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WP2 SAMPO Task 2.2
- Sensitive analysing techniques

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RISE project number P114242.AP02DP02.A01

Background

In work package 2 (WP2) of the SAMPO project, one of the objectives is to provide inputs for the ageing of polymeric components used in Nuclear power plants (NPPs). One of the suitable ways is to provide the techniques that can be used to measure thermal degradation in polymeric components non-destructively. One key issue in developing the non-destructive monitoring techniques is to verify how the results obtained using non-destructive testing relate to the polymer condition and its ageing in real life conditions. Task 2.2 under WP2 is focussed on the development of a technique, i.e. isothermal microcalorimetry (IMC), which can measure the thermal degradation non-destructively and closer to the temperature experienced by the material in NPPs.

Methods

Isothermal microcalorimetry

A multichannel microcalorimeter (MC), which is commercially available and known as "Thermal activity monitor" (TAM III), designed by TA instruments, Stockholm, was used. Isothermal microcalorimetry (IMC) is a versatile technique for studying thermal activity. It is one of the most sensitive techniques in comparison to e.g. differential scanning calorimeters (DSC). Both types of instruments can measure a signal in the order of µW, however, the sample mass in IMC can be in grams (1-10 g) whereas, DSC uses milli gram sample mass. Therefore, the specific sensitivity in µW/g for IMC can roughly be at least 1000 times higher than for DSC [1]. This also means that endothermic or exothermic processes due to chemical and/or biological and/or physical changes using TAM III, can be studied at 100 K lower than the DSC. For example, instead of accelerated thermal ageing at 150 °C, thermal degradation using TAM can be studied at 50 °C, which is much closer to the real-life operating temperatures. The heat flow values presented in the report are represented as specific or normalized heat flow values.

IMC measurements were performed as per the standard test procedure recommended by the manufacturer. Steel ampoules along with the samples were held in the calorimeter for 15 min so that both the steel ampoule and sample will be in thermal equilibrium with the calorimeter. After 15 min of preheating, the ampoules were placed into the calorimeter and the measurement was started. Even though the steel ampoules along with the samples were thermally equilibrated as aforesaid, the slight difference between the temperature of the ampoules and calorimeters can produce results with higher uncertainty. Therefore, 45 min of the heat flow values obtained using IMC, from the start of the experiments were not considered.

[1] L. Wadsö, Measuring chemical heat production rates of biofuels by isothermal calorimetry for hazardous evaluation modelling, Fire and Materials, 31 (2007) 241-255.

Work tasks for 2.2 sensitive analysis techniques for 2022 are listed below,

1. To conduct the microcalorimeter trials at different temperatures using a material after being used in the nuclear power plant (NPP). And to compare the results with the model material.
2. To find out how microcalorimeter data can be used for life-time prediction.

Additional work done to support the ageing in polymeric materials in NPP using microcalorimetry (MC).

3. FTIR analysis of the EPDM (Grade 1 or model material) with a known recipe (supplied by James Walker & Co Ltd).
4. Gas chromatograph coupled to a mass spectroscope (GC-MS) of the EPDM (grade 1 or model material as stated in point 3) and EPDM without antioxidant after MC tests.

Status of the manuscript

5. The manuscript title '**Ageing tests closer to real service conditions using hyper-sensitive microcalorimetry, a case study on EPDM rubber'** is under revision after getting comments from the reviewers. The manuscript was submitted to the peer reviewed journal, Polymer testing. Last date for sending a revised manuscript is 10 December 2022.

Status of doctoral degree

6. I, Mohit Pushp have defended and successfully obtained a PhD degree on 21st October 2022. A certificate is attached herewith.

Materials and Microcalorimeter tests

An experiment was conducted using a sample known as Tremco sealing, which was silicon-based material. The joint was Tremco Proseal or Tremco Dymeric. The Tremco sealing was used in the OKG NPP for about 30 years. It was not possible to get a fresh sealing material so that comparative study can be conducted between same materials.

For comparison the Tremco sealing and grade 1 or model material was also tested in MC. MC was operated at 90 °C. A reason for the selection of temperature was to compare the behavior of both materials and to observe what can be learned for the MC test. A quasi-isothermal test using only tremco sealing was also conducted 60-100 °C.

Information about Tremco sealing obtained for NPP. Figure 1 and Figure 2, show the location of Tremco sealing.

