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Long-term performance of polymeric materials in nuclear power plants

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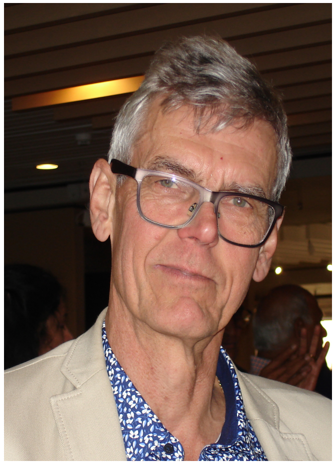

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- ✓ Editor of *Polymer Testing*
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Research interest: Understanding properties of polymeric materials from atomistic, nanoscopic and microscopic structure and how structure at different length scales are interrelated

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List of publications

[I] P. Pourmand, E. Linde, M.S. Hedenqvist, I. Furó, S.V. Dvinskikh, U.W. Gedde, Profiling of thermally aged EPDM seals using portable NMR, indenter measurements and IR spectroscopy facilitating separation of different deterioration mechanisms. *Polym. Test.* 53 (2016) 77–84.

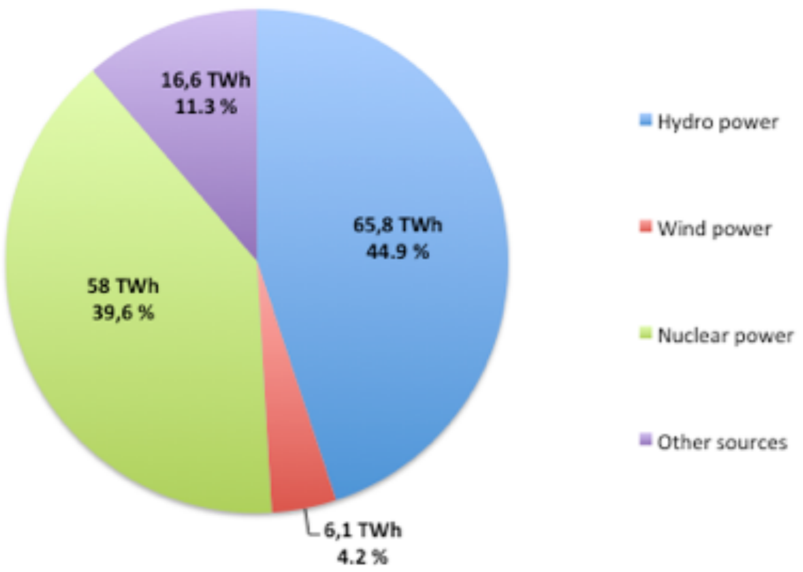
[II] P. Pourmand, M.S. Hedenqvist, I. Furó, U.W. Gedde, Deterioration of highly filled EPDM rubber exposed to thermal ageing in air: kinetics and non-destructive monitoring. *Accepted in Polymer Testing – In press.*

[III] P. Pourmand, M.S. Hedenqvist, I. Furó, U.W. Gedde, Radiochemical ageing of highly filled EPDM seals as revealed by accelerated ageing and ageing in-service for 21 years. *Polym. Degrad Stab.*144 (2017) 473–484.

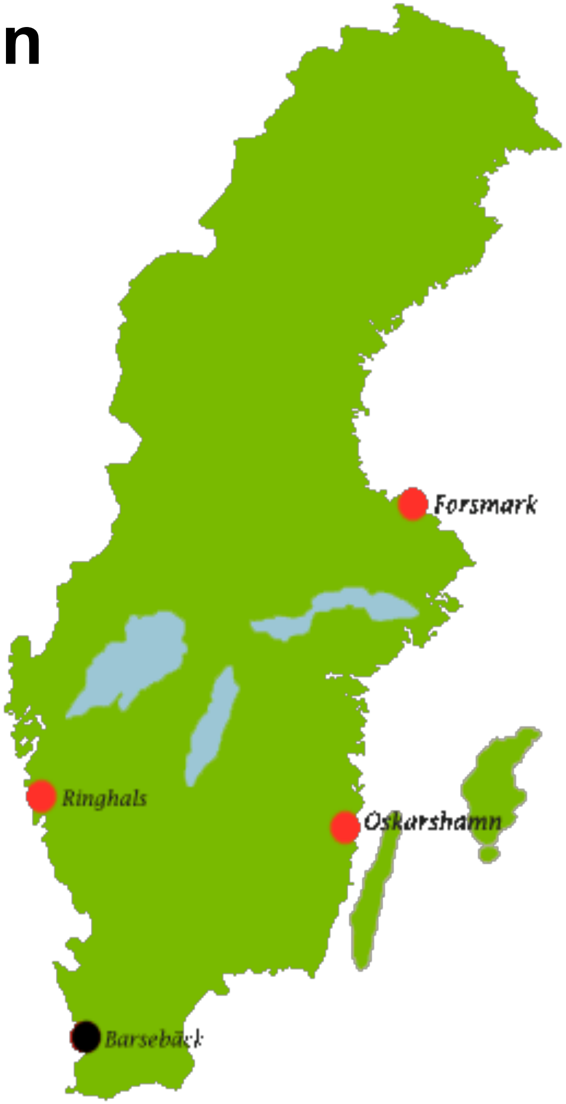
[IV] P. Pourmand, L. Hedenqvist, A.M. Pourrahimi, I. Furó, T. Reitberger, U.W. Gedde, M.S. Hedenqvist, Effect of radiation on carbon-black filled EPDM seals in water and air. *Accepted in Polymer Degradation and Stability – In press.*

Nuclear power in Sweden

Energy production Sweden 2011



Source: Swedish Energy Authority (2011)



Polymers in nuclear power plants

- Commonly found in cables, O-rings, seals, gaskets and hoses

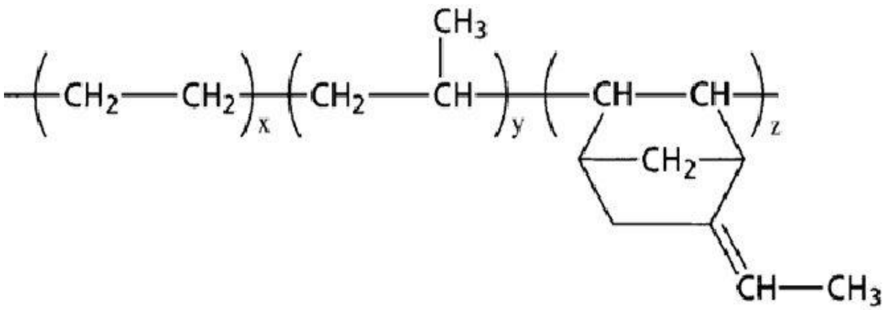
- 1100 km of cable in Reactor O2 in Oskarshamn, Sweden.

