REPORT

Contact person
Marcus Granlund
SP Chemistry, Materials and Surfaces
+46 10 516 51 22
Marcus.Granlund@sp.se

Date 2017-02-01
Reference 6P01138
Page 1 (24)

The Finnish Research Programme on
Nuclear Power Plant Safety 2015 – 2018,
SAFIR2018SAFIR
Energiforsk AB
Swedens Radiation Safety Authority

WP1 COMRADE - Development of condition monitoring methods for polymeric components including low dose rate radiation exposure

(5 appendices)

Abstract

The first year of COMRADE project has been concluded and WP1 is at the final stage of the first ageing test. A peroxide cured EPDM o-ring at standard cord size 3.53 mm and test sheets from the same batch for dumb bells provided by James walker Ltd was used for the test. Test blocks for tightness test of the o-rings were manufactured by SP fitted to the o-ring size to be able to receive the correct compression. The accelerated ageing test was done in sequence irradiation – heat – irradiation – heat at three different temperatures. Both o-rings and dumb bell test specimen were used in the accelerated ageing . In parallel to the samples treated by radiation the same set of samples were aged in heat. The starting point and the second evaluation point was completed and presented at the workshop in September. The third evaluation was completed in middle of January 2017 and the fourth and last will be completed in the middle of February.

The tightness test showed a leak for the o-rings running in 140°C during evaluation 3. The material properties were correlated towards this and an Arrhenius plot was partly completed still waiting evaluation 4. For the upcoming ageing tests a larger cord diameter will be used to be able to evaluate the relaxation of the o-ring. A larger number of samples to be able to have more samples for evaluations are also considered.

A Comparison between samples irradiated at different dose rates in WP1 and WP3 is included in the discussion. Data concerning the effect from the dose rate and how the sequence of irradiation and heat effects the degradation was gathered from the tests. However it may be difficult to draw certain conclusions due to the number of samples, measurement uncertainty and so forth. A further study and discussion is needed during 2017.

In task 1.2 Implementation phase, there was a specific question regarding distinguishing between sulphur and peroxide curde EPDM. The use of XRF-analysis was tested to analyse the sulphur content from the Sulphur cured o-rings. Reference measurements on peroxide cured o-rings were also conducted in order to evaluate whether the method could detect the sulphur from the vulcanisation system used in the o-rings.

A guest article was published in Nordic Energy issue 5 2016 regarding the workshop conducted in September 2016 at SP. The article provided information on the workshop and on the ongoing project COMRADE.

SP Technical Research Institute of Sweden

Postal address
SP
Box 857
SE-501 15 BORÅS
Sweden

Office location
Brinellgatan 4
SE-501 15 BORÅS

Phone / Fax / E-mail
+46 10 516 50 00
+46 33 13 55 02
info@sp.se

Table of content

Background

During a feasibility study [C] acceptance criteria for functional properties for different polymers in system components was studied. Furthermore, the need to study degradation using low dose rates was identified in the study, since previous work described in literature mainly focuses on using a high dose rate to achieve the life time dose during a short period of time. This may cause a different degradation, compared to that obtained with a long exposure at a low dose rate.

The study will focus on accelerated ageing through heat and radiation to EPDM o-rings. The evaluation for a specific set of material properties and for the function of the o-ring is done at 5 evaluation times. The theory for the different methods is further described in the Methods chapter. By doing a correlation between the material properties and when the function of the component ends information of the end of life criteria is identified. To be able to better compare the effect the radiation has on degradation, a parallel test ageing only with heat is added.

The o-rings will be mounted in a test block during the exposure and not to be dismounted and mounted until exposure has been completed. The irradiation is done in an airtight container so there is limited oxygen available. The actual o-ring when in use at the plant also have limited oxygen available. This means that the environment is similar between the test and the reality. The tightness is tested in the hose testing equipment using water at 110 bar. Testing in water is chosen since the high pressure when using air poses a greater risk for blasts. With this test the sealing performance will be measured as water pressure without leakage.

By testing several material properties and the function of an o-ring an understanding of the correlation between them can be made. The aim is to be able to use this to set acceptance criteria for an o-ring using, for instance, compression set as a property.

The following materials are to be included in WP1:

1. o-rings (EPDM) Temperature* 90, 120, 140 ºC, peroxide vulcanized and subject to low radiation.
2. o-rings (Nitrile) Temperature* 60, 80, 100 ºC, vulcanized and subject to low radiation.
3. o-rings (Silicone or Viton), Temperature* to be decided depending on the chosen polymer. 3 different temperatures to be used, vulcanized and subject to low radiation.
   *Temperature may vary slightly due to the formulation of the polymer.

The dose rate radiation exposure is set to 29 Gy/h giving a total dose of 14 - 18 kGy to be compared to a component during normal operation subjected to a high radiation environment of 0,1 Gy/h for around 16 - 20 years. In future work (2017 and onwards) ageing parameters can be chosen in a way that functional properties of these components can be evaluated in situations like service failures and severe accidents in order to provide acceptance criteria if the component has designed function during these situations.

To get an idea of how much of the polymeric materials used in the NPPs that would be covered using the results from this project, actual numbers from Ringhals o-rings (EPDM, Nitrile, Viton) indicate a coverage in order of 85-90%. If choosing silicone instead of Viton the coverage will decrease but still is approximately 65-70% at Ringhals.

Figure 1 shows the time line for one ageing including the evaluation points. The test will be done using 24 o-rings (single sample) and 48 dumb bells (double sample). Only the EPDM o-ring will be tested using two cord diameters. This is estimated to be enough for the modelling to be done in task 1.3 but more tests could be proposed as future work if determined to be of interest. There are 5 points for evaluation including starting point. The time between evaluation is decreased at the later stage of the test since it is the region where the acceptance criteria or end of life will be found. It is estimated that a minimum of 80% compressions set is needed before the function will fail. If 80% is not met during the 6,5 month test the evaluation will help guide in how much longer heat treatment is needed to reach this area.

The result may be possible to use in technical documents setting requirements for polymeric components for the nuclear power plants. This can be used for existing components in the NPP or when purchasing new components (a fingerprint through for instance FTIR or DSC should be added). Depending on the components identified in WP2 a comparison can be made to the accelerated test in WP1.

Goal of the work package

The goal of this work package is to identify the acceptance criteria for the function of the polymeric component. The acceptance criteria or "death criteria" is in this project defined as when the component no longer can keep its function. The function to be tested is tightness of an o-ring. To have use of this as condition monitoring a correlation to a material property will also be investigated. The work package includes the following tasks:

1. Develop robust test methods that can be used by the power plants for condition monitoring through a material property. The material property will be correlated to the function of the component.
2. Performing experimental tests to validate the method
3. Development of a theoretical model that can be used to calculate acceptance criteria for components with different geometries
4. Deployment of the results into the daily operations at the NPPs.

The goal is planned to be achieved during 2016-2018 with both modelling and deployment of the results into daily operations during 2017-2018. More detailed description and fulfilment of deliverables can be found in the Results and Discussion chapter.

Methods

The ageing will be completed using both radiation and heat. During the ageing samples will be taken out at from ageing to be analysed at 4 points plus a reference sample. At each evaluation the analysis stated in the following section will be used. After analysis of the sample it will no longer be included in the test. The following description of methods for evaluation of material properties was compiled by SP Technical Research Institute of Sweden for the Energiforsk feasibility study [C]

Materials

An peroxide cured Ethylene Propylene Diene Monomer (EPDM) has been used for the ageing study. This was chosen based on a request from the Industry team where the most suitable material to test was asked for. The delivered samples were

- o-rings (42 pcs of 50-217 with cord diameter of 3.53 mm, batch number LR9444)
- sheets (4 test pieces 2 x 290 x 290 mm, batch number LR9444)

from James Walker Ltd dispatched May 17 2016.

Accelerated ageing

The accelerated ageing was done in sequence with radiation – heat – radiation – heat. The sequence was chosen based on a discussion with Dr. Sue Burnay during the compilation of the application. A study in WP3 is done to the sequence of ageing which can be taken into account for the next ageing test. It has been shown that starting with radiation creates more degradation then starting with heat. A parallel aging was done without the radiation treatment. In total 6 months of heat treatment and 14-18 kGy in total dose was used in the ageing process. One reference sampling and 4 additional sampling points were used.

Thermo – oxidative ageing

The thermo – oxidative ageing was done using 3 different temperatures; 90°C, 120°C, 140°C. Owens used are 401065 (#67) 90°C, 400011 (#70) 120°C and 401129 (#70) 140°C. The ovens did not have any controlled air flow. A monitoring system was used to monitor the temperature and the curves can be seen in appendix 4. The treatment was done according to the following time periods 2 months, 1 month, 2 month, 1 month.

Radiation ageing

The radiation treatment was done at VTT Technical Research Centre of Finland Ltd. The Gammacell® 220 used a Co-60 source with dose rate 67.35 Gy/h (measured 2016-03-06). The typical dose distribution of the sample cell can be found in appendix 5. Because of the dose distribution not being 100 % in the entire chamber a time correction to the irradiation time depending on the size of the sample was done. The cell dimensions are height: 20.6 cm and inner diam.: 15.2 cm. This sets limitations on how large o-rings can be tested. The irradiation treatment is done in 2 sequences, as explained in the Accelerated ageing section, during 13 days per sequence with dose rate of 29 Gy/h leading to a total dose of 7-9.07 kGy per sequence. Dose rate 29 Gy/h was achieved by using lead shielding with 2.74 cm thickness. The dose rate was calculated based on the material in the test block and the wall thickness of the test block. The temperature in the cell is around room temperature (23°C). The chamber is tight and filled with air from the start.

