

POLYMER COMPONENTS EXPOSED TO THERMAL-RADIATIVE ENVIRONMENTS 2020

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Polymer Components Exposed to Thermal- Radiative Environments 2020

Safety criteria and improved ageing management
research

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Foreword

SAMPO project focuses on safe long-term use of polymer components and improving their ageing management. This is done by studying ageing mechanisms in thermal-radiative environments, determining how to set acceptance criterion properly and providing robust tools for condition monitoring. These topics become more relevant as the original planned lifetime of the plants is approaching and extension is considered. Safety criteria assessment and ageing management needs to be at sufficient level in order to prevent premature component breakdown and avoiding endangering the overall safety.

The Nordic nuclear industry has cooperated on polymer research through the Finnish nuclear safety R&D program SAFIR for several years. The current project is called SAMPO, Safety criteria and improved ageing management research for polymer components exposed to thermal-radiative environments. This report summarizes results from the second year out of four in the project. Detailed results are found in task deliveries from the project, available on the Energiforsk web under the Polymers in nuclear applications program page.

Project leaders are senior researchers Konsta Sipilä from VTT and Anna Jansson/Jason Ryan from RISE. The activities are financed by the SAFIR program, The Swedish Radiation Safety Authority and Vattenfall, Uniper/Sydkraft Nuclear, TVO, Fortum, Skellefteå Kraft and Karlstads Energi through the Polymers in nuclear applications program.

These are the results and conclusions of a project, which is part of a research programme run by Energiforsk. The author/authors are responsible for the content.

Summary

SAMPO is a joint project in collaboration with VTT in Finland and RISE and is run in close collaboration with the Nuclear industry. Polymer researchers work together with experts in sensor technology and sensitive analyse techniques to learn more about degradation of plastics and rubber materials used for long periods of time in Nuclear Power plants. The objective is to set relevant acceptance criteria for end of life of components, and improved material management by use of online monitoring of materials.

Sealings and o-rings are interesting components to study, to be able to increase the interval of exchange. To be able to do this, relevant acceptance criteria is essential. In the case of O-rings, it is relevant to study their deformation, that is "set", when mounted in valves etc. and compare to the degree of deformation to leakage. Material properties are compared to leak tests in specially designed test rigs. During 2020 O-rings with somewhat lower quality have been studied to verify the test method. The initial tests were performed on a high-end material quality and therefore the O-rings did not degrade. Also, the test rigs were modified to better imitate the real application. Investigated material and equipment behave like expected.

Workshops with the NPPs were arranged to discuss suitable products, to extract from the plants for analyses to learn more about residual lifetime, ageing and end of life criteria. A workshop was a good forum to discuss and select materials rather than separate interviews. Membranes were analysed by mechanical tests, tensile testing, hardness etc. Spread in results were observed for some of the materials. Membranes was a suitable product to study since they are large enough for sample preparation and has a safety function in the NPP.

Permittivity is a property possible to measure on polymers online, without sample outtake or destroying the product. It is therefore an attractive method to monitor material degradation and residual service life online. Initial experiments show that the technique works for the tested rubber material and suitable equipment will be achieved for further testing.

To study accelerated ageing and degradation of polymers at lower exposure temperatures is of great interest. It could in the future give better lifetime predictions than accelerated ageing at the high temperatures used today. Micro-calorimetry is a sensitive analysing method which was tested during 2020 with promising results. Changes of reaction mechanisms were detected as well as differences in reactivity in new and previously aged materials.

Keywords

Acceptance criteria, NPP, rubber, sealings, o-rings, polymer ageing, permittivity, antenna technology, micro-calorimetry

Acceptanskriterier, Kärnkraftverk, gummi, o-ringar, polymer åldring, permittivitet, antennteknologi, mikrokolorimetri

Sammanfattning

SAMPO är ett samarbetsprojekt mellan VTT i Finland och RISE och det utförs i nära samarbete med kärnkraftindustrin. I projektet samarbetar polymerforskare med experter inom sensorteknologi och känslig analysteknik för att lära sig mer om vad som händer med plast- och gummimaterial som används i kärnkraftverk under lång tid. Målet är att sätta relevanta acceptanskriterier för end livslängd och i framtiden även kunna övervaka status hos material online.

Tätningar och O-ringar är intressanta att studera för att kunna utöka utbytesintervallen. Detta kan göras om det finns bättre och relevanta acceptanskriterier, dvs vilka materialegenskaper materialet ska ha för att fungera. I fallet O-ringar tittar vi på hur mycket de kan deformeras och "sätta sig" innan de inte längre har någon tätande förmåga. Man jämför materialegenskaper med läckagetester i en specialdesignad rigg. Under 2020 har gummitätningar av lite "sämre" kvalitet testats för att kunna se om testmetodiken fungerar då de första materialen var av väldigt hög kvalitet och inget hände med dem. Även de specialtillverkade testriggarna har modifierats för att bättre efterlikna verkligheten. Det undersökta materialet uppför sig som förväntat och metodiken verkar fungera.

Vi har ordnat workshops tillsammans med deltagande kärnkraftverk för att diskutera vilka produkter de anser viktiga att lära sig mer om, det kan vara sådana som har en viktig säkerhetsfunktion. Utvalda produkter från drift undersöktes för att lära oss mer om kvarvarande livslängd och hur de har åldrats under driftsförhållanden. Workshop var ett bra forum för att välja material. Membran har analyserats med mekaniska tester, t ex dragprovning och resultaten är ganska spridda för vissa av dem. Det är en bra produkt att analysera då många membran är stora och provkroppar kan tas ut från dem.

Permittivitet är en egenskap som skulle kunna mätas på polymera produkter online utan att ta ut prov eller förstöra produkten, och på så sätt hålla koll på materialets egenskaper och kvarvarande livslängd. Initiala försök visar att tekniken är möjlig att använda och lämplig utrustning ska anskaffas för fortsatta tester.

Att kunna studera åldring av plast vid lägre temperaturer än de som används idag är intressant för att mer korrekt kunna bedöma livslängd. Mikrokalorimetri är en känslig analysmetod som vi testat med goda resultat och som visar vilka temperaturer som ger förändrade nedbrytningsmekanismer. Försöken har också visat att nedbrytningsreaktioner som ger utslag i utrustningen inte syns på redan nedbrutna plastmaterial.

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1 Background to the SAMPO project

The interest in polymer ageing issues has increased nationally and internationally as the original planned lifetime of NPPs is about to be reached and extended lifetime is desired.

Since polymers are used in numerous different applications within NPPs and each polymer type can have different compositions depending on its use, a vast amount of unique polymer blends which contribute to the overall safety of the plants needs to be managed. Thus, it becomes essential to identify the most important topics among so many components and phenomena that contribute to the overall safety of the plants. In order to do this identification, a collaborative group between experts from Finnish and Swedish plant operators, regulators and researchers has been established during the last SAFIR-program period. The group is interacting with each other to identify the most relevant topics in NPP polymer component research and as an outcome, the most relevant topics relate to sufficient acceptance criteria and safety margin assessments and reliable ageing management procedures. SAMPO is funded by the SAFIR-program and some of the research performed at RISE is funded by Energiforsk and SSM.

1.1 POLYMERS AND AGEING IN NUCLEAR POWER PLANTS (NPP)

Polymers degrade (polymer ageing) as they are used over long periods of time, losing their mechanical strength and performance. The most important stressors recognized for the ageing are temperature and ionizing radiation, but also the effect of moisture is recognized. In addition, the presence of oxygen has significant effect on the ageing process and the difference in ageing has been recognized between oxygen containing and inert atmospheres [Spång 1997].

The polymer condition is usually thought to be correlated to its mechanical properties, that is a commonly used acceptance criteria for polymers is considered to be 50% absolute elongation at break. However, in practice functionality is required from the polymer components and the acceptance criterion should be assessed based on the functionality of the component. This would require an understanding of the ageing environment, prevailing ageing mechanism itself and the functional property of the component. Thus, setting up an acceptance criterion and safety margin assessment can be complicated.