2. Purpose of the study

- To focus on common components used in NPPs in this case highly-filled EPDM sealants of particular interest
- To understand the effect of γ-radiation on EPDM in oxygen (different p_{O2}) and water
- To perform accelerated ageing and understand underlying deterioration processes (profiling the material behaviors)
- To find a possible non-invasive condition monitoring method for testing (NMR mouse)
- Increase the general awareness about polymers in Swedish NPPs

3. Materials and test methods.

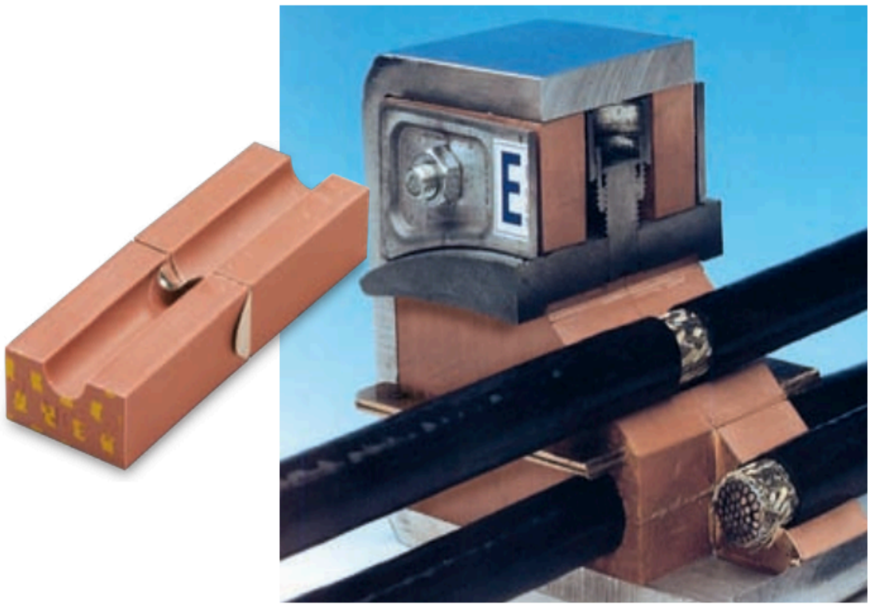
Ethylene propylene diene (EPDM) rubber.



- Diene source of crosslinking
- Small amounts 2–12 wt.%
- Ethylidene Norborene (ENB) most common.

Typical applications:
radiator and garden hoses, door seals for cars and roofing etc.

MCT Brattberg insert blocks (Lycron)



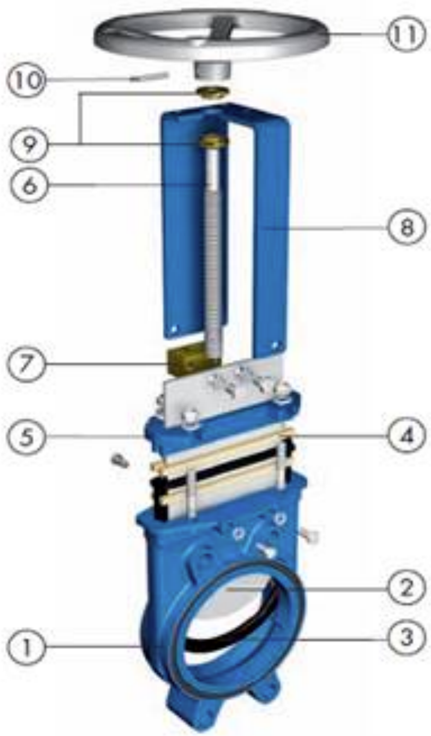
MCT Brattberg Sweden

- ATH = flame-retardant

EPDM (Vistalon 8504)	30 wt.%
Chalk	6 wt.%
Aluminum trihydrate (ATH)	35 wt.%
Magnesium carbonate	3 wt.%
Zinc salts	2 wt.%
Titanium oxide	2 wt.%
Extractable components (stearate)	7 wt.%
Sulphur	2 wt.%
Accelerators/activators	3 wt.%

EPDM sealant for knife-port valves

Diameter: 0.5 m

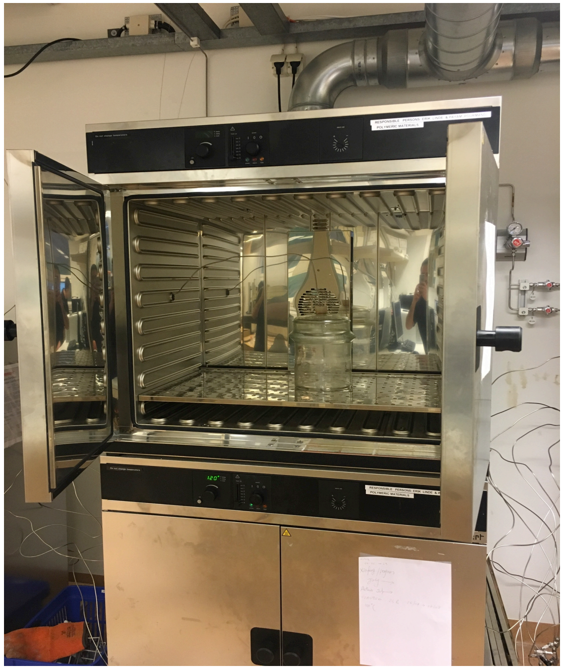


Orbinox S.A., Spain

EPDM (Vistalon 6602)	47 wt.%
Carbon black	39 wt.%
Calcium carbonate	5 wt.%
Extractable components (Paraffin oil)	7 wt.%
Sulphur	1 wt.%
Accelerators/activators	3 wt.%
Zinc oxide	0.5 wt%
Magnesium oxide	0.5 wt%

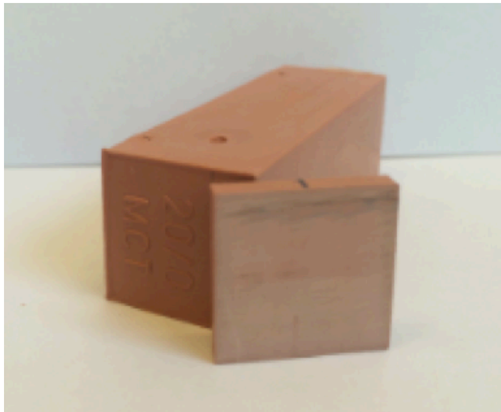
3. Test methods – Thermal ageing

- In ventilated ovens with air as medium
- Temperatures 110, 120, 150 and 170 °C.
- 6 different aging times (max 1.3 years, 110°C)



