Ageing tests closer to real service conditions using hypersensitive microcalorimetry, a case study on EPDM rubber

Presented by

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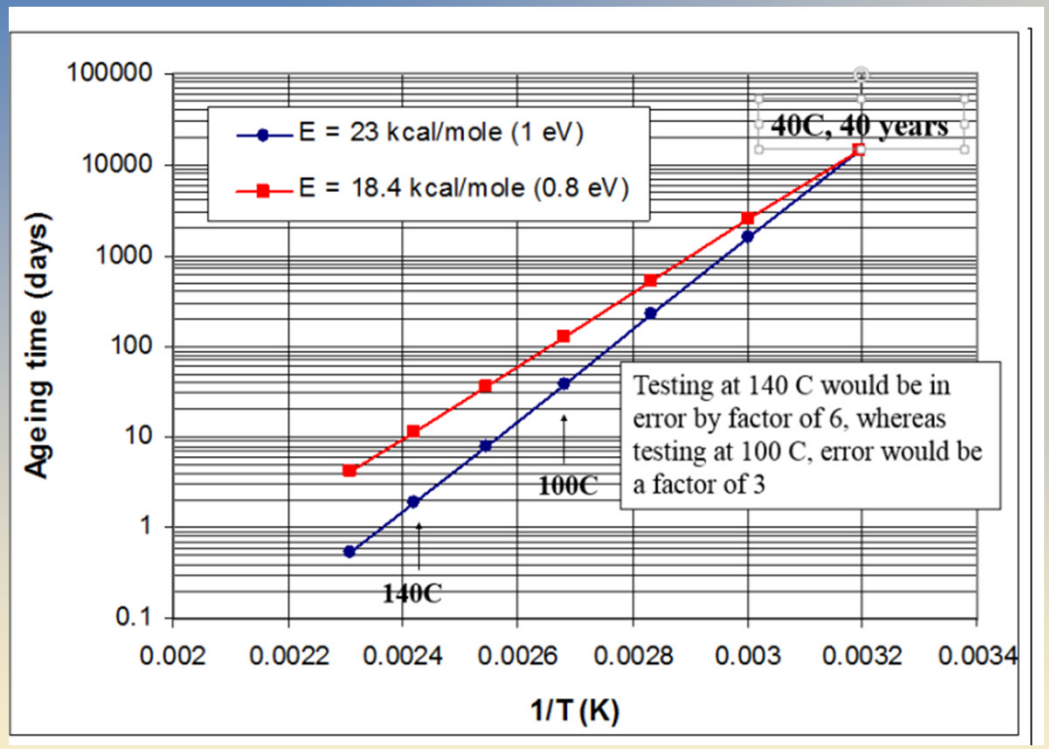
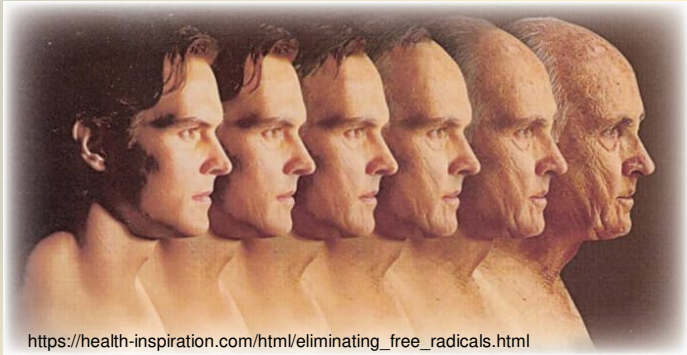
Rationale for using MC



Effect of different activation energy on the time required to simulate a service life of 40 years at 40 °C

