning Calorimetric (ISO 11357-6) – Indirect measure of oxidative stability or antioxidant content.

Evaluation methods - Stress Relaxation test

Example stress relaxation measurement on EPDM

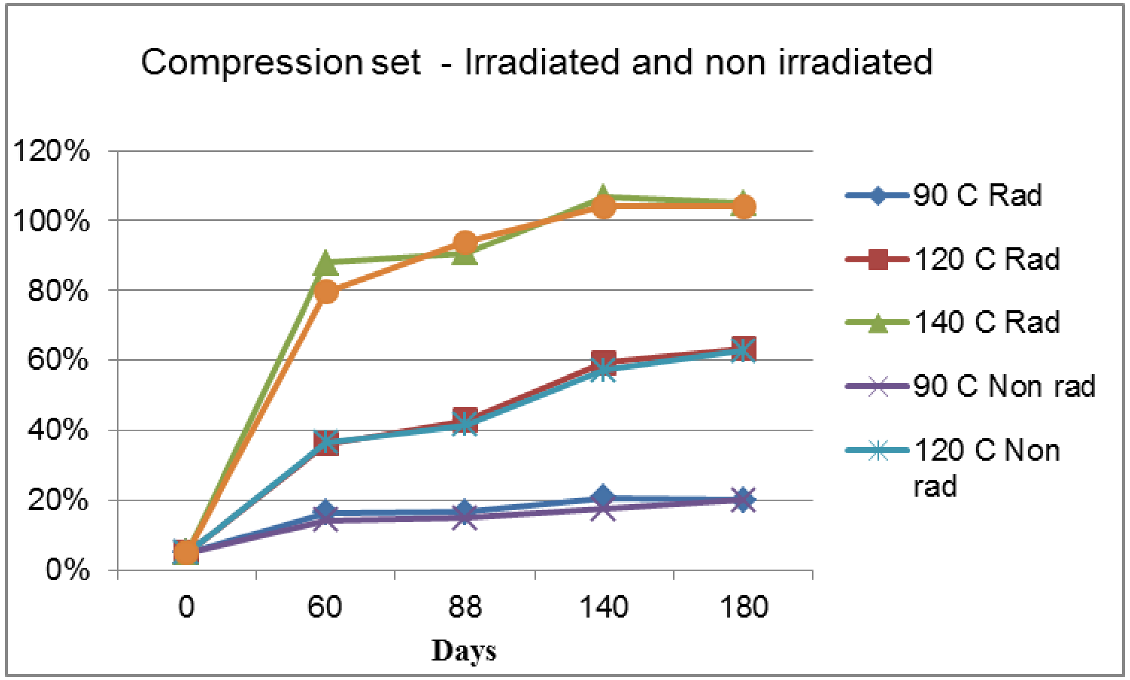
Advantages Stress Relaxation

- More sensitive compared to Compression set
- Contiuous measurement in the oven. Not necessary to remove the sample from the oven.
- You may measure in different media, different liquids.