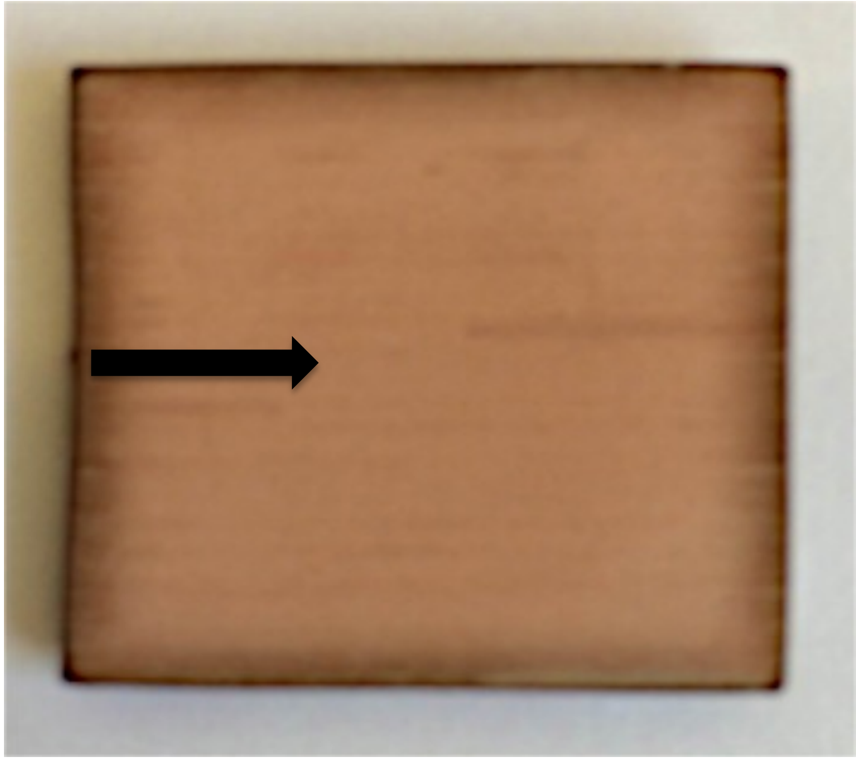
(MEMMERT ULE-600)

Profiling methods



- Indenter modulus
- IR-profiling (carbonyl index)
- Portable NMR
- Extraction profiles

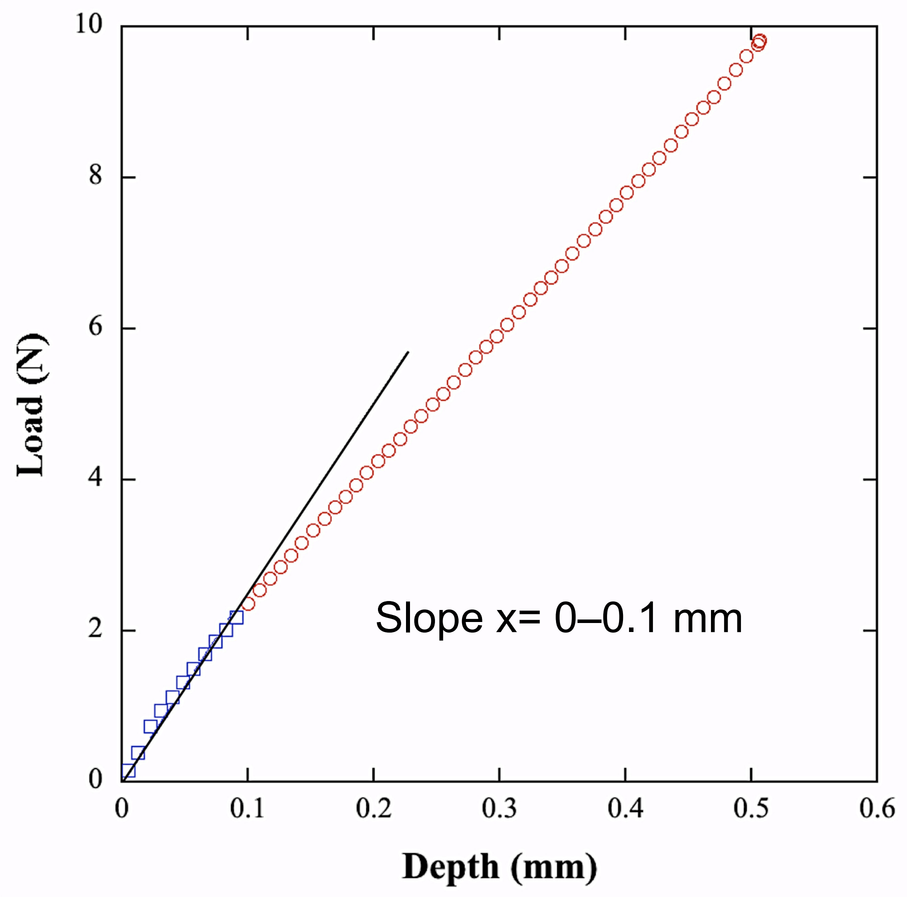
• Unidimensional profiles in cross-sections