Challenge

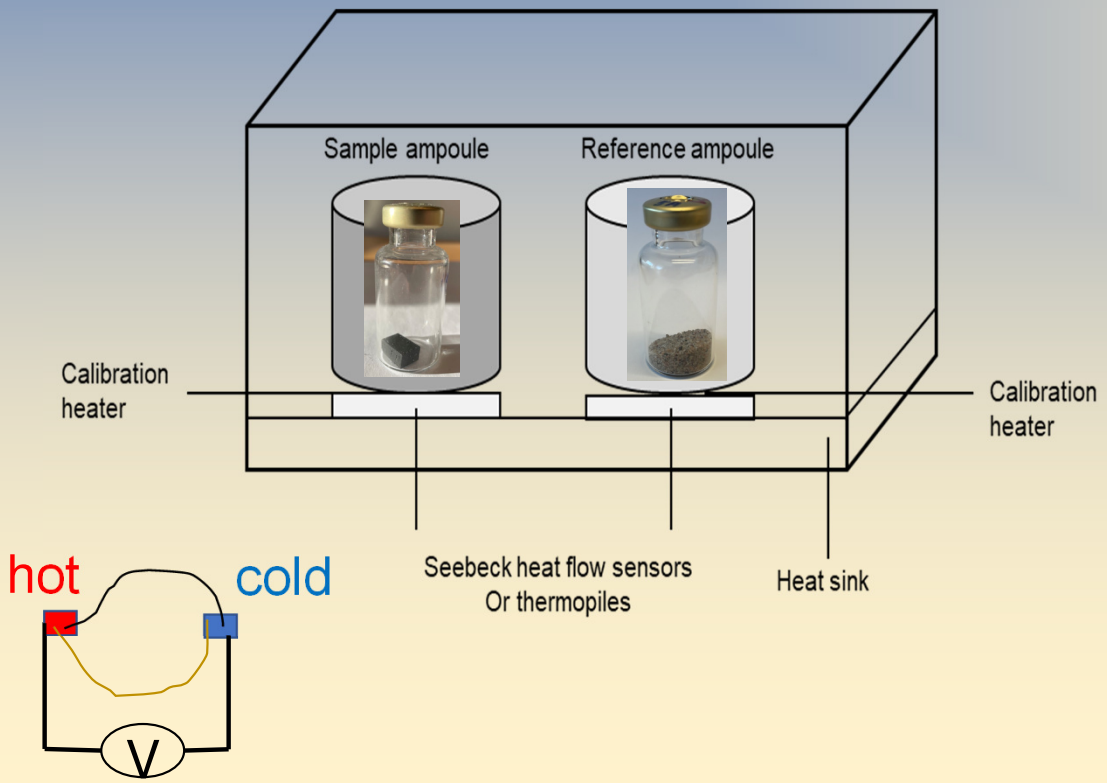


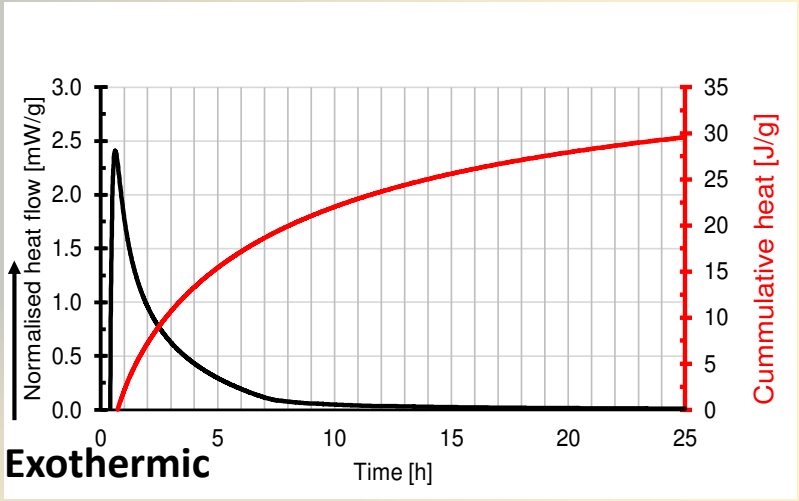
Sensitive technique is required

Introduction to Microcalorimetry (MC)

DSC ~ 1 µW/10 mg and MC ~ 1 µW/1000 - 10 000 mg

Specific sensitivity ~ 1000 times higher than DSC



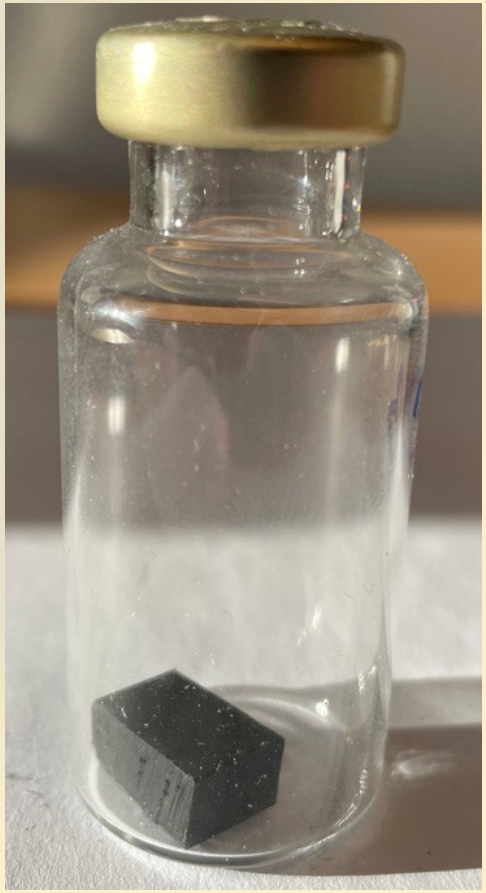


Normalised Heat flow(mW/g) and Cumulative heat (J/g)

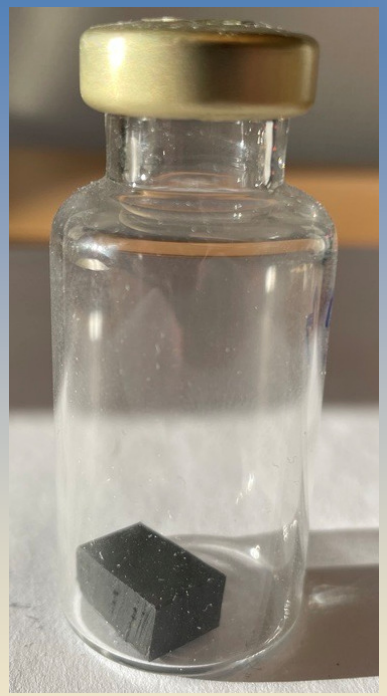
Limitation of MC for polymeric materials