1.2 ACCEPTANCE CRITERIA

Within this project acceptance criterion and safety margins are assessed in four different cases. Firstly, we aim to provide safety margins or evaluations on remaining lifetimes of critical polymer components that are identified as being difficult or almost impossible to replace. This is possible by collaborating with the Swedish plants that are planned to be decommissioned. Secondly, safety margin assessment is conducted with the O-ring condition monitoring technique developed in COMRADE project. Thirdly, ageing between air and nitrogen atmosphere is compared and evaluation is conducted to determine whether

“storage ageing” of components is significantly affecting the safety margin assessment. Fourthly, physico-chemical analyses of previously aged materials are conducted (mechanical analyses were completed during COMRADE, which preceded SAMPO) and work started in COMRADE will continue explaining how the structural changes in sample materials induced by separate thermal and irradiation ageing differ from the changes induced by simultaneous thermal and irradiation ageing.

1.3 AGEING MANAGEMENT OF POLYMERS

An essential part of ageing management is to have the means and techniques to monitor the condition of components. Acceptable condition monitoring techniques have a well-established acceptance criterion which defines whether the component can be still used in its designed application. The acceptance criterion set should be sensitive to ageing and correlate with the component condition. Condition monitoring techniques have been studied mostly for cables used in NPPs and several summarizing reports describing their use can be found [EPRI 2005, Gillen et al 2005, IAEA 2012, OECD NEA 2011, Simmons et al. 2013, Yamamoto et al. 2009]. The common trend seems to be that the condition monitoring techniques used should be non-destructive or they should require only very small amount of the tested material, that is techniques based on micro-sampling. This would be highly beneficial for the ageing management programs where sample deposits are not available, or they are limited.

In this project, the aim is to further develop a non-destructive technique by determining the correlation between the measured non-destructive response and the polymer condition. Thus, it is possible to propose an acceptance criterion that is based on the functionality of the polymer and measurable non-destructively. The aim is also not just to develop condition monitoring techniques to be used on-site and during outages, but also develop sensors that can be applied online during power operation.

2 Objective

The main objective of the project over a four-year project period, is to produce data and techniques that help improve the overall safety of NPPs and improve their long-term and reliable use. This can be done via improved acceptance criteria and safety margin assessment as well as by enhancing ageing management. In order to achieve this, knowledge on polymer ageing mechanisms is required. As a result of the project, the following developments are expected:

- An example case for improved safety margin assessment for a critical polymer component
- Provision of a list containing novel techniques for polymer quality verification
- Comparative study on ageing in air and nitrogen atmospheres
- Improve ageing management via enhanced condition monitoring techniques
- More detailed analysis of synergistic effects due to thermal and irradiation ageing

3 Work plan

In SAMPO two work packages (WP) are built around the topics acceptance criteria and polymer ageing management and an additional third work package for international cooperation. No activities are done in WP3 for obvious reasons, the spread of the Corona virus. Each work package contains sub tasks, which are formed around a more specifically identified issue, related to polymer ageing, safety criteria assessment or ageing management. In the following sections, a more detailed description of each task and the main results from 2020 are reported.

3.1 WP1 ACCEPTANCE CRITERION AND SAFETY MARGIN ASSESSMENT

The objective of this work package is twofold. The first objective is to evaluate what different factors need to be taken into account when an acceptance criterion is set for a polymer component. The second objective is to improve safety margin assessment. It is important to understand how the material ages in thermal-radiative environments and also, how different additives contribute to the ageing mechanism in order to set the acceptance criterion properly. The improved safety margin assessment will be conducted for the O-rings studied in previous COMRADE project and for critical components available from the decommissioned plants. The improved safety margin assessment should result in improved residual lifetime estimations.

In task 1.2 the aim is to understand how different additives affect the ageing of a polymer and how sensitive the polymer properties are when an additive, for example pigment, antioxidant or filler is changed, or its amount is altered in a polymer blend. In addition, possible methods that can verify whether small changes in polymer blend ingredients cause significant changes to ageing behaviour are studied. A survey is conducted that will inform in more detail the role of each additive in the ageing process and what are the analysis techniques applicable to different additives. This task is performed by VTT and is not reported here.

Task 1.3 is based on the work performed during 2016-2018 (COMRADE project) in which O-ring ageing data was produced and their acceptance criteria was determined. The material property "compression set" was compared to leakage in specially designed test rigs where the O-rings sealing performance was tested. Compression set is a measure of deformation of sealings and O-rings caused by the deformation when they are mounted in a pipe connection, valve etc. Traditionally 50 % compression (of initial thickness) is set as acceptance criteria for an O-ring, but it is known that significantly higher compression set values, up to 90 %, is enough to provide functionality of an O-ring. In our measurements O-rings with compression set of almost 100 % did not show any leakage.

In task 1.3 this work will be continued to be able to set realistic safety margins for O-rings that is how well the acceptance criteria are set and safety margin assessment is added. Laboratory conditions are normally static whereas O-rings in service are exposed to thermal fluctuations and vibrations. Therefore, aged O-rings will also be leak tested after exposure to simulated thermal and mechanical

disturbance in order to set relevant acceptance criteria. Stress relaxation tests have also been used in the ongoing project in order to evaluate the O-ring material. This method is similar to compression set, but instead of dimension changes, the sealing force of the rubber or O-ring is measured. Test data is recorded online and the specimen are exposed to heat during the measurement, that is ageing and measurements are performed simultaneously. The counterforce from an elastic rubber O-ring in compressed state is measured continuously and decreases as the O-ring loses its elastic properties.

In task T1.4 the aim is to understand ageing mechanism and kinetics of the chosen sample polymers inside NPP containments. Here is important to underline that some plants have inert (N_2) atmosphere during service and the availability of oxygen for the oxidation reactions is limited. Experiments in different atmosphere will give an improved safety margin assessment for components used in inert atmosphere and the ones that are stored in air is possible. In addition, the gathered data can be used to evaluate artificial ageing procedures, how the chosen atmosphere contributes to the ageing. This work was performed by VTT and reported elsewhere.

4 Analyses and results from WP1 during 2020

4.1 WP1 TASK 1.1 IMPROVED ESTIMATION FOR LIFETIMES OF CRITICAL POLYMER COMPONENTS

This task makes use of the results and analyses from the completed COMRADE project when suggesting useful and relevant acceptance criteria and safety margins. Results from laboratory aging tests and evaluations have been compared to materials obtained from Nuclear Powerplants (NPPs). Improvements to both test methods and aging environments are required to set acceptance criteria as well as safety margins. Some polymer components are extremely complicated or impossible to change in operating NPPs and thus their endurance during the whole lifetime of a plant is essential. To be able to make reliable lifetime estimations of components, information on material properties on both materials that have been in use at NPPs and artificially aged materials is extremely valuable. The question of residual lifetime assessment of polymer components in service is often raised. Without sufficient material data and service history of the materials, that is temperature, radiation dose, oxygen and moisture content in the atmosphere, this is almost impossible to predict. By studying materials from NPPs available from outages and decommissioned plants that have been in service for a long time, we have a unique opportunity to develop material lifetime prediction methods with correlation to materials from real service environment and long-term use.

The aim of this task is trying to identify critical components and to investigate the possibilities to obtain such components from plants under decommissioning or during maintenance, including material data. An obstacle with getting interesting components from decommissioning of NPPs, such as Ringhals R2 which were closed December 31, 2019 and Ringhals R1 which were closed December 31, 2020, is that it will not be possible to obtain the materials for several years because the fuel will not be removed from the reactor immediately.