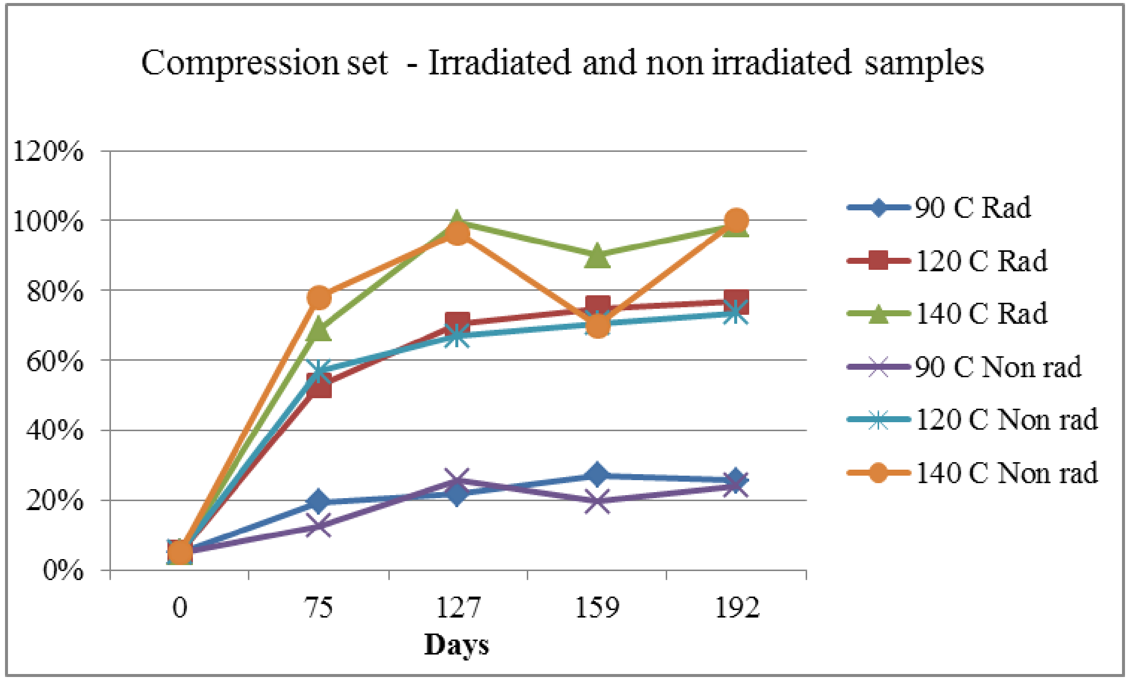


Compression Set EPDM o-rings

Small o-rings

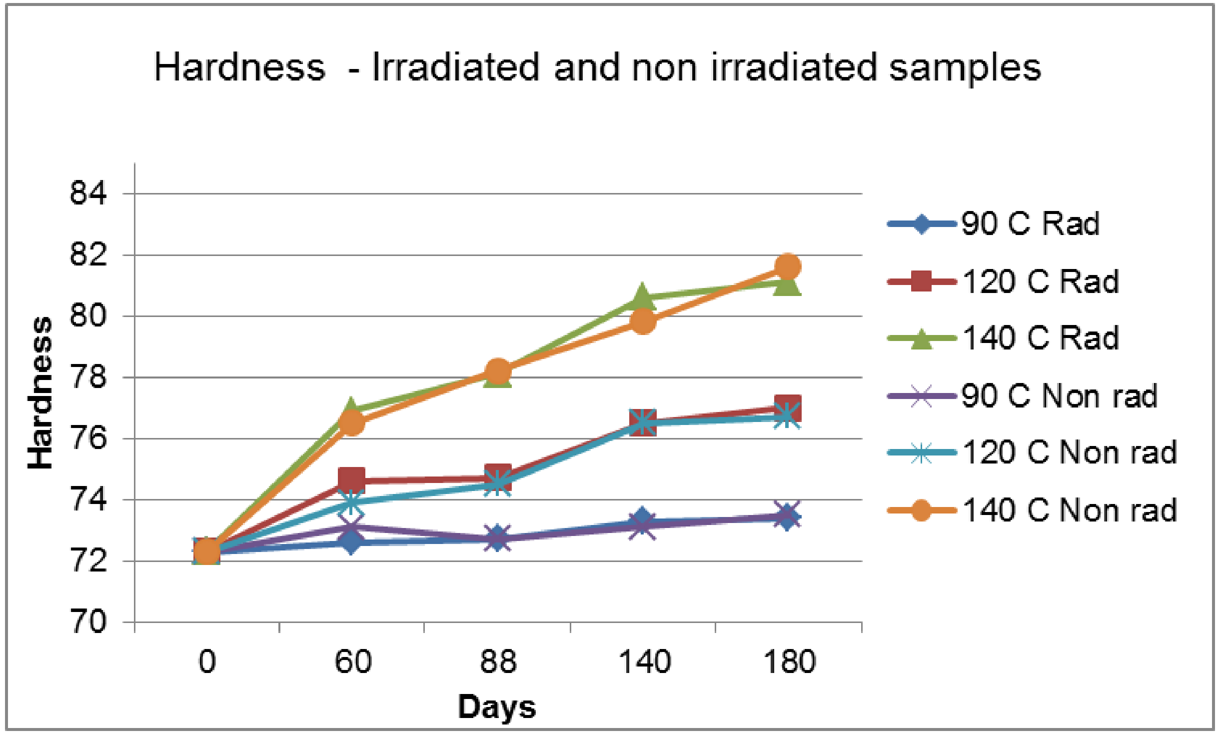


Large o-rings

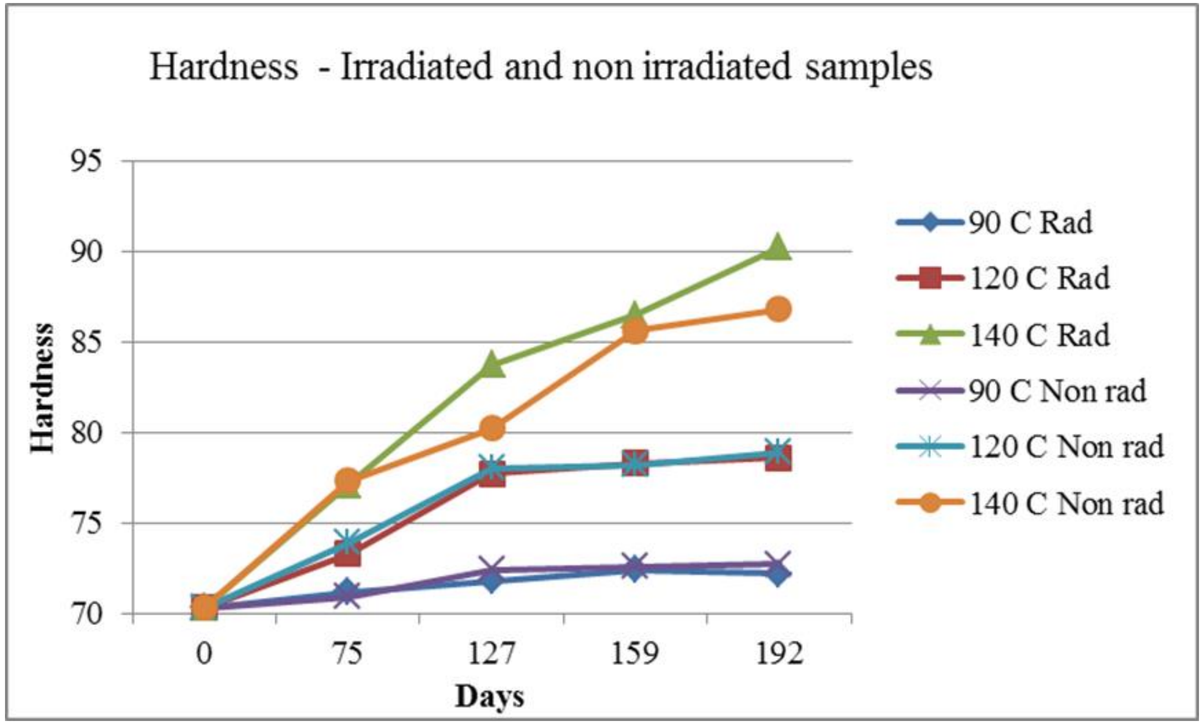


Hardness EPDM

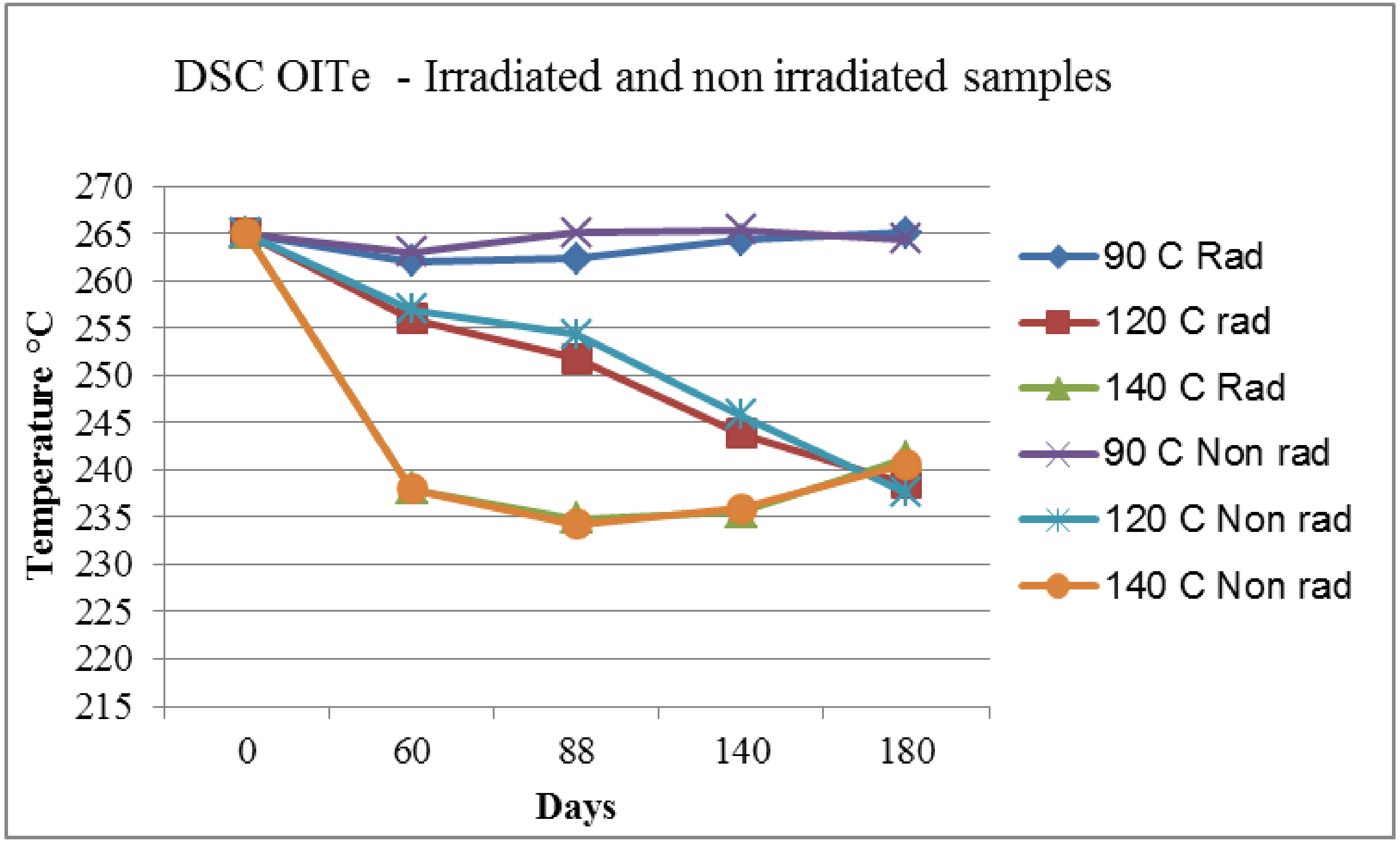
Results from 2016 (small o-ring)



Results from 2017(large o-ring)



EPDM o-rings 3.53 mm



- DSC OIT shows a similar change for both 120°C and 140°C for evaluation 5 even though compression set shows a large difference still.
- Sea shell effect may explain the result at 140 degrees.

EPDM o-rings end-of life

Small o-rings (3,53)

Property	End of life	Initial value
Compression set	105%	4,9%
Hardness	80	72,3
Elongation at break	27% (of initial)	182%
Tensile strength	7,5 MPa	12,8 MPa
DSC – OITe	235,9°C	265°C

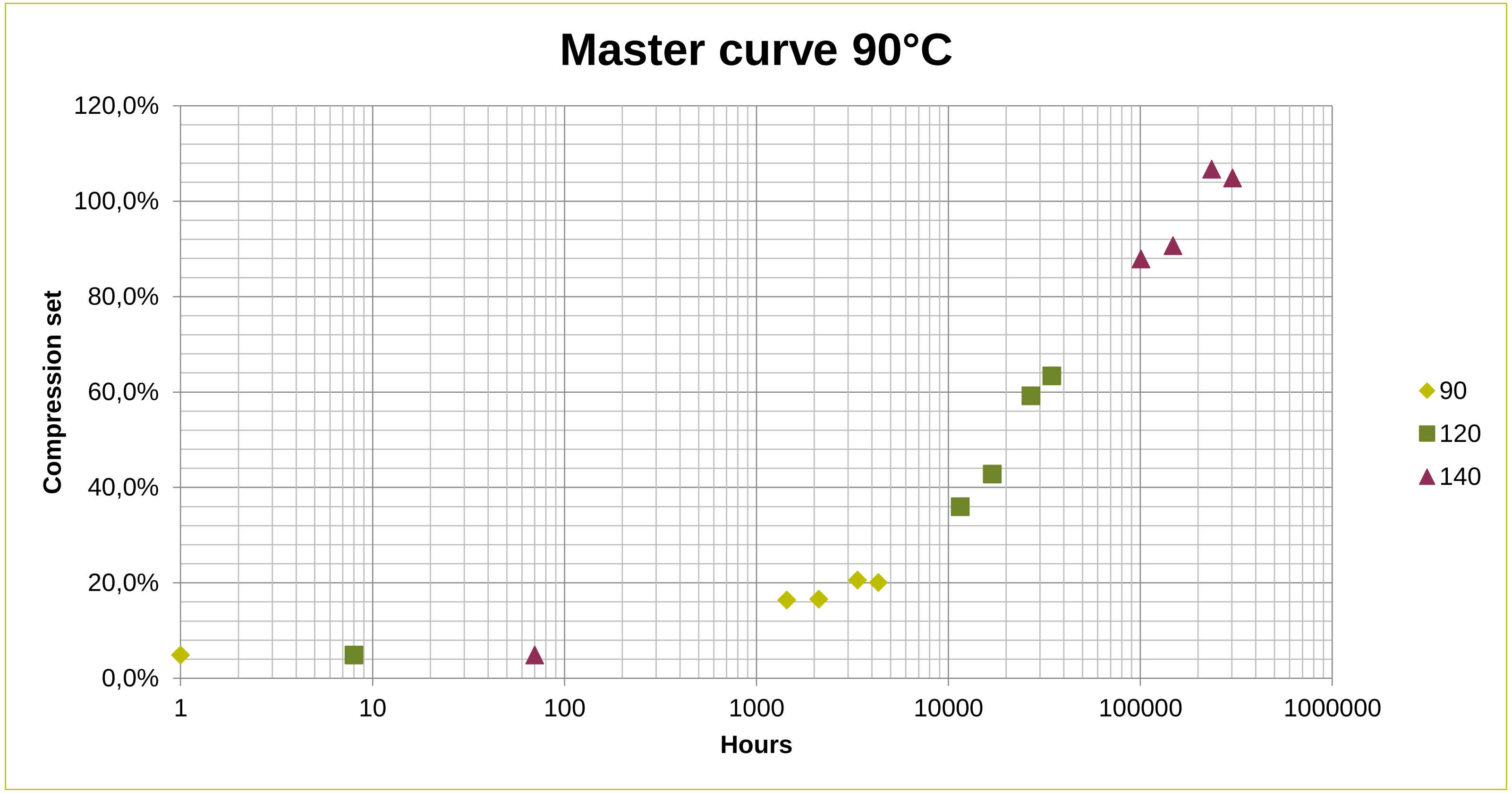
Large o-rings (6,99)