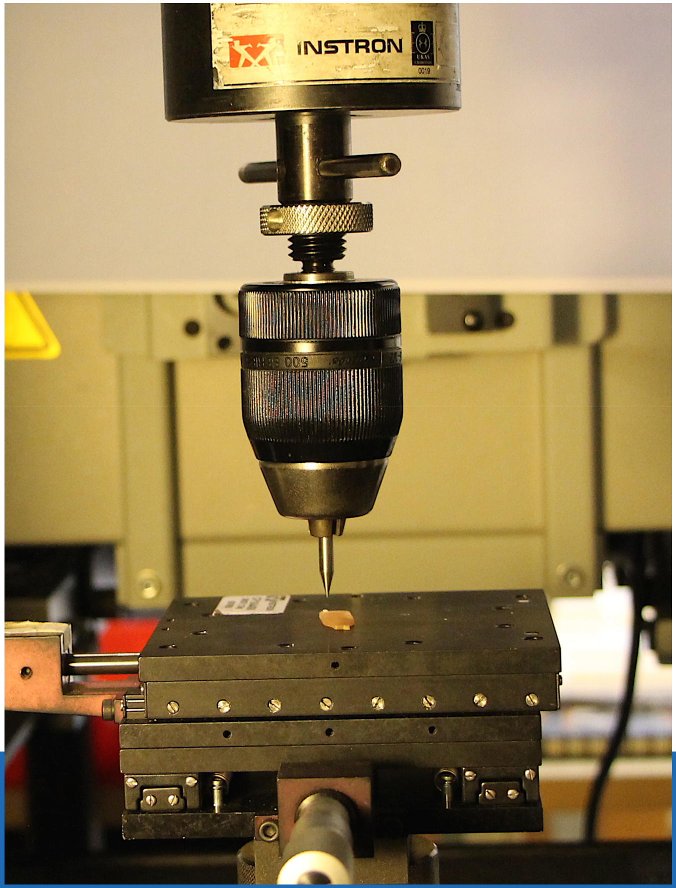


Brattberg seals aged at 170°C for 100 h

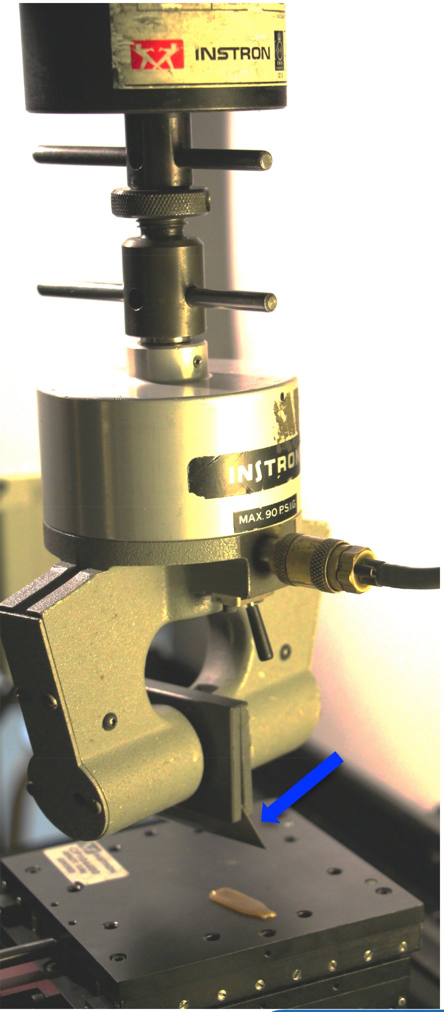
3. Indenter modulus profiling

- Modified Instron 5566 universal testing machine
- Static load cell (10N), modified probe tip (truncated cone 0.2 mm)
- indenter modulus (given in N mm^{-1})





Extraction profiles



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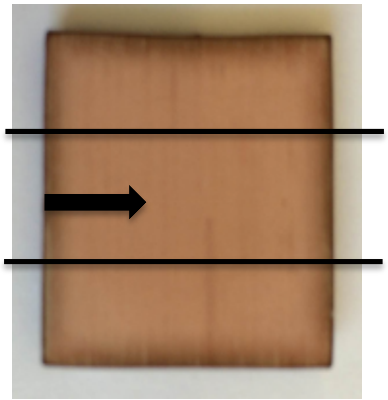

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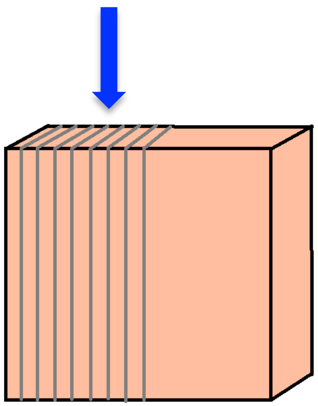


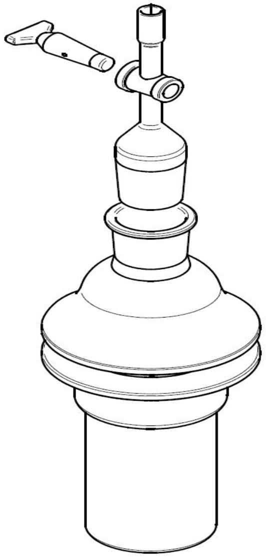
Extraction in *n*-heptane

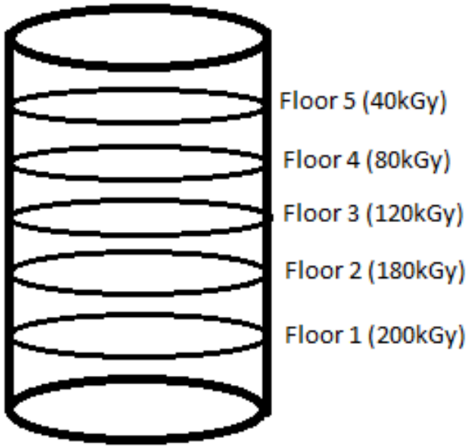
Drying / final mass

γ-irradiation at different oxygen partial pressures

Oxygen partial pressures in the reactor containments:

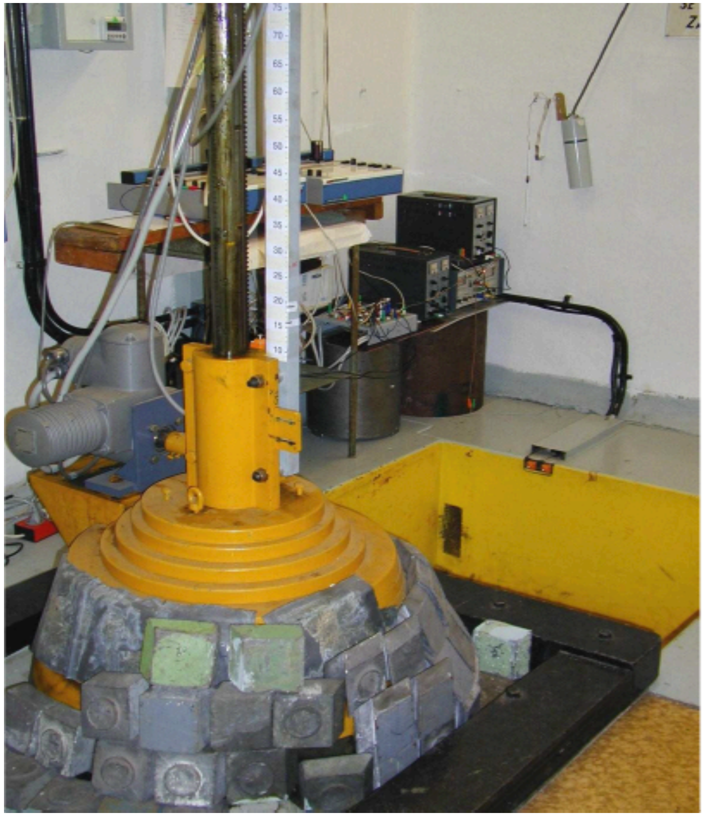
- p_{O2}= 1 kPa normal operation (exposure dose 0.15 kGy)
- p_{O2}= 21.2 kPa during summer maintenance
- p_{O2}= 5 kPa case of failure, up to 200 kGy for 30 days (0.28 kGy h^{-1})

