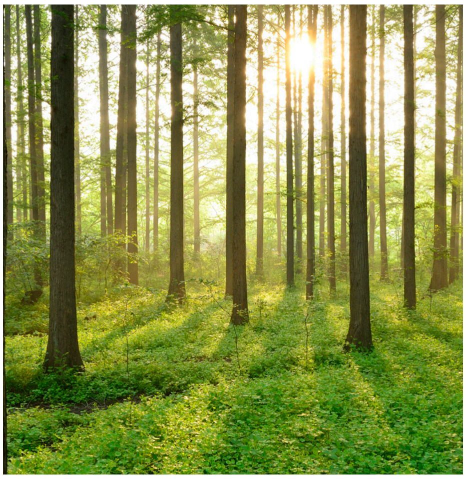
ACCEPTANCE CRITERIA FOR POLYMERS IN NUCLEAR APPLICATONS 2018

REPORT 2019:594



NUCLEAR

COMRADE

Energiforsk

Acceptance Criteria for Polymers in Nuclear Applications 2018

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ISBN 978-91-7673-594-7 |

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Foreword

Polymeric materials are widely used in nuclear power plants. Different kinds of materials are used, and the applications range from O-rings that can easily be changed to components that are more or less built in into the structure and are difficult and costly to exchange. Also, even the components that are easy to change are so numerous, that it is costly to make exchanges. As of today, components like O-rings are often exchanged according to predetermined intervals without considering the remaining lifetime of the component. If a simple and preferably non-destructive method to determine the remaining lifetime of polymeric materials could be established, this could improve both safety margins and reduce the maintenance costs.

This report summarizes the results from the third and final year of the project. There are also more detailed project reports, that can be downloaded from the COMRADE section on the Energiforsk web.

The COMRADE project was initiated following a feasibility study that was launched by Energiforsk. It is a joint project between Energiforsk and the Finnish nuclear R&D program SAFIR. The project team consists of Anna Jansson, Johan Sandström and Anna Bondesson, senior researchers at RISE (Research Institutes of Sweden) and researchers Konsta Sipilä, Jukka Vaari, Antti Paajanen, Tuukka Verho and Harri Joki at VTT Technical Research Centre of Finland.

An advisory group consisting of Annelie Jansson (Forsmark), Tommy Holm (OKG), Emil Boström (Vattenfall), Jukka Sovijärvi/Miia Lampén (STUK), Monika Adsten (Energiforsk), Peter Ekström/Elena Calota (SSM), Andrew Douglas (James Walker), Ritva Korhonen (Fortum), Stjepan Jagunic (Ringhals) and Timo Kukkola (TVO) are acknowledged for assisting the project team.

The project was financed by Energiforsk nuclear research portfolio (Vattenfall, Teollisuuden Voima, Uniper/Sydkraft Nuclear, Fortum, Skellefteå Kraft and Karlstad Energi), Finnish State Nuclear Waste Management Fund (VYR), Swedish Radiation Safety Authority (SSM) and VTT Technical Research Centre of Finland Ltd.

Monika Adsten, Energiforsk

Sammanfattning

Inom COMRADE har vi studerat hur tätningsringar i olika typer av gummimaterial fungerar under längre tid i närvaro av gammastrålning och förhöjd temperatur. Syftet med arbetspaket 1 som rapporten avser var dels att öka förståelsen för hur materialen påverkas av låga till måttliga stråldoser (29 Gy/h) som de utsätts för under drift. Dessutom korrelerades funktion hos komponenten, i det här fallet täthet, med en materialegenskap som enkelt kan mätas enligt standardmetod. Med kunskap om funktionen kan produktens bäst före datum bestämmas med större säkerhet med hjälp av materialtester.

Tre olika gummitätningar studerades i projektet, EPDM (Eten-Propen-Dien gummi), NBR (Nitril-Butadien gummi) och FKM (fluorgummi mest känt under handelsnamnet Viton). Alla materialen exponerades för gammastrålning följt av accelererad termo-oxidativ åldring vid förhöjda temperaturer. Parallellt exponerades proverna för enbart värme. Materialegenskaper liksom funktion hos tätningsringar mättes under totalt 6 månaders exponering. När tätningsringen läckte anses produktens liv vara slut och man har nått ”end-of-life” och produkten måste bytas ut. Läckage korrelerades till materialegenskaper som sättning, draghållfasthet och hårdhet.

Läckagetesterna utfördes i en specialdesignad testrigg där vattentryck applicerades läckage noterades. Efter testerna monterades tätningsringarna ut ur riggen och sättning och hårdhet mättes. Det visade sig att de O-ringar som läckte var mycket nedbrutna och sättningen var runt 100%, alltså maximalt vad som är mätbart. Sättning är med andra ord inte en särskilt känslig metod för att bedöma nedbrytning av materialen som åldrats vid hög temperatur, då sättningen ökar vid exponering för att sedan vara ganska konstant. Inget av de studerade materialen var känsliga för de stråldoser som de utsattes för under exponeringen. Relaxationsmätningar visade sig kunna fungera för att bedöma materialkvalitet.

Som jämförelse studerades O-ringar efter verklig exponering i kärnkraftverk. Ett antal O-ringar hade plockats ut och främst hårdhet mättes eftersom antal och storlek på ringarna var begränsade. Hårdhetsvärdena stämde väl överens med värdena från prover åldrade på lab.

En beräkningsmodell baserad på Finita Element Modellering utvecklades för att kunna beräkna tryck som ger läckage vid olika temperaturer. Resultaten verkar lovande men mer data och försök behövs för detta.

Summary

The COMRADE project studied how different types of rubber sealing rings perform during long periods of time in presence of gamma radiation and at elevated temperatures. The aim of the study was to increase the knowledge about the material behavior at rather low and medium radiation doses (29 Gy/h) which are comparable to radiation doses in their service environment. In addition, function of the component, sealing performance was correlated to material properties measured by standardized test methods. Knowledge about the function facilitate determination about end-of-life for the component by use of material tests.

Three rubber sealing materials were studied in the project, EPDM (Ethylene-Propylene-Diene rubber), NBR (Nitril-Butadiene rubber) och FKM (fluorine rubber, known under the trade name Viton). All samples were exposed to gamma radiation followed b thermo-oxidative ageing at elevated temperatures. In parallell the samples were exposed to ageing only. Material properties as well as function were measured during 6 months of ageing. As leakage was observed end-of-life was reached and the component should be replaced. Leakage was compared to material properties such as compression set, tensile properties and hardness at that stage of degradation.

Leakage tests were performed in a specially designed test rig in which water pressure was applied and leakage noted visually. After testing the samples were removed and compression set and hardness measured. Leaking O-rings turned out to be heavily degraded with compression set close to 100%. Hence, compression set is not suitable for measuring rubber degradation after ageing at high temperatures. Stress relaxation seems to be a better method to investigate material quality. None of the investigated materials turned out to be very sensitive to the radiation doses used.