Secondary intermediate floor sealing

Description of the original structural design given below.

The secondary seal consists of a soft joint with a retainer strip. The soft joint is covered with 1 mm thick stainless steel sheet as protection, see figures 3 and 4.

According to drawing 3A-26-020, the soft joint originally consists of sealing compound of the type Tremco Proseal and Tremco Dymeric.

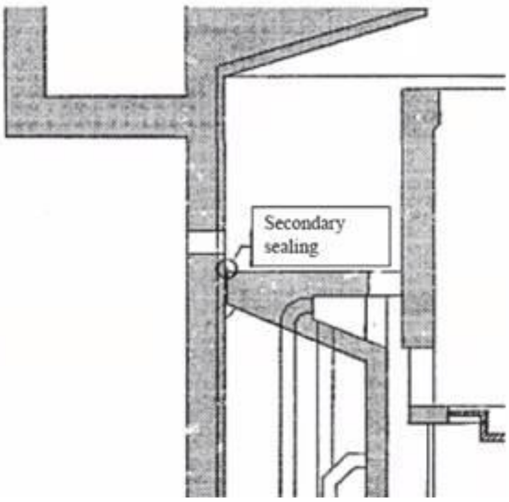

Figure 1. Tremco sealing location used in NPP

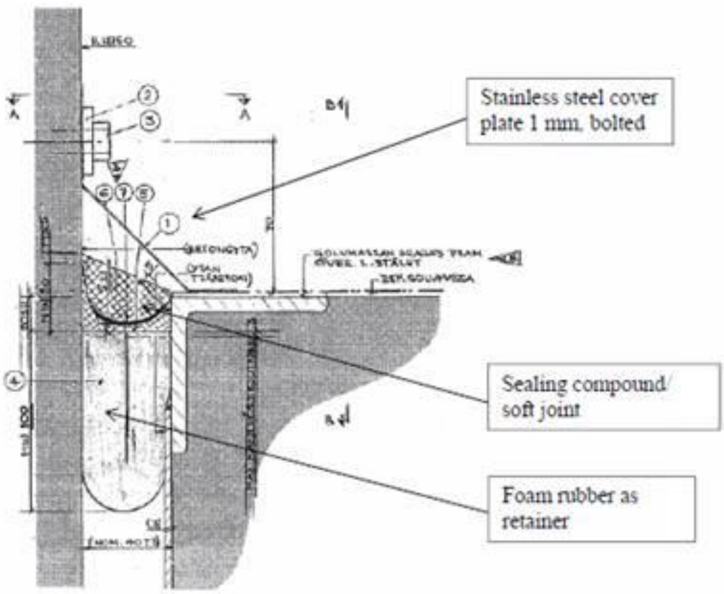

Figure 2. Tremco sealing location used in NPP

Results

A MC test result for model or grade 1 material and Tremco sealing is shown in the Figure 3. The normalized heat flow (thermal power) was measured for about 25 days. The normalised heat flow for grade 1 material as expected has shown a constant value around 2 µW/g and the measured heat flow is in good agreement with the MC test conducted using same material in 2021 (normalised heat flow was 1 µW/g). This shows that result for grade 1 is reproducible and difference of 1 µW/g (is expected) is most likely within uncertainty by MC and may be the inhomogeneity in the sample. The normalised heat flow for tremco sealing was almost double, that is around 4 µW/g for about 430 hours and then a step increase in the heat flow can be observed. The normalised heat flow after 430 hours remained significantly higher. In principle positive values of heat flow as measured for both the materials is an indication of exothermic processes and most likely be the oxidation. The tremco sealing was oxidising at significantly higher rate that grade 1 material. The reasons for what was oxidising in the tremco sealing cannot be explained because recipe of not known however, oxidation is most likely the reason for exotherms (normalised heat flow) using tremco sealing. A step-rise in the normalised heat flow after about 430 hour is an interesting phenomenon and need further investigation.