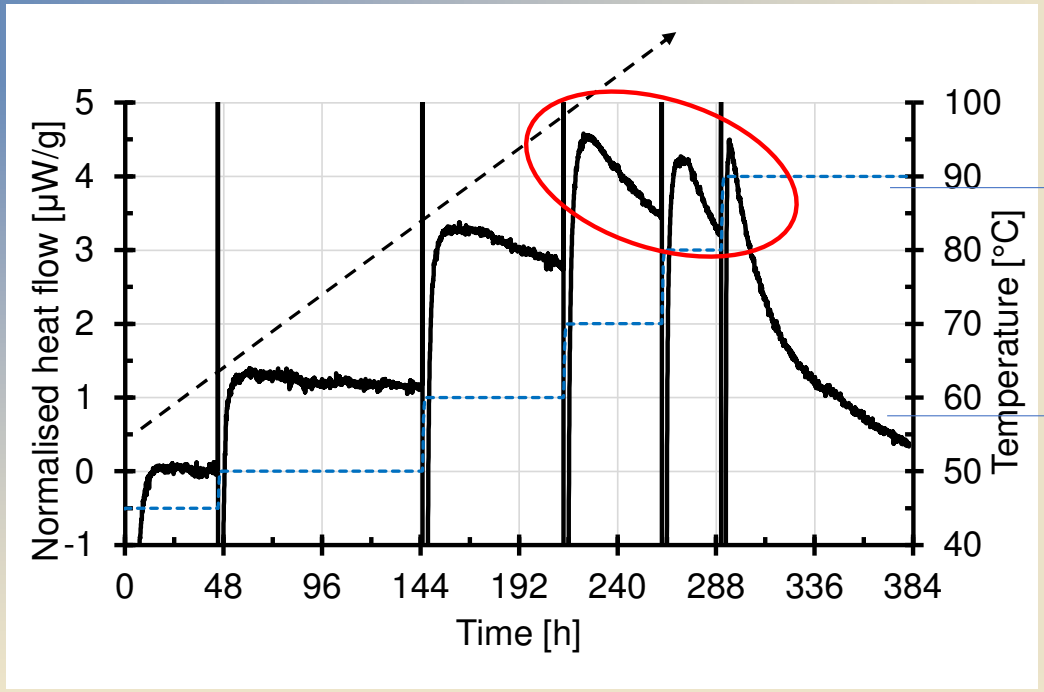
Heat flow is a lumped parameter

To understand different mechanisms post analysis may be helpful, for example using SEM-EDX, GC-MS, FTIR etc.



MC test using EPDM

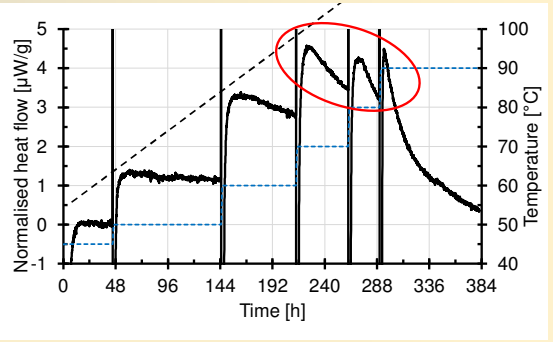




Normalised heat flow for EPDM at 45, 50, 60, 70, 80 and 90 °C using Microcalorimeter for about 2 weeks. Temperature steps are shown by a blue dotted line.

Different components of EPDM rubber

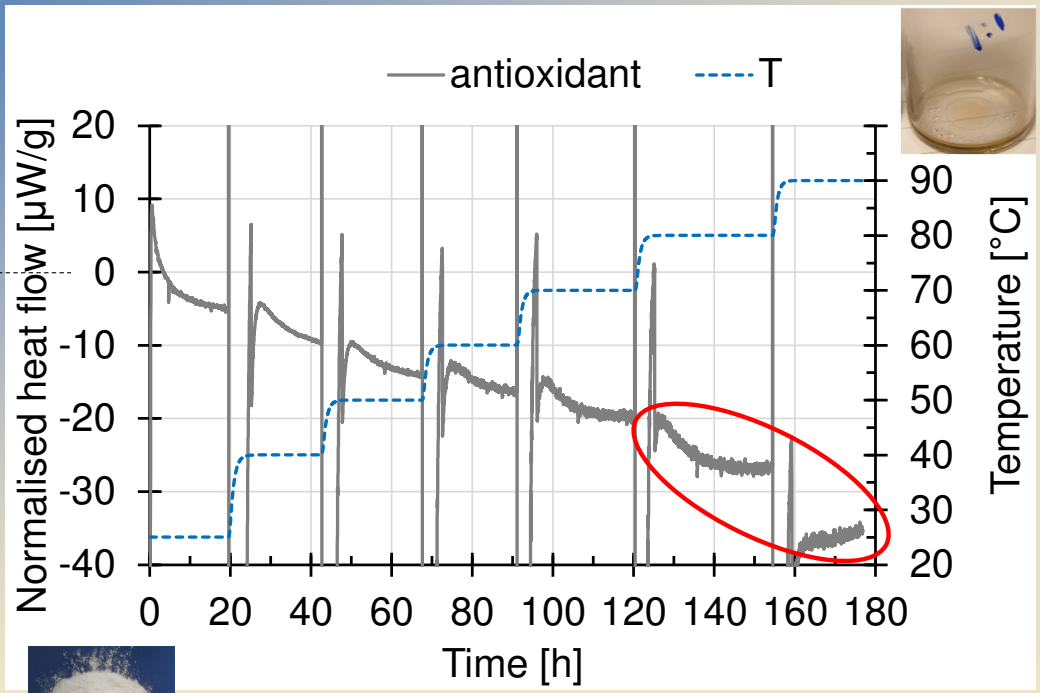
Contents	*EPDM rubber, phr*
EPDM with 55% ethylene, 40% propylene, 5% Ethylidene norbornene (ENB)	100
Zinc oxide	5
Carbon black (N550)	55
TAC-70 peroxide coagent (70% active, 30% is a silica carrier)	0.8
Luperox F40 – peroxide	3.5
Naugard 445 – antioxidant (4-4'-bis (phenylisopropyl) diphenylamine	0.8