As a comparison used O-rings collected from NPPs were analyzed. Hardness was measured because the number and size of the O-rings were limited. The hardness values corresponded well to the hardness of artificial aged and degraded samples.

A FEM (Finite Element Model) model was developed for calculation of leakage pressure of O-rings at different temperatures. The results are promising but more data and experiments are needed to evaluate and calibrate the model.

List of content

1 Background

The COMRADE project is based on input from feasibility studies from Energiforsk AB[1] and STUK and through discussions between VTT, RISE former SP and the Nordic NPPs through Energiforsk. When developing COMRADE it was understood that there are gaps in knowledge for setting functional based acceptance criteria at the nuclear power plants. Furthermore, there is a need in gaining a better understanding about polymer degradation upon exposure to different levels of low dose ionizing radiation and synergistic effects between thermo-oxidative and radiation degradation. These issues are further studied in three different work packages (WPs):

- WP1: Development of condition monitoring methods for polymeric components including low dose rate radiation exposure.
- WP2: Survey on polymeric materials available for ageing studies from Barsebäck plant under decommissioning (RISE Report)
- WP 3: Polymer ageing mechanisms and effects inside NPP (Nuclear Power Plant) containments (VTT Report)

In this report the results from WP1 and WP 2 is presented and discussed. WP1 also include development of a FEM method making it possible to calculate the service life of o-rings of different dimensions. The FEM-modelling is reported in more detail separately (RISE Report)[2].

1.1 DURABILITY AND LIFE TIME PREDICTION OF POLYMERS IN NPP:S

Plastics and rubber generally are durable materials. The durability depends on the polymer structure and additives i.e. antioxidant content. For rubber materials cross-link chemistry also have an impact on the durability. At the end of life plastics and rubbers typically becomes more brittle, and visible cracks may occur on the surface.

The most common degradation process is oxidation, reaction with oxygen leading to is an autocatalytic process, meaning that radicals formed during the ractions catalyze further degradation. The reaction is slow at the start but accelerates with the increasing concentration of resulting hydroperoxides and highly reactive radicals. In order to prevent oxidation and degradation antioxidants are added to plastics and rubber during manuafctureing. Rubber materials may also be protected by their structure, i.e. double bonds. Materials used in Nuclear Power Plants (NPP:s) usually high grade materials with excellent durability.

When designing a polymer product it is of utmost importance to estimate its service life and then stabilize the material sufficiently to last throughout the product lifetime. If the estimated lifetime is several decades, as for example in NPP:s and construction industry, accelerated test methods are necessary. Durability studies and lifetime predictions for polymeric materials are therefore

[1] Energiforsk report 2015:157, "Acceptance Criteria for polymers" Granlund et.al

[2] RISE Report 2019:19 "Simulation of rubber materialsfor seals in nuclear power plants" Johan Sandström

usually performed by studying accelerated ageing at elevated temperatures. 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 at ambient temperature using the Arrhenius equation. The reaction rate for almost all chemical reactions increases with increasing temperature. This is described by the Arrhenius equation:

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

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 a constant if the studied temperature interval is not too large. A failure criterion (ususally 50% of initial value) is set, where the material is no longer useful, and the time (t) to failure is measured experimentally (Figure 1).

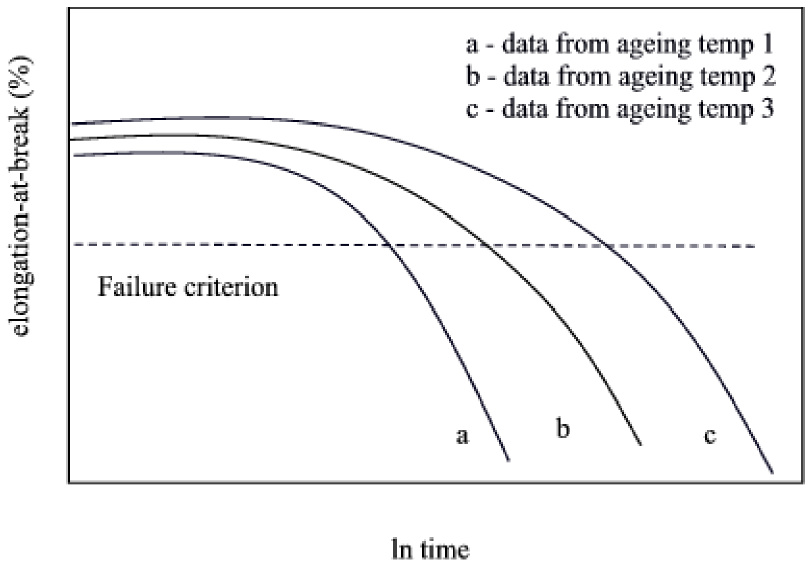

Figure 1: Elongation at break for samples aged at three different temperatures. Temperature 1, is the highest and hence the time to failure a, the shortest.

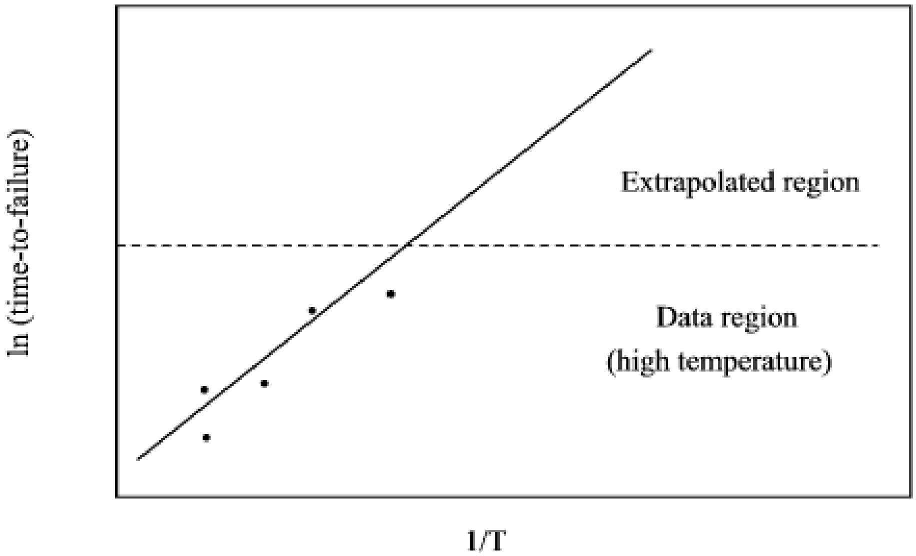

Figure 2: Schematic Arrhenius plot. The slope of the plot is equal to the activation energy.