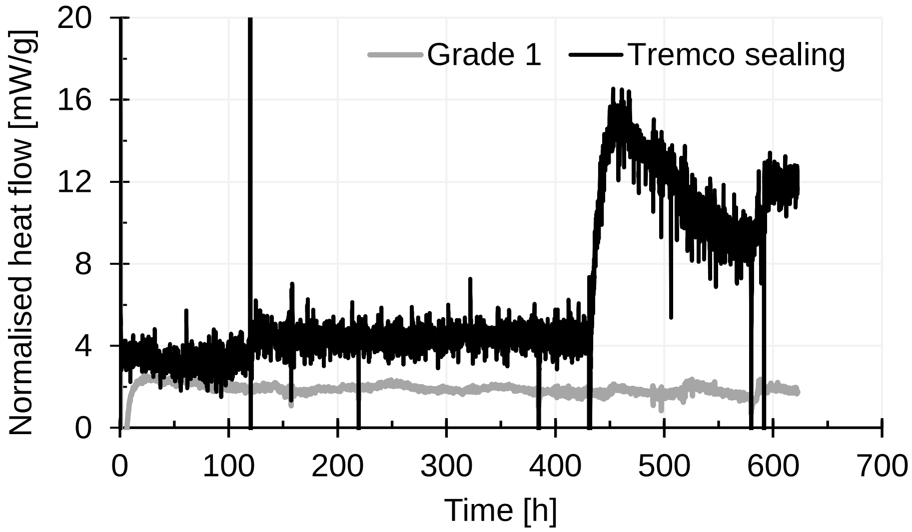

Figure 3. An Isothermal MC test at 90 °C using grade 1 and Tremco sealing.

Physical investigation of the material after MC test at 90 °C shows that the sample was deformed and significantly softened at 90 °C as shown in the Figure 4.

Figure 4. Tremco sealing after MC test at 90 °C.

This indicates that for the polymeric materials like tremco sealing ageing at 90 °C was most likely harsh and should be avoided unless material may experience similar temperatures in NPP. The ageing test should be conducted closer to the real-life service conditions in NPP that is around 40-50 °C. Figure 5 shows the cross section of the tremco sealing, with respected to the oxidised surface show in Figure 6, material was appeared to be at least significantly less oxidised from the inside (cf. Figure 5).

Figure 5. A cross section of Tremco sealing

Figure 6. The oxidised surface of tremco sealing.

Quasi-isothermal test using tremco sealing

The normalised heat flow for a quasi-isothermal test is shown in Figure 7. It can be seen that slow oxidisation (positive normalised heat flow on y-axis) can be seen at 70 °C. With respect to 70 °C, normalized heat flow at 80 °C, 90 °C and 100 °C are higher as expected and indicates oxidation in tremco sealing. As presented above that tremco sealing was soften and seemed like started melted after MC test at 90 °C. The quasi-isothermal test indicates that if in real service-life material may not experience higher than 50 °C, oxidative ageing should not be performed at higher temperatures for example higher than 50 °C. Normalised heat flow at 60 °C was endothermal (normalised heat flow is about 2 µW/g) and at least oxidation was below the detection limit of the instrument in a short time duration test (a day). The quasi-isothermal test shows that if there was oxidation at 50 °C, it was significantly slower than for example 90 °C.

