Polymer ageing mechanisms and effects inside NPP containment – Results from COMRADE project

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Background for COMRADE

- Feasibility studies conducted at RISE and VTT → How to set acceptance criterion properly and irradiation resistance of polymers used inside containments
- Questions related to irradiation resistance of polymers arose:
  - How severe is the irradiation induced ageing compared to thermal ageing during the normal service conditions?
  - Are there any synergistic effects arising from simultaneous exposure to radiation and heat?
  - How severe is the dose rate effect during the normal service conditions?
- These topics were included in the third work package of COMRADE project within the SAFIR2018 framework

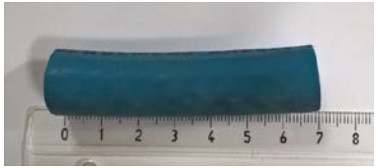
Background for COMRADE

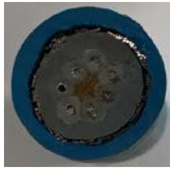
- WP1 O-ring condition monitoring technique
- WP2 Material acquisition from plants
- WP3 Polymer ageing mechanisms and effects inside NPP containment:
  - Task 3.1 Modelling tools for synergic effects of radiation and heat
  - Task 3.2 Polymer ageing during LOCA
  - Task 3.3 Synergy effects between radiation and heat and oxidation depth
  - Task 3.4 Evaluation of methods used in extrapolation of dose rate effect
- This presentation summarizes the results from T3.2 and T3.4

Synergy effects between radiation and heat

Studied materials and ageing

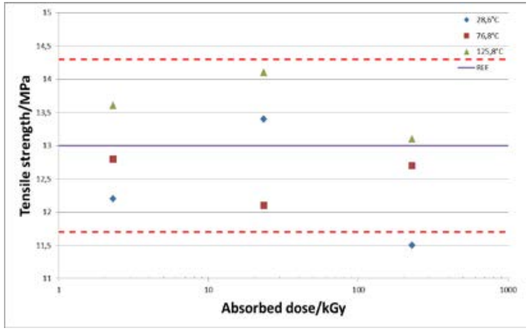
- Samples studied included peroxide cured EPMD (James Walker) and CSM Lipalon cable jacket, tradename Hypalon (from TVO)
- Ageing conducted at Rez, RISE and VTT
- Various doses, dose rates and temperatures

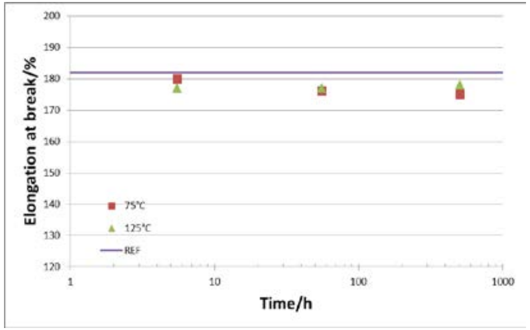


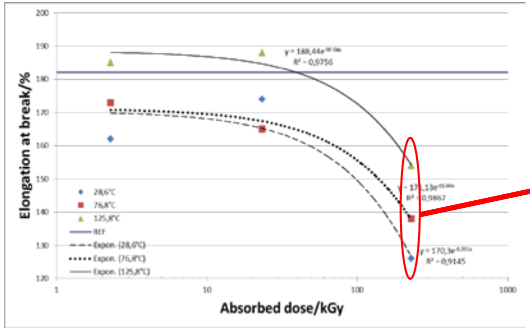


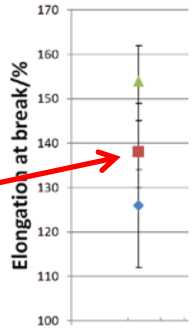
Ageing of EPDM simultaneously under irradiation and at elevated temperature

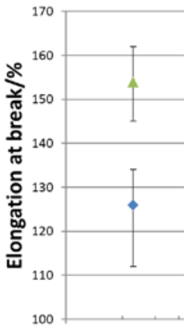
- EAB more sensitive parameter for material degradation than tensile strength or hardness
- Plane thermal ageing (i.e. three weeks at 125°C) did not yield in significant decrease in EAB
- Elevated temperature seems to be beneficial for the studied EPDM when simultaneous radiation treatment is applied