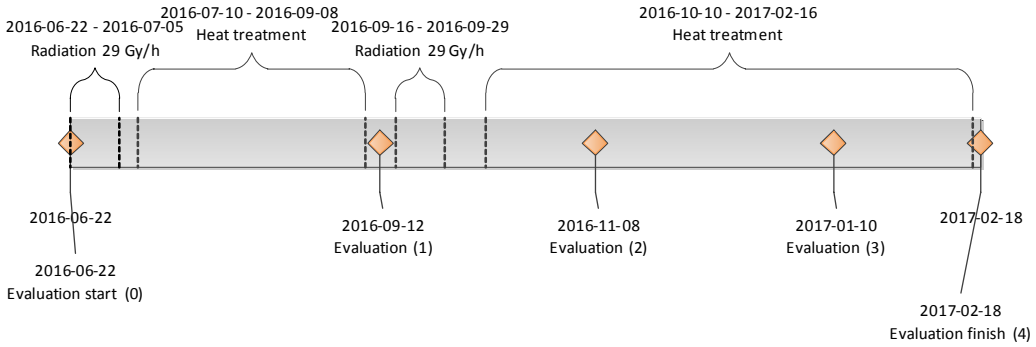


Figure 1 Time line for ageing process

Tightness test

The tightness test was done using a blaster for hoses. The pressurized medium was water at room temperature and the maximum pressure was set to 110 bar for 45-60 seconds. The ramp up from 1 to 110 bar was done in 60 seconds. The test was done using the sample holder in figure 2. The o-ring was mounted in its position (red arrow figure 2) and screwed together. The o-ring was placed on a flat surface with support on the outer diameter. An air screw on top of the test block was closed after filling of water. The test block was tested initially without a o-ring to see at what pressure leak started. At 10 bar first leak indication was shown and at 30 bar a continues flow of water came through the leak indicators. The leak indicator can be seen in figure 3 marked by red arrow.

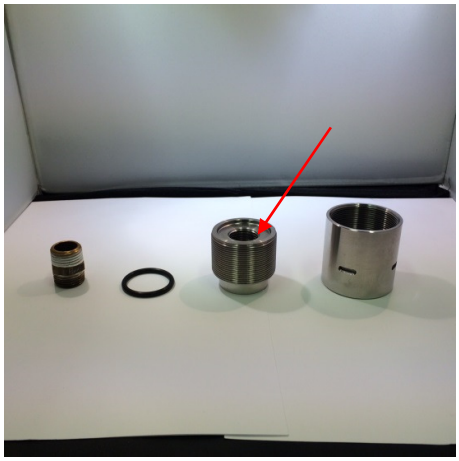


Figure 2. Test block not mounted.

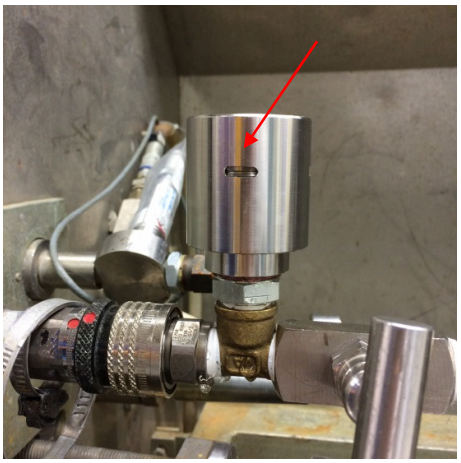


Figure 3. Test block mounted

Differential Scanning Calorimeter – Oxidation Induction Time (DSC – OIT)

Differential scanning calorimetry (DSC) is a thermal analysis technique. A sample is heated at a constant temperature rate and the energy consumption is recorded. All processes that require or generate heat, like crystallization melting or chemical reactions, can be detected.

It is also possible to study oxidation reactions. To protect polymers from ageing by oxidation anti-oxidants are added. How well they work or if they are consumed can be analysed using DSC with oxygen atmosphere.

The test was done in accordance to standard ISO 11357-6. Each sample step included a DSC run from parts of the dumb bells. The change in temperature were oxidation occur gives information on the status of the polymer. 2 tests was done for each sample and master curve can be found in appendix 2.

Fourier Transform Infrared Spectroscopy (FTIR)

IR-radiation excites molecular bonds causing absorbance of the radiation. Scanning through the IR-band generates an absorbance diagram. From this a lot of chemical information about a material can be obtained. This is carried out using an IR-spectrophotometer, usually designated Fourier Transform Infrared Spectroscopy (FTIR). When it comes to ageing, oxidation can be studied by selection frequencies that are absorbed by oxygen-carbon bonds. Ageing generates increased absorbance for those frequencies. It is necessary to have reference values from new material as well as some kind of correlation to physical properties.

Using a reflective absorbance technique like ATR it is possible to measure IR-absorbance on very small samples (2×2×1 mm), making the method useful for installed components.

Radiation causes surface degradation and therefore depth profiling is valuable to get information about how deep the degradation has progressed. It might be possible to slice a sample with a microtome for this purpose. On thicker materials a cross section can be analysed.

A common problem with IR-analyses is interference from additives like carbon black and fillers absorbing too broad in the IR-range. Black rubbers can be pyrolyzed prior to analysis to avoid this problem.

Nuclear Magnetic Resonance (NMR)

Nuclear Magnetic Resonance (NMR) is a physical phenomenon in which nuclei in a magnetic field absorbs and re-emits electromagnetic radiation. The NMR spectroscopy measurements is done using a solid state NMR. Measurement of Magnetic Resonance Imaging (MRI) and Magic Angle Spinning (MAS) are included in this project. The samples are cut from the o-rings. A test using a handheld NMR equipment is presented in a paper by Erik Linde, KTH [D] where they study chain mobility. The paper describes a correlation between NMR and FTIR and the possibility to use this as condition monitoring. A further study on selected samples will be done at one of the evaluation points in this project.

Tensile

A tensile test is to pull a test sample until it breaks and record the force. It can be carried out on both products and more commonly material samples. The maximum measured force divided by the minimum cross section area is the ultimate strength of the material. For rubbers it is measured in MPa. Ultimate strength can be used to measure degradation and ageing but it is seldom to recommend as the correlation is weak and a decrease is often quite sudden.

A better property to correlate to ageing is elongation at break. It is the maximum possible elongation of the material before it ruptures, measured in percent of the initial length. Normally a polymeric material has decreasing elongation at break when ageing.

The standard used for the test was ISO 37 common for rubbers. Two dumb bells are used at each evaluation point fort the test. Values for elongation at break and tensile strength are noted. Each sample is manually punched out from the test sheets using a puncher. A Zwick tensile tester is used for the tensile test.

Modulus of elasticity

The modulus or stiffness of the material can be measured at small deformations when the material is still elastic and not plastic. The modulus of elasticity is the increase of stress (MPa) at a certain increase of strain (mm/mm), commonly measured in MPa. Most polymeric materials have increasing modulus with ageing. Modulus can often be tricky to measure. There are a lot of practical parameters that affect the results.

An alternative to modulus of elasticity, that are commonly used for rubber materials, is to measure stress at a certain strain, like stress at 100 % elongation. Even if this can be far above the elastic region it can generate reliable reproducible results. An elongation of 100 % is commonly chosen for rubbers but for plastics an elongation of 1-10 % can be used.

An advantage with measurement of modulus or some other stiffness is that it is far less sensitive to sample preparation than elongation at break and ultimate strength. Modulus in tensile correlates to modulus in compression. It can sometimes be easier to prepare samples for compression tests. The modulus can sometimes also correlate to hardness.

Hardness

Hardness is actually measured on the surface part of a product and may be used for surface degradation studies. The ageing of rubber is correlated to increasing hardness. Some plastics can also show such correlations.

The technique is based on the measurement of how deep a certain needle can penetrate a surface within a certain time. The most common standard is IRHD (ISO 48) for rubbers. There

are handheld “durometers”. Those tend to generate results with poor repeatability. When it is possible to remove some material and measure the hardness in laboratory, it is preferable.

Hardness can sometimes correlate to measurements of modulus in tensile tests. An advantage is that small samples can be used and it can be done one final product, for instance o-ring.

Compression set

The most central property of sealing rubber products is compression set. Compression set is a test method (ISO 868) in which a circular rubber piece or an o-ring is compressed by typically 25% of initial thickness. The compression set rig may be stored at temperature relevant to the service environment. After a specified time the test piece is released and allowed to relax. The thickness is measured before and after compression and exposure. The material of good quality should retain its initial thickness or almost the initial thickness. Compression set is normally caused by subsequent crosslinking reactions and occurs during relatively short period depending on the temperature. Upon polymer degradation, which is the long term process the elasticity decreases and as a consequence, the sealing performance decrease. Poor compression set may also be caused by crystallization or high filler concentration.

Knowing the dimensions of installed sealing products like o-rings, it is possible to measure actual compression set by measuring the dimensions after demounting. It does take some practice to perform this in a repeatable way but it could be a usable method. The timing is important, meaning that the sample must relax a specific time after demounting typically 30 minutes.