It has proven that it is difficult to get clearance of materials used in the NPPs and it is sometimes also difficult to achieve sufficient amounts of materials to perform relevant tests, therefore a full year project including workshops together with the NPPs is planned for this task to be able to discuss what components to choose. One group of materials mentioned in the running project are cables. Moreover, replaced materials from outages will be considered. In COMRADE many samples were too small and not in sufficient amount to be analyzed. Therefore, artificially aged materials will be investigated in parallel. This work package will be run in collaboration with micro-calorimetry (MC) tests in order to calculate activation energies and verify the MC technology.

4.1.1 Project plan

The work package task will follow the plan below:

1. Identification of critical components in all plants
2. Possibility to extraction the components from plants
3. Estimating their residual and total lifetime.
4. If possible, order samples made from the same material from the supplier

For year two the plan was to continue with the workshops with NPPs. Based on these discussions' selection of interesting materials from closed NPPs and/or from outages should be made and find suitable reference materials.

4.1.2 Methods

The workshops that were held at Ringhals NPP and Forsmark NPP have been the main method to identify critical and interesting materials for further investigating. In a first stage focus was set on Ringhals because of their upcoming decommission of two reactors but during the decommissioning time it will be hard to get out materials because critical components will still be in used in the reactors for several years to come.

Discussion of materials of special interest for the project were also held at the SAMPO workshop at Fortum, Espoo in November 27-28th 2019.

For investigating residual lifetime of the chosen and obtained materials some testing has been initiated. This initial investigation of the materials included testing of hardness, tensile strength, and elongation at break.

4.1.3 Results and discussion

Workshops with NPPs

Workshops have been held at Ringhals NPP (29 Oct, 2019), at the seminar days at Fortum, Espoo (27-28 Nov, 2019) and online with Forsmark NPP (21 Sept, 2020).

Below some of comments on interesting materials and other inputs from all workshops are summarized:

Product	Material	Evaluation	Comment
Cable	PVC	Indenter, work poorly	PVC is changed to other polymer material.
Valve membranes	EPDM, natural rubber (NR)	Tensile testing	More critical than o-rings for leakage. Replaced according to schedule. Different exchange intervals. Some studies are made at Ringhals
Re-inforced membranes		Adhesion between reinforcement and material is important.	Reinforcing material may be the weakest part of the construction.
Joint mass between concrete elements			Has recently been replaced.
Brattbergare			Already under investigation.
Joint seals	Reinforced EPDM or Chloroprene	Test dummies are placed in the NPP for regular analysis.	
Dome seals	Shieldseal 663 James Walker		Changed annually.

Comments

A LOCA (Loss of Coolant Accident) test or other accident simulation on replaced materials, as well as on accelerated aged material is interesting to perform. . . Probably not possible to get clearance to take out the material from the NPP

Shieldseal 663 is similar to the EPDM designated LR9444 provided by James Walker for the COMRADE project.

Selected materials for testing during 2020

Neoprene membranes from Ringhals NPP: Ringhals has collected membranes from earlier revisions and the collection contains several membranes of similar type and of similar conditions and time in use.

- Outtake was made in September 2018
- They have been in the plant for 8 years (which is maintenance interval)
- There is membranes of three dimensions 40, 19 and 17.5 cm in diameter
- All neoprene membranes come from two systems: (liquid waste processing system (WP)) and (Sampling System (SS)). The sampling system is a giant system consisting of many different parts. Neoprene membranes come from pneumatically operated valves, which means that the membrane is at the top of the valve and does not come into contact with process water. Thus, it does not experience the temperature of the water medium. The exposure temperature is the ambient and air that pushes the membrane that triggers the opening or closing of the valve.

4.1.4 Test program*Neoprene membranes*

Tensile test; tensile strength and elongation at break – was done in year 2 (2020) and reported

Hardness – was done in year 3 (2021)

Stress relaxation – year 3

High temperature test – year 3

EPDM joint seal

Artificial aging in 45 days – was done in year 2

Tensile test; tensile strength and elongation at break – was done in year 2

Micro calorimetry – was done in year 2 (see report for task 2.2)

Hardness – was done in year 2

Stress relaxation – year 3

LOCA test – year 3

4.1.5 Results from testing*Test methods*

The membranes were punched into dumbbell test specimen.

Tensile testing was made according to ISO 37 with type 2 dumbbell on a Zwick Z1 tensile tester at a rate of 500mm/min and with a clip-on extensometer.

Testing of Neoprene membranes from Ringhals

Membranes d = 17.5 cm

Figure 1 below show elongation at break, which vary considerably between the different test specimen indicating degradation of the material, which is

inhomogeneous and therefore the results differ. The samples may also have been unevenly exposed to different ageing stressors.

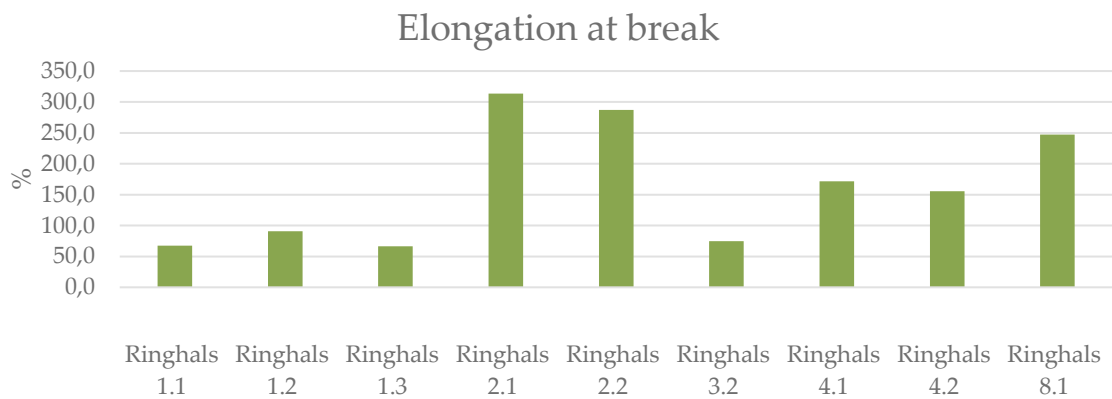


Fig 1: Elongation at break

Tensile strength is not as sensitive as elongation to detect degradation of a material.

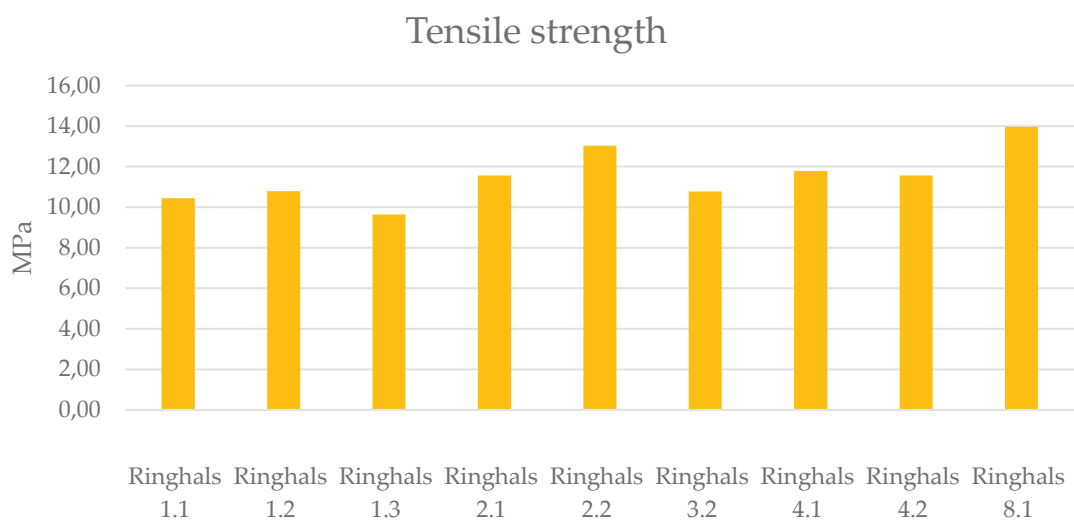


Figure 2. Tensile strength for the 17 mm membranes.