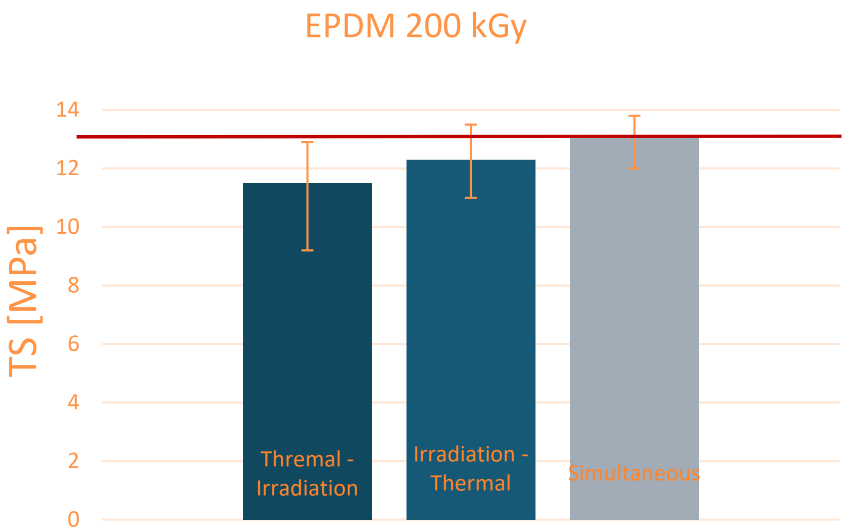


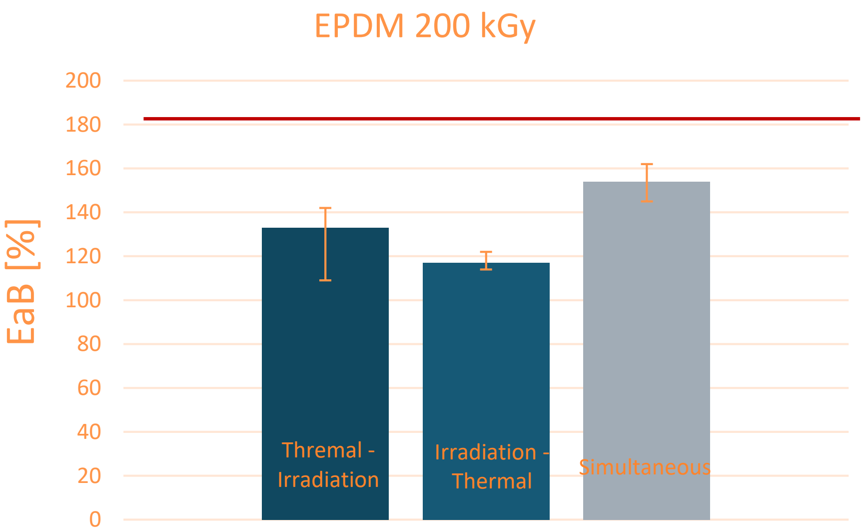




Ageing of EPDM simultaneously under irradiation and at elevated temperature

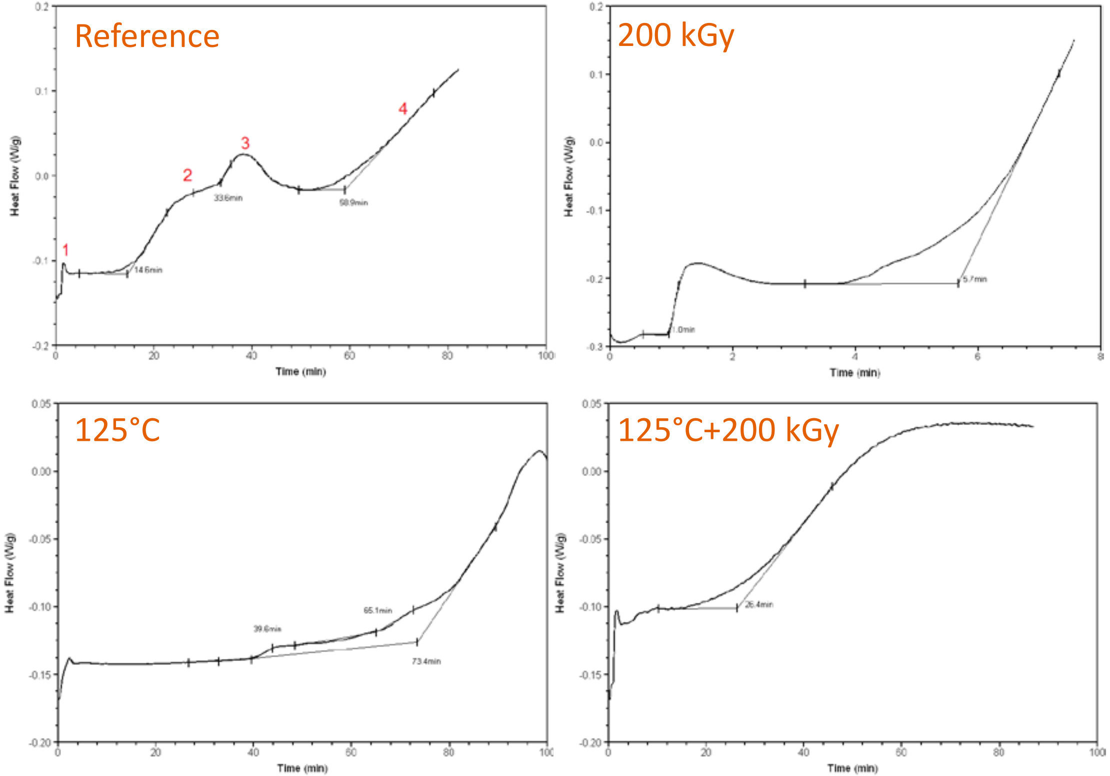
- Comparison of sequence in thermal (three weeks at 125°C) and irradiation
- Irradiation first, thermal second -sequence slightly decreases EaB





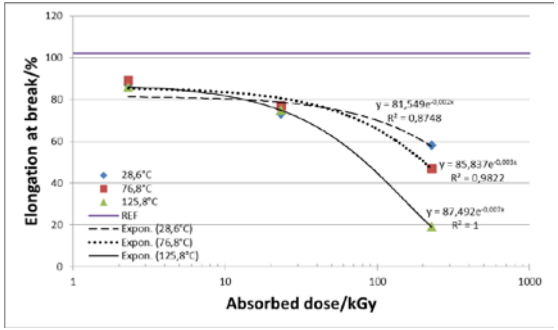
Oxidation induction time (OIT) for EPDM

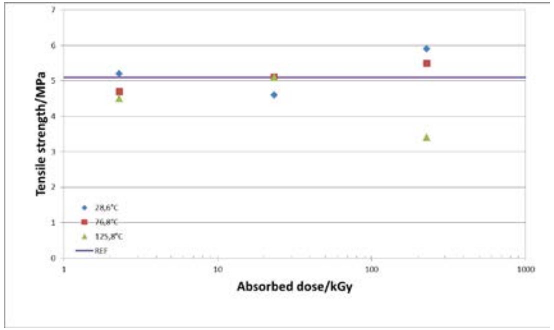
- Four EPDM samples was analysed
- Analysis of the spectra gives info on the thermal stability of our samples
- Processes 1-3 most likely decomposition of different additives
- Process 4 decomposition of the base polymer
- Irradiation decreases OIT and thermal exposure increases OIT

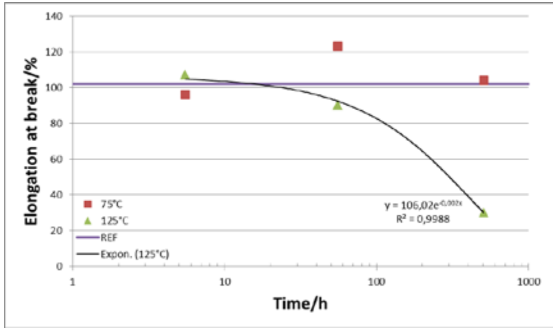


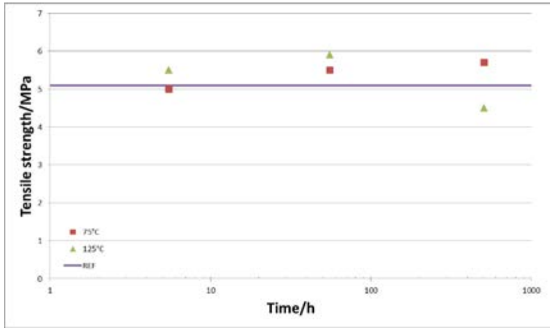
Ageing of CSM simultaneously under irradiation and at elevated temperature