Relaxation

A complementary measurement to compression set is stress relaxation. This is a more direct way to measure sealing properties of rubbers. Instead of dimension change, the sealing force is measured over time. When the sealing force is zero there are no physical sealing. Compression set is more common to measure as it is easier, but stress relaxation gives a better picture of sealing properties. In dynamic environments with changing temperature or dimensional fluctuations, or in chemical environments that can give physical changes in the material, stress relaxation is preferable.

It is possible to carry out an approximate measurement of actual stress relaxation on demounted sealing components by compressing the component to the actual seat height and measure the force after the initial relaxation. Another possibility is to run stress relaxation in cyclic temperatures if the working temperature is varying in the product application.

A common standard is ISO 3384.

Dimensions

Measurements of dimensions such as thickness and diameter of the o-rings was not done before starting of the ageing test. Instead this was done on 10 other o-ring samples from the same batch and delivery to see the variation. At each evaluation point measurements have been done.

The Arrhenius equation

The Arrhenius equation can be used to calculate an estimated service life at ambient temperature. The deterioration of a material property, for example elongation-at-break, is followed over time, and the results are used for calculating an estimated service time using the Arrhenius equation.

The reaction rate for almost all chemical reactions increases with increasing temperature. This is described by the Arrhenius equation as:

$$k = A \exp [-Ea / (RT)] \qquad [1]$$

where k is the rate constant for the chemical reaction, Ea is the Arrhenius activation energy, R the gas constant, and T the absolute temperature. The pre-exponential factor A, the molecular collision frequency, is considered to be a constant if the studied temperature interval is not too large. A failure criterion is set, where the material is no longer useful, and the time (t) to failure is measured experimentally (Figure 4).

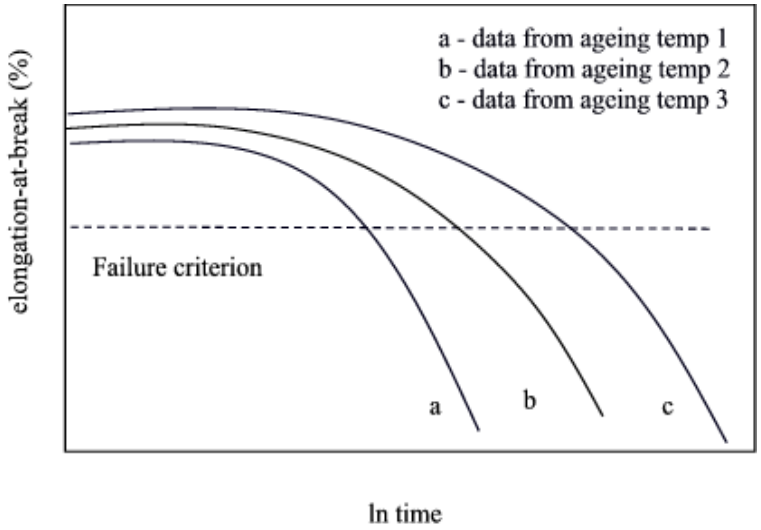


Figure 4. Example of an ageing plot using elongation at break as the property to trend over time.

In Figure 5, the logarithm of time-to-failure at the different testing temperatures can be plotted versus 1/T, a so called Arrhenius plot. The data points should fall on a straight line and the activation energy can then, according to equation 1, be calculated from the slope of the line. Furthermore, extrapolation to other temperatures can be made, enabling lifetime prediction.

Extrapolations according to the described method should, however, be done with caution, since different reactions with different activation energies may dominate at different temperatures. This gives Arrhenius plots with different slopes in different temperature regions.

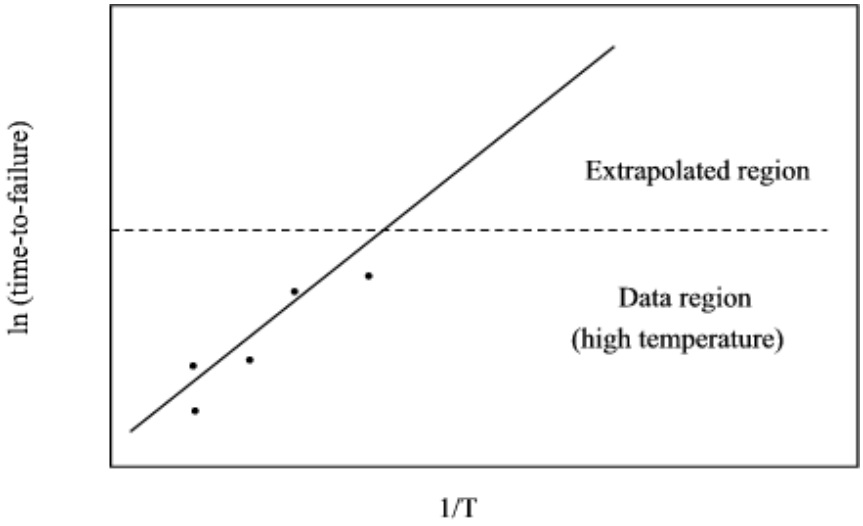


Figure 5. An example of Arrhenius plot.

X-ray Fluorescence (XRF)

To distinguish peroxide and sulphur vulcanized EPDM qualities from each other, several different techniques can be used. The most promising one, x-ray fluorescence (XRF), was chosen for more detailed evaluation. XRF technique is based on wavelength measurements of reflecting x-rays from the studied material. Basically it is a semi-quantitative analysis of a material surface and is applicable on 70 of the 80 commonly occurring elements in the periodic table (B, C, N, O and F are excluded). The method gives an approximate quantification of an analysed element, in this case sulphur. RISE possesses a portable XRF pistol which was used in the analyses and which would also be convenient to use at onsite measurements. Uniquant software was used in analyzation of the measured data.

Results and Discussion

In the following diagrams when using days as the x-axis only the days in heating is used and not the days in radiation treatment.

Accelerated Ageing

The accelerated ageing started the 22nd of June 2016 and follows the dates noted in figure 1. Below table 1 provides the sample IDs used during the test. In addition to 0-samples 24 o-rings and 48 dumb bells was used. The dumb bells had double samples whereas the o-rings used single samples. Table 1, 2 and 3 summarizes the different treatment steps each sample had.

Table 1. Showing the sample ID of o-rings and dumb bells and the temperature it was submitted to.

O-ring		Dumb bell			
Sample	Temperature (°C)	Sample	Temperature (°C)	Sample	Temperature (°C)
0	0	0	0		
1	90	1	90	25	90
2	90	2	90	26	90
3	90	3	90	27	90
4	90	4	90	28	90
5	120	5	90	29	90
6	120	6	90	30	90
7	120	7	90	31	90
8	120	8	90	32	90
9	140	9	120	33	120
10	140	10	120	34	120
11	140	11	120	35	120
12	140	12	120	36	120
13	90	13	120	37	120
14	90	14	120	38	120
15	90	15	120	39	120
16	90	16	120	40	120
17	120	17	140	41	140
18	120	18	140	42	140
19	120	19	140	43	140
20	120	20	140	44	140
21	140	21	140	45	140
22	140	22	140	46	140
23	140	23	140	47	140
24	140	24	140	48	140

Radiation

O-ring and dumb bell samples were aged as summarized in table 2. The samples still not tested waiting for the irradiation treatment was stored in room temperature. Since the irradiation chamber has a dose rate distribution a rearrangement of the samples was done after half time in each 2-week treatment. The X in the table marks the treatment done and as the ageing pro longed samples was taken out in each sampling step going from 0-4.

Heat

O-ring and dumb bell samples were thermo-oxidative aged as summarized in table 2 and 3. The X marks the treatment done and as the ageing prolonged samples was taken out in each sampling step going from 0-4. Sample 4, 8, 12, 16, 20 and 24 had the longest heat treatment for the o-rings.

Table 2. Showing the sample ID:s of o-rings and their sequence of ageing.

O-ring	Irradiation 1	Heat 1	Irradiation 2	Heat 2	Heat 3	Heat 4
0						
1	X	X				
2	X	X	X	X		
3	X	X	X	X	X	
4	X	X	X	X	X	X
5	X	X				
6	X	X	X	X		
7	X	X	X	X	X	
8	X	X	X	X	X	X
9	X	X				
10	X	X	X	X		
11	X	X	X	X	X	
12	X	X	X	X	X	X
13		X				
14		X		X		
15		X		X	X	
16		X		X	X	X
17		X				
18		X		X		
19		X		X	X	
20		X		X	X	X
21		X				
22		X		X		
23		X		X	X	
24		X		X	X	X

Table 3. Showing the sample ID:s of dumb bells and their sequence of ageing.