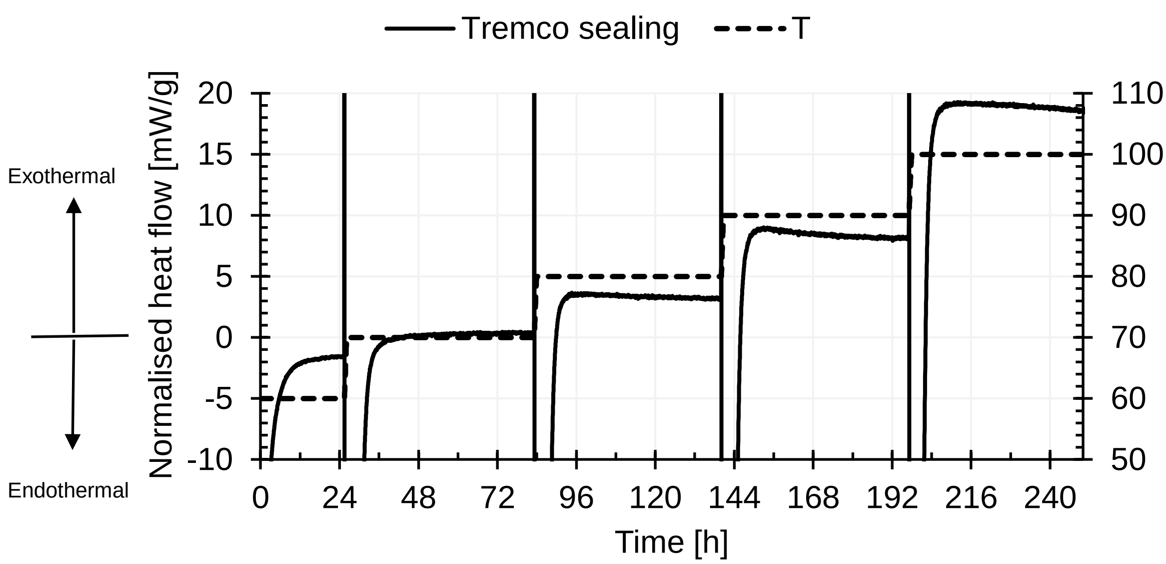

Figure 7. Normalised heat flow from a quasi-isothermal MC test at 60, 70, 80, 90 and 100 °C using tremco sealing.

FTIR analysis of the tremco sealing

FTIR analysis of the tremco sealing was conducted from inside (cf Figure 5 and Figure 6). The result for FTIR analysis is shown in Figure 8. As shown in the Figure 8 spectra between 3300-3000 cm^{-1} and a distinct peak at 1100 cm^{-1} are signs of oxidation on the surface with respect to the inside of the material. The significantly different oxidation on the surface with respect to inside is most likely be explained by diffusion limited oxidation.

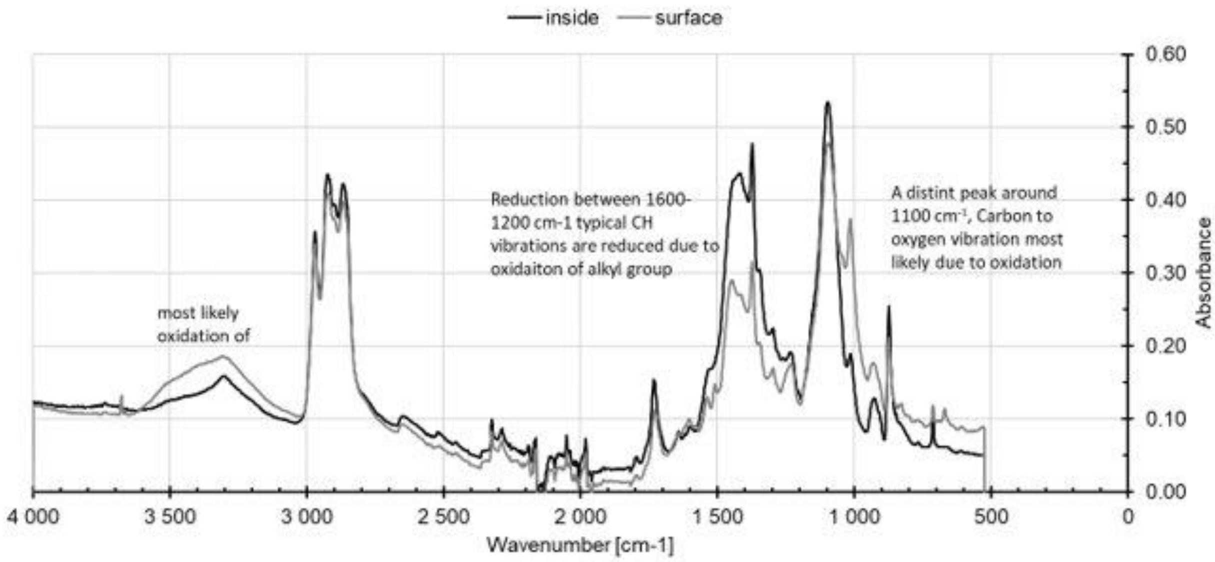

Figure 8. FTIR analysis of tremco sealing from inside and oxidised surface.

Microcalorimeter and life-time prediction

Aim was to find how MC data can be used to obtain the lifetime of the material. A brief of what has been done is listed below.

- Activation energy using MC data for grade 1, 2 and 3 materials is compared with a widely accepted accelerated thermal ageing (ATA).

Result

The activation energies for different grades using MC and ATA data are presented in Table 1.

Table 1. Activation energy for different grades using MC and ATA.

Material	Activation energy KJ/mol	Temperature range	remarks
Grade 1, MC	81	80, 100 and 140 °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	

Grade 1

Activation energy obtained using MC is listed in Table 1. Detailed information can be read in the manuscript or will be enclosed later after the acceptance of the manuscript. However, a summary of the findings are listed as below.