The 19 cm diameter membranes showed similar results, but with less spread in results compared to those reported above.

4.2 WP 1 TASK 1.3 SETTING UP SAFETY MARGINS FOR O-RINGS

4.2.1 Background and aim

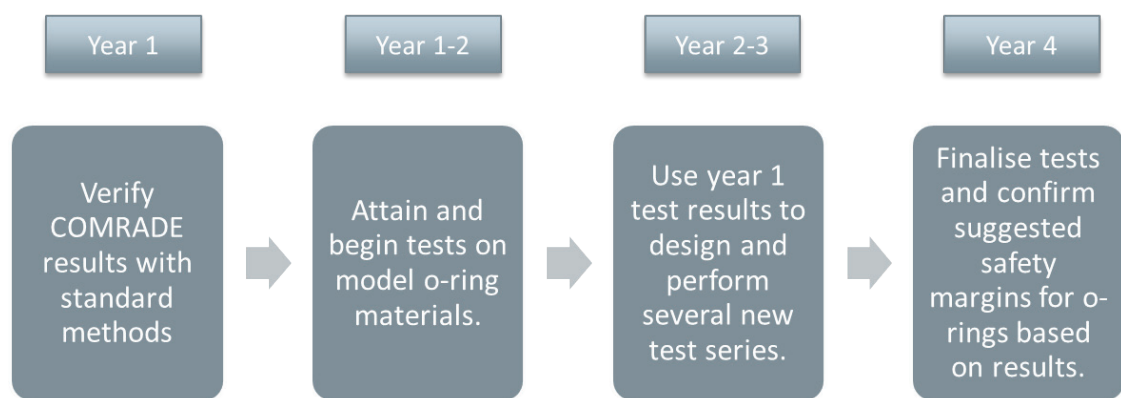
This task primarily aims to attain usage lifetimes for rubber O-rings which are present in critical functional capacities in Nuclear Powerplants (NPPs). SAMPO

2019 focused upon verification of COMRADE results and was successful in doing so. SAMPO 2020 focuses on utilising model materials to attain material failure, further verifying methods and better representing average power plant material.

Rubber O-rings can be found in some critical components such as pumps and pipe connections. If these pipes were to fail, a so-called 'loss of coolant accident' (LOCA) could occur. This could obviously be disastrous to the Powerplant and surroundings.

4.2.2 Project plan

The project plan can be best summarised as followed:



4.2.3 Experimental

Materials

Ethylene Propylene Diene Monomer (EPDM) was supplied by James Walker Ltd. Two grades are present and defined here as 'top-level', which is the same material as used in COMRADE and SAMPO 2019, and 'bad' which is a bespoke material fabricated from James Walker for SAMPO.

Compression set

Compression set test was performed on standard test specimen of cylindrical shape with a diameter 13 ± 0.1 mm and a thickness 5.6 ± 0.2 mm according to ISO 815-1. The standard test specimens were cut from the rubber sheets with a standard cutting mould. Three test specimens were placed between the plates of one compression device with the spacers with a height of 1.4 mm. The bolts were tightened so that the percentage of the compression was 75% of the original thickness. In total, three assembled compression devices were prepared for EPDM and nitrile sample, respectively.

The compression was performed in air.

The compression set was calculated as:

$$\frac{h_0 - h_1}{h_0 - h_s} \times 100\% \quad (1)$$

where h_0 , h_1 and h_s is the initial thickness of test specimen, the thickness of the test specimen after recovery, and height of the spacer, respectively.

Leak test rigs had O-rings compressed to approximately 20 % and calculated as above.

Stress-relaxation

Testing was performed in duplicate for each temperature (90, 120, 140 °C). The samples were compressed initially to 75 % and the force was measured continuously until 50 % of initial force was reached (test of samples in 90 °C was discontinued before reaching 50 %).

4.2.4 Results and discussion

Compression set and leak test

Previous work in 2019 focused on the overall verification of the data attained in the prior project COMRADE, that is the method used in COMRADE (measurement on O-rings), and the standardised method for measuring compression set (cylindrical cut-outs from a sheet). This experimentation showed that the data is reliable in both circumstances. In Task 1.3 2020, work has been undertaken on compression set of a model material provided by James Walker (JW), at a level which has been described by JW as 6/10 (denoted 'bad' material), where the material measured in SAMPO 2019 is considered at top levels, 9-10/10. The purpose of this was two-fold. Firstly, we wanted to assure that a material could reach failure, unlike the prior COMRADE project, where the top-level material was used, and failure was rare – thus casting into doubt at time whether the experiment was at fault, or if the material was just simply that good. Secondly, it is unknown whether power plants will at all times use top level material, so experimentation upon a more realistic, yet still proficient material, was deemed wise.

Figure 3 depicts a result from 2019 (120 °C EPDM) compared with 2020 results upon this model 'bad' material. For the comparable 120 °C one can observe the 'bad' performing worse than the top-level material, with, as far as the data goes, ~60 vs. ~85 % respectively. This is a good sign, and the data follows the trend that we would expect.

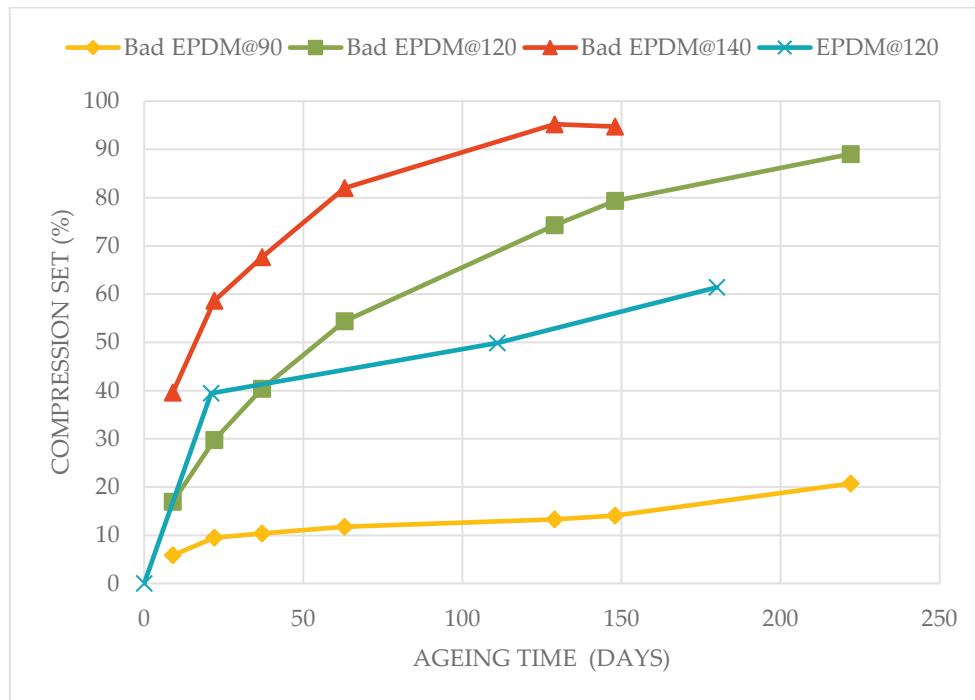


Figure 3. Data of compression set for model 'bad' material, and one set of data of top-level material at 120 °C for comparison.

Experimentation moved on to compression set within leak test rigs, having verified compression in this manner is appropriate. During a symposium summarising 2019 data for stakeholders, it was brought to our attention that the 'old' test rigs may not be deemed satisfactory enough for duplicating the environment that O-rings find themselves in inside a power plant. Thus, the rigs were redesigned as per figure 4, where one can see a groove has been cut out for the ring to sit within, compared to the 'old' test rig with much more empty space in the centre.



Figure 4. O-ring test rigs. Left: old test rig from COMRADE. Right: new test rig re-designed for SAMPO.