Dumb bell	Radiation 1	Heat 1	Radiation 2	Heat 2	Heat 3	Heat 4
0						
1	X	X				
2	X	X				
3	X	X	X	X		
4	X	X	X	X		
5	X	X	X	X	X	
6	X	X	X	X	X	
7	X	X	X	X	X	X
8	X	X	X	X	X	X
9	X	X				
10	X	X				
11	X	X	X	X		
12	X	X	X	X		
13	X	X	X	X	X	
14	X	X	X	X	X	
15	X	X	X	X	X	X
16	X	X	X	X	X	X
17	X	X				
18	X	X				
19	X	X	X	X		
20	X	X	X	X		
21	X	X	X	X	X	
22	X	X	X	X	X	
23	X	X	X	X	X	X

Dumb bell	Radiation 1	Heat 1	Radiation 2	Heat 2	Heat 3	Heat 4
24	X	X	X	X	X	X
25		X				
26		X				
27		X		X		
28		X		X		
29		X		X	X	
30		X		X	X	
31		X		X	X	X
32		X		X	X	X
33		X				
34		X				
35		X		X		
36		X		X		
37		X		X	X	
38		X		X	X	
39		X		X	X	X
40		X		X	X	X
41		X				
42		X				
43		X		X		
44		X		X		
45		X		X	X	
46		X		X	X	
47		X		X	X	X
48		X		X	X	X

Tightness test

Only the o-rings were tested for tightness. The test blocks were manufactured at SP work shop based on the size of the o-ring and a design done by SP work shop in collaboration with James Walker Ltd. A test without an o-ring was done to verify the leak indicators. At 10 bar first leak indication was shown and at 30 bar a continues flow of water came through from the leak indicators. At each sampling point the test blocks where taken out for the leak test. The result can be found in the table 4.

Sample 11 and 23 leaked at 30-35 bar pressure at evaluation 3. A test to raise to 110 bar was done on sample 23 and the leak stopped.

Table 4. The result of the leak test of o-rings

Sample	Evaluation	Result
1	1	No leak indication
2	2	No leak indication
3	3	No leak indication
4	4	
5	1	No leak indication
6	2	No leak indication
7	3	No leak indication
8	4	
9	1	No leak indication
10	2	No leak indication
11	3	**Leak at 30 bar**
12	4	
13	1	No leak indication
14	2	No leak indication
15	3	No leak indication
16	4	
17	1	No leak indication
18	2	No leak indication
19	3	No leak indication
20	4	
21	1	No leak indication
22	2	No leak indication
23	3	**Leak at 35 bar**
24	4	

Differential Scanning Calorimeter – Oxidation Induction Time (DSC – OIT)

DSC test was conducted on samples prepared from the used dumb bells. ISO 11357-6 was followed and a cycle of 5 minutes at 25 °C, going from 25°C to 275°C 10 K/min and going from 275°C to 25°C 10 K/min was done. There is very little difference between the irradiated and not irradiated samples. It seems to be the temperature that provides a greater difference to the OIT.

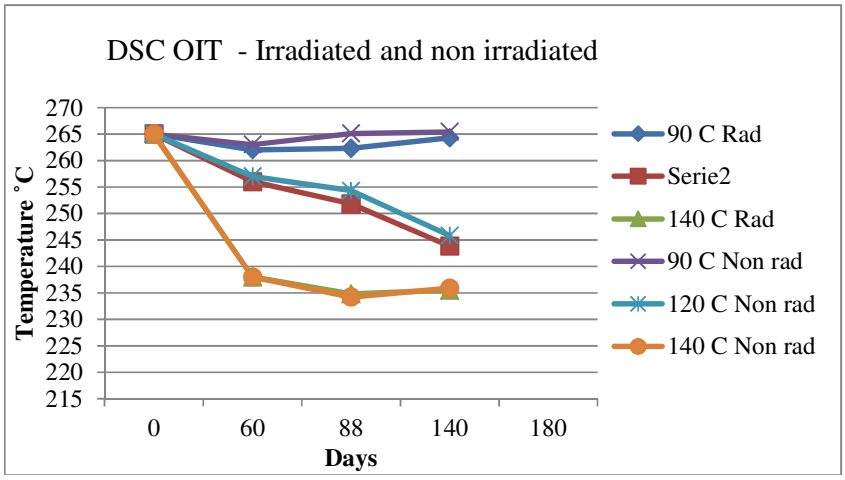


Figure 6. DSC OIT for irradiated and non-irradiated samples. Two evaluations have not yet been completed.

FTIR

FTIR was conducted on the o-rings. A measurement on the surface of the o-ring would have provided us with information on the oxidation at the surface. However this was not possible due to the carbon black being the filler. One possibility could have been to use pyrolysis first which will be considered in the next ageing experiment.

Nuclear Magnetic Resonance (NMR)

The NMR test was conducted at the Swedish NMR Centre in Gothenburg. The test was done on three samples of o-rings sample 0 (reference sample), sample 6 (120 °C and irradiated) and sample 18 (120 °C not irradiated). To access the impact of ageing two approaches were used: Magnetic Resonance Imaging (MRI) and Magic Angle Spinning (MAS) solid state NMR. In the MRI the T_2 could not be measured due to being very short. Instead T_1 was used. T_1 appears to be different between the 3 samples and T_1 is in general longer for treated samples. However, the irradiated samples has a T1 that stands out compared to the non-irradiated samples.

In the MAS spectra samples 6 sticks out again. A small peak is revealed which is not identified. It could be due to the radiation treatment. Further analysis would be needed to identify the peak.

See appendix 3 for full test report.

Tensile

The tensile test was done according to ISO 37. Sample dimensions of 85 x 10 x 2 mm were used. At the initial sampling (reference point) a series of 10 samples were tested. This was done to achieve a better understanding on how much the samples may differ. For each sampling point 2 samples were available for testing. The tensile strength and the elongation is presented in below diagrams.

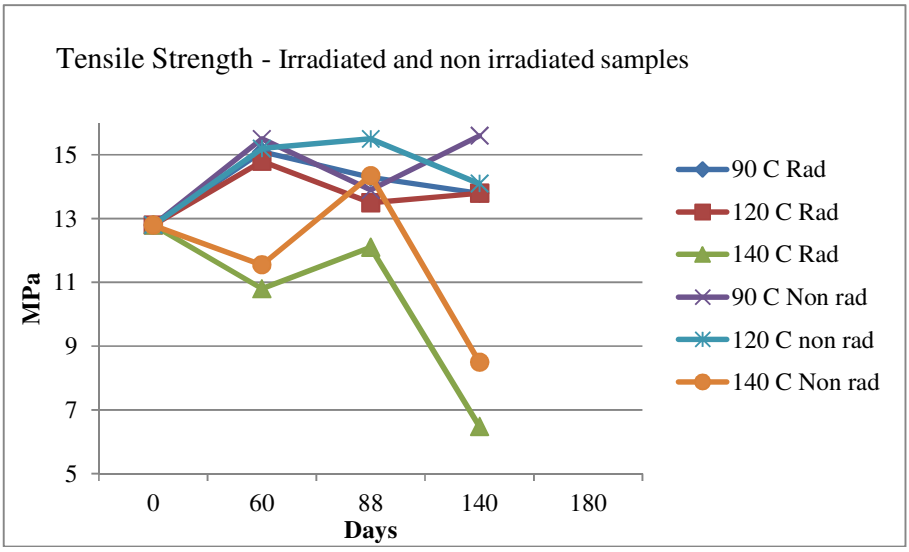


Figure 7. Tensile strength for irradiated an non-irradiated samples.

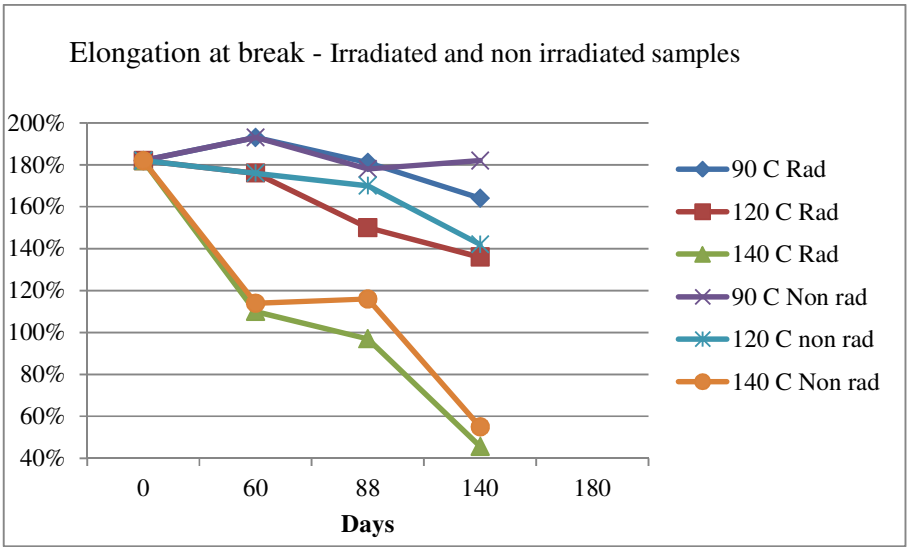


Figure 8. Elongation at break for irradiated and non-irradiated samples.

Hardness

Hardness was measured using the dumb bells. The measurement followed standard IRHD-m (Shore A). 3 measurement points leading to an average value.