In Figure 2, 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 be calculated from the slope of the line. Furthermore, extrapolation to other temperatures can be made, enabling lifetime prediction.

Time temperature superposition is another method to estimate the service life of a polymer. The graphs of the materials are shifted for form a master curve from which the activation energy is calculaten and life time estimation at ambient temperature may be extrapolated.

When data series has been collected for different ageing temperatures they may be super positioned by using shift factors[3]. This means that all the data points collected at different temperatures is shifted along the x-axis to create a master curve, figure 3.

[3] K. G. R. Bernstein, "Prediction of the lifetime of flourosilicone O-rings," *Polymer Degredation and Stability,* vol. 94, pp. 2107-2113, 2009.

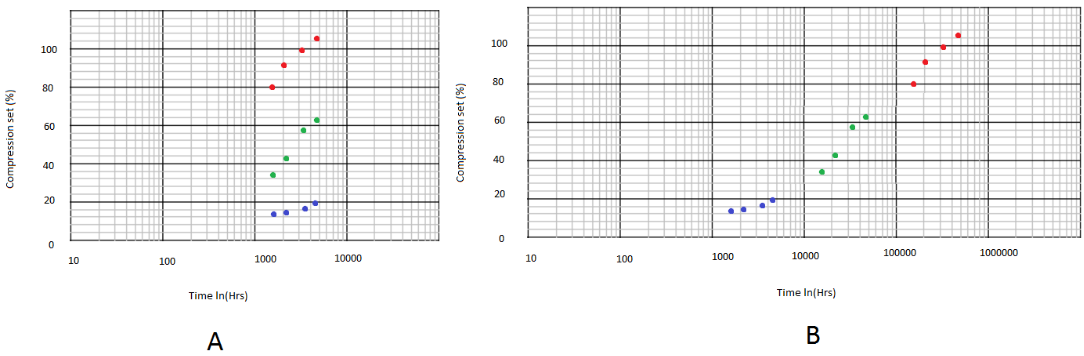

Figure 3: An example showing superpostione using a shift factor. Data from graph A to the right is shifted along the x-axis, graph B. Blue-lowest temperature. Green- medium temperature. Red- Highest exposure temperature.

The shift factors used for superposition is then plottes versus temperature and ideally a straight line is achieved. The activation energy is calculated from the slope of the straight line.

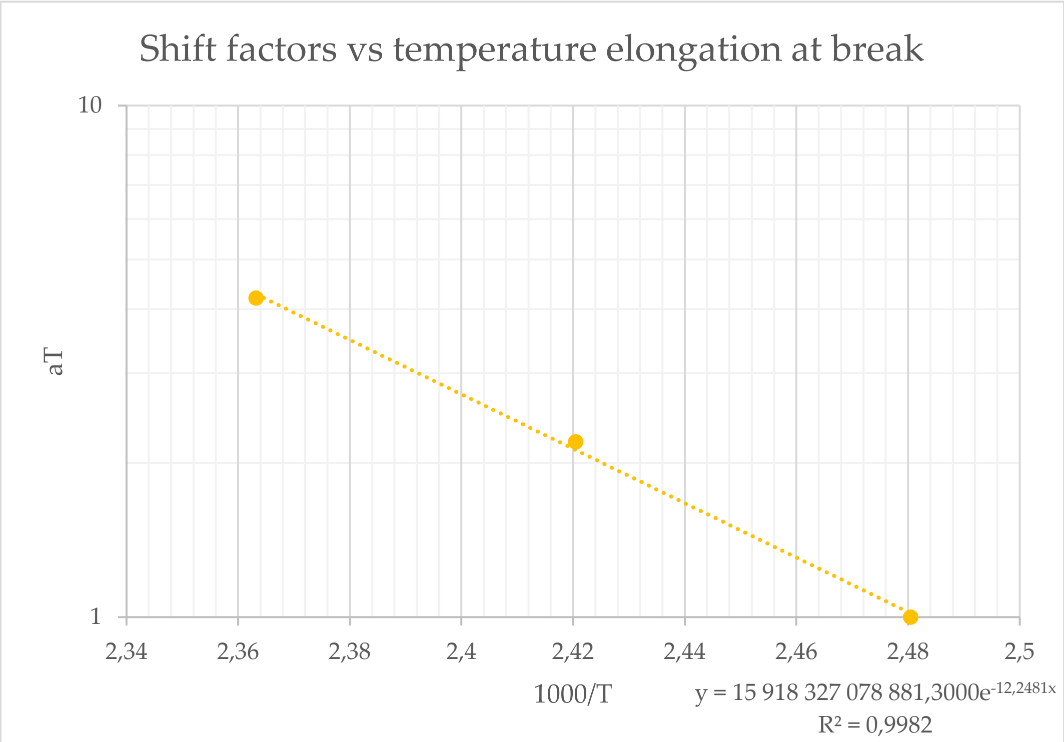

Figure 4: Activation engergy calculated from elonigation at break for EPDM material.

Extrapolations according to the described methods should, however, be done with caution, since different reactions with different activation energies may dominate at different temperatures. This gives Arrhenius plots and s with different slopes in different temperature regions. Importantly, the change in slope may occur outside the investigated temperature interval, and lifetimes estimated through extrapolation should therefore be perceived as approximations[4]. Hence, Dixon emphasizes the use of low activation energies in lifetime predictions in order not to overestimate the service lifetime[5]. The presence of antioxidants can also influence the activation energies and consequently the Arrhenius plot.

[4] Gillen Et.al. TRIP 1997:5:250

[5] Dixon R.K. ed. IEEE Transaction on Elec Insulators Vol El-15 vol 4. 1980

2 Materials

2.1 EPDM

EPDM was chosen based on a request from the Industry team, asking for investigations on EPDM.

The study focuses on O-rings exposed to accelerated ageing in heat and irradiation (gamma) according to the test scheme in figure 1. Test materials were kindly supplied by James Walker Ltd in the UK. EPDM is a high volume, specialty elastomer which is found in many various applications in buildings as roofing material, in automotive components, cable insulation material and many other applications. The material is often found in nuclear applications since it is known to be resistant to gamma irradiation. In this study peroxide crosslinked EPDM material was used.

EPDM, designated LR 9444, O-rings of two different core diameters were studied in 2016 (3,53 mm) and 2017 (5,99 mm). The reason to study two different O-ring sizes to be able to calibrate the FEM (Finite Element Method) modelling for leak tests to different O-ring dimensions. Tensile and hardness tests were performed on test slabs punched out from 2 mm thick test sheets. The results from the EPDM studies have been reported in detail in Energiforsk reports 2017:389 and 2018:486. Therefore, these results are only summarized in this report.