Property	End of life	Initial value
Compression set	90%	4,9%
Hardness	86,5	70,3
Elongation at break	10% (of initial)	183%
Tensile strength	5,6 MPa	12,5 MPa
DSC – OITe	229,5°C	252°C

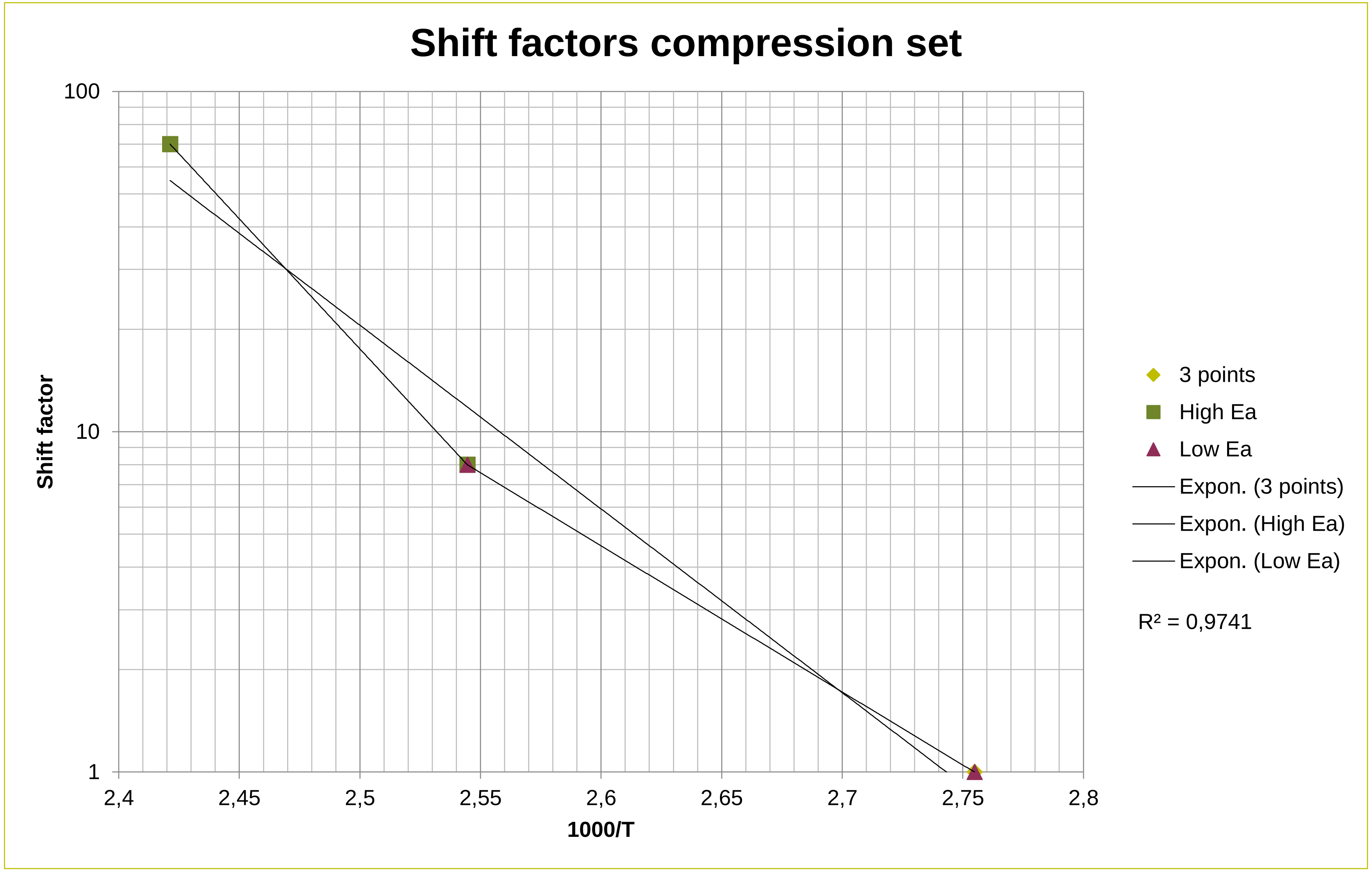
Stress relaxation F/F0 after 6 months at 140 degrees was 0,2

Master curve compression set (EPDM o-rings 3.53 mm)

- Shift factors
  - 90°C – 1
  - 120°C – 8
  - 140°C – 70



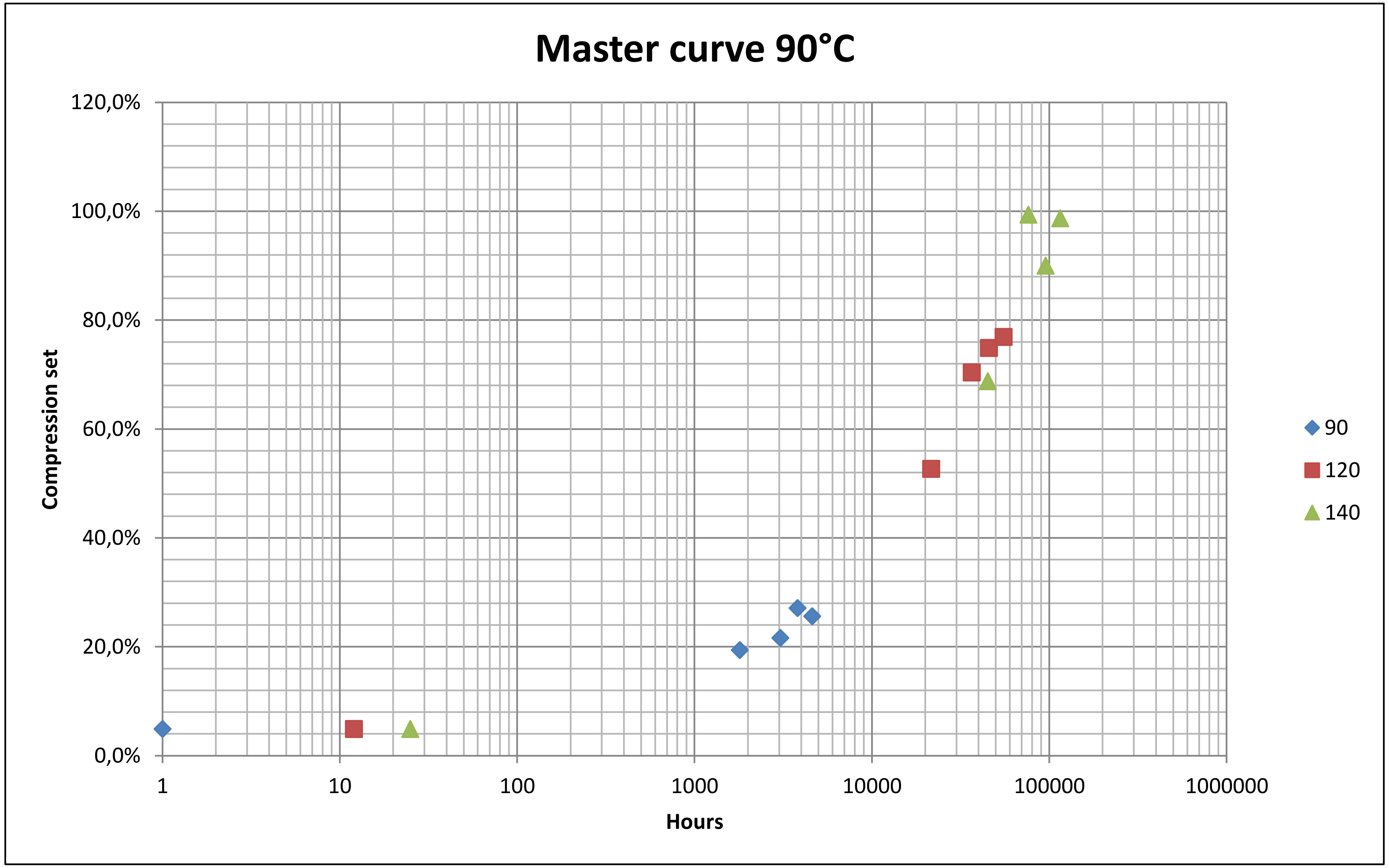
Shift factors compression set (EPDM o-rings 3.53 mm)