- Using MC it was possible to measure the thermal degradation in grade 1 material at 60 °C and above.
- Activation energies obtained at 60, 70, 80 °C (lower temperature) and 80, 100 and 140 °C (higher temperature), has shown different values. For example, activation energy at lower temperature was about 30 KJ/mol however at higher temperature it was about 81 KJ/mol. The activation energy obtained at higher temperature is not same as it was with ATA testing and ageing temperatures were not exactly same either. However, trend in the activation energy obtained using MC and ATA is same that is for grade 1 material activation energy is lower than for grade 2.
- An important finding after ageing in MC and post analysis of the EPDM material indicates that activation energy obtained closer to the service conditions that is around 60 °C is primarily due to the reactions by the peroxide system and antioxidant. No sign of oxidation of base polymers was seen at 60 °C. a mild oxidation was seen only after 120 °C.

Grade 2

Activation energy was obtained using MC at two different temperatures 120 and 140 °C. The selection of both temperatures was made, so, that data can be compared with ATA that was conducted at same temperatures (120 and 140 °C). The MC tests at 120 and 140 °C was conducted for about 1.5 weeks and the values of activation energy was obtained for same degree of conversion. It can be seen that activation energy value obtained using MC is in reasonably good agreement with compression set and stress relaxation method. For better understanding of the changes in the material deeper investigation using alternate technique may be useful. The post analysis is not conducted in this study as it was beyond the scope of the project. The Arrhenius fit for two different degree of conversion is shown in the Figure 9.

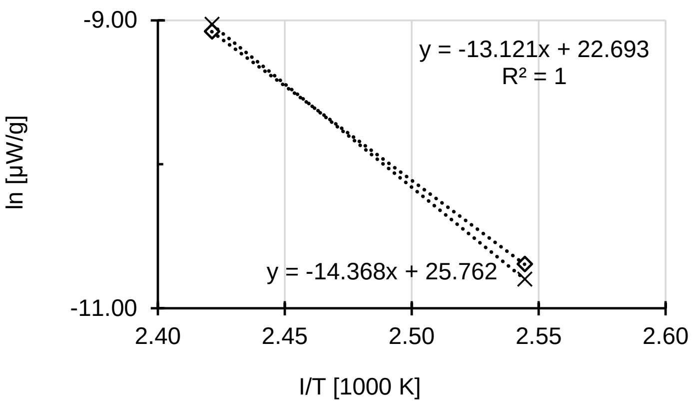

Figure 9. Activation energy for two different degree of conversion, 3 and 3.4 J/g at two different temperatures 120 and 140 °C.

Grade 3

Two different grade 3 materials were tested using MC. Arrhenius plot for both is shown in the Figure 10 and Figure 11. A straight line fit for both materials are reasonably in good agreement as all three points lying on straight line. The activation energy presented in Table 1 for MC, for example is obtained by multiplying slope from the Arrhenius fit that is 11.63 with the gas constant 8.314 J/K.mol, which has provided activation energy equals to 97-95 KJ/mol.

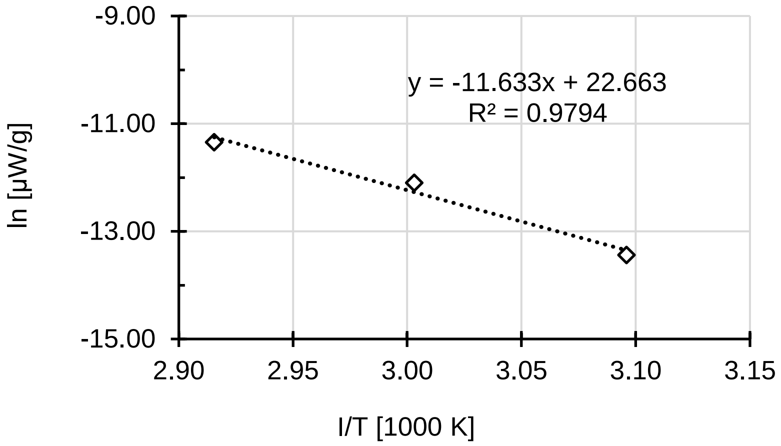

Figure 10. Arrhenius plot for commercial or grade 3 material.