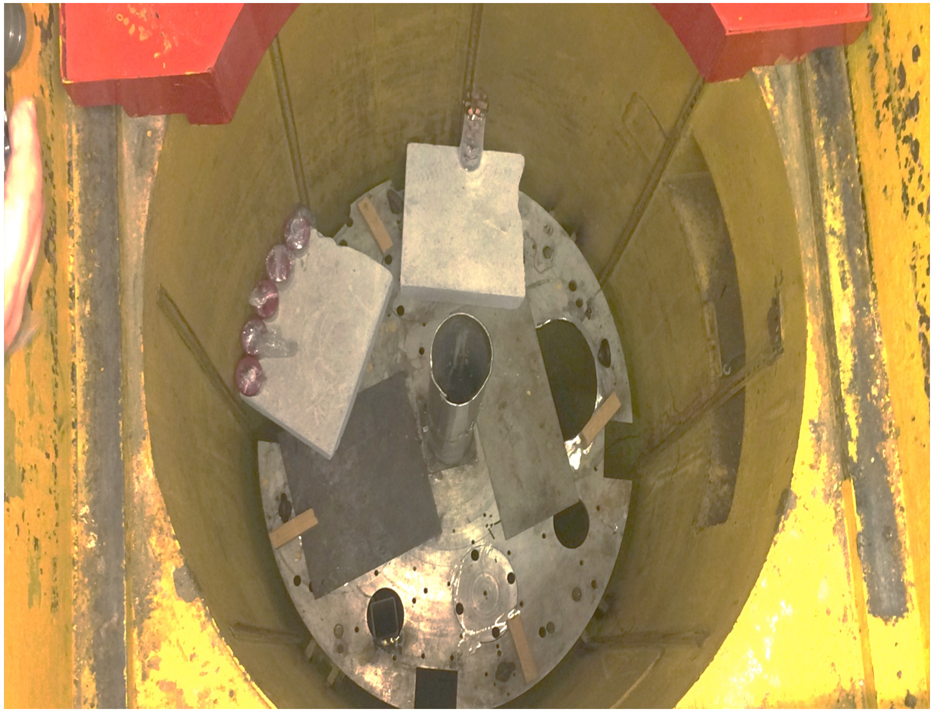




Gamma Irradiation chamber

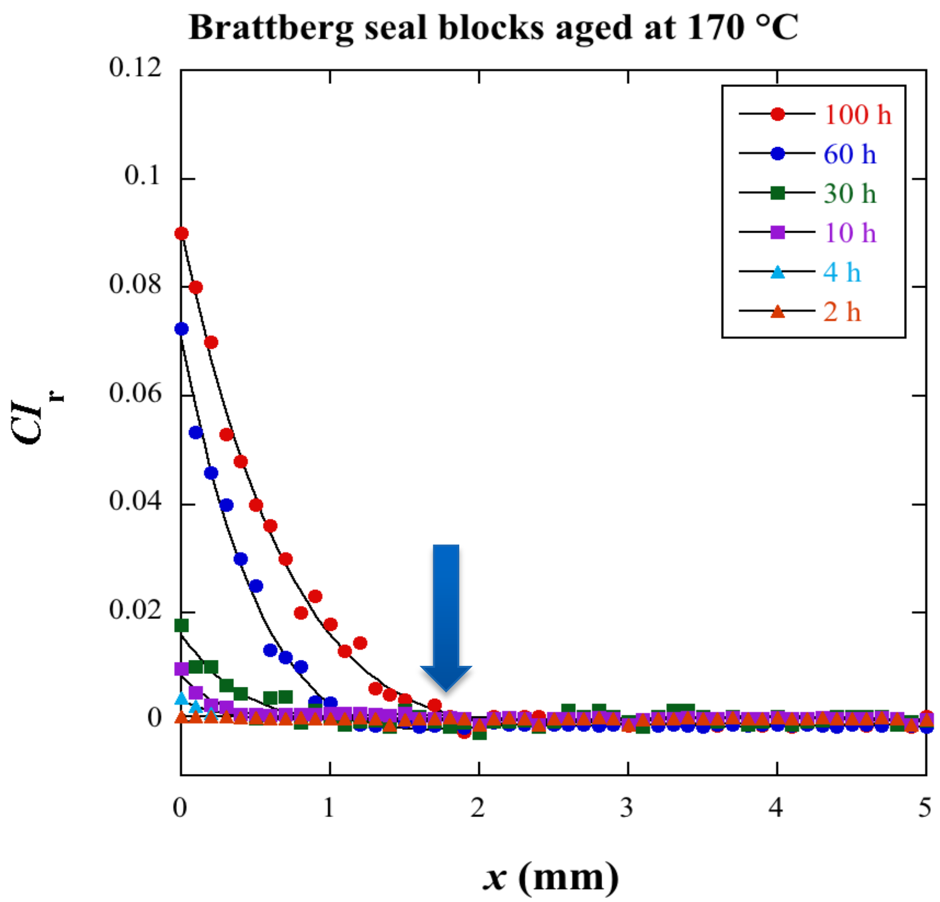
- Samples placed at 2 locations

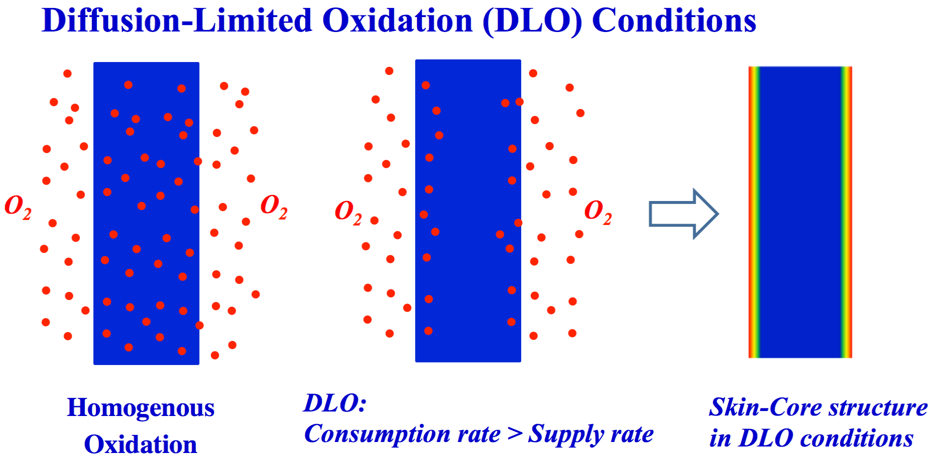




4. Results

Thermal ageing of EPDM (Paper I and II)