- During simultaneous exposure elevated temperature increased degradation
- Thermal ageing at 125°C yielded in similar result as combined ageing
- Opposite behavior to EPDM
- Some decrease in tensile strength when exposed to 200 kGy and 125°C simultaneously



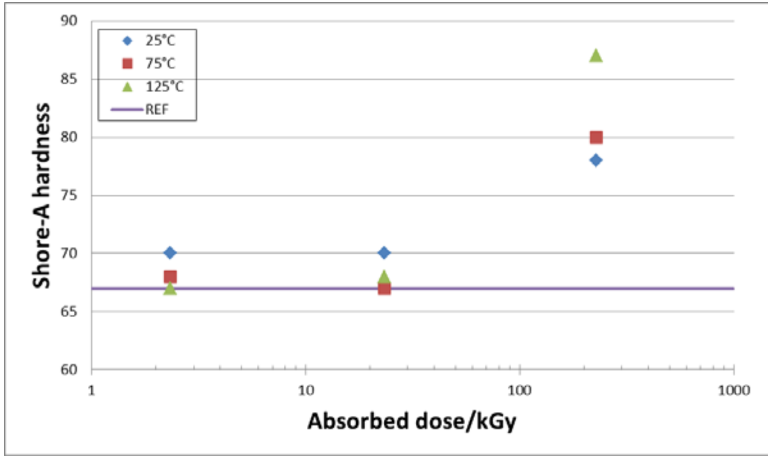


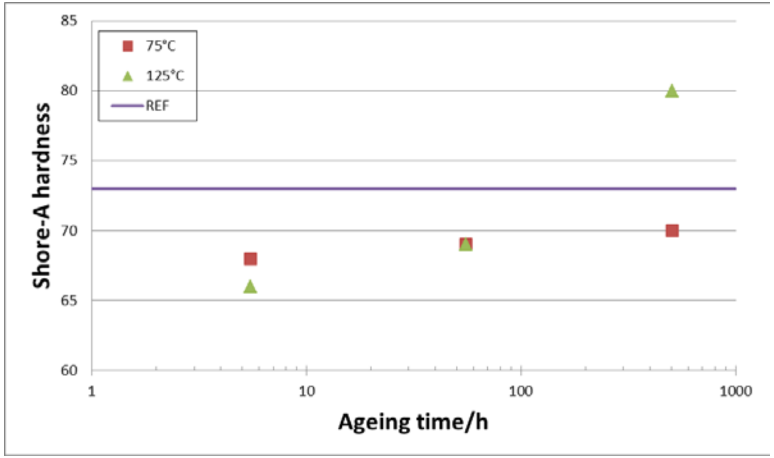




Ageing of CSM simultaneously under irradiation and at elevated temperature

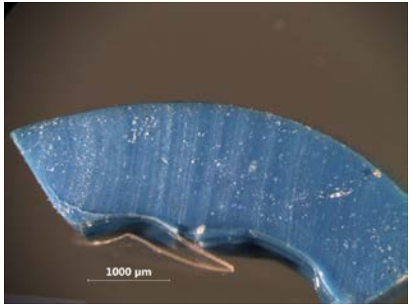
- Hardness increased as the ageing time increased → Cl content and crystallinity degree

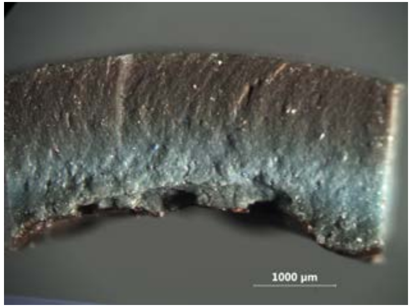




Visual changes induced by the ageing treatments

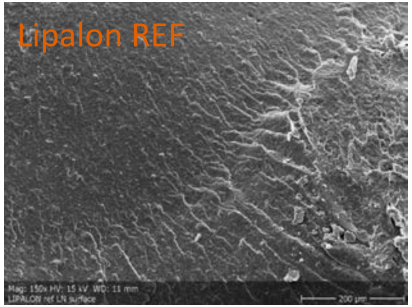
- Photographs after exposures
- No visual changes in EPDM samples
- Clear color changes in CSM samples after simultaneous thermal and irradiation exposure (due to the thermal exposure)
- Cross section revealed a gradient in color change

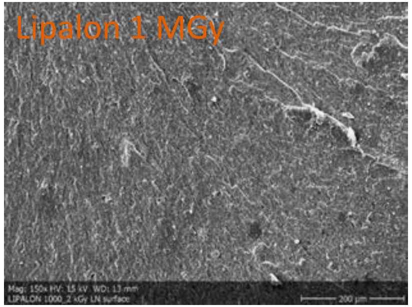


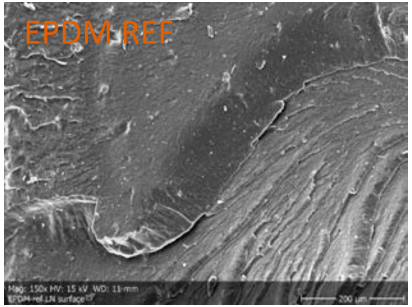


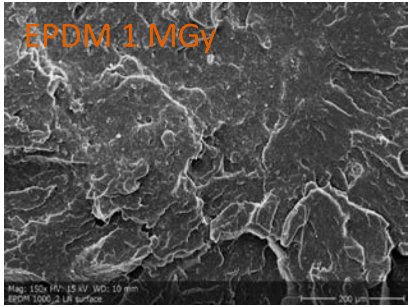
Visual changes induced by the ageing treatments

- SEM images of the fracture surfaces
- Irradiated samples showed more rough surface properties