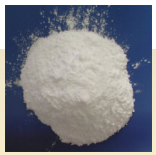


MC test using Antioxidant

Exo

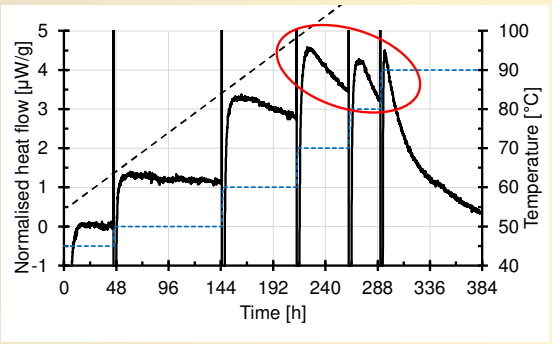
End



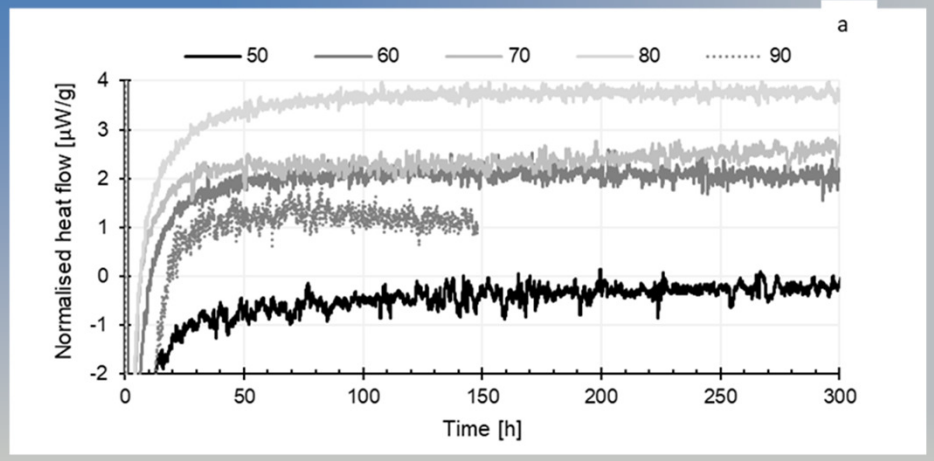


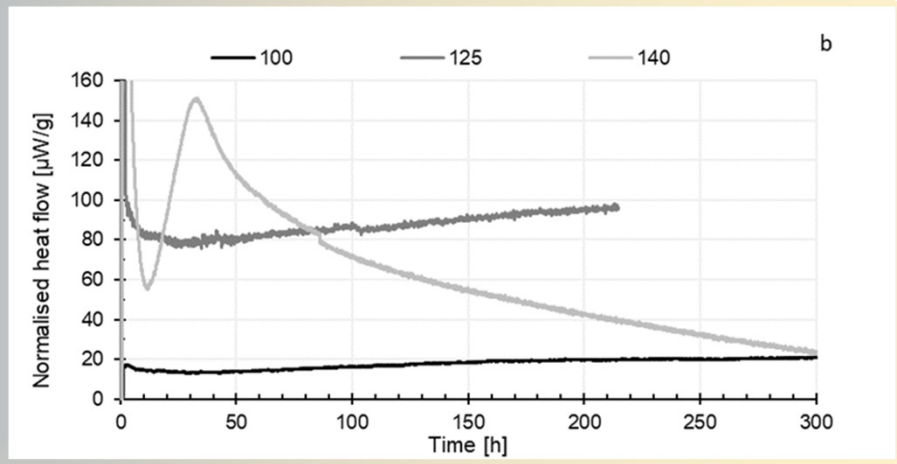
Quasi-isothermal microcalorimetry for antioxidant in an inert atmosphere (N_2)