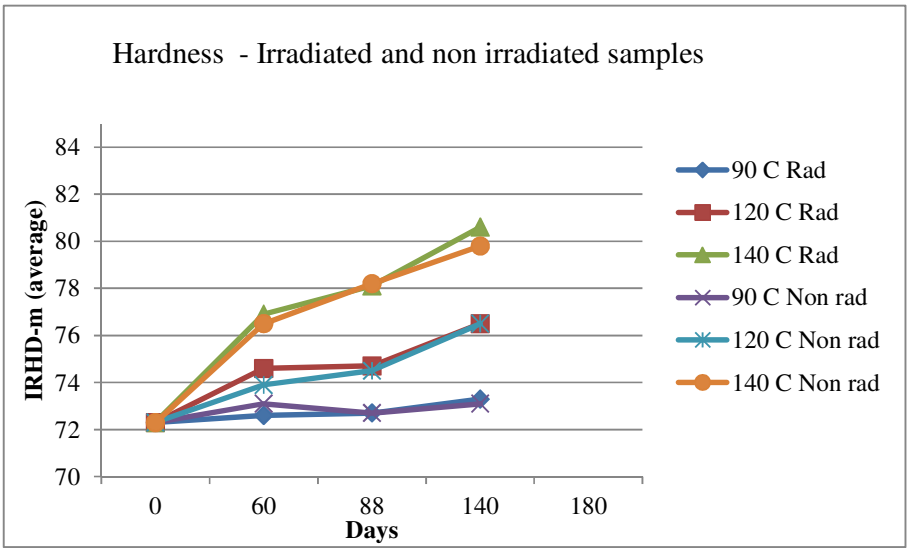


Figure 9. Hardness for irradiated and non-irradiated samples.

A comparison between samples in WP1 and WP3 was done for hardness. The hardness for the sample was 72 (Shore A). This is similar to the value obtained using low does rate and heat treatment in 90°C.

Compression set

Compression set was measured on the o-rings. After the tightness test the o-rings were placed in the constant climate enough time to dry up. The test was done according to standard

ISO 815. A reference sample was made in 23°C with holding time of 72 hours resulting in 4,9%. Average thickness for the o-rings were used measured on 10 samples being 3,517 mm. There is a variation in the testing with 17%-22% compression giving us a similar measurement error in the reported values.

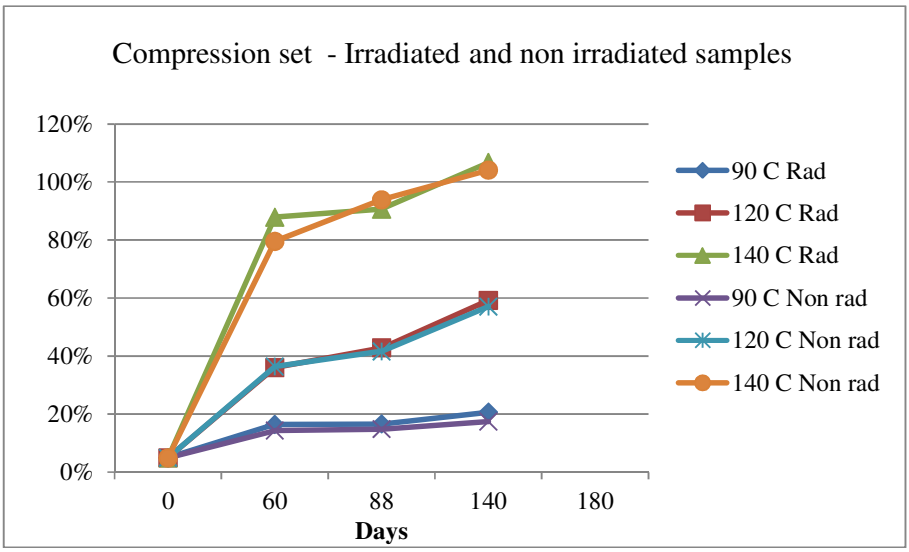


Figure 10. Compression set for irradiated and non-irradiated samples

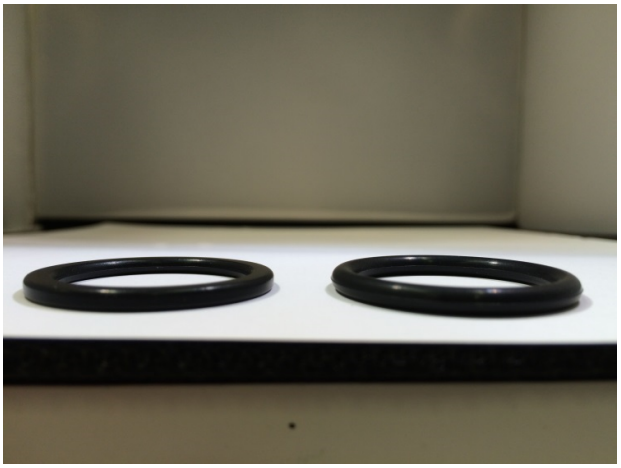


Figure 11. Evaluation point 3 sample 23 (105% compression set) to the left and un-aged to the right.

Relaxation

The samples were not thick enough to be able to perform relaxation test. This will be completed in the next ageing run when the o-ring thickness will be increased to 6,99 mm cross section. The dumb bells will also have the same thickness.

Dimensions

The following dimensions were measured on the o-rings. The reference samples were measured.

Table 5. Dimension measured on the o-rings.

Sample	Evaluation	Result Cord diameter (mm)
0	0	3,537 Mes on 10 pcs
1	1	3,41
2	2	3,41
3	3	3,39
4	4	
5	1	3,29
6	2	3,25
7	3	3,13
8	4	
9	1	2,99
10	2	2,81
11	3	2,85
12	4	
13	1	3,42
14	2	3,42
15	3	3,41
16	4	
17	1	3,29
18	2	3,26
19	3	3,08
20	4	
21	1	2,89
22	2	2,93
23	3	2,73
24	4	

Arrhenius plots

The Arrhenius plot using compression set as the trending property can be seen in figure 12 and 13. Figure 12 shows a compression set of over 100% for the o-rings treated in 140°C. As the leak test indicated leak for these two o-rings the failure criterion is for this case 100 % compression set. To be able to create the Arrhenius plot as in figure 5 all three temperatures should have surpassed the failure criterion. Since that has not yet happened an estimation could be used instead. This will be included in the revised report.

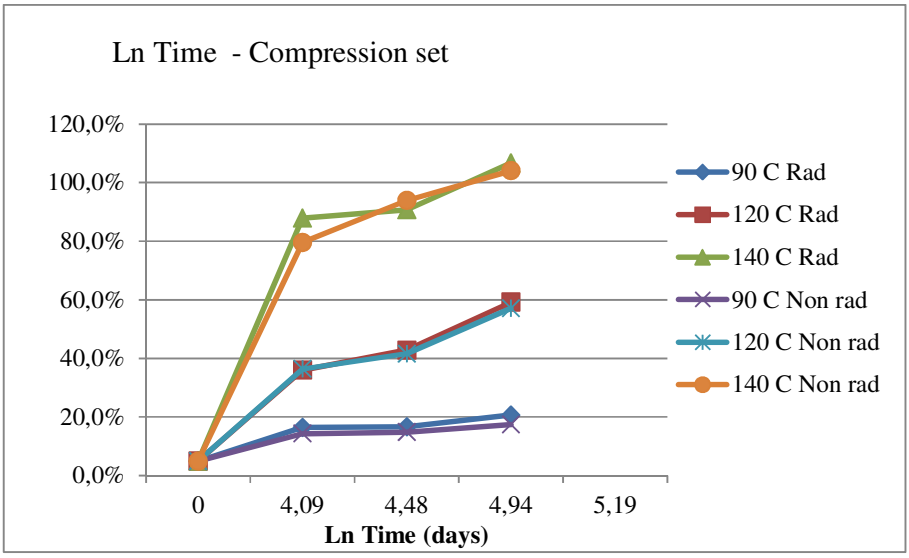


Figure 12. Arrhenius plot of compression set and Ln Time (days). By identifying the failure criterion being at compression set 105% a Ln Time to failure – 1/T plot can be made. This will be included in the revised report.

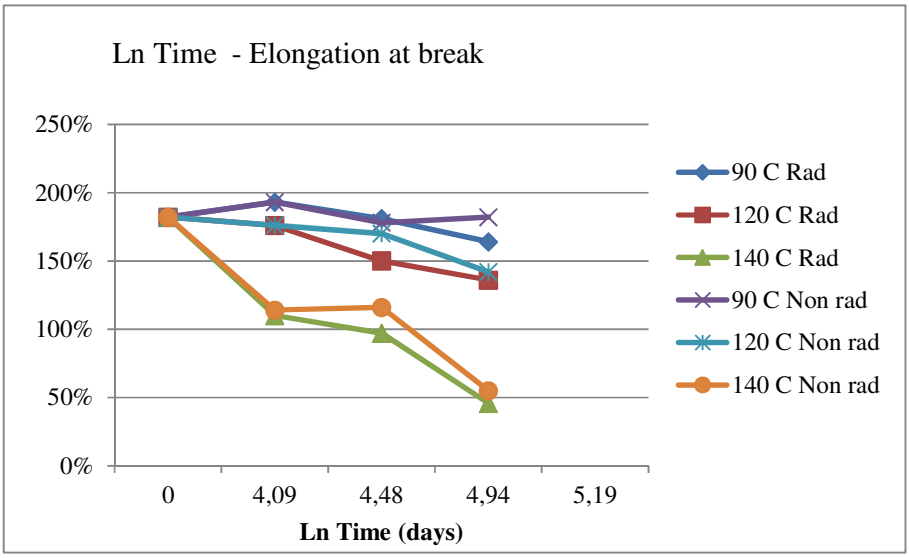


Figure 13. Arrhenius plot of Elongation at break and Ln Time (days). By identifying the failure criterion being at elongation at break 50% a Ln Time to failure – 1/T plot can be made. This will be included in the revised report.