Compression set is underway for EPDM material within both leak test rig designs, and the data can be found in figure 5. The data follows the expected trend, with raising temperature, a higher compression set is attained. The testing will continue to attain more data points. Note that leak testing has been performed at the 2 latter time points as per figure 5, no leaks were detected except for the 'old' rig, at 140 °C. For the first of the two time points the leak was detected under low pressure (~5 Bar) and once the operating pressure for the test was attained (~60 Bar), the leak was no longer detected. It could be deduced that the higher pressure allowed the O-ring to attain a tighter seal within the test rig. For the last point, the rig was leaking continuously and could not hold any higher pressure.

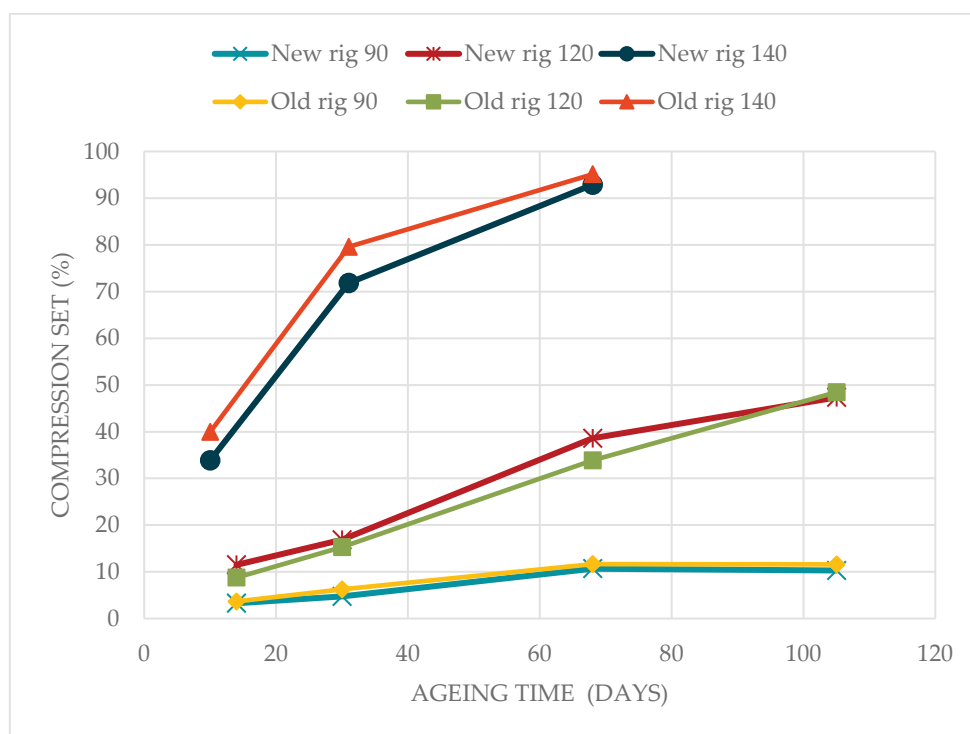


Figure 5. Compression set of model 'bad' EPDM material within test rigs, both 'old' and redesigned.

Stress-relaxation

Stress relaxation was conducted to determine failure (F_{50} , 50% compression) for the model 'bad' material, EPDM. The values of which can be found in table 2.

Table 2. EPDM material: time for F_{50} , failure, at 50% compression.

Temperature	Sample no	Time to F_{50} [days]
120 °C	1	89
	2	134
140 °C	1	19
	2	23

The values follow an expected trend that at higher temperature the material fails sooner. Top-level EPDM rubber, as determined in COMRADE, gave for 140 °C an F_{50} of 49 days. Whereas, for 120 °C, compression reached 75 % after 58 days.

4.2.5 Conclusions

1. Expected trends are present for all data – higher temperature leads to greater/faster failure.
2. Model ‘bad’ material performs worse, as expected, than the top-level material from SAMPO 2019 and COMRADE before.
3. The model ‘bad’ material is important as it better represents the average material in use at a power plant. Additionally, allowing for shorter test times whilst working with similar degradation mechanisms.
4. The new rig seems to hold against leakage longer than the old rig.
5. Perhaps more experimentation should be performed on commercial grade material, which JW denotes as being a 2-3/10 level material. Stress-relaxation particularly would be useful to determine key aging points in the material. This could lead to the use of a material that allows for shorter testing time, which ties in with WP2 requirements.

5 Results from 2020 WP 2 Improvements in ageing management of polymer components

In this work package, the objective is to provide improvements to ageing management in order to enhance the long term and safe use of the plants. The most suitable way to do this is to provide techniques that can be used to measure component condition non-destructively. For practical reasons, these techniques are typically non-destructive or require very small piece of sample material. One key issue developing novel non-destructive condition monitoring techniques is to understand how the non-destructively measured material parameter relates to polymer condition and its ageing. Such correlations are of interest in this research, combined with the objective to develop techniques for on-site measurements.

5.1 TASK 2.1 ONLINE CONDITION MONITORING TECHNIQUES

5.1.1 Background and state of the art

Ageing management of polymer materials takes time and effort and we believe that new technologies such as digitalization and online measurements would make this easier in the future. These possibilities will be examined in task 2.1. In NPPs, where it is difficult to change and sometime also to inspect parts, it would be particularly valuable. For example, in pipes for water supply and wastewater placed underground in cities, online monitoring is already used to spot leakages of water. Flow meters are placed in the pipes and monitored by computers and a leakage may be detected before it is observed above ground. We will try to monitor changes in polymer properties in for example cables and O-rings by measuring the dielectric properties. Changes in the chemical structure and overall composition of the materials are likely to affect the dielectric properties and there are previous examples where changes in dielectric properties have been linked to aging of polymeric materials [Daily 2015]. The effects of ageing on the dielectric behavior of the materials in question could be measured using that is impedance/dielectric spectroscopy. A very convenient method to monitor the status of rubber or polymer materials would be to measure material changes online. If there are large enough changes in dielectric behavior of the materials that can be directly related to the ageing process, it should be possible to follow these changes using antenna dielectric sensors [Huang, 2016]. By mapping the dielectric behavior of the materials under test, antennas could hopefully be designed to fit the frequency providing the highest sensitivity. Placement, environmental factors and calibration of sensors would likely also be issues necessary to address as well as monitoring moisture and temperature to avoid overlapping effects of moist content and degradation of the monitored polymers.

If ageing of the materials leads to cracking or inhomogeneities in the materials these could possibly be detected by designing a method utilizing partial discharge. State of the art measurements of impedance are not ready for products, only for

test samples. The research question is how to design specific measurements methods and test samples sizes that are suitable for aging tests. The electric properties will be correlated to relevant material properties such as elongation, compression set and tightness etc. before and after ageing in order to verify the methodology.

5.1.2 Goal of the study

The goal of this study was to assess if the accelerated ageing performed within the project induced measurable dielectric changes in some of the rubber materials and, if possible, identify specific frequency regions with more pronounced as well as systematic changes. We also wanted to investigate the feasibility of the concept of online monitoring of dielectric changes in similar rubber materials over extended periods of time.

5.1.3 Methods

As the frequency region of interest is unknown for any new material under investigation a broad band measurement method is needed. For this reason, a coaxial probe was chosen for the dielectric characterization of the materials. The coaxial probe is in principle a monopole antenna sensor, albeit not the type of antenna sensor we hope to see implemented as a result of this work. Instead of incorporating the antenna in or on the material the dielectric probe is pressed against the material. This approach facilitates measurements on several samples without extra fabrication steps, but also introduces some uncertainty in the quality and consistency of the contact between the probe and the material under test.