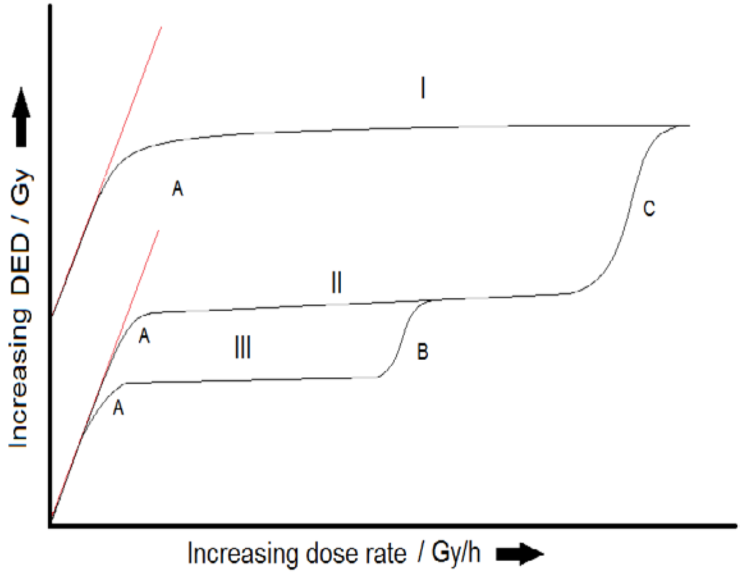




Dose rate effect studies

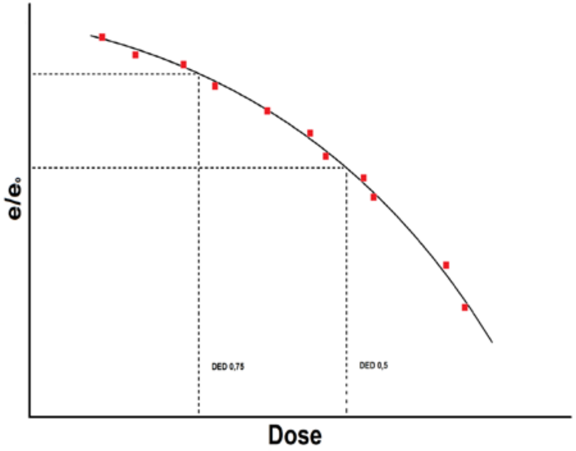
How to estimate dose rate effect?

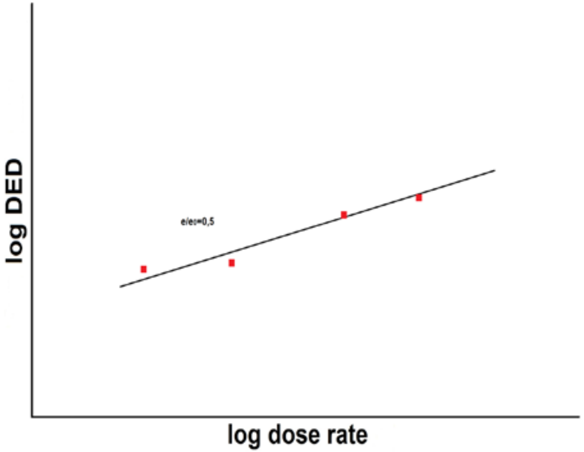
- Lower dose rate causes more damage to the polymer than a higher dose rate
- Low dose rate irradiations are time consuming and expensive
- Existing tools to predict dose rate behaviour in open literature are semi-empirical → Could they be used to estimate the severity of the phenomenon



Semi-empirical models

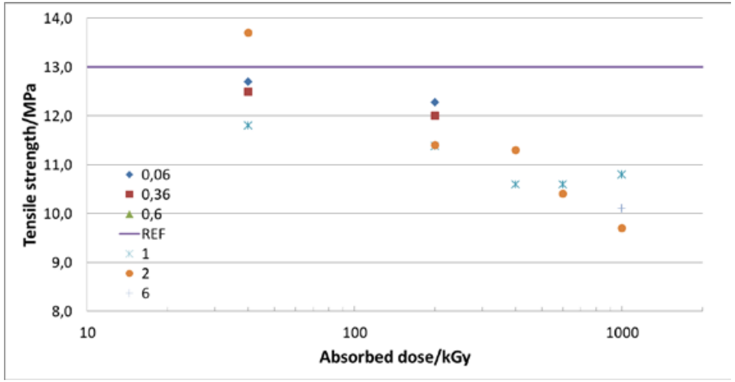
- They use experimental data to predict degradation as function of dose rate
- Interesting models include power law and superposition models
- Dose to equivalent damage (DED) are defined based on a function of a material property (here EaB) describing the material condition and dose
- DED parameters are plotted versus the dose rate

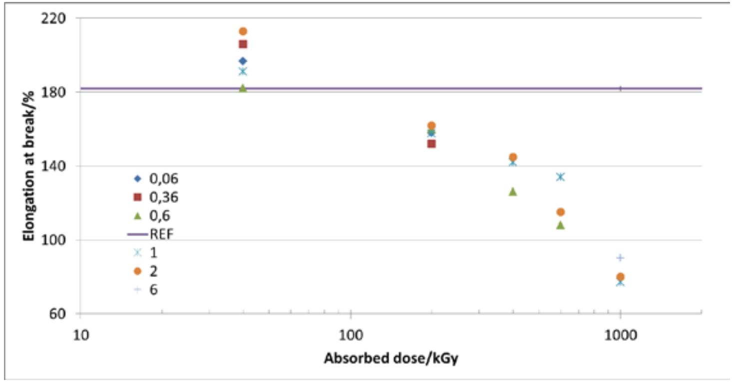




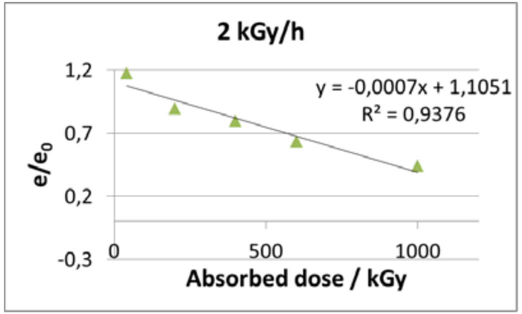
Application of power law model on EPDM

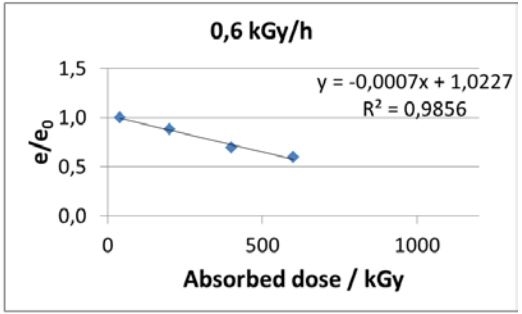
- Data for EPDM obtained at single temperature, with different dose rates and absorbed doses