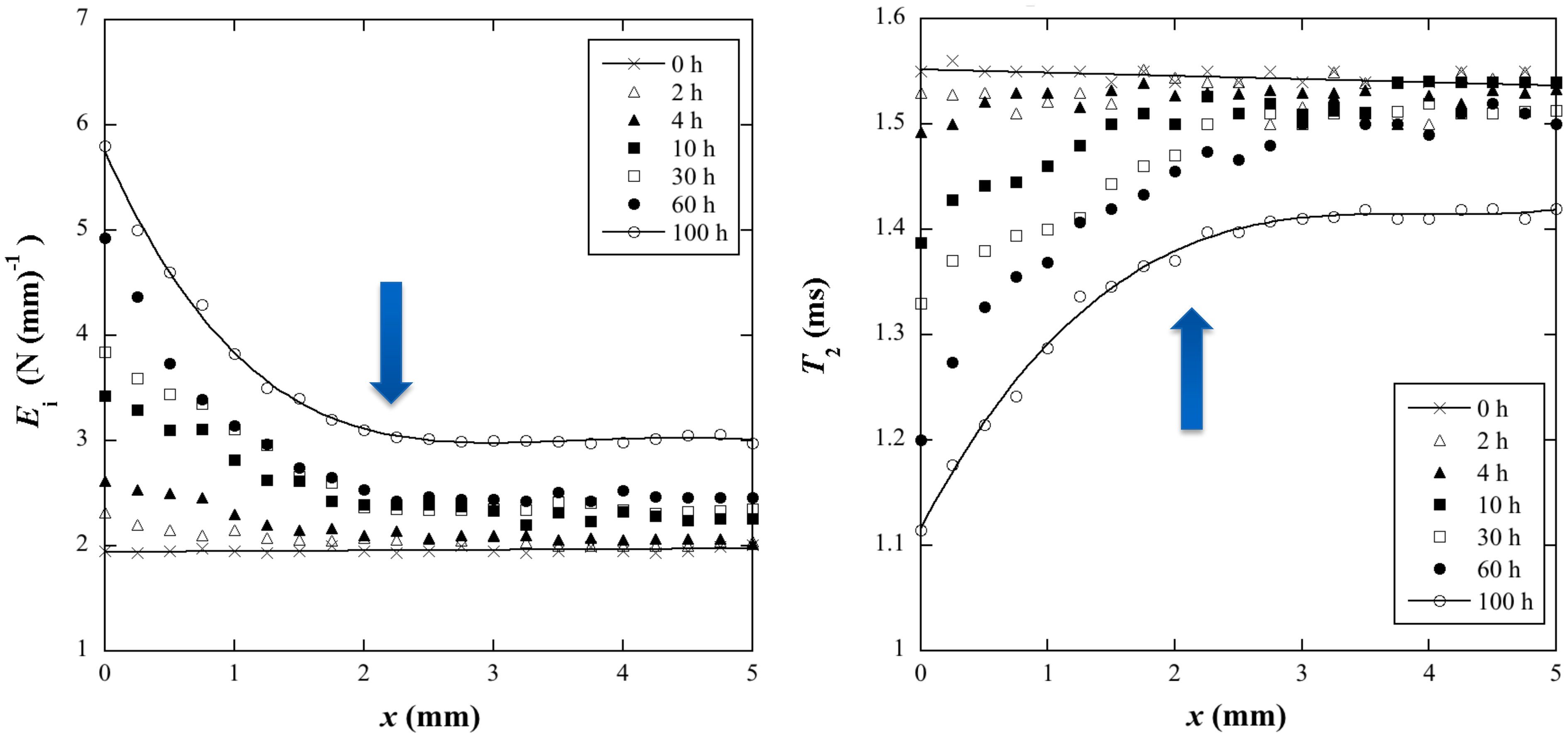


Reduced carbonyl index:

$CI_r = CI - CI_0$

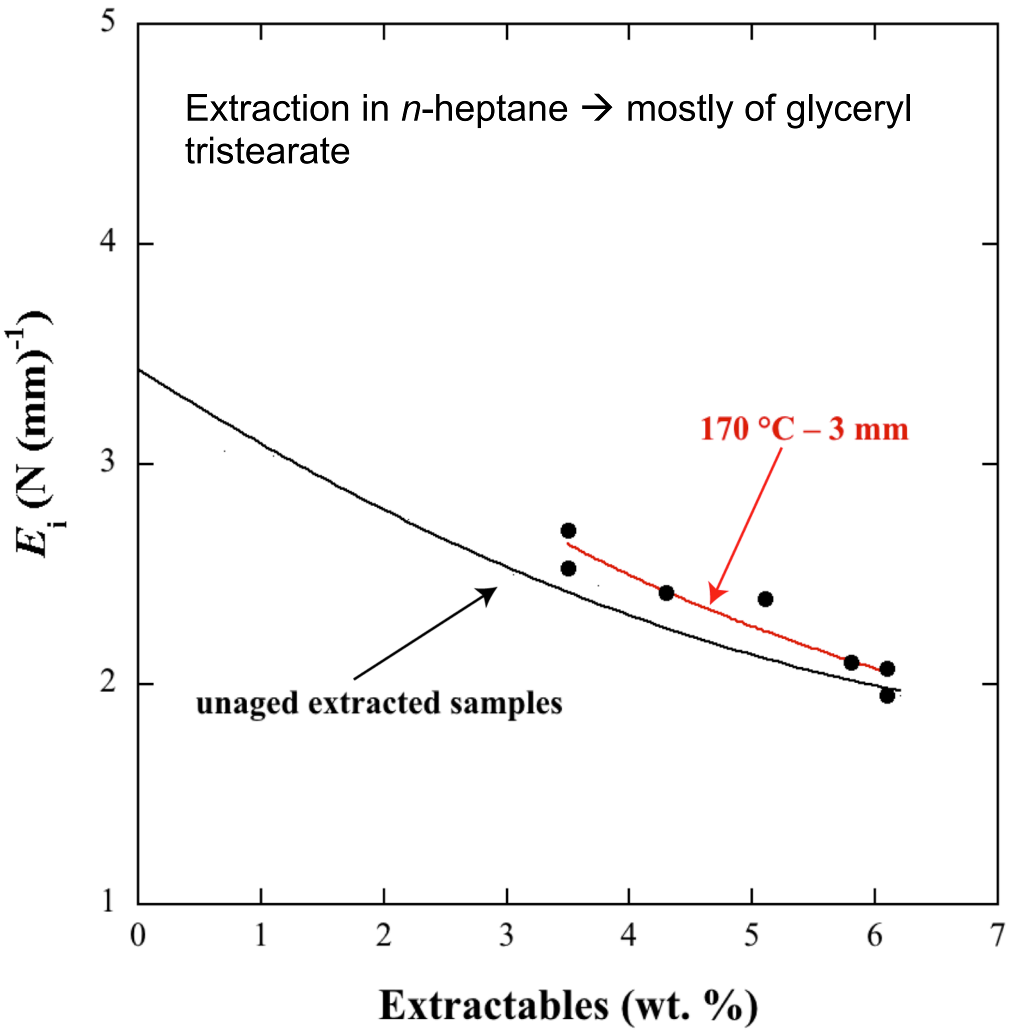
- Carbonyls → produced from oxidation
- Carbonyl range 1690 –1760 cm^{-1}
- Reference peak 800 cm^{-1} (ATH)

Modulus profile – Brattberg sealant aged at 170 °C



Figs. 20 and 21.