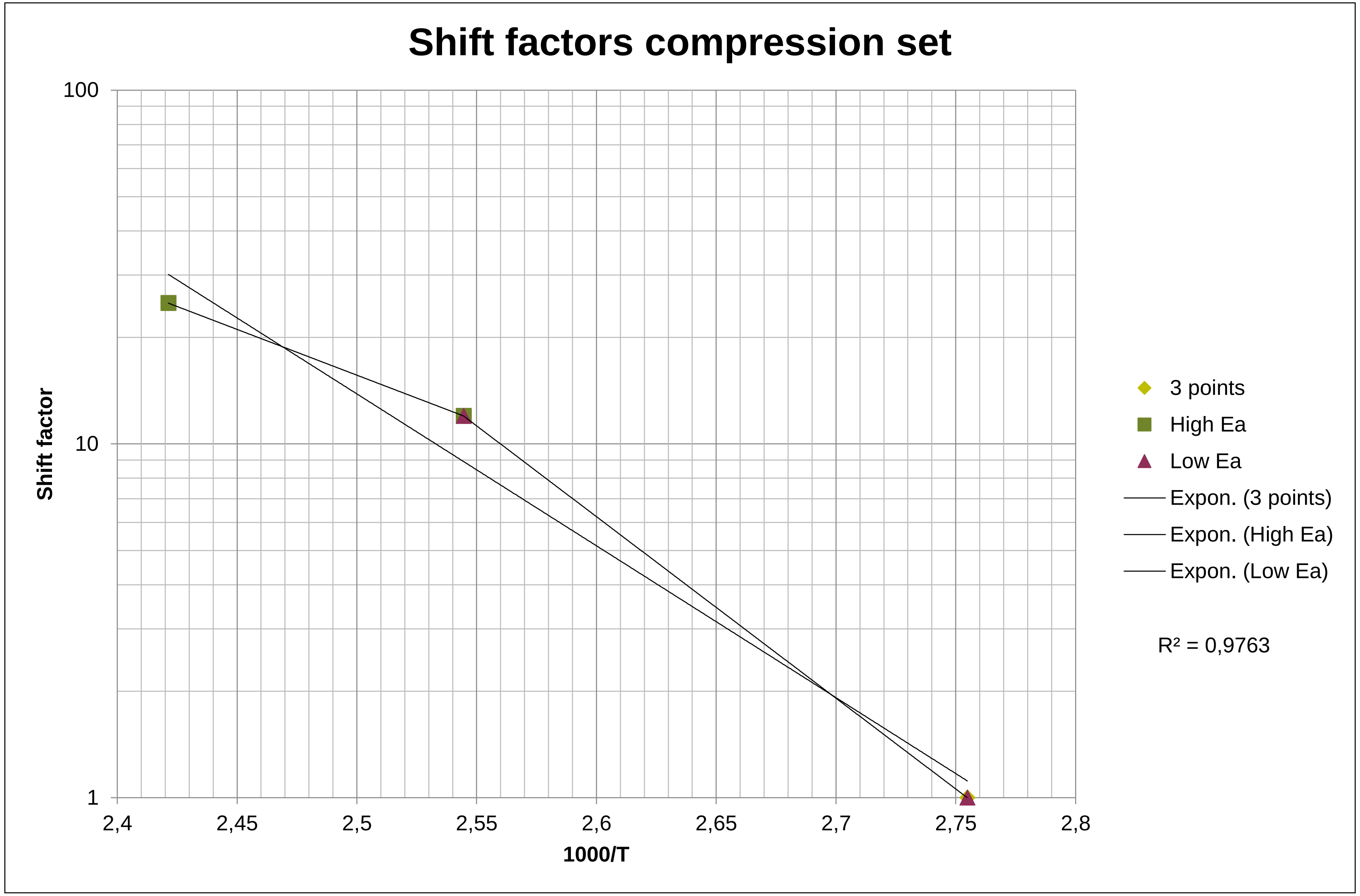
- Activation energy
  - All 3 ageing temperatures
    - E_a= 103kJ/mol 1,07 eV (R^2=0,97)
  - Lower 2 ageing temperatures
    - E_a= 82 kj/mol, 0,85 eV
  - Higher 2 ageing temperatures
    - E_a= 146 kJ/mol, 1,51 eV

Master curve compression set (EPDM o-rings 6.99 mm)

- Shift factors
  - 90°C – 1
  - 120°C – 12
  - 140°C – 25

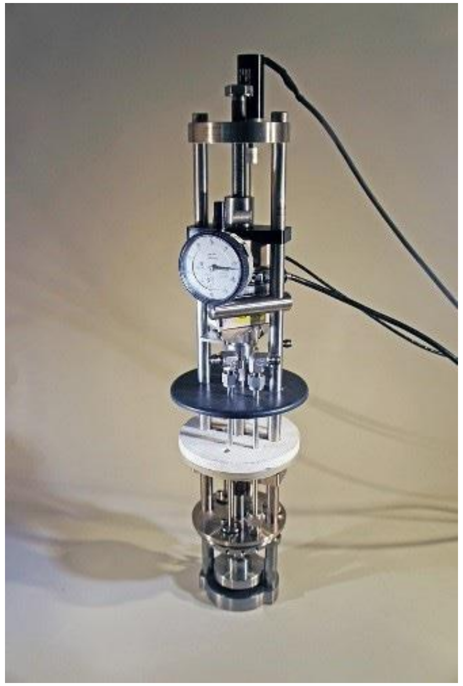


Shift factors compression set (EPDM o-rings 6.99 mm) – an example data

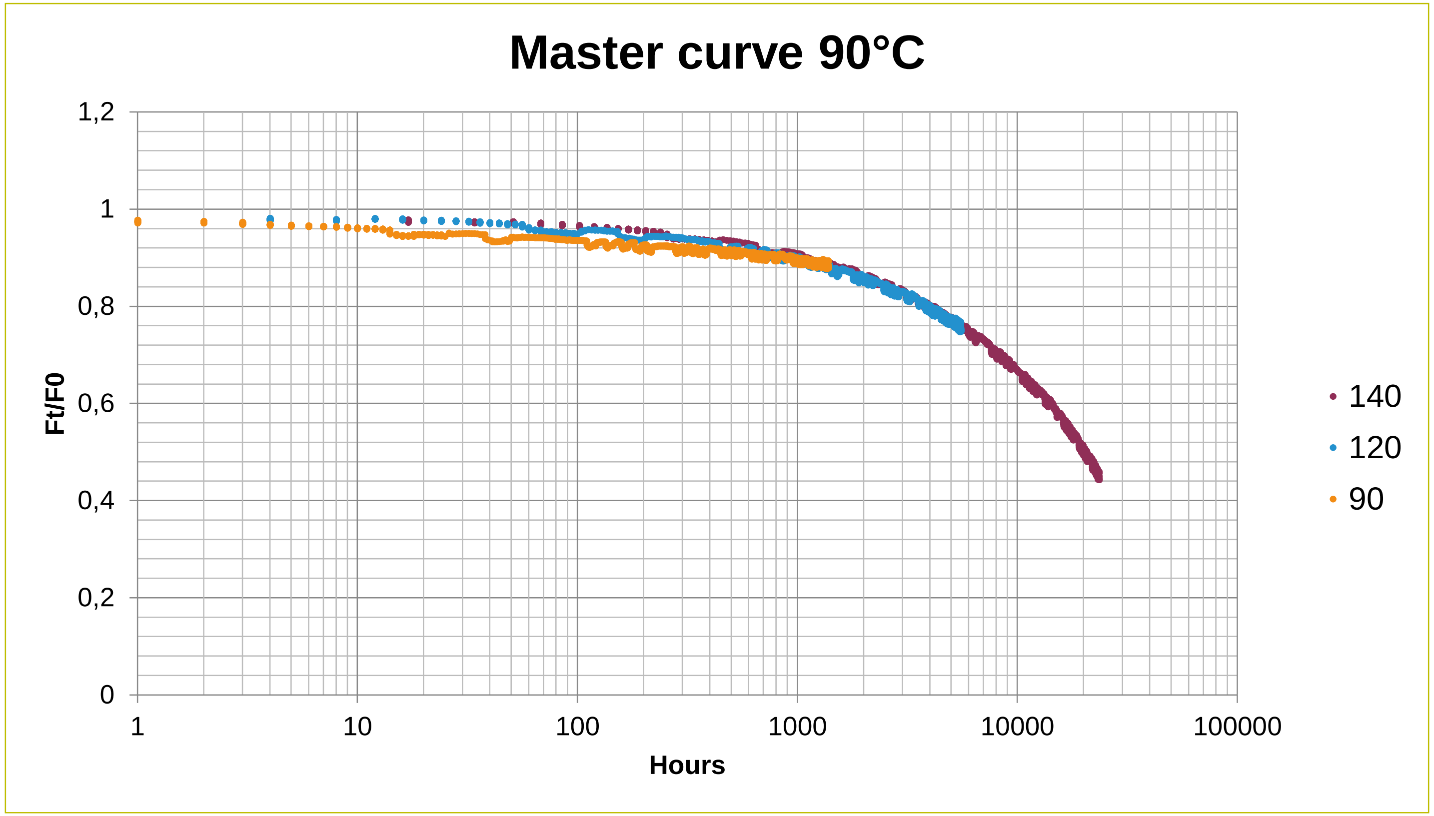


- Activation energy
  - All 3 ageing temperatures
    - E_a= 82kJ/mol, 0,85 eV (R^2=0,97)
  - Lower 2 ageing temperatures
    - E_a= 50 kj/mol, 0,52 eV
  - Higher 2 ageing temperatures
    - E_a= 98 kJ/mol, 1,02 eV