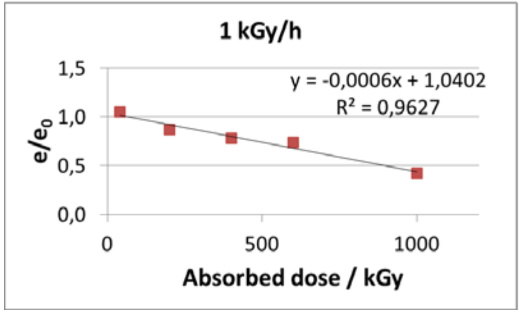


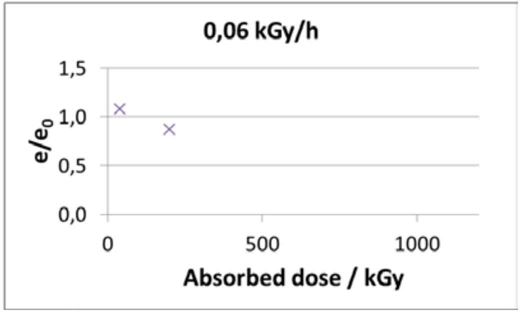


Power law – interpolation of the end-point dose for EPDM





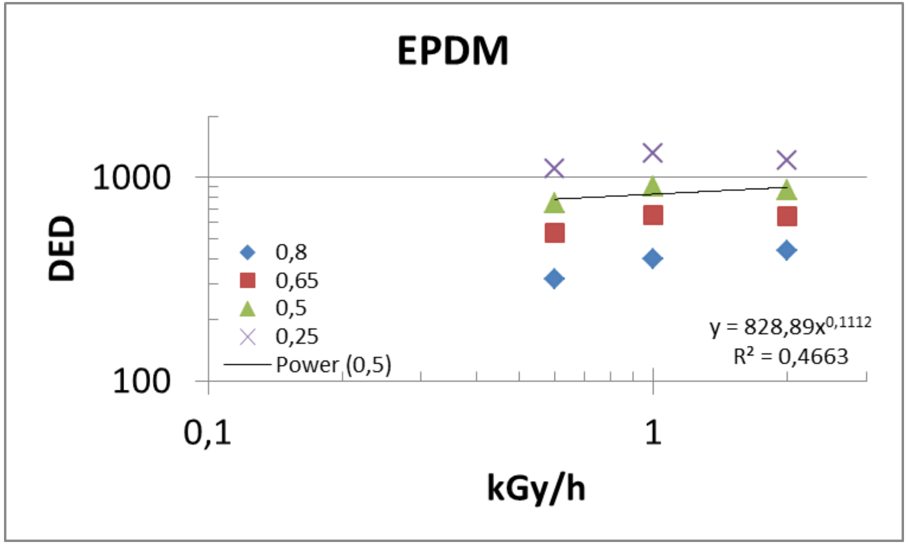




Application of power law model on EPDM

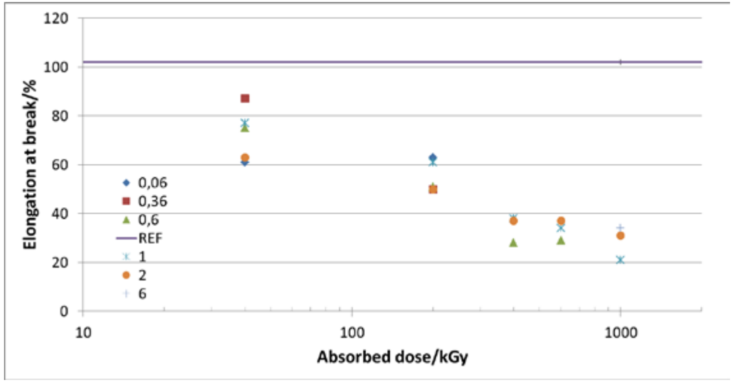
- DED = K D^n, where K and n constants, D dose rate
- Linearity of the log-log plot is required – not very good fit
- Heterogeneous oxidation at high dose rates (2 mm sample thickness)?
- e_0 = 182%

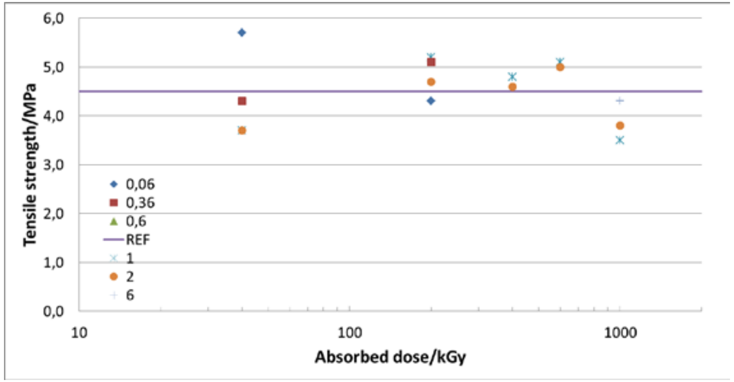
EPDM	DED at Dose rate / kGy/h		
e/e0	0,6	1,0	2,0
0,9	175	234	293
0,8	318	400	436
0,7	461	567	579
0,65	532	650	650
0,6	604	734	722
0,5	747	900	864
0,4	890	1067	1007
0,3	1032	1234	1150
0,25	1104	1317	1222