Remarkable sensitivity

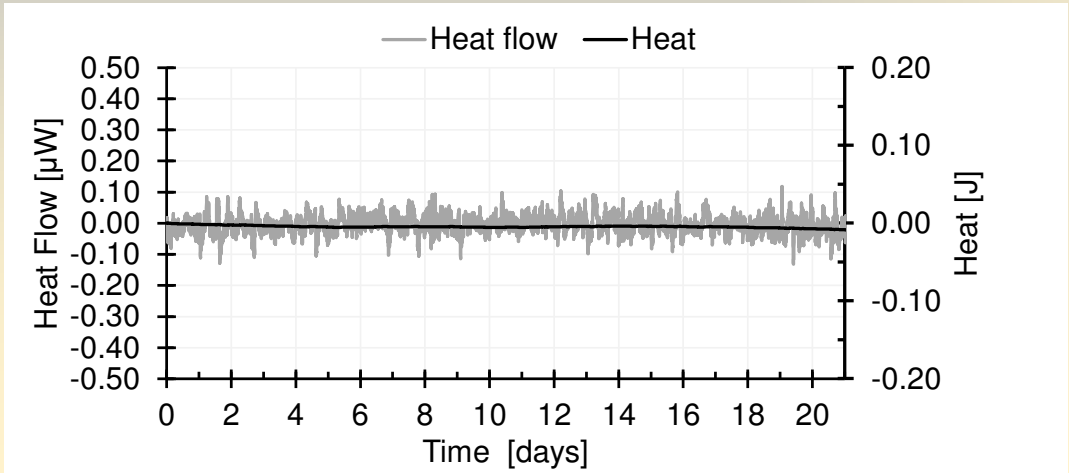


MC tests using EPDM (a) 50-90 °C and (b) 100-140 °C

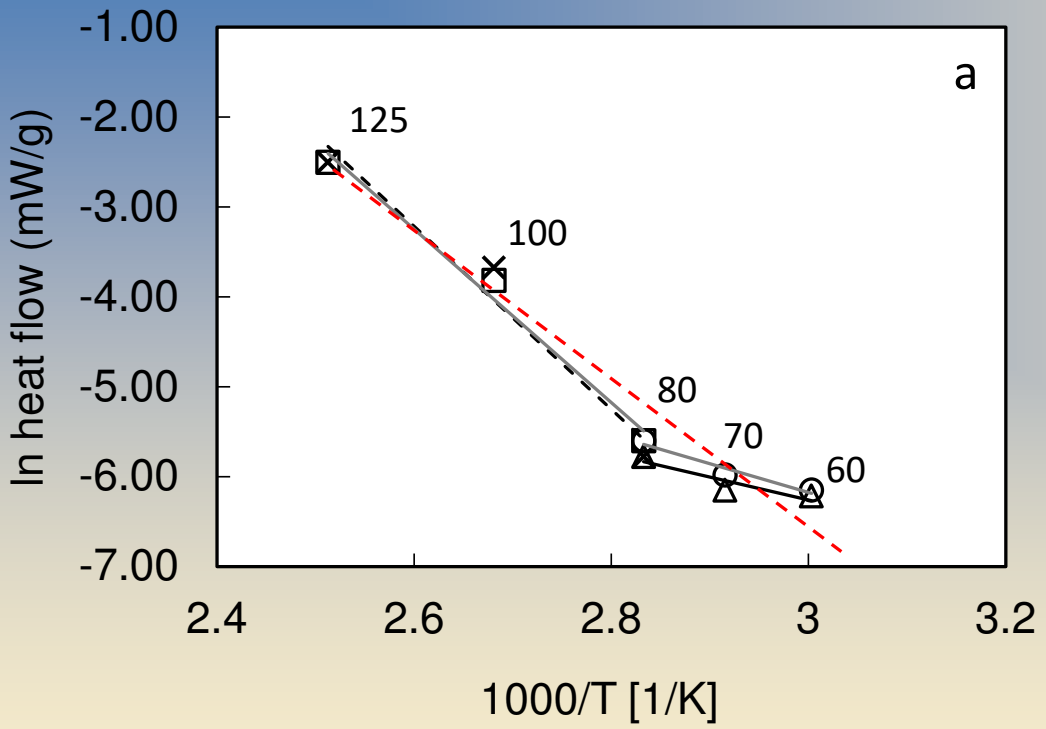




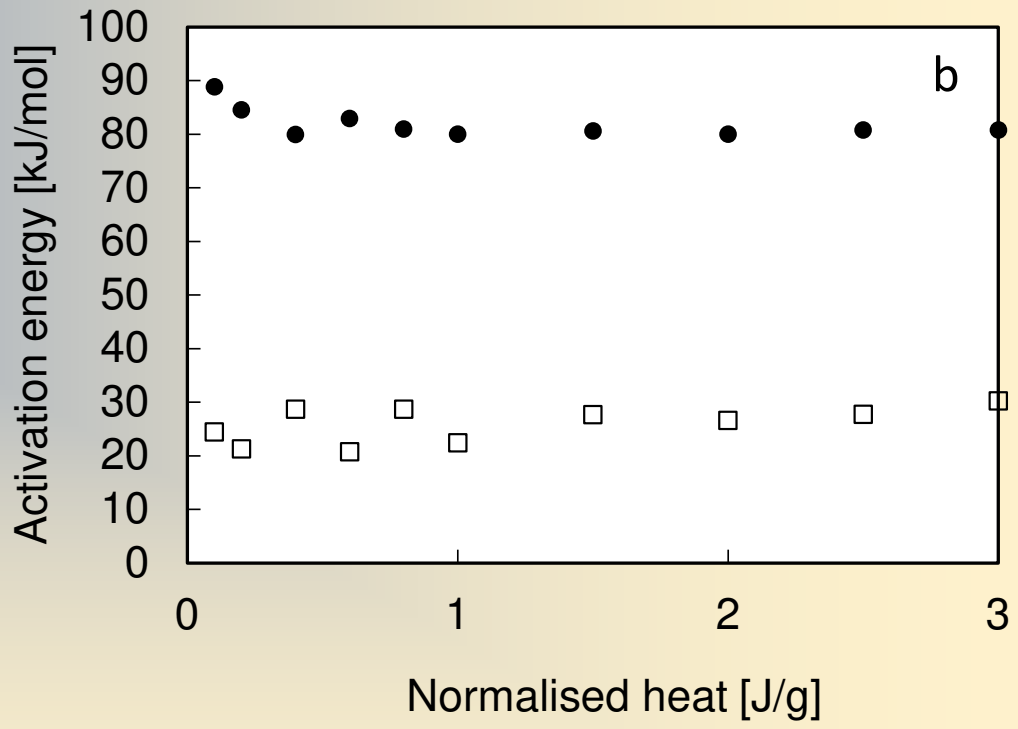
Baseline stability (drift) of calorimeter for about 3 weeks



Activation Energy



Arrhenius plot of the heat flow data, and linear fit, for two different degrees of conversion, 0.2 (black) and 2 J/g