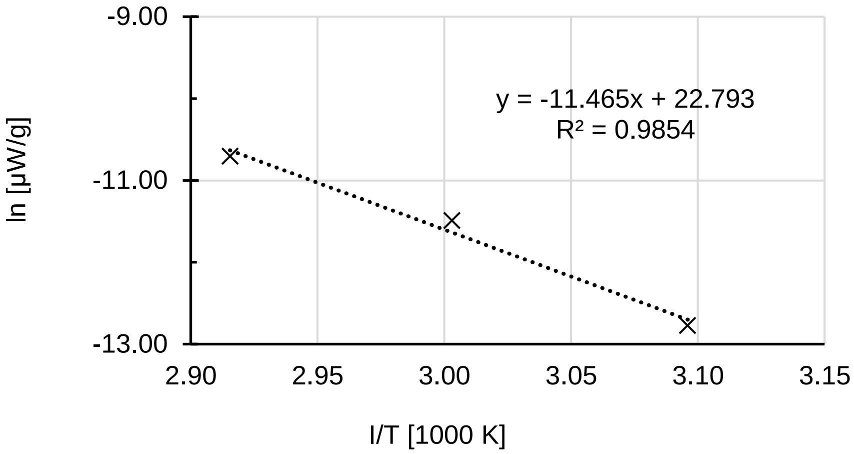

Figure 11. Arrhenius plot for commercial or grade 3 material with reinforcement.

NOTE: The activation energies obtained using MC and ATA techniques are matching within experimental error despite temperature range are different. Weather both techniques and difference in temperature range have same basis of comparison needs deeper investigation. For example, it is must to identify the chemical changes in the material and to related it with activation energies obtained at different temperature ranges or using different techniques.

Status of the manuscript.

A manuscript with the title, '**Ageing tests closer to real service conditions using hyper-sensitive microcalorimetry, a case study on EPDM rubber'** was submitted to the peer reviewed journal Polymer testing. The comments from 3 reviewers have been received and revised manuscript will be submitted before 10 December 2022. Before submission of the manuscript post analysis of the EPDM material after aged in MC and ATA techniques was carried out using FTIR and GC-MS etc. **NOTE**: data or the work carried out is not presented in this report to avoid plagiarism. We hope that the revised manuscript may be accepted but it's not sure and if it will be rejected, we may have to submit for another journal. This may take significant time therefore, extensive work done on EPDM in this year will only be available after acceptance of the manuscript. A screen shot of the manuscript is shown in **Error! Reference source not found.**.

A brief summary or abstract for the manuscript is as below.

The high sensitivity of MC (μW/10000 mg) means that chemical changes can be measured at least 100 K lower than DSC (μW/~30 mg). The increased sensitivity opens up the possibility of measuring the ageing/degradation of polymers at closer to real-life temperatures and conditions. This is advantageous, since the normally used accelerated testing at significantly higher temperatures leads to degradation conditions that do not resemble service conditions. It is shown here, with the MC technique on a highly filled ethylene propylene diene monomer (EPDM) material, that the ageing processes, as well as the activation energy of the ageing processes, at close to real-life temperature are different from those at high temperature. With the high sensitivity of the MC, local thermal processes on a small scale could be readily observed, such as the melting of the antioxidant and further reactions in the peroxide cross-linking system. Hence, the results indicate that MC is a promising technique for measuring chemical changes and reaction parameters closer to the real-life temperatures in complex systems like highly filled EPDM rubber. To relate heat flow data to chemical mechanisms, post analysis of polymeric materials should be carried out with alternate techniques, for example, infrared spectroscopy (FTIR), gas chromatography and scanning electron microscopy coupled to energy dispersive X-ray.

Conclusions

Based on the MC tests and comparison with the ATA technique some conclusions can be drawn.

- MC can be used as a promising technique for the ageing tests closer to the service life of the polymeric material in NPP.
- Ageing tests can be conducted in real time and in significantly shorter duration for example 1 month activation energy can be obtained,
- Post analysis of the polymeric material at least using standard techniques for example SEM-EDX and FTIR may provide valuable information about the ageing mechanisms.

Acknowledgement

The funding of this work by the Finnish Ministry of Economic Affairs and Employment within the frames of the SAFIR 2022 Finnish Research Program on Nuclear Power Plant Safety (2019–2022) is gratefully acknowledged.