Separation of ageing effects



Migration:

$$E^*_{ir,\,migr} = \frac{E_\mathrm{i}\ (\mathrm{extr}\ \%,\ t=0)}{E_\mathrm{i}\ (t=0)}$$

Anaerobic contribution:

$$E^*_{ir,\,anaerobic} = \frac{E_i\ (x=3\mathrm{mm})}{E_\mathrm{i}\ (\mathrm{extr}\ \%,\ t=0)}$$

Sum of all contributions:

$$E_i = E_i(t=0) \times E^*_{ir,\,migr} \times E^*_{ir,\,anaerobic} \times E^*_{ir,\,c}$$

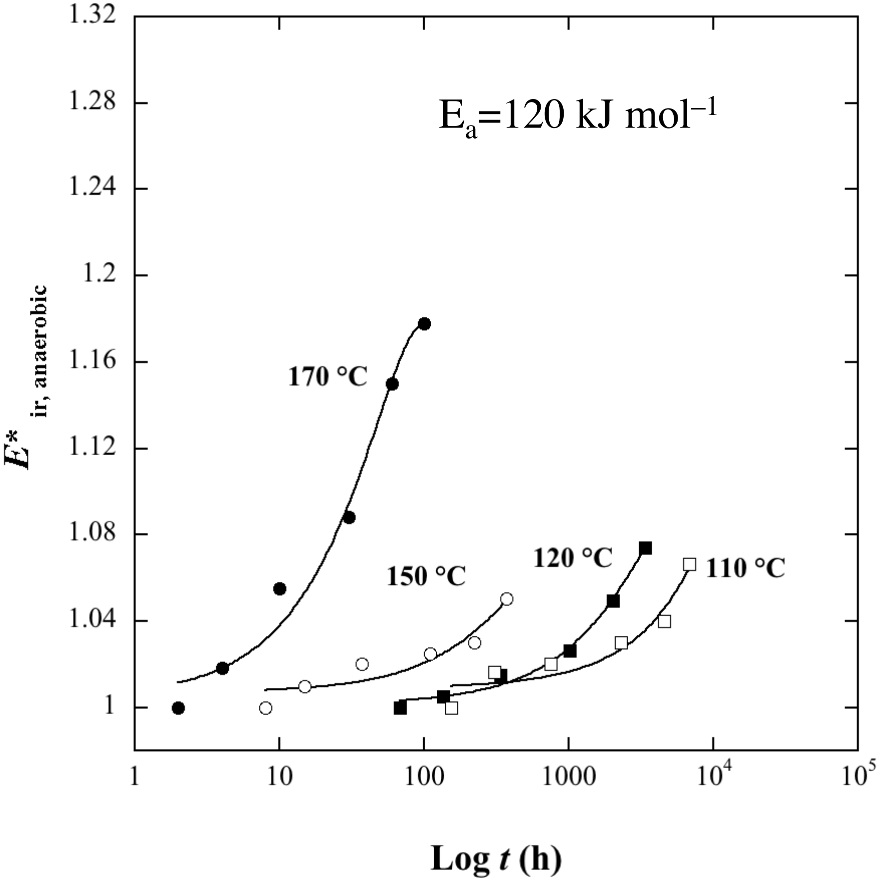
Oxidation:

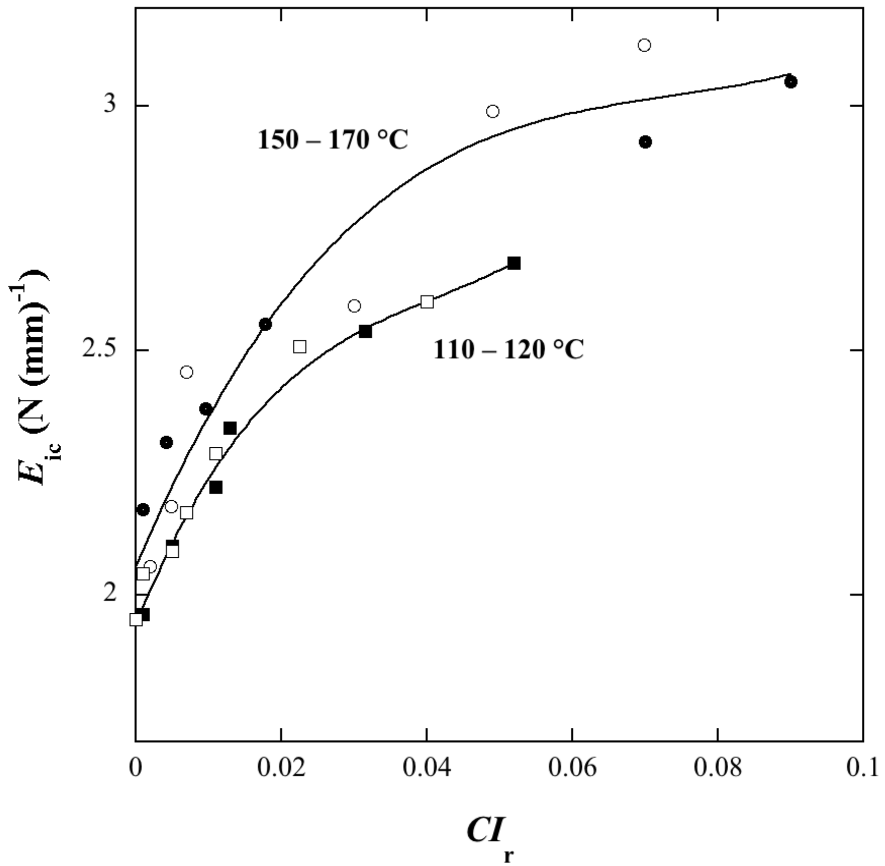
$$E^*_{ir,\,c} \times E_i(t=0) = E_{ic} = \frac{E_i}{E^*_{ir,\,migr} \times E^*_{ir,\,anaerobic}}$$

Thesis, section 4.1.5, Fig. 24, p. 53.

Brattberg seals thermally aged –
Anaerobic effects.