Master curve Stress Relaxation

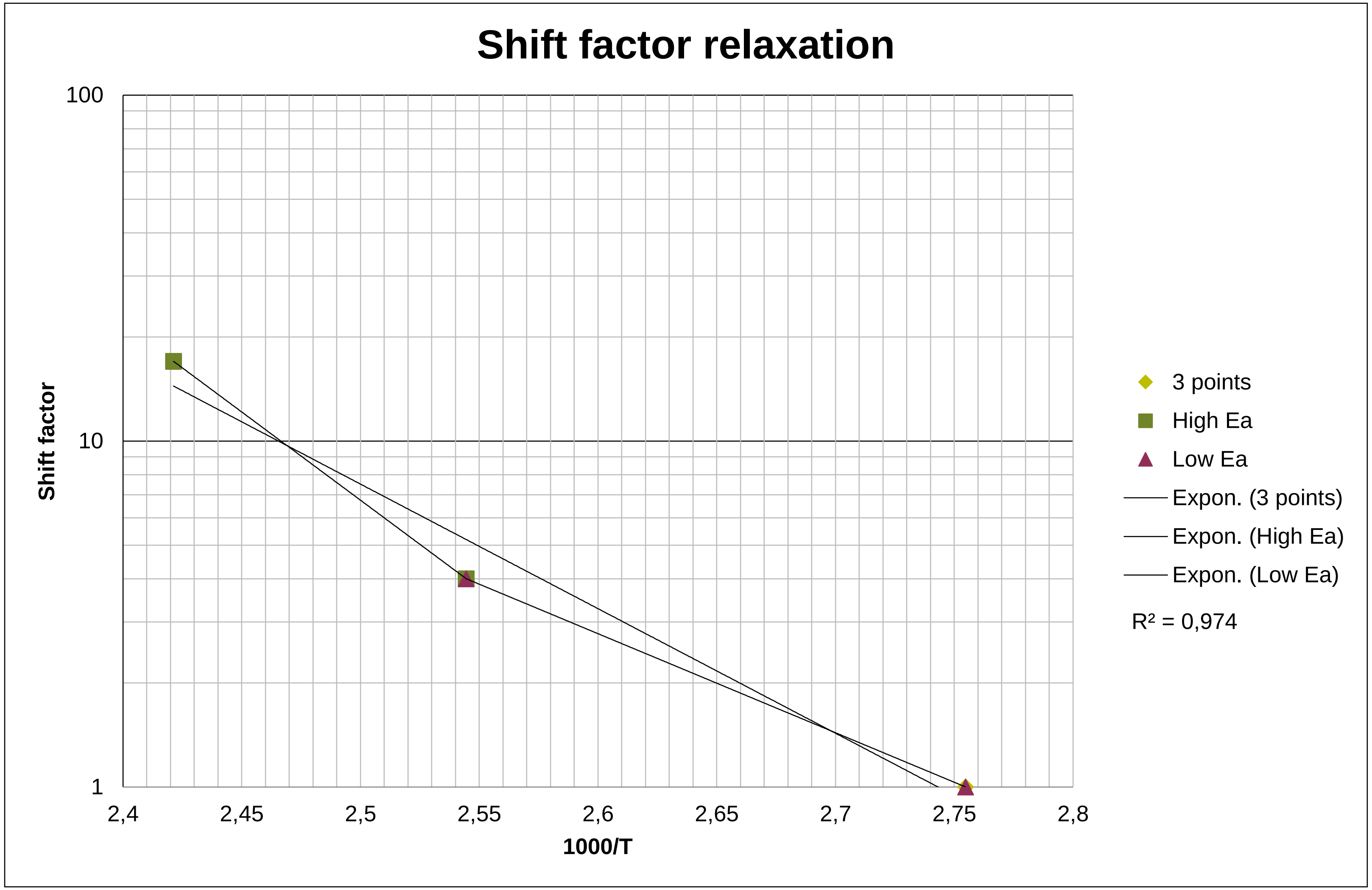


- *From azom.com*



- **Shift factors**
- 90°C = 1
- 120°C = 4
- 140°C = 17

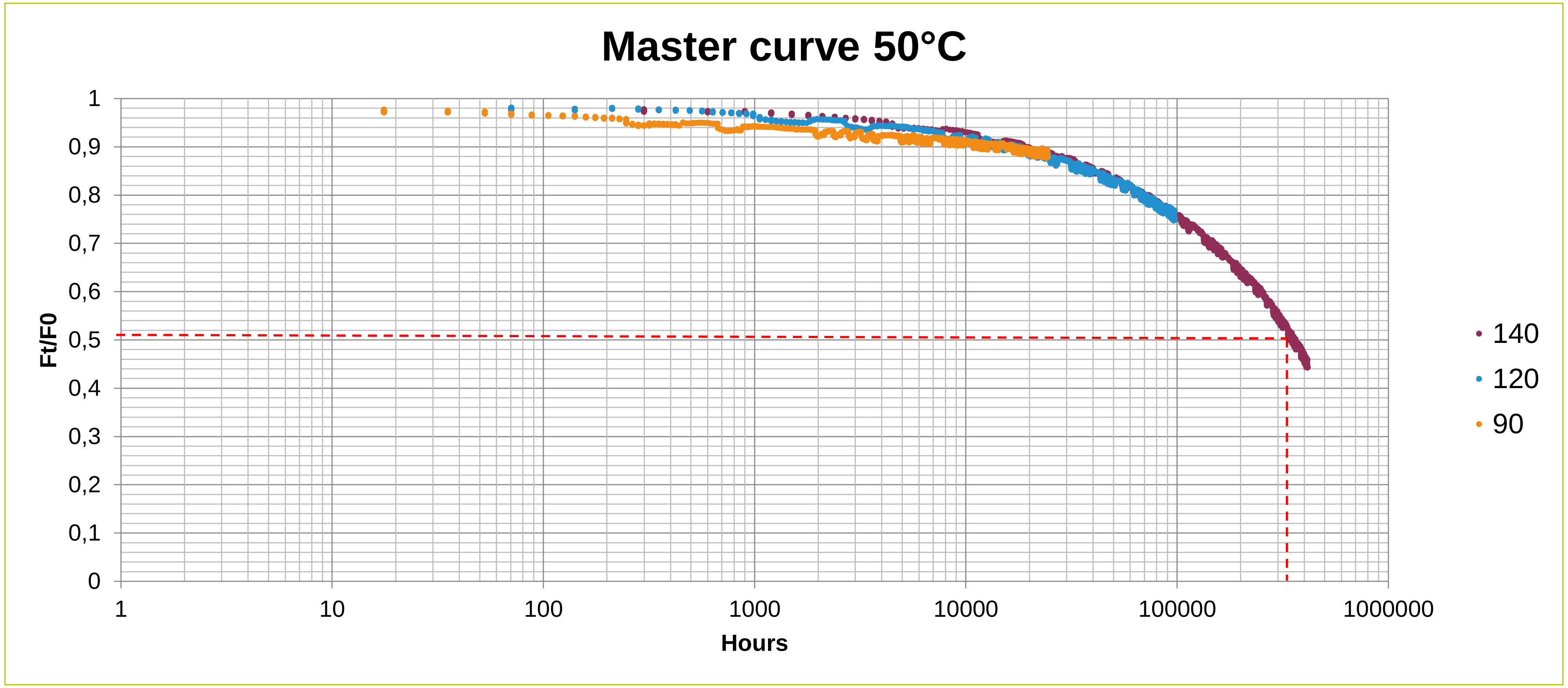
Shift factor Compression Stress Relaxation



- Activation energies
  - All 3 ageing temperatures
    - E_a=69 kJ/mol, 0,72 eV R^2=0,97
  - Upper 2 ageing temperatures
    - E_a=98 kJ/mol, 1,02 eV
  - Lower 2 ageing temperatures
    - E_a=55 kJ/mol, 0,57 eV

Master curve 50°C

- How long would this o-ring last at 50°C?
- First of all – What´s your end of life criteria.
- If 50% of initial – approx. 40 years



Different test methods – different activation energies

Method	Sample	Activation Energy kJ/mole	Activation Energy eV
Compression Set	Small o-ring	103	1,07
Compression Set	Large o-ring	82	0,85
Stress relaxation	Small o-ring	69	0,72