5.1.4 Measurements on aged samples

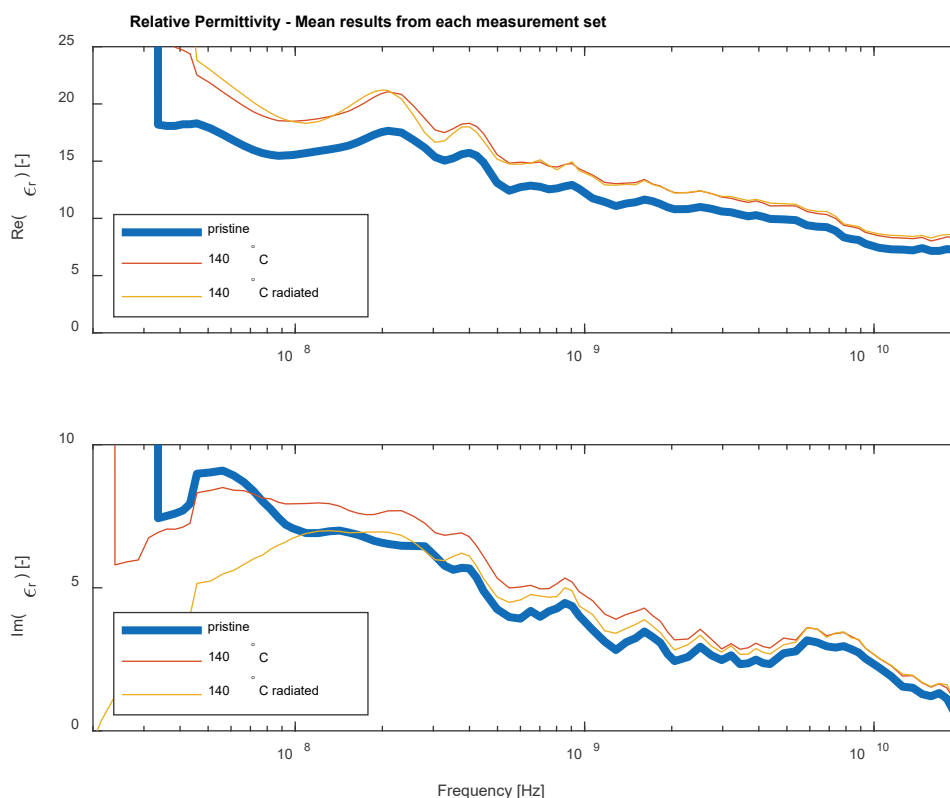
Measurements have been performed on provided EPDM samples that were cut out from the same piece of test material after which they were put through accelerated ageing to different degrees. The shape and thickness of the samples were not optimal in regard to compatibility with the dielectric probe method. They did not appear to quite fulfil the condition of being semi-infinite (thick enough to not measure out the other side of the material) and there were some difficulties in ensuring a uniform contact between sample and probe. For this reason, the absolute values of the measured data should not be taken as the true values for the permittivity of the materials. However, we believe that trends in changes can be taken as indicative if they are systematically detected over both several measurements at different sites on the same sample as well as between different samples of the same type.

Measurements were performed for three unaged samples and four samples aged at 140 °C for 6 months, of which two were also irradiated in cycles between ageing. The probe was disconnected from the samples and then reconnected between measurements to ensure measurements were performed at more than one specific sample location. This also helps in ruling out that the variation in results between samples could simply be due to differences in the contact between probe and sample.

Before the first measurement the cable was placed in a fixed position to the extent possible. The measurement set-up was then calibrated for the entire measured frequency spectrum using air, milli-Q water and a short as reference points. The placement of the measurement equipment unfortunately turned out to be sub-optimal and it is difficult to rule out cable drift due to other activities in the vicinity of the measurement set-up. This may also be one reason why it was difficult to realize a good calibration for the lower frequencies.

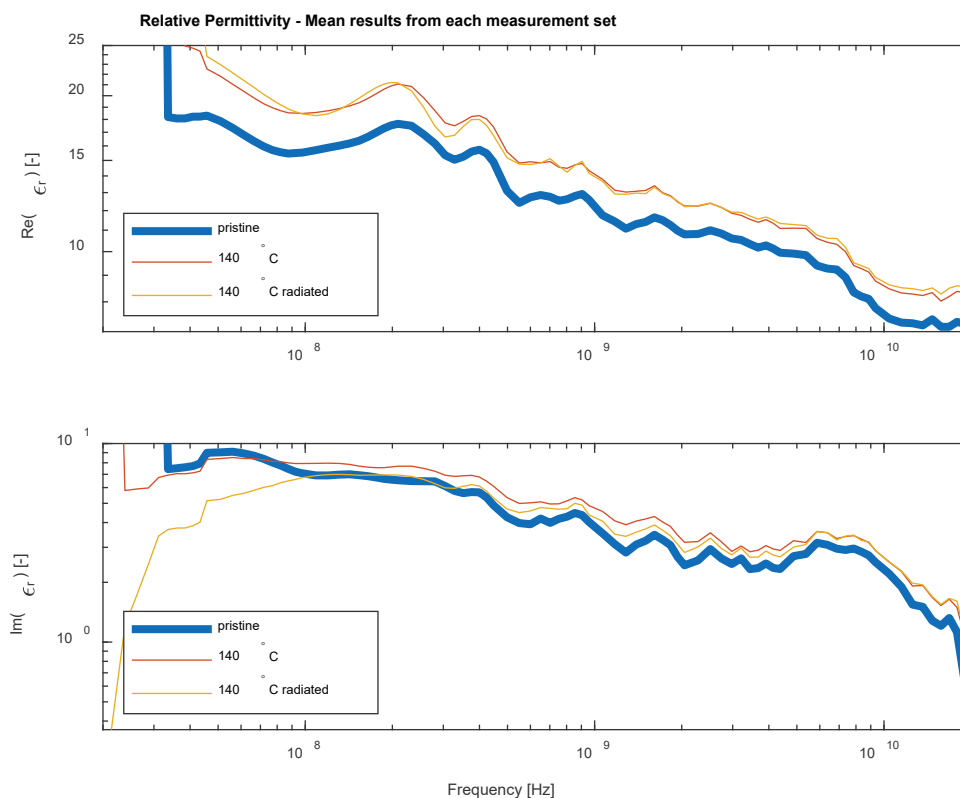
5.1.5 Measurements on aged samples

A simple mean over all measurements made on each sample/sample group is presented below. Material pre-irradiation appears to have very little effect on the results for the samples aged at 140 °C. This is consistent with the results from the mechanical studies. A slight increase in the real part of the permittivity could indicate an increased density of dipoles. There appear to be no clear frequency shifts for the peaks of the imaginary part of the permittivity. Without knowing the exact blend of the rubber material under test it is difficult to make any statement on if the results are plausible or not.