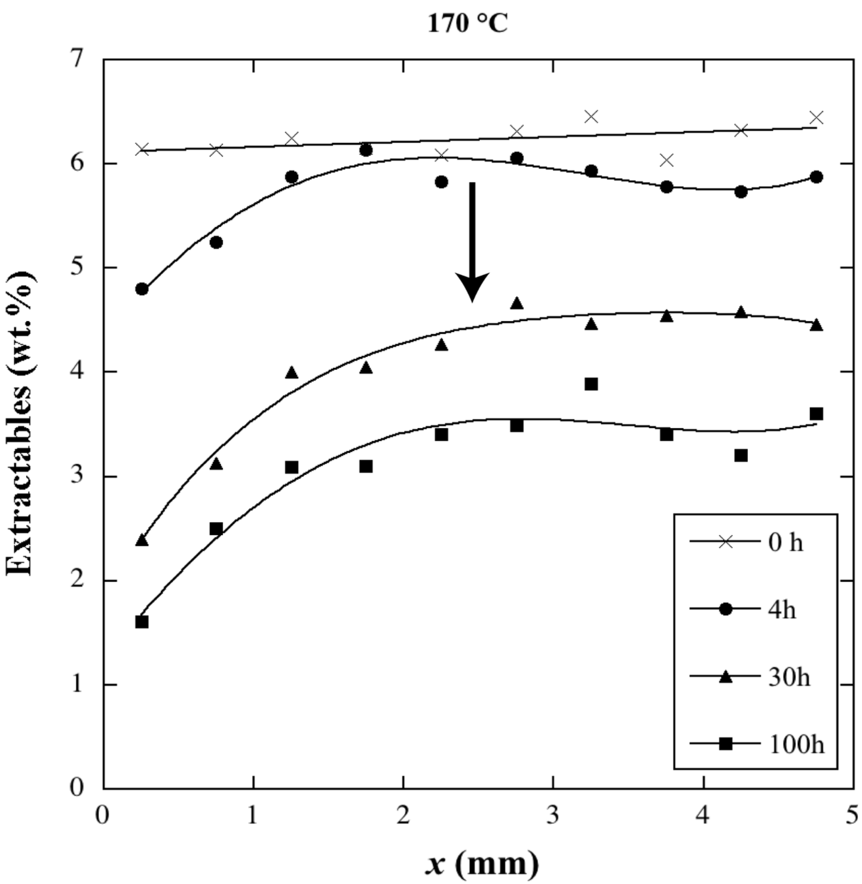
Indenter modulus associated with oxidation

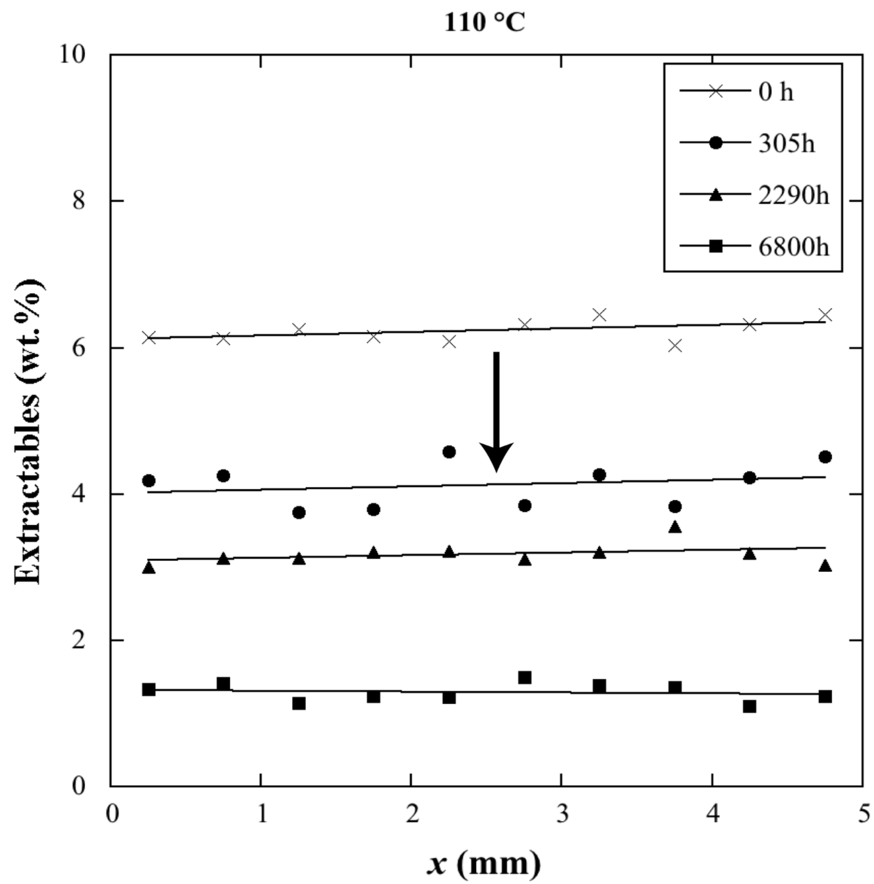




Paper II, Figs. 10 –11

Migration of low molar mass species





ΔH_{vap} = 175 kJ mol^{-1} (Glyceryl tristearate)

$E_{a(evap)}$= 85 kJ mol^{-1} , see section 4.1.6, p.58

$E_{a(diff)}$= 62 kJ mol^{-1}

E. Selke, W. Rohwedder, H. Dutton, Volatile components from tristearin heated in air, J. Am. Oil Chem. Soc. 52 (1975) 232–235.

5. Conclusions

- Results clearly show the complexity of the degradation process of highly filled EPDM. Profiling methods proved to be essential to understand the the process in detail i.e. migration, anaerobic effects and oxidation.

- The importance of oxygen partial pressure during γ-irradiation was revealed, strongly affecting the migration of low molar mass species and by which directly affecting the modulus and T_2.

- γ-irradiation in air and water highlighted the importance of oxygen availability to the EPDM rubber. Water was shown to be a less aggressive environment, reflected by the small changes in *CI*, modulus and T_2 .

7. Acknowledgements

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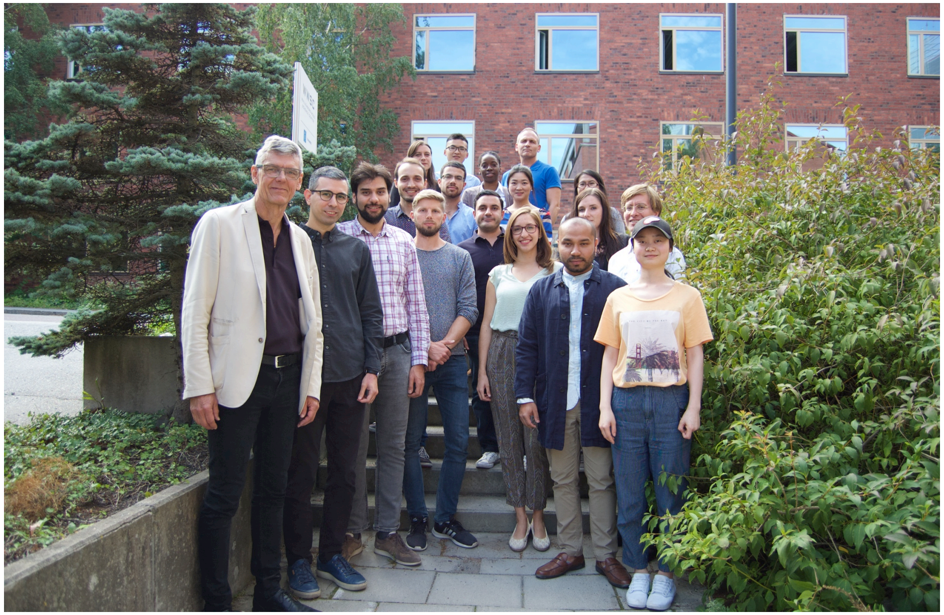
okg - part of the energy business Uniper

Strål säkerhets myndigheten
Swedish Radiation Safety Authority

VATTENFALL

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