2.2 FKM FLUORINE RUBBER

FKM is of known under the trade name Viton and is a fluorine rubber. There are many different Fluorine elastomers and they are typically used in high temperature applications or harsh environment where chemical resistance is necessary. Additives are used in minor amounts to design hardness and compression

For this material O-rings of 3,5 mm cross section and 2 mm test sheets supplied by James Walker Inc were studied. The material was a Fluorocarbon FR 10/70 but no detailed information about the material composition was available.

2.3 NITRILE RUBBER

Nitrile rubber is a co-polymer based on butadiene and acryl- nitrile and is a common rubber material used in for example O-rings. Typical for this material is oil resistance and some NBR materials are durable at rather high temperatures. Carbon black, plasticizers and oils are often used to tailor hardness and facilitate processability. The material also accepts many anti-degradants which may improve the stability of the material.

The larger O-ring type (5,99 mm core diameter) was studied for Nitrile rubber and 2 mm thick test sheets were used for tensile test specimen. The material was designated Nitrile NM27/70.

3 Exposure

All rubber materials were exposed to ageing in two parallel sequences, one using irradiation – heat – irradiation – heat and one with only heat. Figure 5 below shows the combined heat and radiation exposure. 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), see fig 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 diameter: 15.2 cm. This sets limitations on the maximum O-ring size to be exposed. The O-rings were exposed inside a leakage test rig designed by RISE as seen in fig 6.

The irradiation treatment is done in 2 sequences, as explained in figure 5, 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.

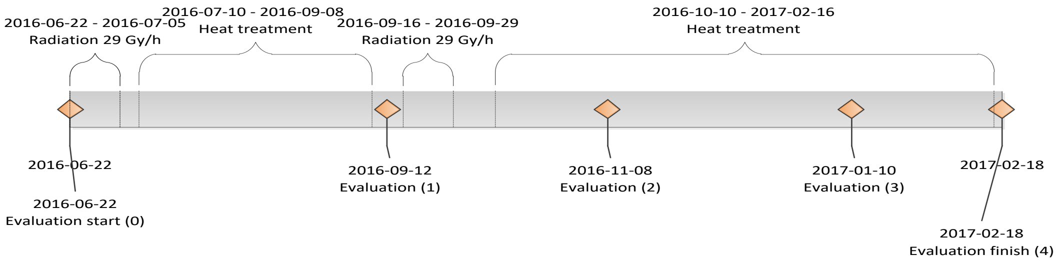

Fig 5: Exposure scheme for radiation and oven ageing.

In addition to the radiation the samples were aged in heating cabinets in air at three different temperatures. O-rings were aged inside the leak test rigs and the dumb-bell pieces were hanging freely. The heating cabinets, ma used had controlled laminar air flow and the temperature did not vary more than ± 2°C. Tests were performed after the first irradiation followed by 3 months of ageing. Thereafter a second irradiation takes place and is then followed by accelerated ageing. Sample 3, 4 and 5 is taken after one, two and three months of additional ageing (Fig 5). Total ageing time is six months.

The ageing temperatures used were chosen based on the heat resistance of the polymers, according to the table:

Material	Temperature 1 (°C)	Temperature 2 (°C)	Temperature 3 (°C)
EPDM	90	120	140
FKM	160	180	195
NBR	60	80	100

Fig 6: Samples placed in the gamma-cell at VTT.

4 Analyses

The samples were evaluated by several different methods in order to verify the test results and properties of the material to their function, in the case of an O-ring; leakage

4.1 LEAKAGE AND COMPRESSION SET

Compression set is the most central property of sealing rubber products since the permanent set of a product decreases the sealing performance. ISO 815 describes the test in which a circular rubber piece or an O-ring is compressed by typically 25% of initial thickness (for hardness below 80 IRHD). The compression set rig consists of two metal plates and a spacer to achieve the correct compression of the sample. The samples are exposed to irradiation, elevated temperatures mounted in the test rig. After a specified exposure time the test piece is released and allowed to relax for 30 minutes. Initial sample thickness is compared to final thickness after exposure and relaxation. High quality rubber shows low set, i.e. thickness close to initial thickness. Permanent set may be caused by crosslinking reactions which occurs during relatively short period depending on the temperature. Upon polymer degradation, which is a long term process the elasticity decreases due to chemical changes in the polymer such as chain scission, and as a consequence, the sealing performance decrease. Poor compression set may also be caused by crystallization or high filler concentration and loss of low molecular plasticizer. Compression set is calculated according to the equation below and is reported in %:

$$\frac{h_0 - h_1}{h_0 - h_s} \times 100$$

h_0 is the initial thickness of the specimen, in millimeters

h_1 is the thickness of the specimen after recovery, in millimeters

h_s is the height of the spacer, in millimeters

In this project compression set was measured on the O-rings mounted in the specially designed test rigs shown in figure 7 below. This is not according to standard method but the reason for this was to measure compression and leakage on the same test specimen.

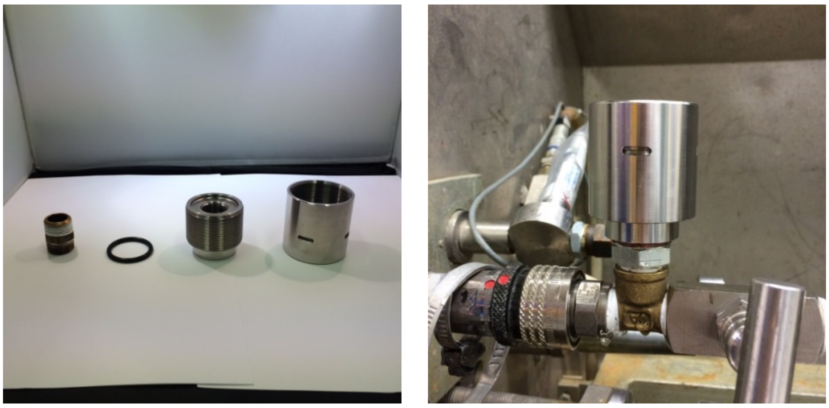

Fig 7: Test rig for leakage tests. To the left test rig before mounting the O-ring and to the right the rig is mounted for leakage test.

The test rigs with O-rings inside were exposed both to heat and irradiation according to fig 7. Samples were mounted in the test equipment and water pressure was applied. Leakage was observed as water appeared in the holes in the test rig.

4.2 TENSILE TESTING

Tensile testing was performed on a Zwicki Z1 tensile testing machine according to ISO 37 on dumb- bell shaped test specimen punched out from 2 mm thick test slabs. The preload was 2 N and the test speed was 500 mm/min, stress-at-break and elongation-at- break was reported. Elongation was measured by using a long stroke extensometer.