Application of power law model on CSM

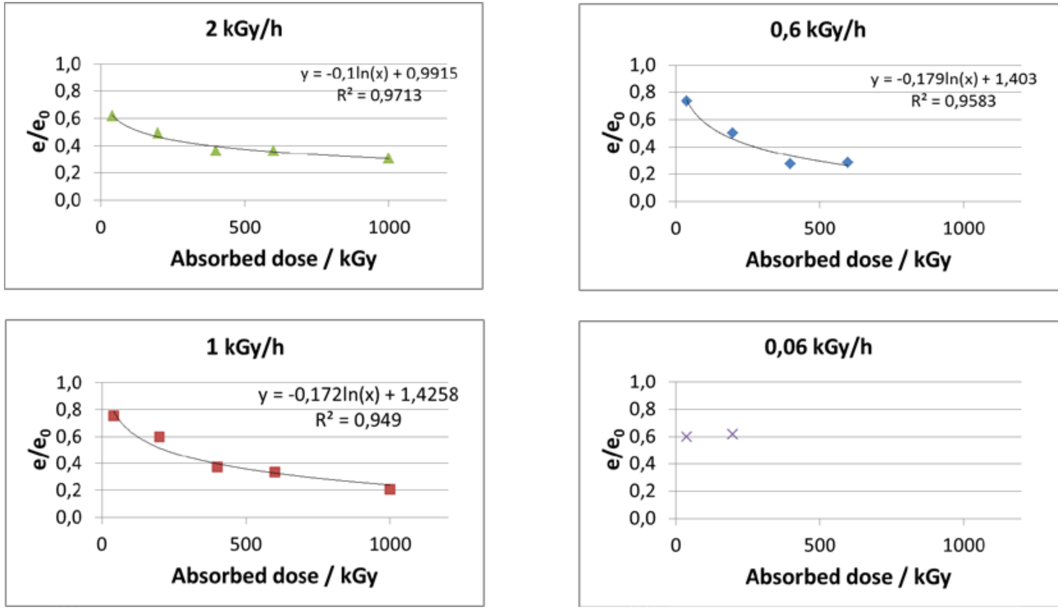
- CSM tensile testing results





Power law – interpolation of the end-point dose for CSM

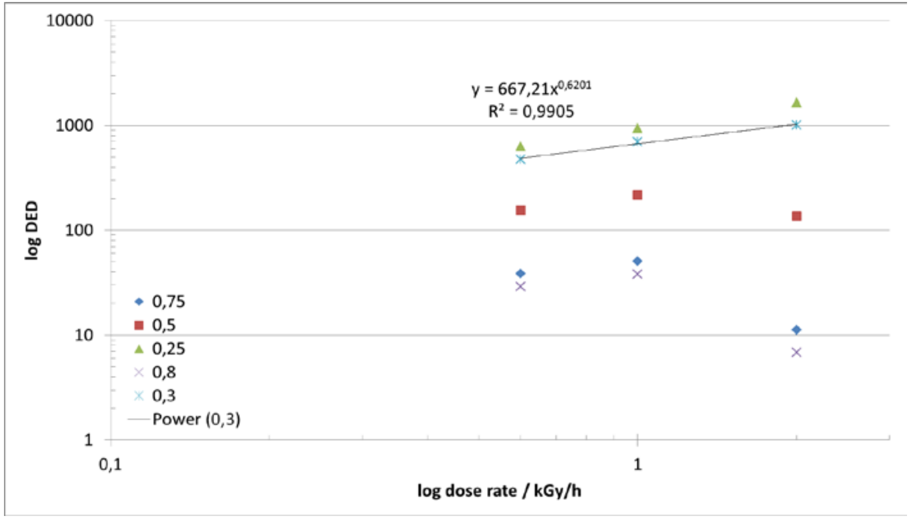
- Definition of the end-point criteria



Application of power law model on CSM

- DED = K D^n, where K and n constants, D dose rate
- Linearity of the log-log plot is required – good fit when end-point criterion is low, i.e. <0,3
- Heterogeneous oxidation at high dose rates (cable jacket ca. 2 mm thick)?
- e_0 = 102%

Lipalon	DED at Dose rate / kGy/h		
e/e0	0,6	1,0	2,0
0,9	17	21	2
0,8	29	38	7
0,75	38	51	11
0,7	51	68	18
0,6	89	122	50
0,5	155	218	136
0,4	271	389	371
0,3	474	696	1007
0,25	627	931	1661



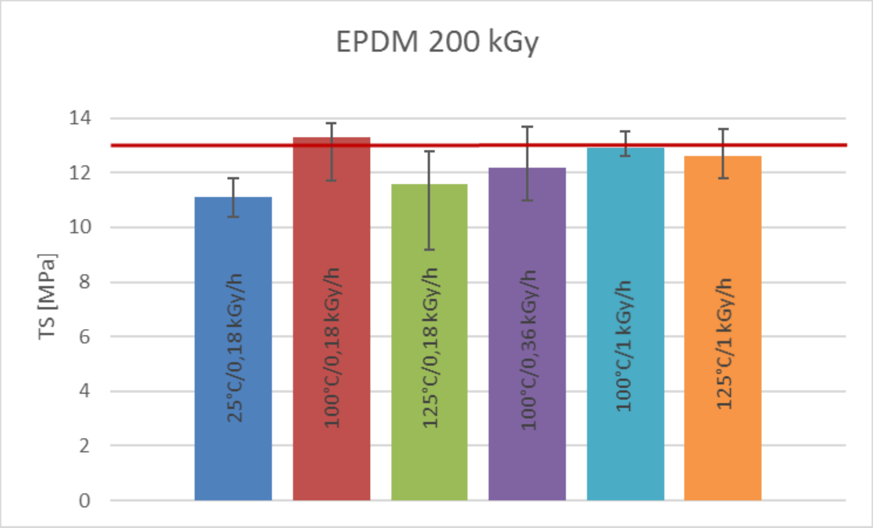
Application of superposition model on EPDM and CSM (2018)