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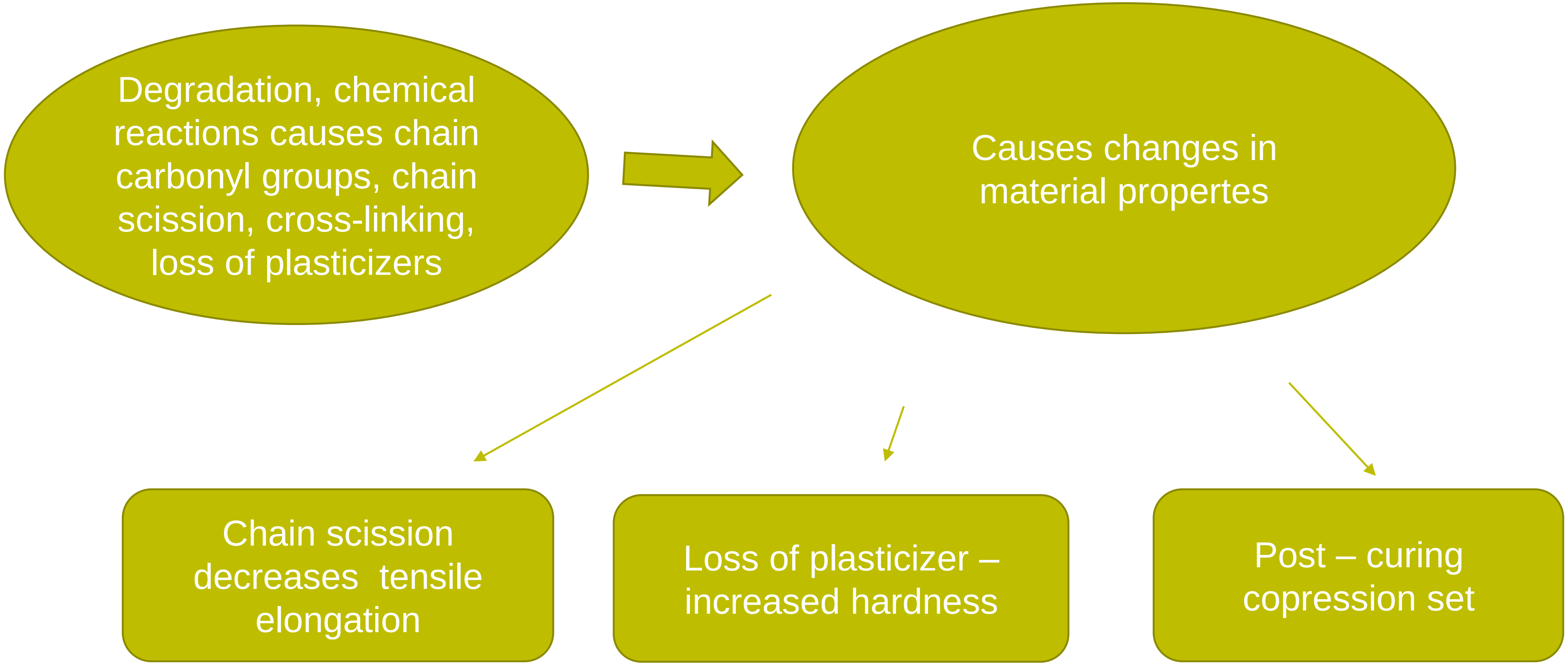
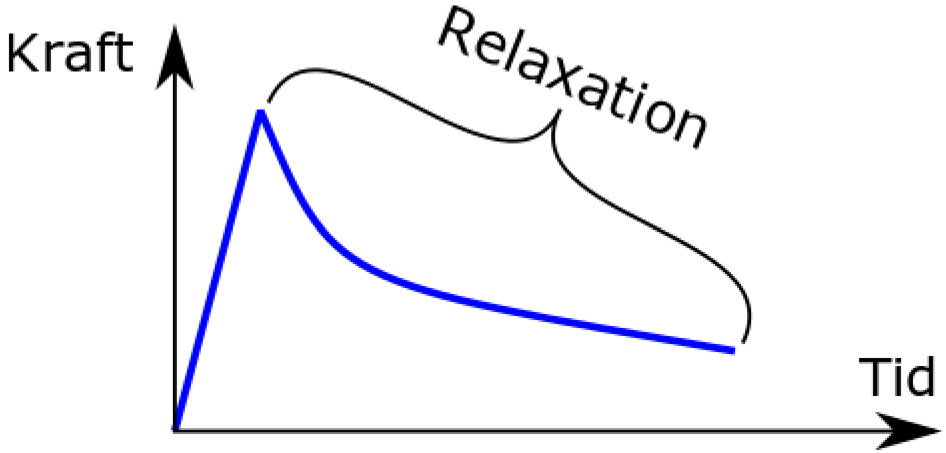
Why do different test methods result in different activation energies?

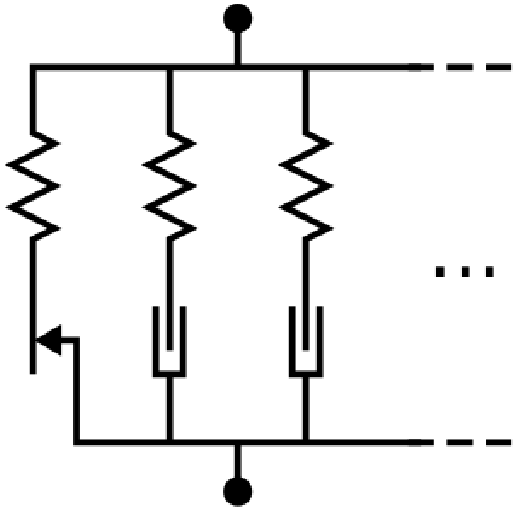


Polymer degradation affect different polymer properties differently

Modelling of rubber sealings and their tightness

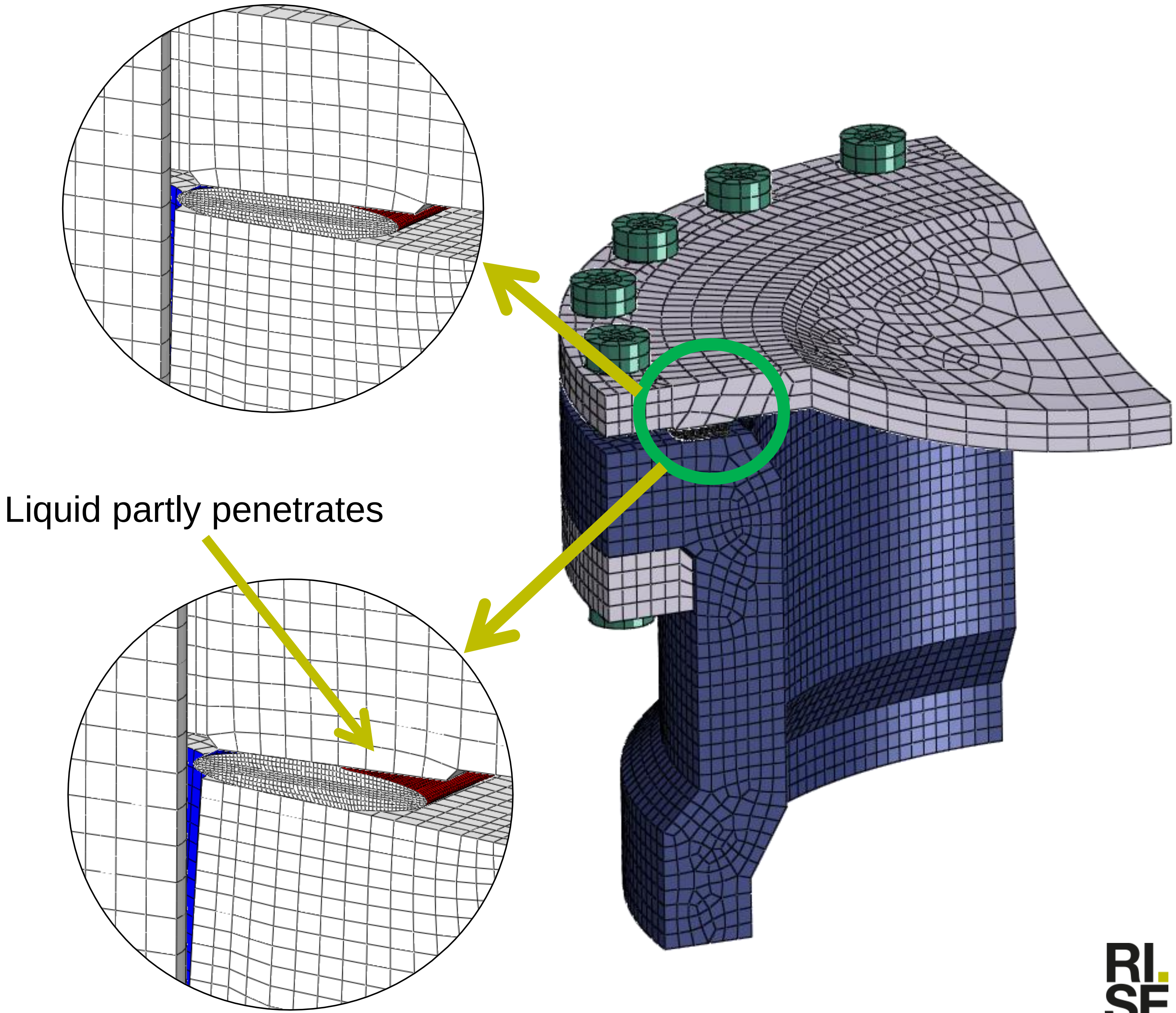
- Simulation of a sealing may be performed by using FEM (Finite Element Method)
- Simulation demands a material model that can describe the complex behaviour of a rubber material
- ***Stress Relaxation*** – Stress decreases over time under constant deformation
  - **Permanent set** – the material does not retain its original shape after load.
  - Non linear non-visco-plastic material model
  - Reologic network with several paralel chains
  - Hyperelastic
  - Several paralel chains for visco-elasticity
  - Plasticity for permanent set
- Calibration
  - Directly on model and experiment for sealing ring
  - Adaptation with measuring data and simulation of sealing rings.





Simulation of tightness

- By using FEM there is a possibility to simulate tightness.
  - The pressure of the sealed liquid causes separation of the contact surfaces.
  - Example for a sealing ring in a flanged joint.