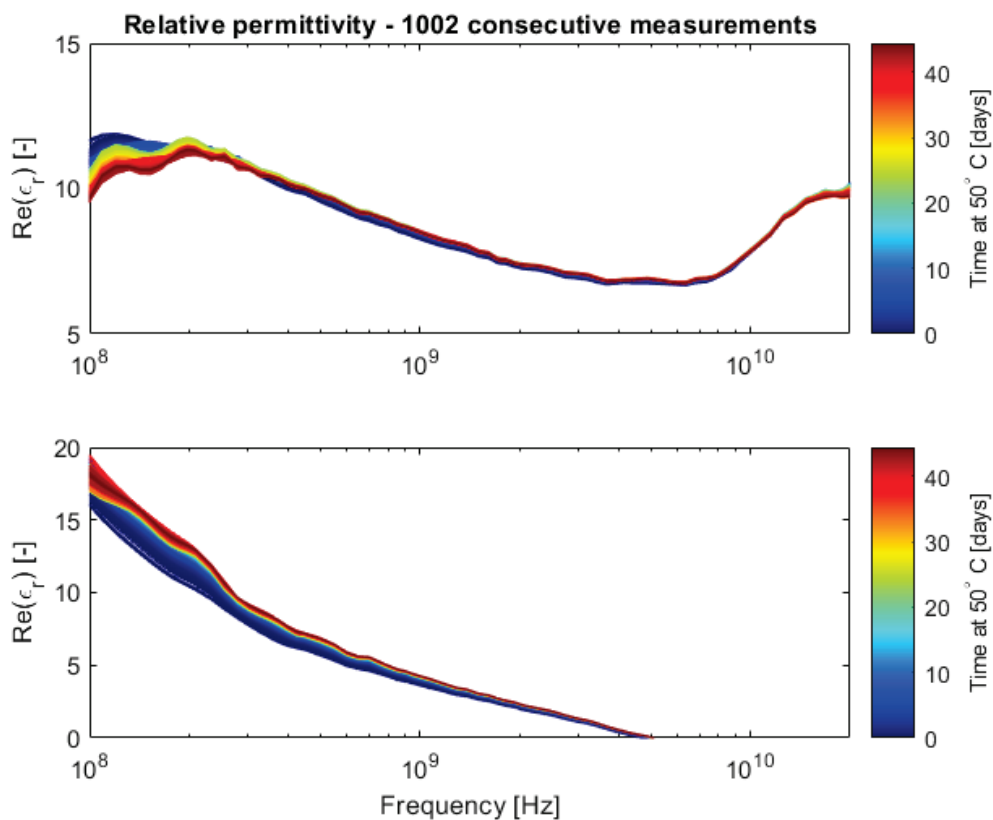
Looking at the data on a log-log scale there appears to be a shift in the dominant polarization mechanism at 6-10 GHz for this specific material, seen as a more pronounced reduction in the real part of the permittivity over those frequencies as well as what looks like a corresponding peak in the imaginary part of the permittivity in that same frequency interval. If the changes seen in the data is in fact due to the ageing mechanisms it appears that the ageing at higher temperatures affect the entire spectra, while the lower temperature aging only

appears to affect the lower frequencies. This could indicate a possibility to use different frequencies for identification of different types of ageing.



5.1.6 Online measurements

The measured relative permittivity as function of frequency taken approximately every hour for a total of 44 days was plotted together with the color axis indicating progression in time [days]. In most of the investigated frequency span it appears that the relative permittivity increases as time progresses. At this timescale the change is quite small, and the rate of change is highest at the start of the measurement series. The overall trend appears to be consistent with the results observed for the samples aged at 140 °C although the change seen at this timescale might be too small to draw any definite conclusion.



5.1.7 Results and discussion

As the wavelength becomes shorter with increased frequency it is more likely the samples could fulfil the semi-infinite thickness condition at higher frequencies. The results from these frequencies should thus be considered more reliable. We also had more difficulties achieving a stable calibration at lower frequencies and for these reasons we will focus more on the results at higher frequencies for our analysis. This does not necessarily mean that those frequencies would be more sensitive to material changes, and thus better suited for sensing the changes, but thicker samples and a better measurement set-up would be needed to draw further conclusions about the lower end of the spectrum.

The overall quality of the measurement conditions and thus measurements was unfortunately unsatisfactory. As such the results should thus be seen as indicative more than scientifically sound.

5.1.8 Conclusions

Measurement results achieved can be seen as indications that the permittivity might prove a useful indicator for aging monitoring of some polymeric materials. To better determine the effect of ageing on the permittivity of the material measurements either need to be performed over very extended periods of time or at higher temperatures for a more accelerated ageing process. For this to be possible it would be beneficial to acquire a probe and/or probe system which is

more robust and may function at higher temperature and have better handling of cable drift and sample contact variations.

As it has not been possible yet to identify any specific frequency region of interest, for the materials provided, frequency specific antenna sensor design and simulation has been postponed.

5.2 TASK 2.2 SENSITIVE ANALYSING TECHNIQUES

In this task we will look at a sensitive technique that is MC to be able to measure material deterioration/ageing at temperatures, as close as possible to the temperature experienced by the material in NPPs. MC like DSC (Differential Scanning Calorimetry) can register oxidation exotherms or any exothermic chemical and physical changes. The specific sensitivity is thus 10^3 times higher than DSC. Small sample sizes allow studies on materials such as coatings, adhesives and seals. Using newer techniques, measurements can be performed over a shorter period and at lower temperatures in comparison to the conventional oven tests. Polymers used in NPPs are usually very durable and hence traditional lifetime prediction measurements are very time consuming. Therefore, a sensitive technique able to detect degradation in an early stage is required.

The aim within task 2.2 is to verify the use of this MC as a condition monitoring technique as well as lifetime prediction for cables and other polymeric materials. This is conducted with a series of sensitivity studies, coupled with other techniques (that is detailed chemical analysis of the rubber before and after the trials) which can be used for the validation of the technique. Also, correlation with traditional monitoring techniques such as hardness, compression set is needed.

5.2.1 Methods

Isothermal microcalorimetry

Isothermal microcalorimetry is used to age the different polymeric materials at different temperatures for different time duration. The corresponding heat flows (exotherm or endotherm) were measured while the materials have been aged. 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 that is 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 $\mu\text{W/g}$ 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.

Scanning electron Microscope (SEM) coupled with and energy dispersive X-ray (EDX).

SEM technique is used for the elemental analyses for the selected aged samples. SEM instrument: ZEISS SEM Supra 40vp, equipped with Oxford Instruments EDX detector X-Max with 50 mm² window was used in this study. EPDM samples were attached to a circular stub using double sticking carbon tape. These stubs were then mounted on a circular sample holder and inserted in the vacuum chamber. For SEM imaging an acceleration voltage of 1 kV was used in high vacuum condition (around 1×10^{-6} mbar in the chamber), working distance around 3.5 mm, aperture 30 μ m. Detector SE2 (Scattered Electron).

While running EDX the voltage was increased to 15 kV and a low vacuum condition was required (around 35 Pa = 0.35 mbar) as the samples were not covered with a conducting film. Working distance around 8.5 mm, aperture 60 μ m. Software used for EDX mapping was AZtec version 4.3 (Oxford Instruments). VPSE (Variable Pressure Secondary Electron) detector for SEM-images together with EDX-maps.

5.2.2 IMC experiments

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 preheated 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.

Figure 6 below shows integrated heat release from three rubber samples. Rubber aged at 90°C releases most heat and the one aged at 140°C the least heat. The non-aged rubber falls in between. The reason is probably that no degradation reactions occur any longer in the 140°C aged material.

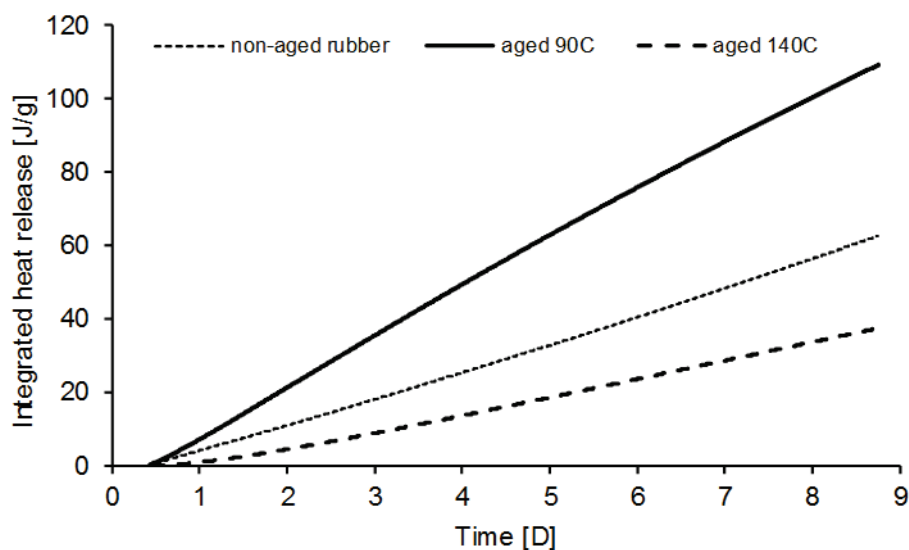


Figure 6. Previous MC results from COMRADE project on EPDM aged at 90 °C and 140 °C versus the non-aged sample.

IMC test using EPDM rubber samples.