4.3 HARDNESS TESTS

Hardness, IRHD (International Rubber Hardness Degrees) was measured according to ISO 48, method M (micro) on the 2 mm thick tensile test specimen. A ball indentor is applied on the test piece surface and the difference between a small contact force and the large indenting force is measured. In the micro test the reading is multiplied by a scale factor 6 and the IRHD value is obtained from tables in ISO 48. The test is convenient since it is quick and small samples can be measured. All tests were performed using a Bareiss hardness tester.

4.4 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

In DSC evolved or absorbed energy in a small sample is plotted versus time or temperature. Exothermal and endothermal changes in the material such as, melting, crystallization and oxidation is recorded. Oxidation is the most common degradation mechanism in plastic and rubber degradation and the oxidation induction time or temperature as measured by DSC is an indirect measure of the residual active antioxidant in a material before and after ageing. More antioxidants and stability in the material push the oxidation of the samples towards higher oxidation temperatures or longer times at elevated temperatures. In this study

Oxidation Induction Time (T_{ox}) was measured on the EPDM material. The temperature was increased by 10°C per minute and the onset temperature where oxidation starts is reported. All samples were analyzed using a Mettler DSC1 with oxygen as purge gas.

4.5 STRESS RELAXATION

A complementary measurement to compression set is stress relaxation. Instead of dimension change of the sample, the sealing force is continuously measured over time. The samples are initially compressed to 25% of initial thickness and the compression force is continuously measured, figure 8 shows a test rig. The measurements are usually performed at elevated temperature and the accelerated aging is performed simultaneously with the analysis. Test results are usually reported as F/F0 where F0 is the maximum initial force recorded. End of life for a sealing material is typically set to be F/F0 = 50 %. Whether this is correct needs to be verified by for example leakage tests. When the sealing force is zero there is no physical sealing.

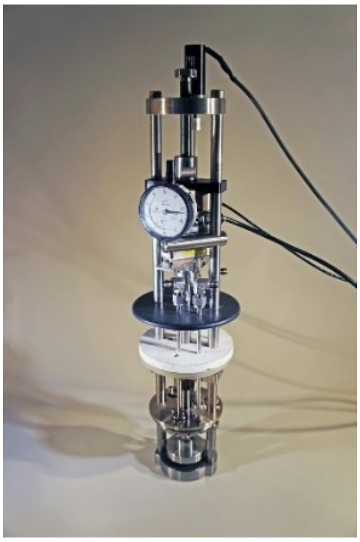

Figure 8: Compression Set test rig. The samples are mounted between the test plats on the bottom of the rig, which is then placed in an oven.

Stress relaxation test has been performed in parallel to the oven ageing for the EPDM material, using the same oven temperatures but without gamma radiation. Tests were performed according to ISO 3384 method A, with the exception for the minimum sample thickness of 6 mm when the 3,5 mm O-rings were measured. Elastocon EB02 stress relaxation test rigs were used and placed in a cell oven from the same manufacturer. The test results were mainly used for FEM modelling of leaking.

5 Results

5.1 EPDM O-RINGS

EPDM was supplied as 2 mm thick test slabs and O-rings two dimensions 2,99 mm and 6 mm cross section diameter, respectively. Results from the EPDM O-rings are previously reported in Energiforsk Report 2017:389[6]. Therefore, only the most important results on the EPDM material are reported here.

The results show that the relatively low radiation used in this study has no effect on the material. As expected, the higher ageing temperatures i.e. 120°C and 140°C have more effect on the material properties. It is important to remember that different oxidation and degradation reactions dominate at different temperature and the data from the highest ageing temperatures are uncertain when extrapolating and predicting the durability at service temperature.

5.1.1 Leakage test and Compression Set

Leakage were observed after ageing at 140°C after five and six months. At that stages Compression Set was around 100%, meaning no elasticity or sealing performance in the O-ring. Leakage and compression set was measured on O-rings after exposure inside the test rigs. Corresponding elongation-at-break had decreased from around 200% to only 20-40 % and hardness of the material had increased from 70 to between 80-90 IRHD (International Rubber Hardness Degrees). Elongation and hardness were measured on dumb-bell shaped test pieces. The abovementioned test results could be used as end of life criteria since they correspond to the leakage.

Leak test results for EPDM are summarized in table below:

O-ring size	Exposure 5 months 140°C	Leakage 6 months 140°C
3,53 mm diameter, radiation exposure	Leak 30-35 bar	Leak 5-50 bar
3,53 mm diameter, heat only	Leak 30-35 bar	Leak 25-90 bar
5,99 mm diameter, radiation exposure	Leak 6 bar	Leak 6 bar
5,99 mm diameter, heat only	Tight	Leak 6 bar

All compression set results for the small EPDM rings are shown in figure 9 below. The results are the same for the large O-rings and deviations within the sources of error. After initial heat exposure compression set increases most probably due to additional curing at elevated temperatures.

[6] www.energiforsk.se Report 2017:389

The data in fig 9 below is achieved from measurements on the O-rings exposed in leakage test rigs. These measurements are not as accurate as if standardized test rigs are used. The dimensions of the test rigs deviates, and after heat exposure some of the test rigs were rather difficult to open and the O-rings may have been distorted.

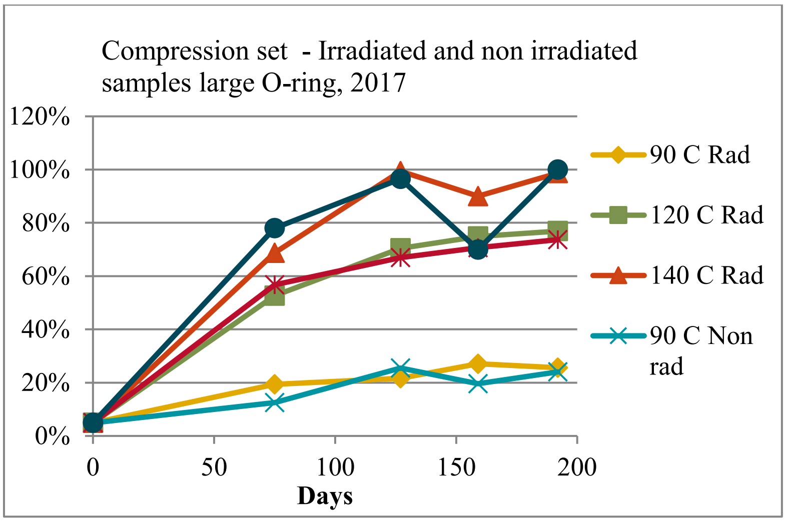

Figure 9: Compression Set for large O-rings.

The compression set results were shifted and used to calculate service life according to the time-temperature superposition method. Figure 10 shows the master curve and figure 10, compression set vs log time.