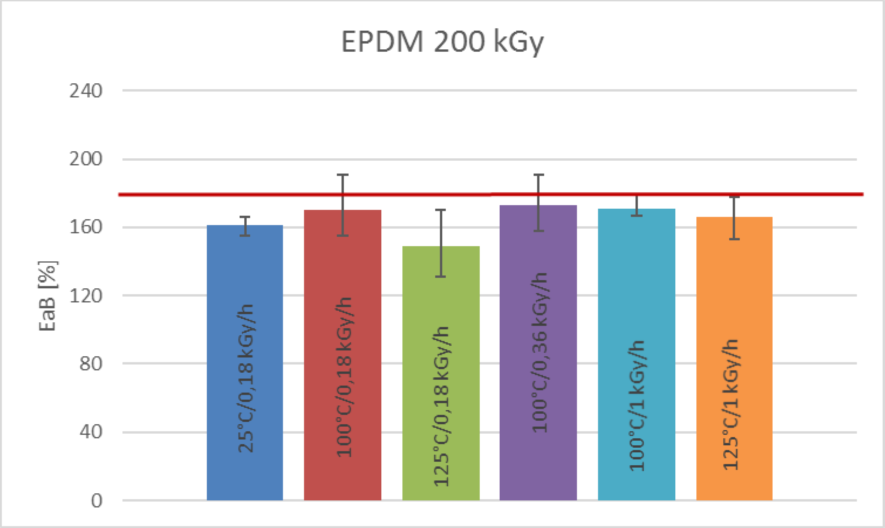
- Data produced at elevated temperature and irradiation environments → combined to the data from earlier years, application of the model should be possible

Temperature (°C)	Dose rate required (kGy/h)	Dose rate measured (kGy(h)	Absorbed dose required (kGy)	Absorbed dose measured (kGy)
25	0,36	0,38	400	418
25	0,18	0,27	200	209
100	1,0	0,71	400	470
100	0,36	0,44	400	401
100	1,0	0,75	200	219
100	0,36	0,41	200	200
100	1,8	0,26	200	201
125	1,0	1,11	400	411
125	0,36	0,41	400	406
125	1,0	1,02	200	203
125	0,18	0,26	200	202

Application of superposition model on EPDM – Tensile testing results 200 kGy

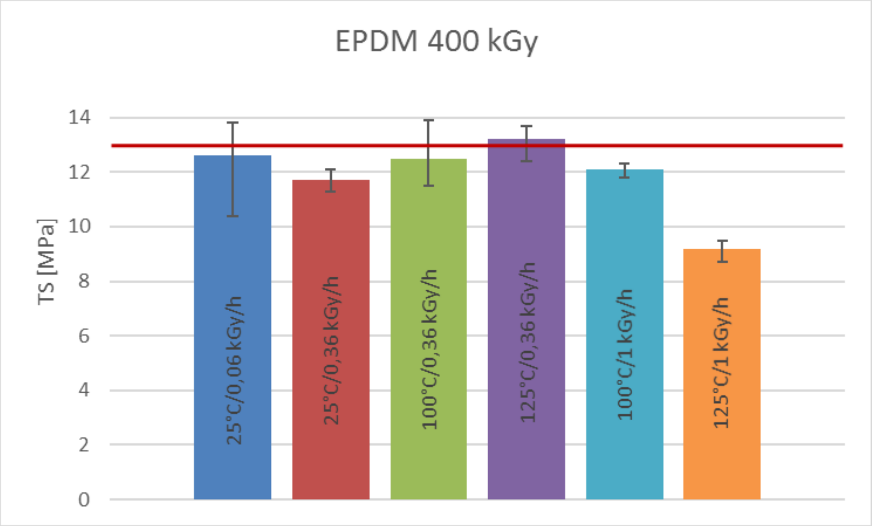
- Genreally only minor decrease in the measured properties

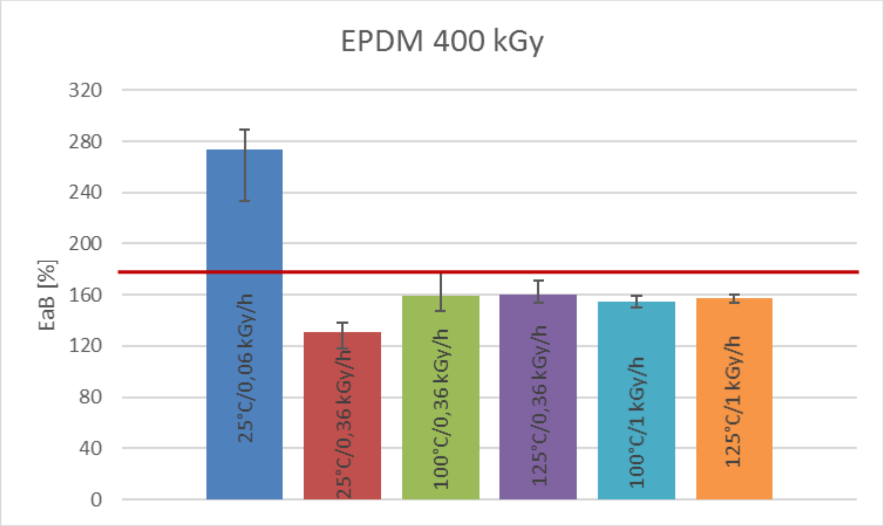




Application of superposition model on EPDM – Tensile testing results 400 kGy

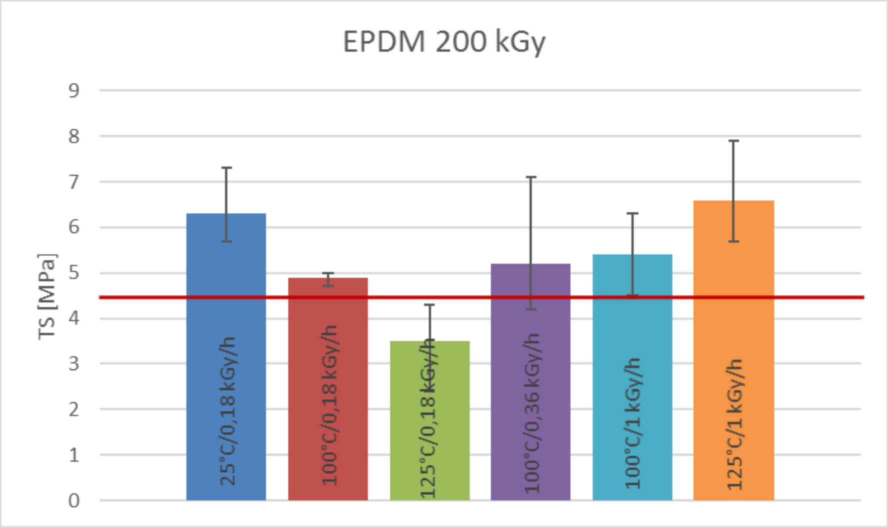
- Irradiation at low dose rate (<0,06 kGy/h) yielded in increase in EaB