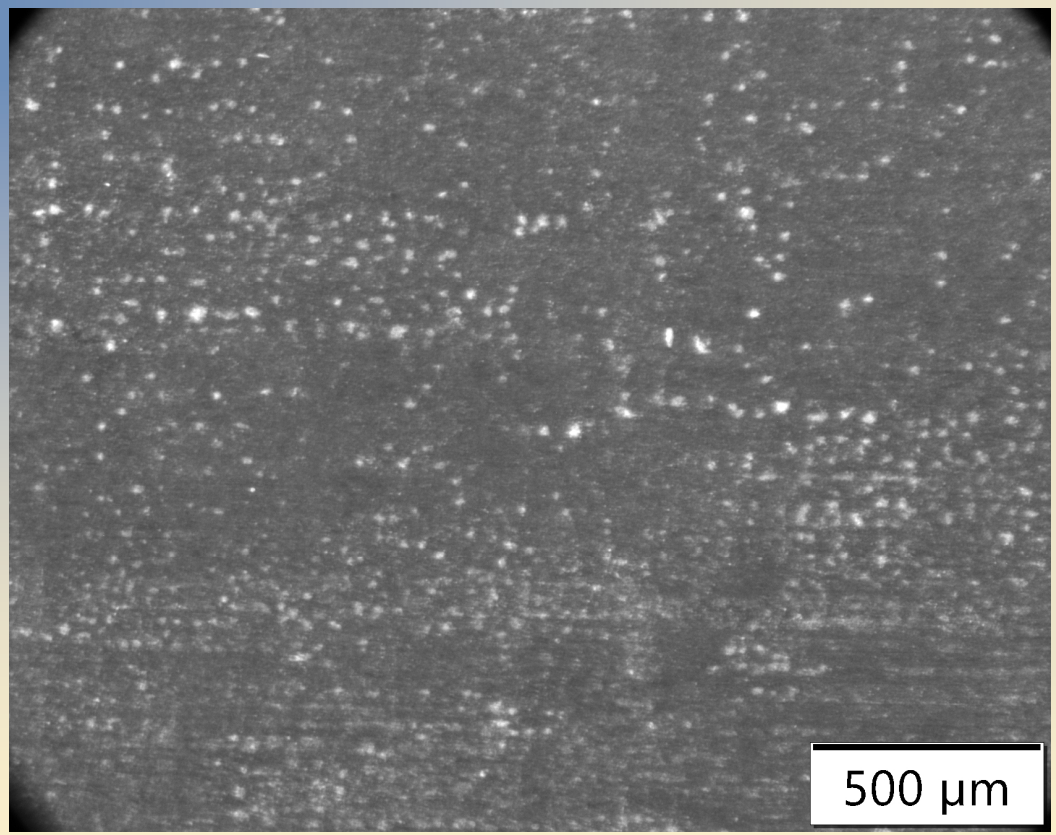


Activation energy for different degrees of conversion at 80-100-125 °C (filled circles) and at 60-70-80 °C (unfilled squares)

Light in darkness

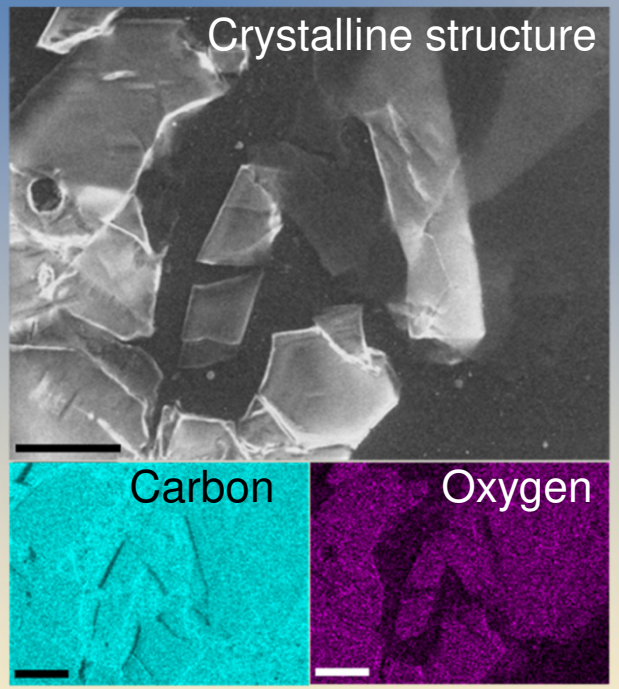
https://videohive.net/item/door-opens-and-a-bright-light-flooding-a-dark-room/31549638

Shiny flakes on EPDM surface



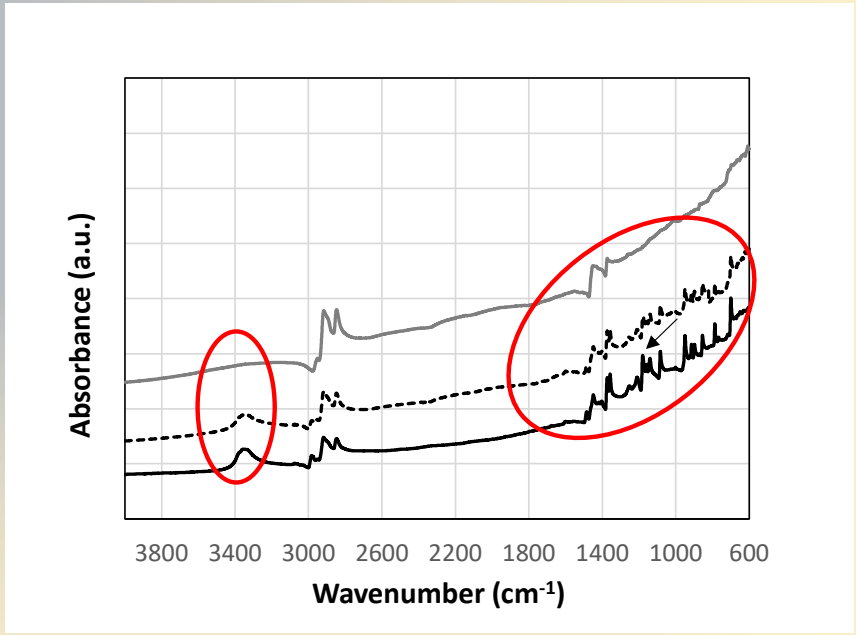
Post analysis using SEM-EDX, GC-MS and FTIR