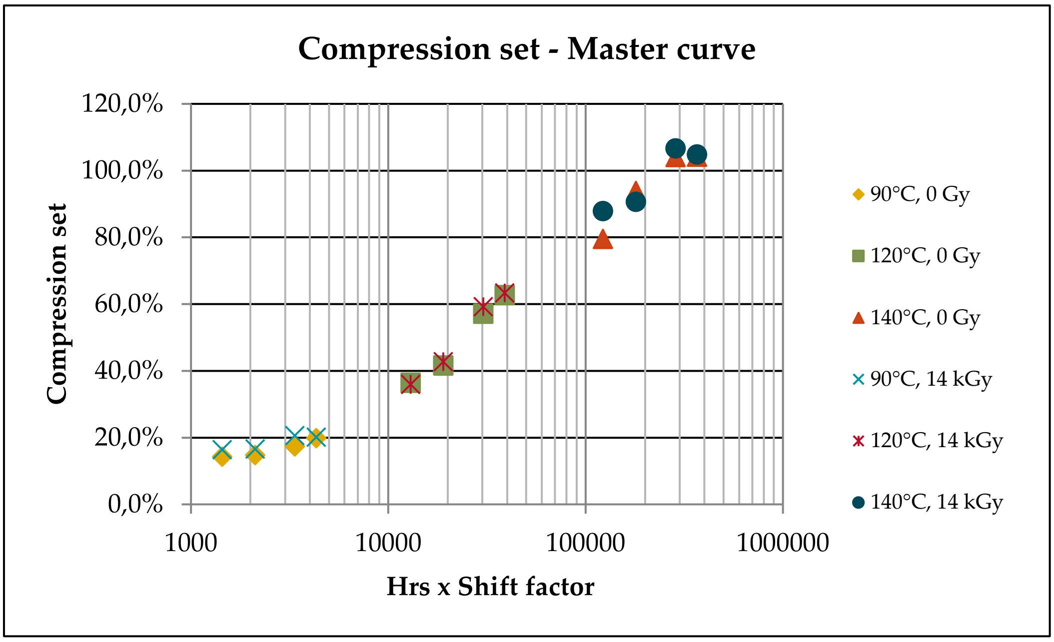

Figure 10: Master curve for the small size O-rings.

5.1.2 Tensile testing

For both EPDM test series tensile tests were performed on dumbbell shaped test specimen and the results are very similar and within sources of error and therefore only one of the two test series are reported here. Results from 2016 is reported in Energiforsk report 2018:486[7]

Decrease in stress and strain at break is caused by degradation in the material, chain scission in the polymer chain and the crosslinks. Ageing at 90 and 120°C does not cause any significant decrease in tensile strength. The samples exposed to 140°C are significantly more degraded.

5.1.3 Hardness

Like for tensile testing hardness were measured on 2 mm thick test slabs in both EPDM test series. Results from 2017 is reported here.

Hardness increases upon ageing as expected and the increases from around 70 IRHD up to 75 and 80 IRHD for 120 and 140°C respectively. Also, at 90°C ageing a minor increase in hardness can be observed, as seen in figure 11.

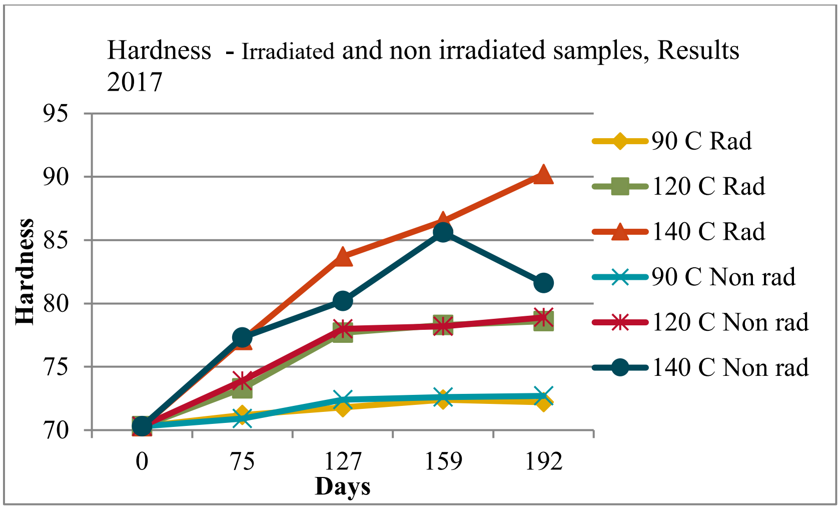

Figure 11: Hardness results for EPDM.

5.1.4 Differential Scanning Calorimetry

Antioxidants are used in limited amounts in EPDM rubber since residual double bonds act as a stabilizing functional group in the material. Since the studied material is high quality material, antioxidants are most likely added to some extent. Some antioxidants i.e. hindered amines are known not to function efficiently at elevated temperatures and may explain the results. No oxidation is noticed at 90°C and gradual decrease occur at 120°C. At 140°C the oxidation

[7] Energiforsk report 2018:486 "Acceptance Criteria for polymers in Nuclear applications" Molaner et.al.

temperature remains constant after the initial drop (fig 12), and at the last data points oxidation temperature increases. This may be explained by the so called "seashell effect" meaning that a protecting layer is formed on the material surface which prevents oxidation. This effect is well known in the rubber industry and is typically observed for EPDM exposed to 140°C.

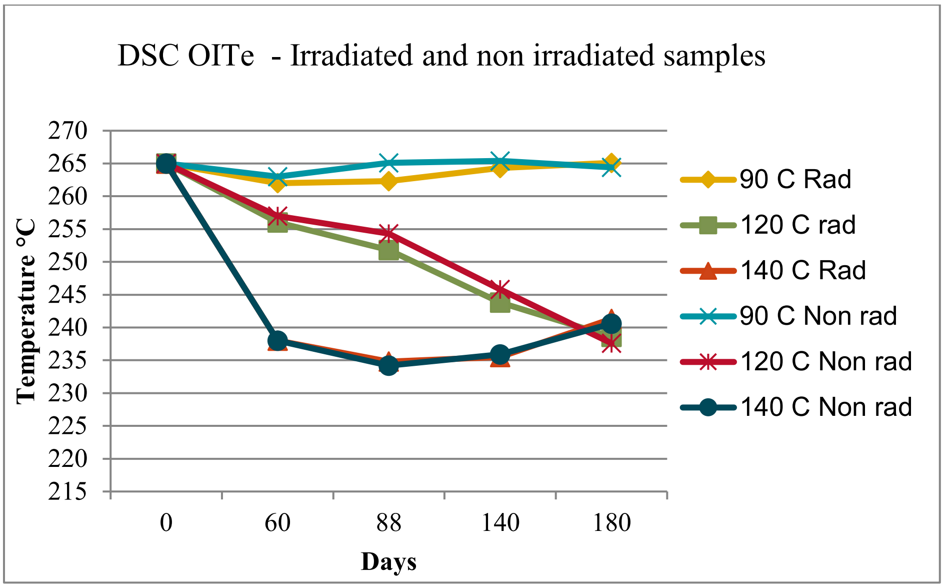

Figure 12: Oxidation Induction Temperature for EPDM.