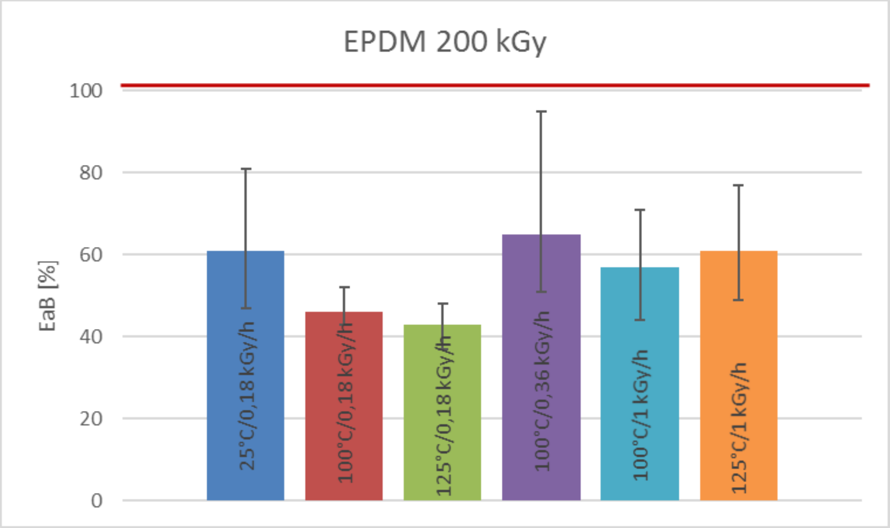




Application of superposition model on CSM – Tensile testing results 200 kGy

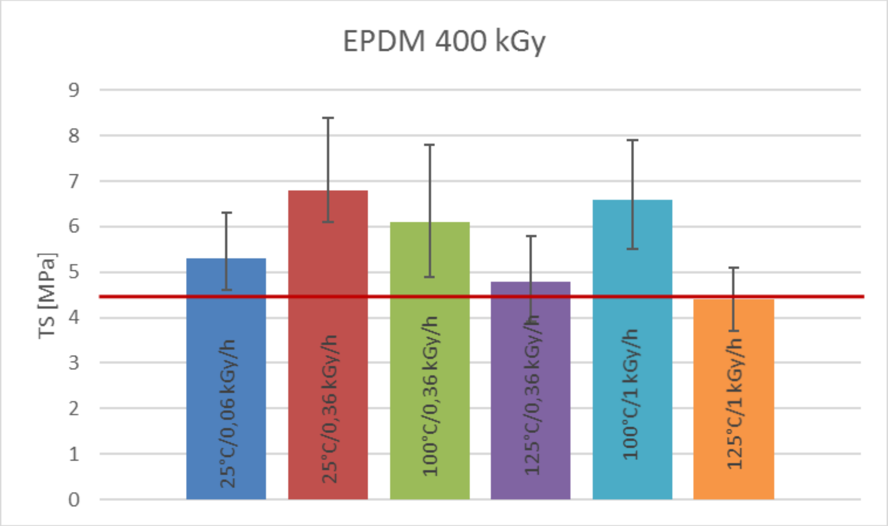
- Slight increase in TS values and decrease in EaB

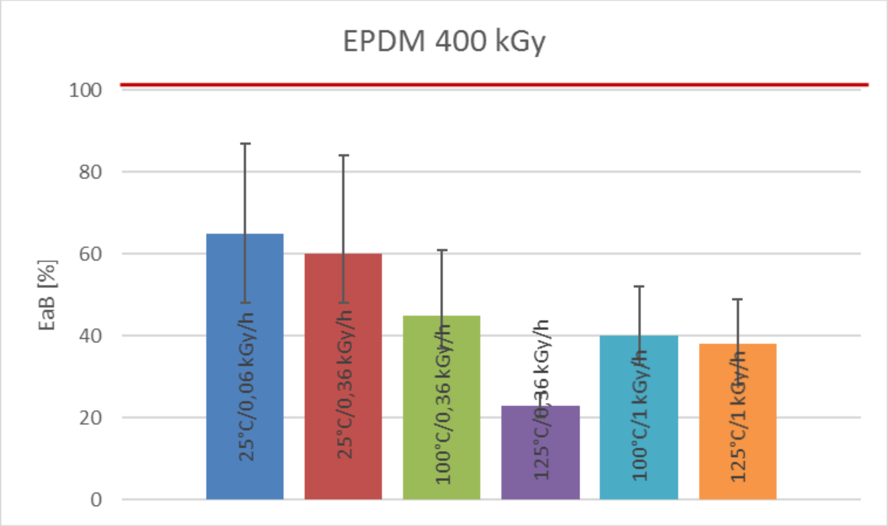




Application of superposition model on CSM – Tensile testing results 400 kGy

- EaB decreases as the dose increases





What to say now about superposition models and the data gathered

- EPDM seems to be too radiation resistant that reliable estimates on dose rate effect using the collected data is not possible
- CSM seems to be more promising and the application will be finished as sufficient amount of thermal ageing data is acquired (December 2018)

SUMMARY

- Irradiation and thermal effects and dose rate effect were studied with EPDM and CSM samples
- Ageing of EPDM seemed to hinder at combined irradiation + thermal environment as the ageing temperature was increased to 125°C
- The sequence of ageing seems to have an impact when EPDM is aged
- With CSM, increasing temperature in combined irradiation + thermal environment increased the degradation → Increasing hardness and decreasing elongation are signs of embrittlement
- The application of power law model seemed to work for CSM samples, i.e. dose rate effect could be seen → however the role of heterogeneous oxidation was not defined on samples causing some uncertainties to the interpretation of the results
- Sufficient degradation levels needs to be achieved in order apply semi-empirical models properly
- EPDM seemed to be too radiation resistance on these irradiation parameters → applying models for radiation resistant materials can be very expensive

Thank you!