By products from peroxide system



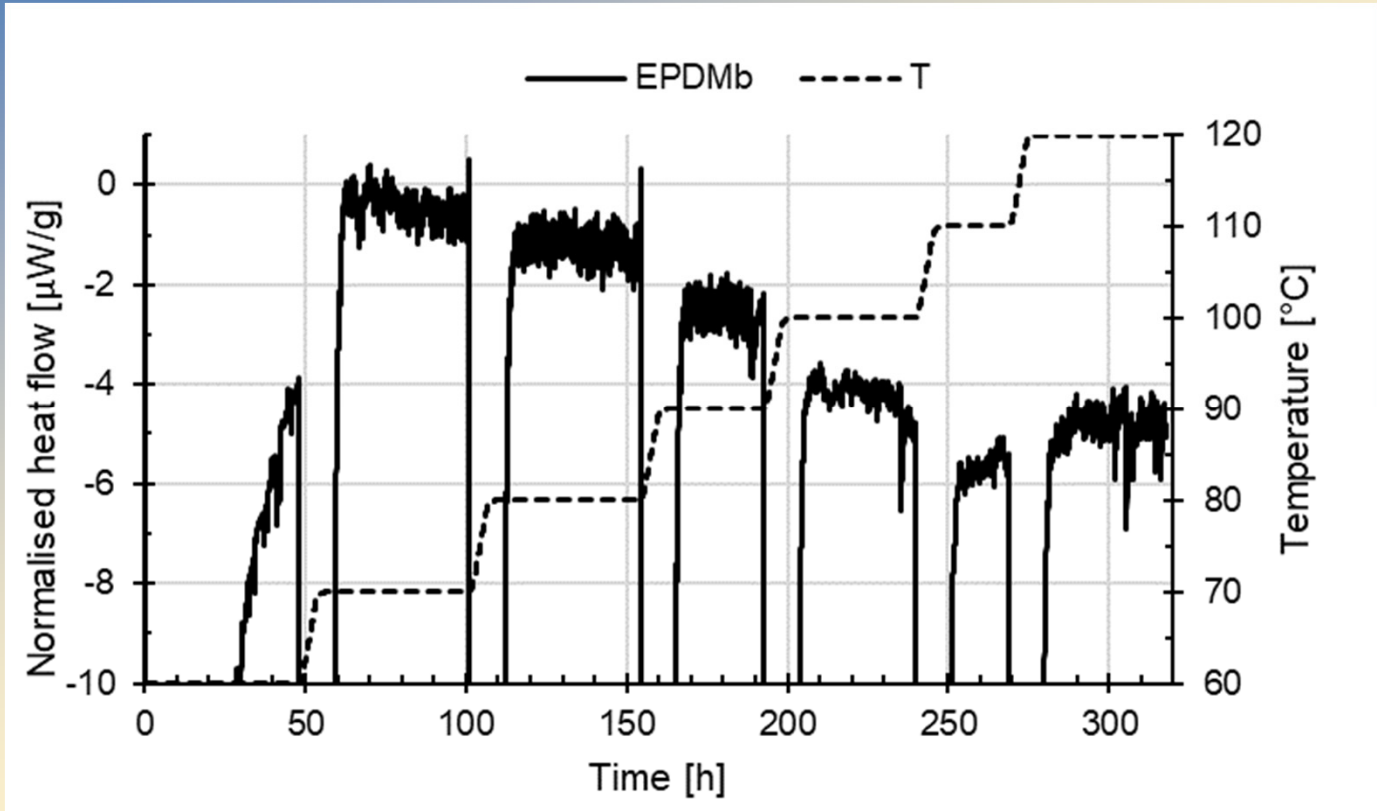
SEM-EDX images on the surface of an EPDM sample after the quasi-isothermal test.

Absence of peroxide system and antioxidant at higher temperature



FTIR spectra of unaged EPDM in black and EPDM after MC test at 70, 140 °C (1 week) and quasi-isothermal ended at 90 °C. The arrow is indicating the peaks for antioxidant.

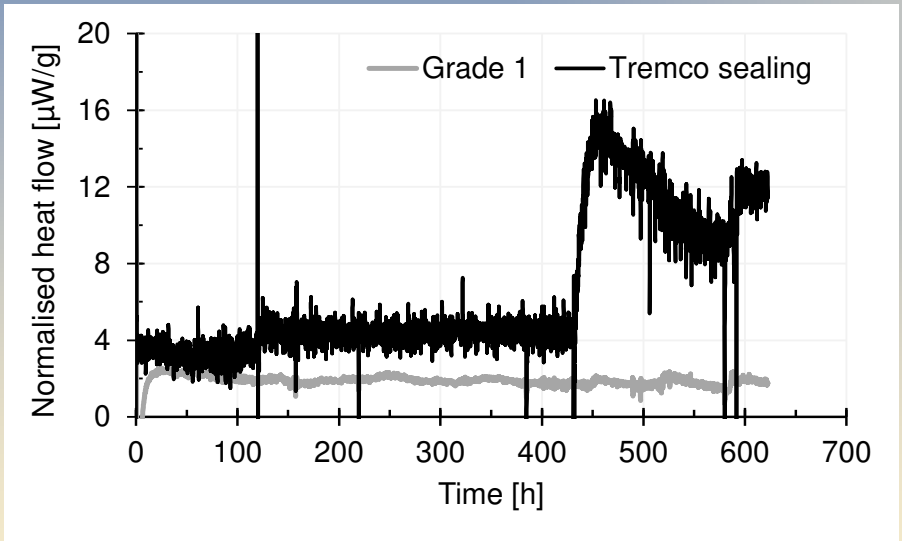
Heat flow of the base polymer during the step-wise MC test between 70 and 120 °C



Conclusions

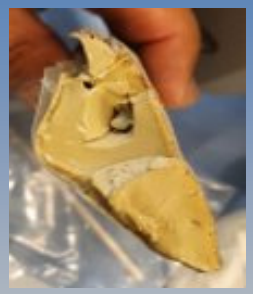
- **Ageing of polymer materials can be performed (using MC) closer the service life in nuclear power plants and in significantly shorter duration than Accelerated Thermal Ageing.**
- **Post analysis of the polymeric materials using different techniques for example SEM-EDX, FTIR, GC-MS, GC-TCD may be used to understand the thermal degradation/mechanisms.**