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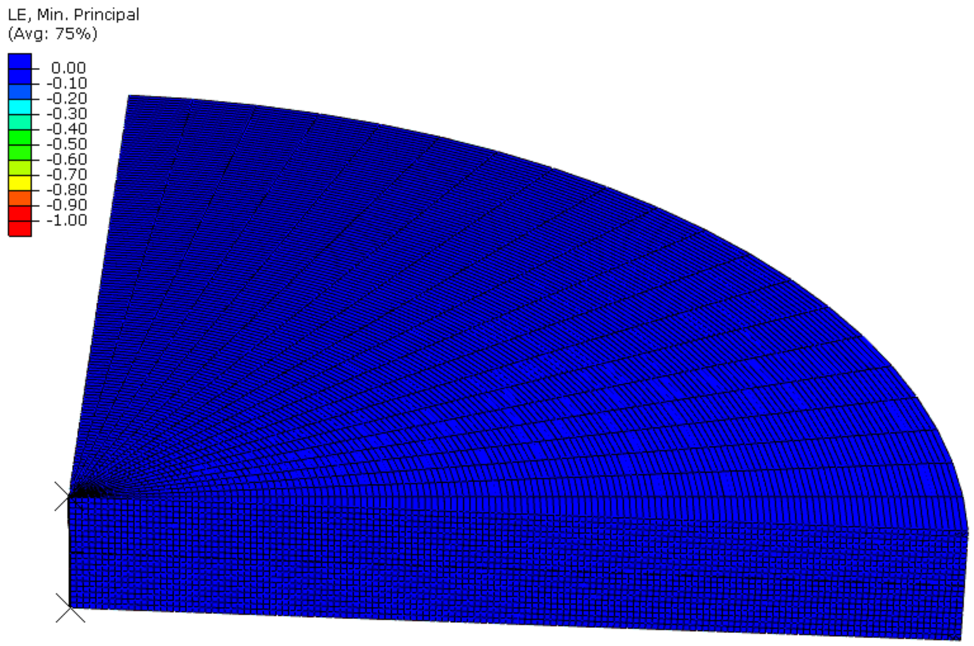
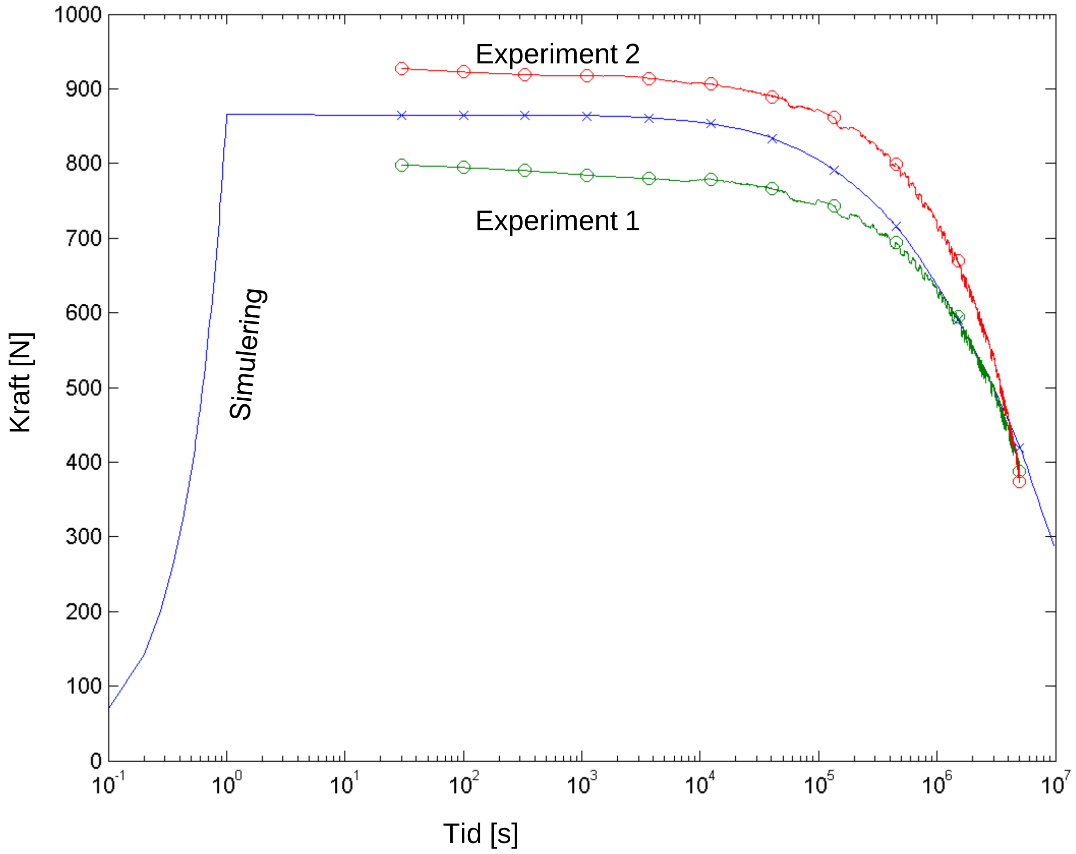
Simulation and Calibration

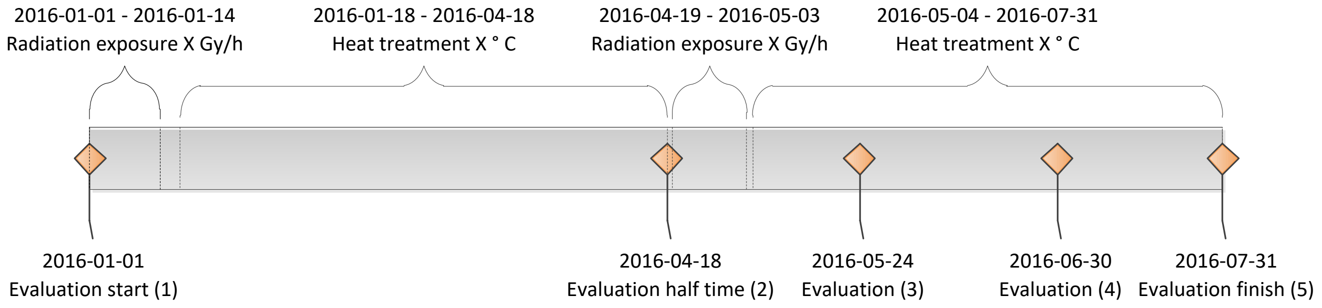
- Compression of the sealing ring is simulated by FEM
- Optimisation algoritms are used to calibrate the rubber material model.
- Resulting respons falls within the experimental area.



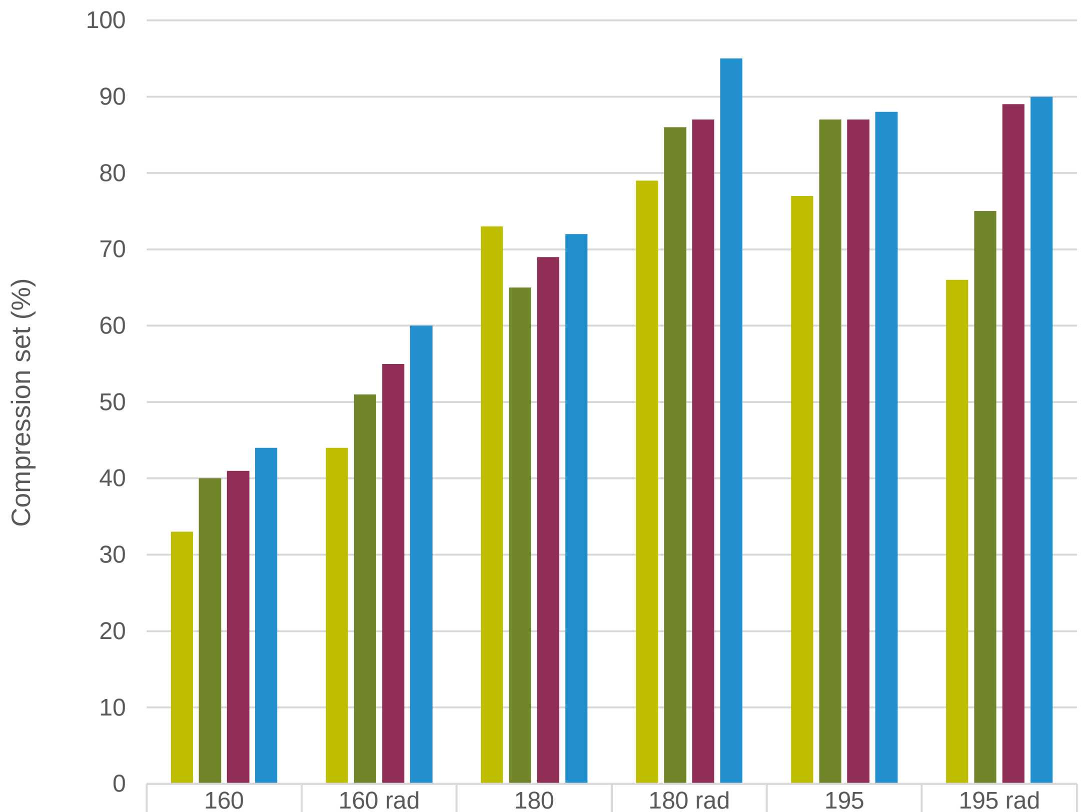


FKM results _

- Ageing temperatures
  - 160°C
  - 180°C
  - 195°C
  - Small Leakage test rigs.