5.1.5 Stress Relaxation

In this project stress relaxation was measured at three different temperatures, the same temperatures as for the oven exposure. Figure 13 shows a plot where recorded force F/F_0 is potted versus time at 140°C. End of life value is typically set to F/F_0=50 but whether this is the true end of life is not verified in most cases. Stress relaxation data from EPDM was used for life-time prediction and in-data for FEM modelling.

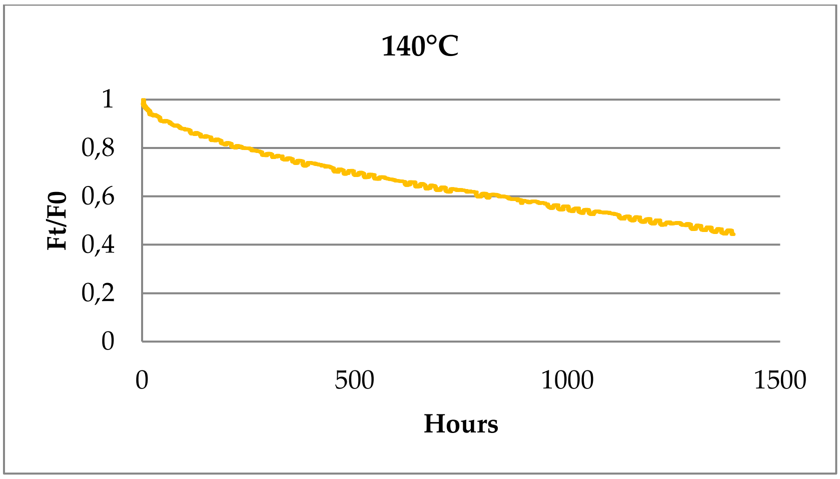

Fig 13: Example of Stress relaxation curve for EPDM.

5.1.6 Life-time prediction

When a material is aged at elevated temperature the material properties deteriorate. Different properties change more or less rapidly at elevated temperatures. For example, tensile elongation is more sensitive to oxidation and chain scission compared to for examples OIT. Therefore, it is important to choose a material property relevant for the use of a product when selecting a test method for calculation of activation energy and life-time prediction. For an O-ring compression set or Stress relaxation are relevant material properties to study when performing life-time predictions. The table below shows different activation energies for EPDM based on compression set and stress relaxation tests performed in the project.

Sample	Test method	Activation energy E_a kJ/mole	Calculated Service life at 50°C, years
Small O-ring	Compression Set	103	460
Large O-ring	Compression Set	82	114
Circular test piece	Stress relaxation	69	34

The results in the table are based on an ageing at 120°C and that end of life is reached after six months of oven ageing. The results clearly indicate that low activation energies should be used in order not to over-estimate the service life.

5.2 FKM RUBBER

FKM is a fluorine rubber often known under the trade name Viton and it is known for high resistance at high service temperature and in harsh environment. Sealing material and O-rings are common applications for FKM rubbers.

5.2.1 Leakage and Compression Set

The leakage tests proved the excellent durability at high temperatures for the FKM material studied in this project. No leakage was observed even after 6 months of ageing at 195°C and exposure to radiation.

Compression Set measurements show that gamma radiation has some impact on the test result at ageing temperatures 160 and 180°C, the compression set increased somewhat for those samples exposed to gamma radiation (Fig 14 below). At the highest temperature 195°C the effect of gamma radiation was not observed.

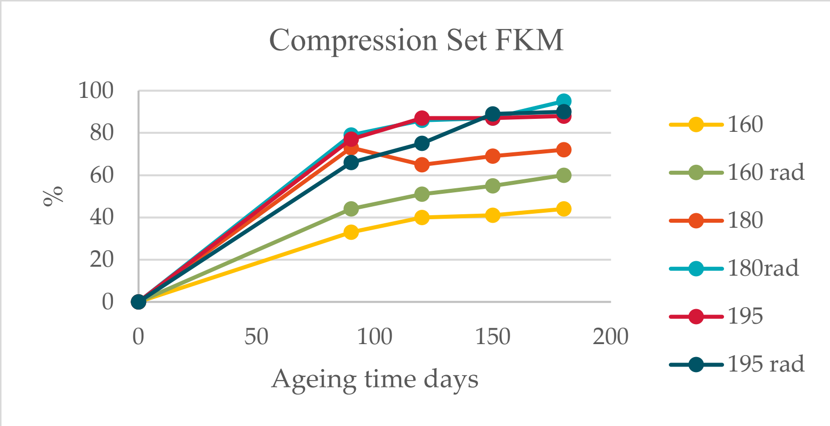

Fig 14: Compression Set for FKM after exposure to heat and gamma radiation.

Since leakage was not detected for the studied FKM material end of life criterium was not possible to determine.

5.2.2 Tensile testing

As shown in fig 15 the tensile elongation for the FKM (Viton) material did not change significantly and neither did stress at break.

The ageing temperatures were not high enough to degrade this very stable material. If the ageing temperatures were elevated further hydrofluoric acid is formed which is very harmful and higher ageing temperature is therefore not recommended. The maximum temperature for the heating cabinets were 195°C.

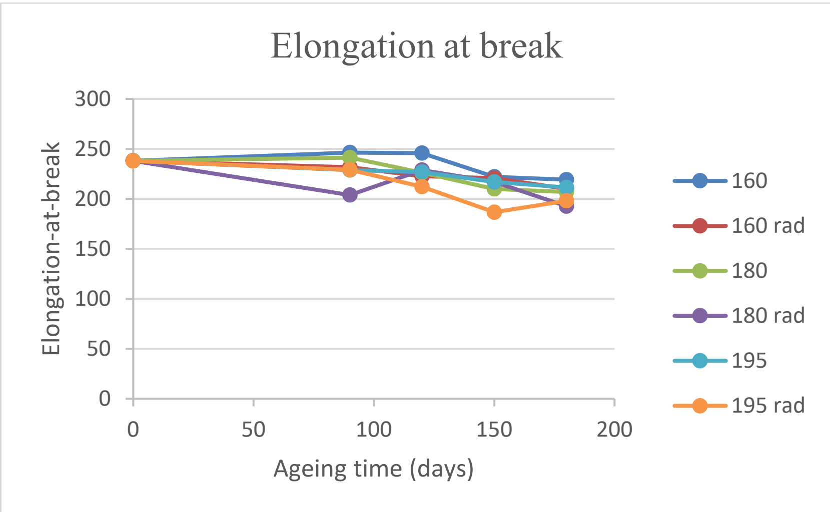

Figure 15: Elongation at break for FKM rubber.