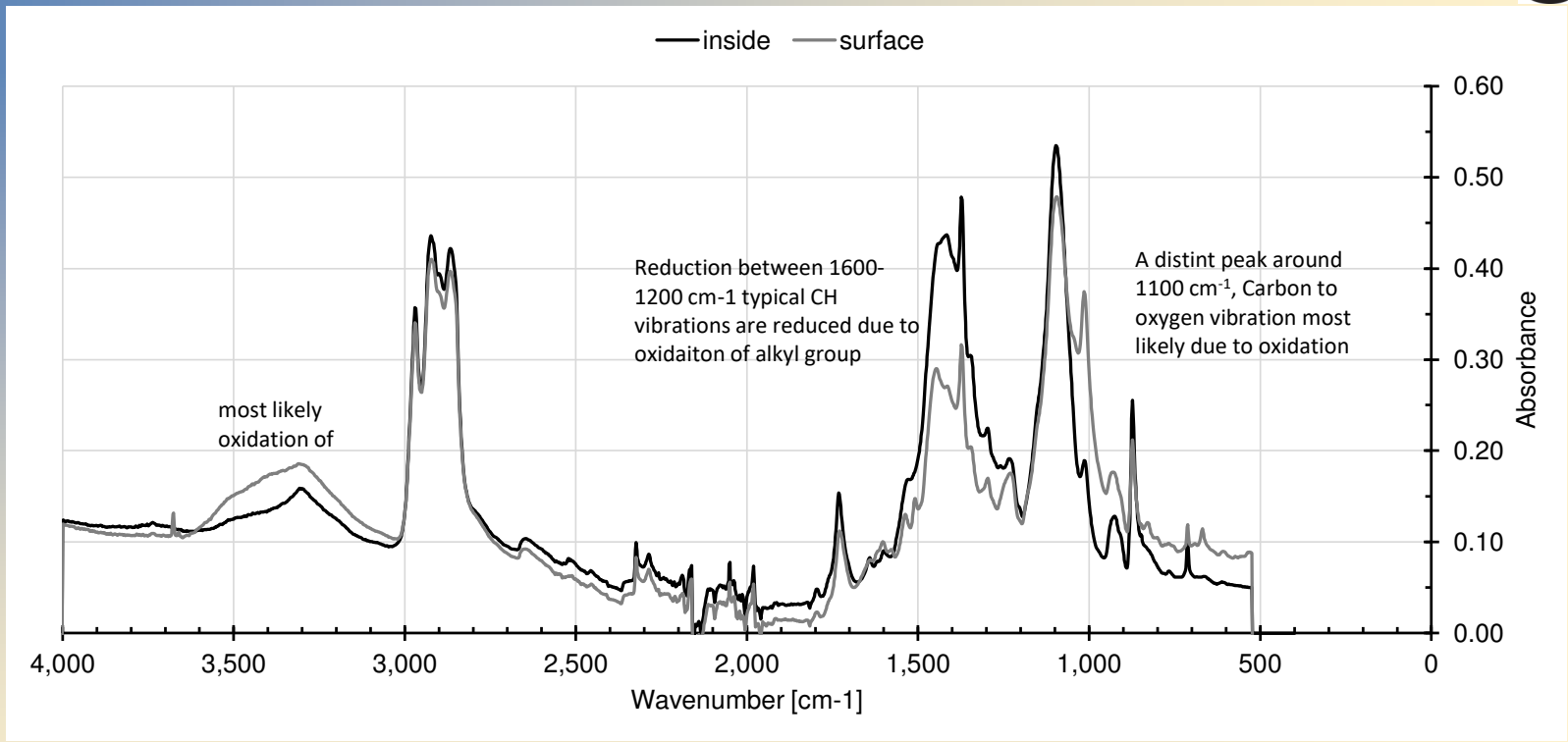
MC test on polymeric materials obtained from NPP



An isothermal MC test at 90 °C using grade 1 (EPDM) and Tremco sealing.

FTIR analysis of tremco sealing from inside and on surface





Messages

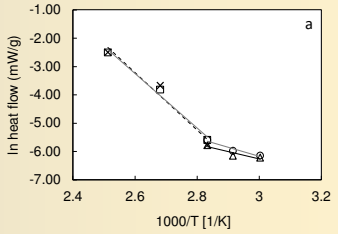
- DLO.
- Ageing tests for tremco sealing should be carefully designed.

Activation energies for different grades using MC and ATA

Material	Activation energy KJ/mol	Temperature range	remarks
Grade 1, MC	81	80, 100 and 125 °C	
Grade 1, ATA	100	90, 120 and 140 °C	Using stress relaxation
Grade 2, MC	115±5	120 and 140 °C	
Grade 2, ATA	≈100 and ≈138	90, 120 and 140 °C	Using compression set and stress relaxation
Grade 3, MC	96±1	50, 60 and 70 °C	Temperature range is not same. Activation energy was obtained using stress relaxation
Grade 3, ATA stress relaxation	98	80, 90 and 100 °C	

MC for NPP, some thoughts

- For the used materials in NPP, activation energies (Ea) over a wide range of temperatures can be obtained and compared with ATA



- MC provides a rate of degradation of the material; this can possibly be used to measure the stability of the material.

Acknowledgement

- Finnish Ministry of Economic Affairs and Employment (Finnish Research Program on Nuclear Power Plant Safety (2019–2022))
- Energiforsk
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Future work

Lot more can be done using Microcalorimetry

I appreciate your patience