Implementation for the industry

Suitable method for detection of the curing system of EPDM

EPDM is widely used material in sealant applications at NPPs due to its good performance in wide range of service environments and relatively low cost. Peroxide and sulphur are two common vulcanizing agents that are used in manufacturing phase of EPDM blends. Peroxide cured EPDM quality generally performs better in high temperature applications [A]. However, at some point in the material supply chain the distinctive differences of the two EPDM qualities may be ignored resulting in delivery of EPDM quality with wrong vulcanizing agent. Thus a suitable method for detecting the wrong EPDM quality before the component

installation would improve the lifetime of the component and prevent premature component failure. One such technique is x-ray fluorescence.

Two samples were analysed, sulphur and peroxide cured EPDM. The studied materials were delivered by James Walker Ltd. The analysis results are shown in Table 7. Mn, Al, Cl and K were found in both samples in quite small amounts. In sulphur cured EPDM amount of Si and Ca were less than 0,1 weight-% as in the peroxide cured quality the amounts were ca. 0,1 and 1,0 weight-%, respectively. The amount of Zn is quite large, 9 and 8 weight-%, in sulphur cured and peroxide cured qualities, respectively. Large amount of Zn is due to its use as an activator in the vulcanization process. In case of S, there is a clear (factor of ten) difference in weight-% between the two curing systems. The current EPDM evaluation standard [B] defines the sulphur content to be 1,5 PHR (parts per hundred rubber) when sulphur is used as a vulcanizing agent. Thus the amount of ca. 2 weight-% of S would be typical amount when the vulcanization of EPDM is done by using sulphur as a vulcanizing agent. Based on such obvious difference seen between the two samples, XRF technique is capable to distinguish sulphur and peroxide cured EPDM qualities from each other.

Table 6 XRF analysis results for the two curing systems.

Element	Sulphur/ weight-%	Peroxide/ weight-%
Mg	0,02	0,02
Al	< 0,01	0,02
Si	0,04	0,1
S	2	0,2
Cl	< 0,01	0,01
K	< 0,01	< 0,01
Ca	0,02	1
Zn	9	8

Comparison between samples irradiated at different dose rates

A comparison between the samples and their experimental data in WP 1 and WP 3 was made. This was done to evaluate any difference in ageing behaviour when using different dose rates. The dumb bells from the same batch of EPDM as in WP1 was tested for tensile properties after radiation treatment in WP3. The sample dimensions was 115 x 25 x 2 mm. The radiation treatment in WP3 was done using a total dose of 23,3 (±2,4) kGy at three different temperatures, see table 7. The used dose rate was 0,39 kGy/h(13 times higher dose rate then in WP1). A similar total dose reached as in WP1 irradiation treatment.

The resulting tensile test resulted in an average tensile strength of 13,2 MPa and elongation at break of 175,7%. Looking at the ageing in WP1 at 90°C and 120°C the same numbers after 2x irradiation treatment and 2 x heat values are around 170-160 % elongation at break and 14 MPa tensile strength. This could indicate that the higher dose rate causes more severe damage than using the lower dose rate. This is even though they have a similar total dose. The basis to conclude on this is to thin though and further study is needed.

Table 7. An overview of one experiment in WP3. Comparison to change in tensile strength between these samples and samples receiving a similar total dose as in WP1.

Ageing temperature/°C	Absorbed dose/kGy	Ageing time/h	Elongation at break/%	Tensile strength/MPa
28,6±1,0	23,3±2,4	55,5	174	13,4
76,5±0,6	23,3±2,4	55,5	165	12,1
126,1±1,5	23,3±2,4	58,5	188	14,1

When comparing ageing between WP1 and WP3 one more aspect needs to be taken into account. In WP1 the thermal and irradiation ageing were done sequentially as in WP3 simultaneously. In WP3 a comparison was done with simultaneous and sequential ageing at 125C and 228 kGy. The simultaneous treatment yielded in 154% elongation at break and tensile strength 13,1 MPa while sequential ageing 117% and 12,3 MPa. Thus ageing mode, i.e. simultaneous vs. sequential, may complicate the aging further. Both ageing at different dose rates and the sequence need further analysis during 2017.

Conclusion

Deliverables

During 2016 WP1 had the following deliverables

- D1.1.1 Start of accelerated ageing and evaluation of material properties
- D1.1.2 Evaluation of half time material properties
- D1.1.3 Evaluation of full time material properties
- D1.1.4 Compile data and analyse result
- D1.1.5 Correlate material property data and function

The start-up of the accelerated ageing in D1.1.1 was completed at a later stage than originally planned. There were difficulties in deciding the design of the test block for the tightness test. After discussing several models an agreement was reached to use the test block seen in appendix 1. The manufacturing of the test blocks and the test materials (sheets and o-rings) was completed during May and beginning of June. Start-up was done in June with leak test and other reference samples.

The deliverable D1.1.2 Half time evaluation was completed after the first radiation treatment of 2 weeks and a following heat treatment of 2 months. It was planned to go for 3 months but since the workshop was planned for in the end of September the first evaluation was done a month earlier. This will however not affect the full test. During 2016 and the beginning of 2017 the remaining evaluations will be completed. The full time evaluation D1.1.3 is pushed to February to be able to have a full 6 months in heat treatment. The second last evaluation was done in the middle of January and presented in this report as evaluation 3. The compilation of the data and the correlation between a function and a property in accordance to deliverables D1.1.4 and D1.1.5 is presented in this report. A revised report will be issued after completion of evaluation 4, final evaluation.

Goals

The first goal of this work package was to correlate a function, in this case tightness, to a material property. The tightness failed for the first time for the o-ring running in 140 °C (both irradiated and not irradiated) at evaluation 3. This is after 5 months of heat and 4 weeks of irradiation. The material property is compression set (105%), hardness (80), elongation at break (50%), tensile strength (7,5 MPa) and DSC (not yet measured). As can be seen in evaluation 2 for the same temperature the function is still working even though material property for compression set being above 90% and elongation at break with a decrease of 41% thus indicating severe material degradation. This indicates that very high material degradation is needed before the o-ring stops to function. The NMR indicates that there are differences

between the irradiated an non-irradiated samples. It is difficult to see though how this would help the end of life estimation but a further analysis to the peak in the irradiated samples would be of interest. An evaluation of the o-rings that started to leak would also be of interest to see if the peak grows.

No experimental test has been done using material from a power plant as planned in the second goal. The pre study in WP2 will show what material is available and after that a small scale test can be started in WP1 to achieve the goal to validate the test method for the function of tightness. This will further be strengthened once the modeling in WP1 task 1.3 has been compared to the result form the small scale test. If a leaking, or otherwise failed polymeric component, can be found in the power plants it would be interesting to have those in the small scale test as well.

The third goal is planned for during 2017 and the beginning of 2018. Data gathered in the second ageing run using o-rings with cord diameter of 7 mm will provide needed data to be able to build the model using Finite Element Method (FEM).

The fourth goal has not been planned for during 2016 and will be initiated during 2017. A master thesis student will join SP to work with this project and also with the deployment in the industry.

The Arrhenius diagram shows 3 different activation energies for the 3 different temperatures. Looking at the curve with or without radiation there is very little difference indicating the gamma radiation absorbed during normal service life to have little effect in the overall change in material property on a macro scale. For the second ageing test a change in sampling will be done due to this. As it was tested in the first ageing the sampling was taken after radiation plus heat. In the second aging the sampling will be done directly after irradiation to see if a larger difference can be seen.

An evaluation of material properties looking at thickness profile of the o-ring was not done since the samples where thin (3,5 mm). The expectation on the samples was that it would be difficult to see the difference on the surface compared to the bulk of the o-ring. . This will however be studied in the next ageing test where the thickness will be around 7 mm.

End of life

The end of life criteria as it seems for this EPDM o-ring is when the material properties are:

Table 8. Summary of properties for the initial value and for when it has reach the end of life for the function tightness.

Property	End of life	Initial value
Compression set	105%	4,9%
Hardness	80	72,3
Elongation at break	50%	182%
Tensile strength	7,5 MPa	12,8 MPa

This is when the function of the o-ring stops to work. This has however yet only been reached for the ageing running in 140 °C. By looking at the trends for the ageing running in 90°C and 120°C it may not be reached in the last month of aging. A faster degradation could occur so until the last evaluation has been completed it cannot be said for sure that it will not reach the end of life criteria.

References

[A] van Duin, Geelen. 2002. Chemistry of EPDM Cross-linking. KGK Kautschuk Gummi Kunststoffe, Volume 55, Number 4, pp. 150-156.

[B] ISO 4097. Rubber, ethylene-propylene-diene (EPDM) - Evaluation procedure. 2014.

[C] Energiforsk report 2015:157 Acceptance Criteria for polymers in nuclear application

[D] E. Linde et.al 2015 Non-destructive condition monitoring of aged ethylene-propylene copolymer cable insulation using dielectric spectroscopy and NMR spectroscopy, KTH Royal Institute of Technology,

SP Technical Research Institute of Sweden
SP Chemistry, Materials and Surfaces - Polymer and Fiber

Performed by

Signed by: Marcus Granlund
Reason: I am the author of this document
Date & Time: 2017-02-01 15:46:10 +01:00

Marcus Granlund

Examined by

Signed by: Anna Jansson
Reason: I am the author of this document
Date & Time: 2017-02-06 10:00:51 +01:00

Anna Jansson

Appendices

Appendix 1, Samples and test block

Figure 1. The above pictures shows the test block taken apart (a,b) and mounted together (c). The last picture (d) shows the test block when in place at the tightness test. The material is Stainless steel 316L.