IMC test using two EPDM rubber samples. The non-aged EPDM rubber sample as received from NPP and after ageing at 120 °C for 40 days were tested. The non-aged EPDM sample was same as tested in the COMRADE project. The aged EPDM was before ageing originally was from Fortum and commonly used in NPP known as TVO. The IMC test was conducted at six different temperatures 45 °C, 50 °C, 60 °C, 70 °C, 80 °C and 90 °C. The sample mass for non-aged EPDM was 5 g and 6 g for aged EPDM.

As shown in the Figure 2, the normalised heat flow from non-aged EPDM is significantly higher than the aged EPDM. This is expected because EPDM aged at 120 °C has already been exposed the higher temperatures than IMC test.

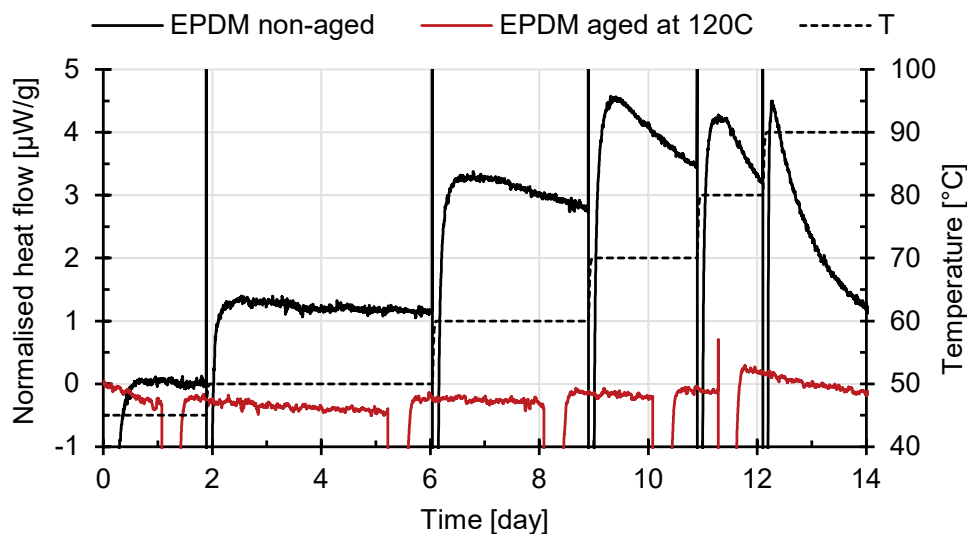


Figure 7. Normalized heat flow ($\mu\text{W/g}$) for EPDM non-aged and EPDM already aged at 120°C . The IMC test was conducted at six different temperatures 45°C , 50°C , 60°C , 70°C , 80°C and 90°C for two weeks. Temperature steps are shown by a dotted line.

It can also be seen that reactivity (Normalized heat flow) for non-aged EPDM has increased at 50°C , 60°C and 70°C in comparison to 45°C . This is expected because thermal power should increase with the increase in temperature provided the mechanism responsible for thermal degradation remains the same. However, a noticeable reduction in the reactivity is seen at 80°C in comparison to 70°C . This indicates a change in the mechanism. The positive values of normalized heat flow for non-aged EPDM indicate exothermic processes and negative values for the aged EPDM indicate endothermic processes or lack of thermal degradation in presence of air.

Electron microscopy images show plate out on samples aged in the micro-calorimeter between 45 - 90°C , see figure 8. This effect is not observed on virgin samples.

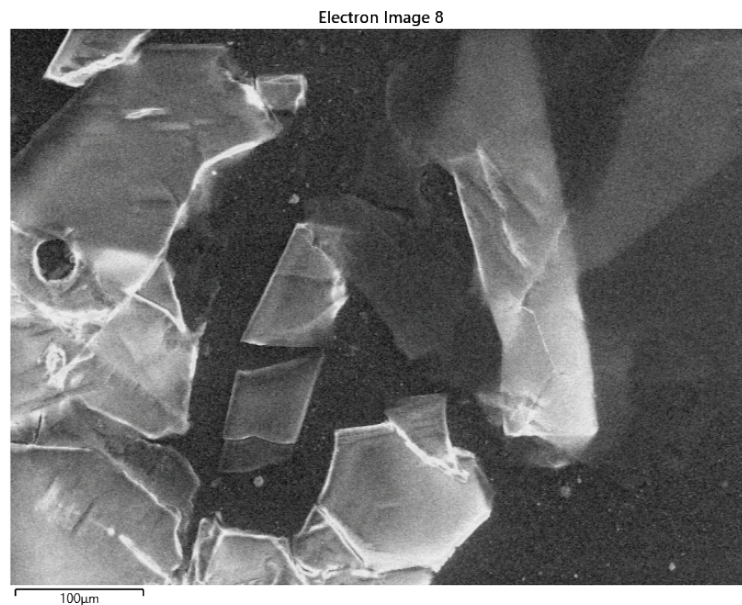


Figure 8. SEM image after EPDM was aged in IMC 45-90 °C, using 100 μm magnification.

The plate-out effect is at present investigated further and several other materials have been investigated by MC in different atmosphere and at different temperatures. These results will be published in a peer reviewed scientific paper during 2021.

6 Conclusions

Workshops at NPP was a better way to select polymer components that has been in service in NPPs for several years. Materials are difficult to achieve but important to investigate to increase knowledge of ageing behaviour in this environment.

A model “bad” material which better represents the average material in use at a power plant was analysed and behaved as expected – higher temperature leads to greater/faster failure compared to the top-level material investigated in 2019.

The model ‘bad’ material is important as it better represents the average material in use at a power plant. Additionally, allowing for shorter test times whilst working with similar degradation mechanisms.

The new rig seems to hold against leakage longer than the old rig.

Measurement results achieved can be seen as indications that the permittivity might prove a useful indicator for aging monitoring of some polymeric materials.

To better determine the effect of ageing on the permittivity of the material measurements either need to be performed over very extended periods of time or at higher temperatures for a more accelerated ageing process. For this to be possible it would be beneficial to acquire a probe and/or probe system which is more robust and may function at higher temperature and have better handling of cable drift and sample contact variations.

Microcalorimetry (MC) has proven to be a useful tool to study ageing behavior of polymer materials. Shift in degradation mechanism is observed as change in energy flow. In combination with Scanning Electron Microscopy migration of additive can be studied.

7 References

- [1] Conference Polymers in nuclear applications 2019, November 27-28, Fortum head office, Keilalahdentie 2-4 (CD-building), Espoo, Finland.
- [2] [2] Sipilä K, Vaari Jukka, Jansson A, Bondeson A. Condition monitoring, thermal and radiation degradation of polymers inside NPP containments (COMRADE), Report for COMRADE project.
- [3] Daily, C., 2015. Dielectric properties and degradation monitoring in polymer-matrix structural composites. Grad. Theses Diss. <https://doi.org/10.31274/etd-180810-3883>
- [4] Huang, H., 2015. Antenna Sensors in Passive Wireless Sensing Systems, in: Chen, Z.N. (Ed.), Handbook of Antenna Technologies. Springer Singapore, Singapore, pp. 1–34. https://doi.org/10.1007/978-981-4560-75-7_86-1
- [5] Li, L., 2011. Dielectric properties of aged polymers and nanocomposites (Doctor of Philosophy). Iowa State University, Digital Repository, Ames. <https://doi.org/10.31274/etd-180810-1135>

POLYMER COMPONENTS EXPOSED TO THERMAL-RADIATIVE ENVIRON- MENTS 2020

SAMPO is a joint project in collaboration with VTT in Finland and RISE and is run in close collaboration with the Nuclear industry.

Polymer researchers work together with experts in sensor technology and sensitive analyse techniques to learn more about degradation of plastics and rubber materials used for long periods of time in Nuclear Power plants.

The objective is to set relevant acceptance criteria for end of life of components, and improved material management by use of online monitoring of materials.

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