Results FKM Compression Set

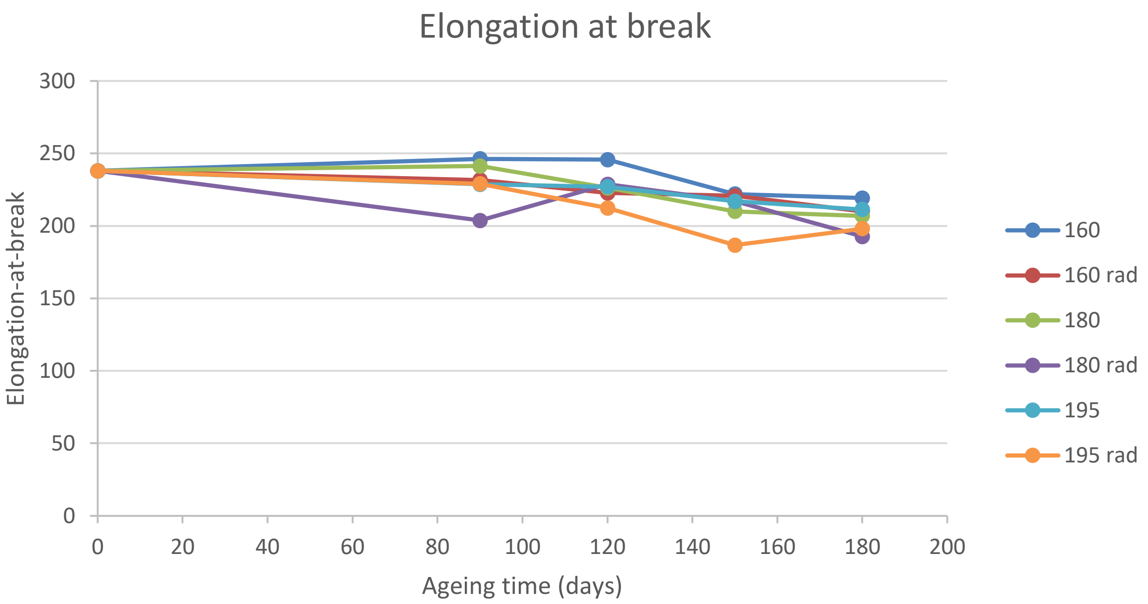


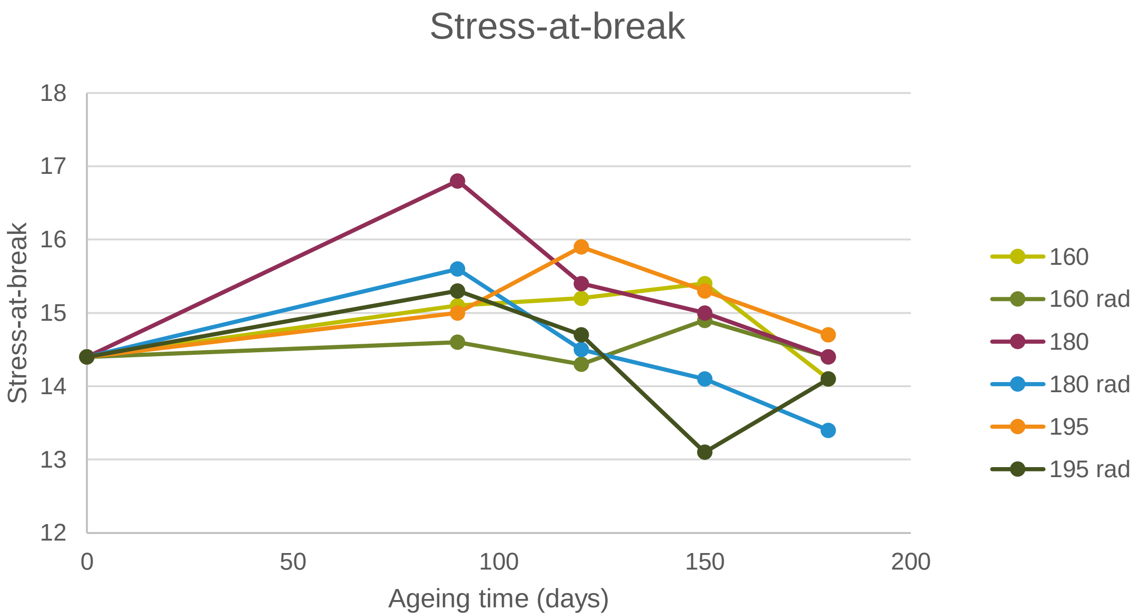
	160	160 rad	180	180 rad	195	195 rad
90 days	33	44	73	79	77	66
120 days	40	51	65	86	87	75
150 days	41	55	69	87	87	89
180 days	44	60	72	95	88	90

Ageing temperature

- No leakage! All sealing rings performed throughout the test, even though the compression set was above 90 %.

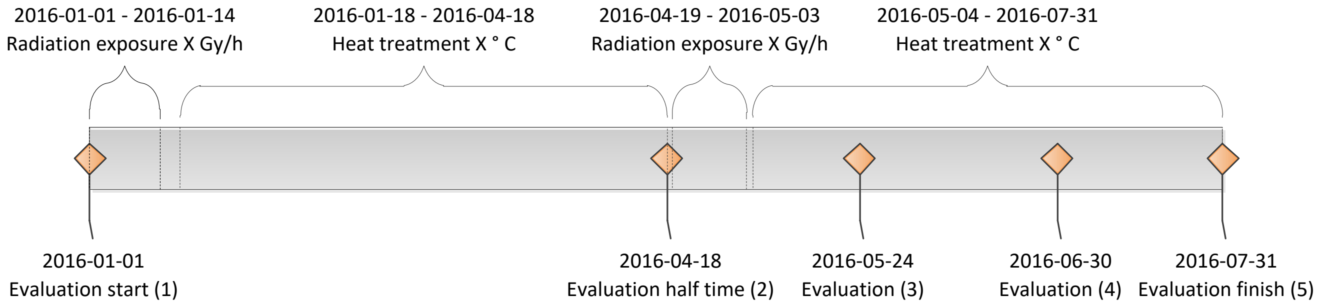
Tensile testing FKM





Nitrile Results _

- Ageing temperatures
  - 60°C
  - 80°C
  - 100°C
  - Large Leakage test rigs.



Hardness Nitrile rubber

Ageing time (Days)	60	60 rad	80	80 rad	100	100 rad
0	79,1	79,1	79,1	79,1	79,1	79,1
90	82,4	80,4	90	89,9	97,5	98,5
120	80,9	84	91,7	93,3	99,5	99,3
150						
180						

Nitrile Rubber – Elongation-at- break (%)

Ageing time (Days)	60	60 rad	80	80 rad	100	100 rad
0	321	321	321	321	321	321
90	246,7	245,8	133,8	137,9	18,8	17,8
120	218,3	218,3	116,8	109,7	3,4	0,1
150						
180						

WP 2

- Deventer Seal
- 6 years
- 50°C operating temp
- 8 bar operating pressure
- Nitrogen surrounding
- A2-96
- 1 year storage after removal

- Find position in SAP art no 8609737
- NBR 70 shore
- Flexible has cracks break upon bending, a number of sealings some of them break some don’t

Rubber sheet from OKG

Material: EPDM or Neopren, rubber sheet.
Installed 1981-83 approximately 35 years of service.
Hardness: 60 Shore
No radiation

Exempel och övningar 40 min

- Upplägg:
  - Frågeställningar placeras ut i olika stationer där deltagarna får 10 minuter per station innan byte sker. I varje skifte/alt efter hela övningen ges möjlighet att kommentera frågorna.
- Frågor:
  - Vilka är de kritiska komponenterna hos er när vi pratar om åldring? Med detta menar vi komponenter som åldras (osäkerhet kring end of life), dyra att byta ut och viktiga för säkerheten/driften.
  - Vilka tekniska krav vill ni sätta för följande komponenter och hur ska dessa fingeravtryckas?
  - På ovan komponenter, vilka funktionskrav har ni i åtanke?
  - Hur kan vi förlänga utbytesintervaller och verifiera att materialen faktiskt kommer hålla?
  - Hur kan ni jobba fram smartare miljökvalificeringar baserat på detta?

Workshops at power plants wishes for the final Report.

- In the final report NPP wants a description about how activation energies were calculated, the difference between shift factors and the Arrhenius equation. Also explain why different material properties give different activation energy values.
- End of life criteria must take into account that the materials must withstand a LOCA accident for minimum 6 months. Definition of acceptance criteria.

Idea list

- Many materials are used at elevated temperature e.g. 50 degrees. Material analysis at this service temperature would be of interest.
- Composition changes - How can changes of additives in polymers qualified.
- Changes of cirquit boards are coming, how could new be qualified?
- Storage in air compared to use in inert atmosphere (Nitrogen), what atmosphere has the most severe effect on the materials.
- Compression Set useful acceptance criteria (rubber sealants), simple method, cheap equipment.
- Ageing inside reactor Containment, control programs at certain intervals interesting.
- Cables are difficult to replace find control programs and condition monitoring for continued use or replacement.

Idea list 2

- Membrane – tear resistance important.
- Rubber in contact with hot water, interesting to study further. A report by Spång, contain background information.
- Sensor technology isinteresting for condition monitoring, humidity, vibrations, temperature etc.
- Switchgears and relay boxes contain fixings and housings in stiff plastic materials. After long service time some of these materials show an oily pleat-out on the surface. This may cause corrosion on the electronic equipment. Embrittlement of these plastics would be interesting to study as well as ageing mechanisms and end of life criteria. Are there any methods to estimate remaining life time? (Idea from Stjepan J, Ringhals)

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CONTACTS

Anna Jansson

Anna.jansson@ri.se

010 516 5329

Marcus Molander

Marcus.molander@ri.se

010 516 5122

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Kemi och Material