Appendix 1

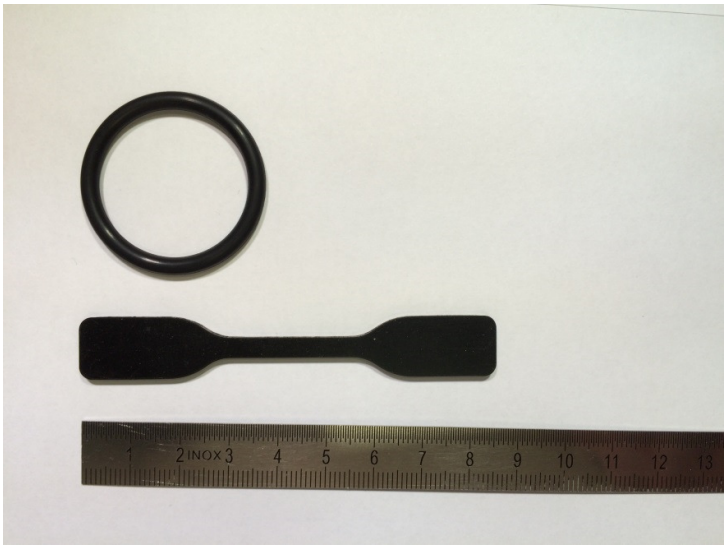


Figure 2. The dumb bell used for tensile test and DSC analysis. The o-ring used for tightness test and compression set.

Appendix 2, DSC summary

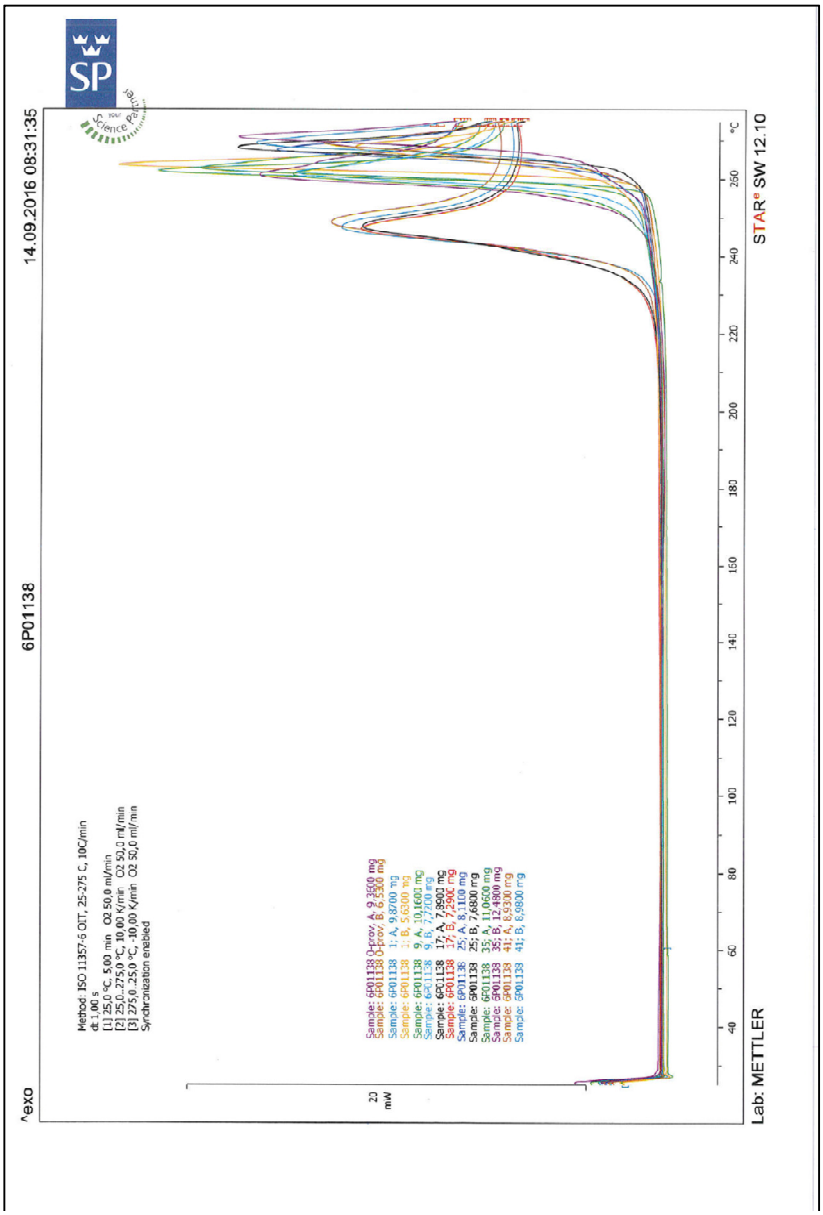


Figure 1. DSC data from sampling 0 and 1.

Appendix 3, Nuclear Magnetic Resonance report

Diana Bernin, Swedish NMR Centre

Diana Bernin, Swedish NMR Centre

Nuclear magnetic resonance (NMR) measurements on aged and non-aged EPDM to monitor the impact of aging

The Swedish NMR Center received three samples in form of O-rings (6P01138):

1. 0-prov
2. 120°C
3. 120°C and 2 x rad

To access the impact of aging, two different approaches were conducted: magnetic resonance imaging (MRI) and magic angle spinning (MAS) solid state NMR.

MRI:

The MRI experiments were recorded at a temperature of 50°C. Roughly 1 cm of O-ring was placed in a 5 mm NMR tube. The T_2, which was reported on in Paper (email), could not be measured because the T_2 is very short to be able to be evaluated trustworthily. The T_2 is generally extracted from fitting 8 or more intensities versus echo time to an exponential function. However, the T_1 could be measured, which showed a bi-exponential behavior for all three samples i.e. there are two "species" in the sample with different T_1.

Evaluation of T_1: Intensities were regressed to increasing repetition times t using $a_1*(1-b_1*\exp(-t/T_{1\_1})) + (1-a_1)*(1-b_2*\exp(-t/T_{1\_2}))$ where a_1 is the fraction of T_{1_1} and b's a scaling factor, which are experiment dependent.

16 images with varying t were recorded with a slice thickness of 2 mm and 32 x 32 points. An example for prov 3 is shown in Figure 1. The voxel resolution is 0.31 mm. The intensity of the same voxel in the 16 images was fitted to the aforementioned equation, resulting in a_1, T_{1_1} and T_{1_2} maps.

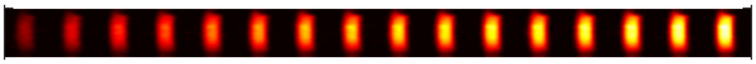


Figure 1: 16 images with varying t.

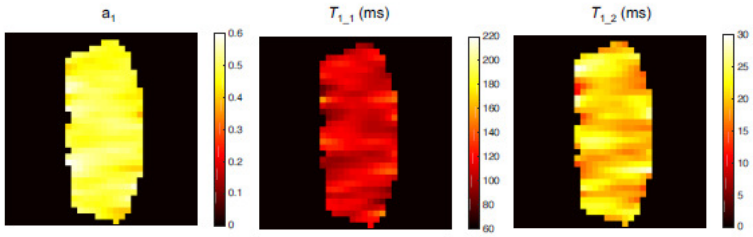


Figure 2: a_1, T_{1_1} and T_{1_2} maps of 0-prov. The size of each map is 10 x 10 mm.

1

Appendix 3

Diana Bernin, Swedish NMR Centre

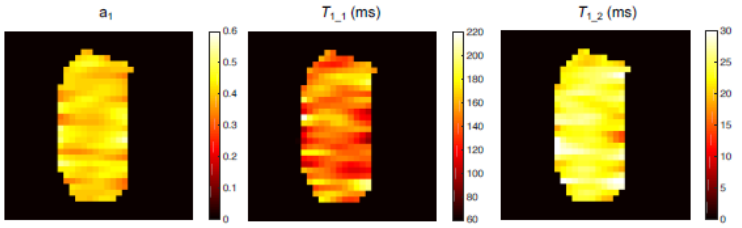


Figure 3: a_1, T_{1_1} and T_{1_2} maps of prov 6 (120°C + 2 x rad). The size of each map is 10 x 10 mm.

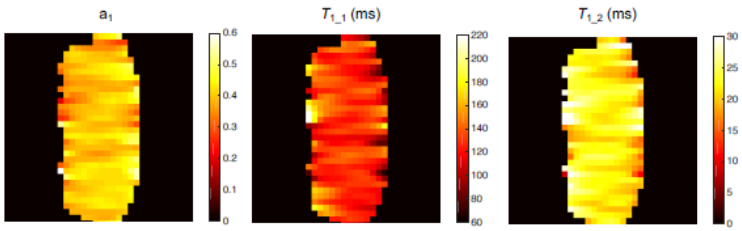


Figure 4: a_1, T_{1_1} and T_{1_2} maps of prov 18 (120°C). The size of each map is 10 x 10 mm.

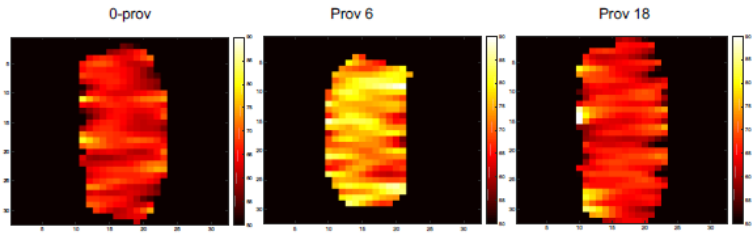


Figure 5: Average calculated as follows $a_1*T_{1\_1}+(1-a_1)*T_{1\_2}$. The size of each map is 10 x 10 mm.

The T_1's appears to be different depending on the treatment. In general the T_1's are longer for the treated samples. However for the average T_1, prov 6, which was in addition irradiated, sticks out while prov 18 is similar to the 0-prov.

Appendix 3

Diana Bernin, Swedish NMR Centre

MAS:

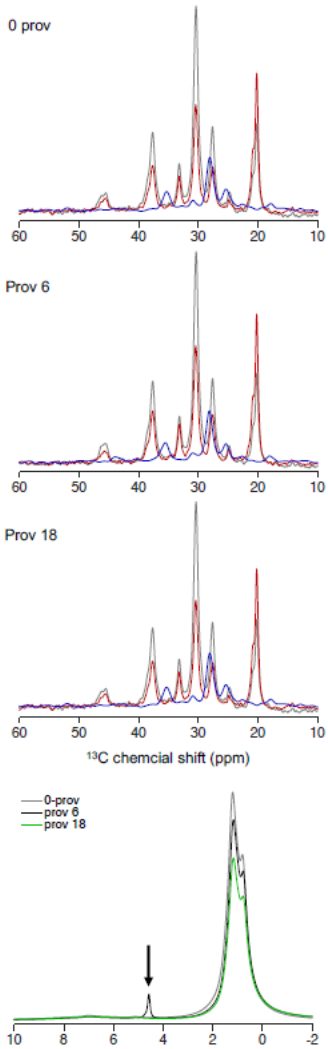


Figure 6: CP (blue), INEPT (red) and single pulse (gray) ^{13}C spectra for 0-prov, prov 6 and 18. ^{1}H spectra for all three samples.

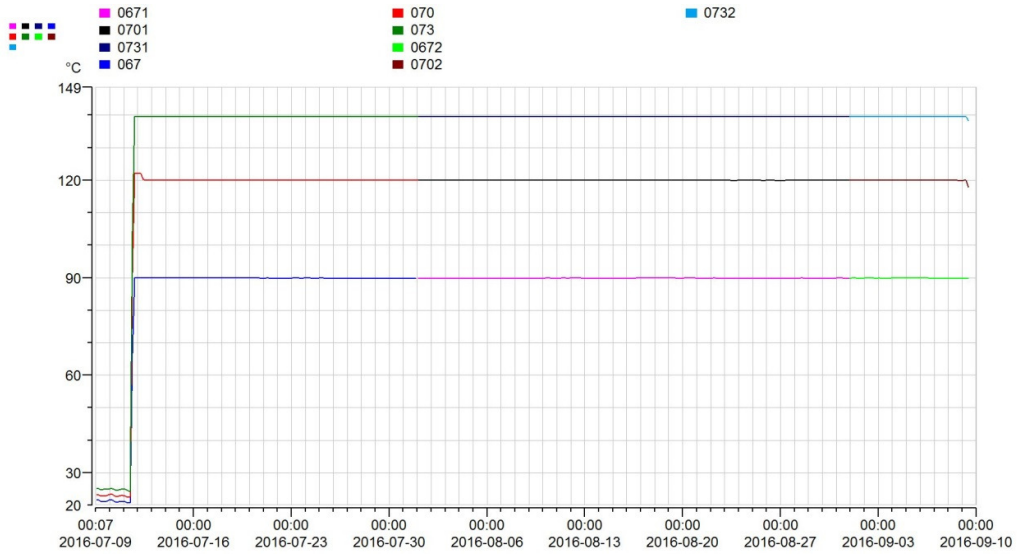
The sample was cut in a long piece and put into the rotor. All experiments were recorded at 15 kHz magic angle spinning speed. The ^{1}H spectrum was not referenced and all ^{13}C spectra were referenced to Adamantane. ^{1}H was a single pulse experiment while ^{13}C was recorded in a single pulse and polarization transfer (INEPT and CP) manner.

Figure 6 shows the ^{13}C spectra, which are overall very similar. However, the peaks belong only to the EPM chain and the diene peaks, which resonate at ~110 and ~143 ppm are not visible most likely because of a too low amount. The ^{1}H spectra of prov 6 reveals a peak, which is neither found in the spectra of 0-prov nor prov 18. The ^{1}H chemical shift is not referenced because I didn't expect any difference there. Thus without any further studies, it remains unassigned. Could it be water or another small molecule that was formed during radiation? This small molecule might also explain the longer T_1 for prov 6.

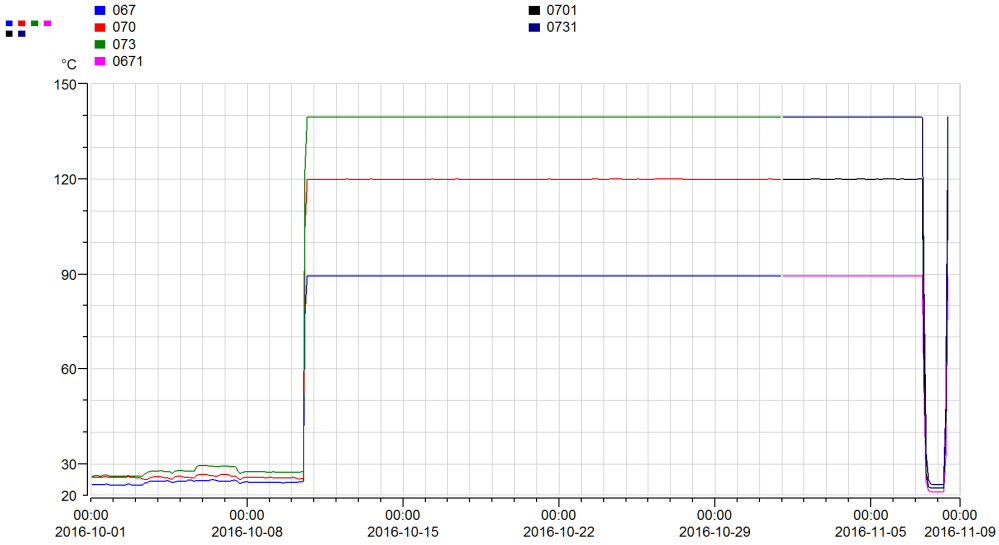
3

Appendix 4, Logging of temperature

067 used for 90°C, 070 used for 120°C and 073 used for 140°C.



Figur 1. 2016-07-09 – 2016-09-10.



Figur 2. 2016-10-10 – 2016-11-10.

Temperature curve for the last two heat treatment will be included in the revised report.

Appendix 5, Dose distribution

Radiation Sources

The Special Form cobalt-60 sources used in the Gammacell 220 *Excel* are double encapsulated in stainless steel and held in a source cage.

Certification and Documentation

MDS Nordion tests each source to ensure freedom from leakage and contamination. A complete package of information including a leak test certificate, and a measurement certificate of activity and central dose rate accompanies every Gammacell 220 *Excel*. As well, a Declaration of Conformity to the appropriate Machinery Directive and Safety of Machinery Standard will be issued for European customers.

A map of the absorbed-dose distribution is available upon request.

Customer Requirements

Customers must obtain a radioactive materials possession license (or equivalent) before the Gammacell 220 *Excel* can be shipped.

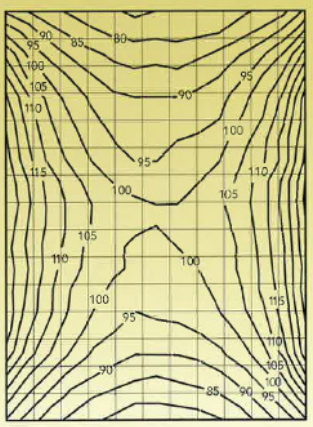
MDS Nordion helps prepare license submission documents required for radioactive materials possession. When applying for a license, customers should quote 10% more activity than ordered to allow for source loading tolerances.

Shipping Information

The Gammacell 220 *Excel* is shipped in a package that meets the requirements of the U.S. Department of Transport, the Atomic Energy Control Board of Canada and complies with IAEA regulations for the safe transport of radioactive materials (1973 Edition, as amended).

The unit with its cobalt-60 source is shipped in one package which can be handled with normal lifting and moving equipment. The shipping weights and dimensions are as follows:

Weight	**4400 kg**	(9700 lb.)
Height	**1700 mm**	(67 in.)
Base	**1560 x 1090 mm**	(62 x 43 in.)



Typical dose distribution illustrates an arbitrary vertical plane through the central axis. All values in percent are relative to the central dose.

Dose Distribution

The Gammacell 220 *Excel* has the typical dose distribution shown on the left. It illustrates an arbitrary vertical plane through the central axis.