5.2.3 Hardness FKM rubber

Hardness increases after ageing, but the increase is very moderate, only 3 hardness degrees. The most pronounced increase is observed after the first ageing period. Part of this increase may be caused by physical changes in the material.

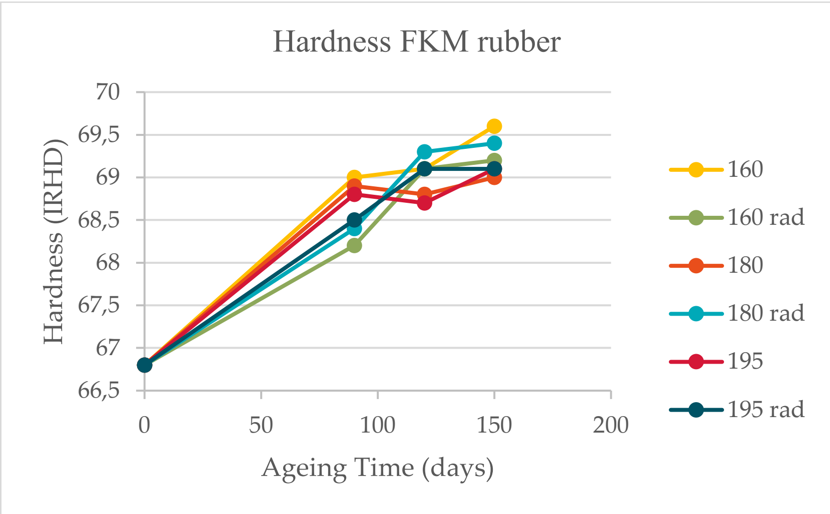

Fig 16: Hardness for the FKM rubber.

5.2.4 Stress Relaxation

One stress relaxation experiment was performed on the FKM material, mainly to see whether the test method was sensitive enough to detect degradation of a very stable material.

Circular samples with diameter 16 mm and thickness 6,5 mm were cut from a test sheet and sent to Elastocon AB for a stress relaxation test at 195°C for 1000 hours, approximately 41 days.

Median stress relaxation after 1000 hours was 37%. Stress relaxation is measured at the test temperature, 195°C. As a rule of thumb stress relaxation of 50 % is set as end of life criterium. For a stable material as FKM a very long exposure is needed to reach this value.

5.3 NITRILE RUBBER

Nitrile rubber was the final material to be studied in the COMRADE project. The large O-ring type, with 5,99 mm core diameter was used. As for the other materials dumb-bell shaped test pieces were used for hardness and tensile tests.

5.3.1 Leakage and Compression Set

Leakage was observed after 6 months of ageing at 100°C. This sample was not radiated. Even if several samples were significantly degraded in terms of increased hardness and decreased tensile properties, no leakage was detected. One explanation for this may be explained by the fact that the samples tend to stick to the test rig surface.

Compression set values increased rapidly to 90% after ageing at 100°C and if compression set is used to indicate end of life, i.e. leakage the Nitrile rubber in this investigation would leak after four and five months of exposure at 100°C as well.

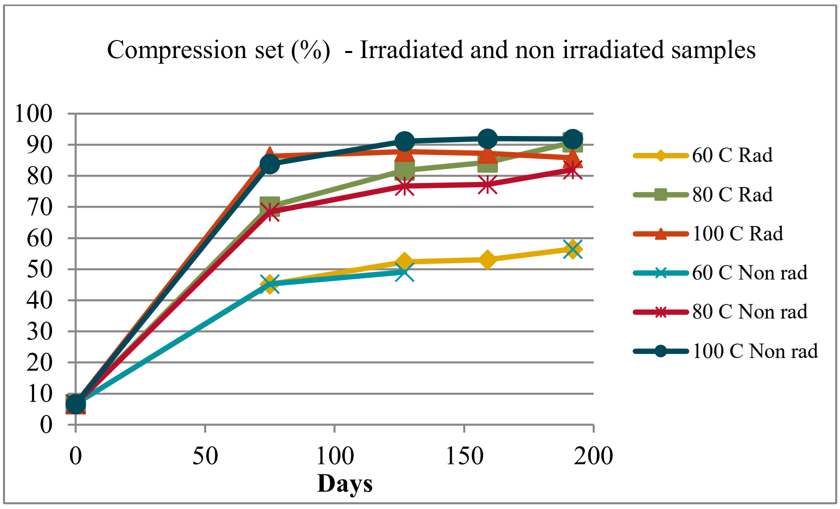

Figure 17: Compression set values for Nitrile rubber.

At 80 and 100°C gamma radiation seems to have some effect on the compression set. The radiated samples showed somewhat higher compression set values compared to the non-irradiated samples.

One data point in figure 17 is missing (60°C radiated sample five months exposure) and the reason for this is that the test rig was stuck and not possible to open

5.3.2 Tensile Testing

Elongation at break decreases initially and then remains at a rather constant level. The samples exposed to 100°C became hard and brittle after ageing. This process was quite rapid, and we believe that some low molecular additive evaporates.

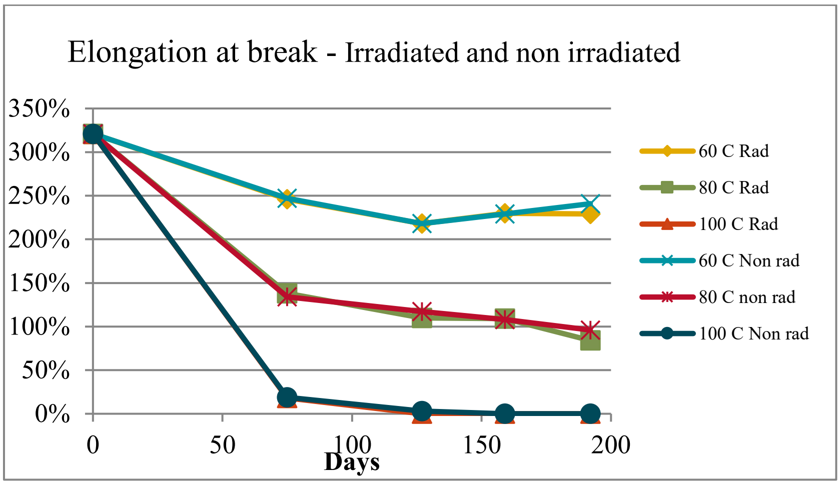

Figure 18: Elongation at break plotted vs ageing time.

Like elongation tensile strength decreases for sample exposed to 100°C. The other two test series remain on a constant level with small variations.

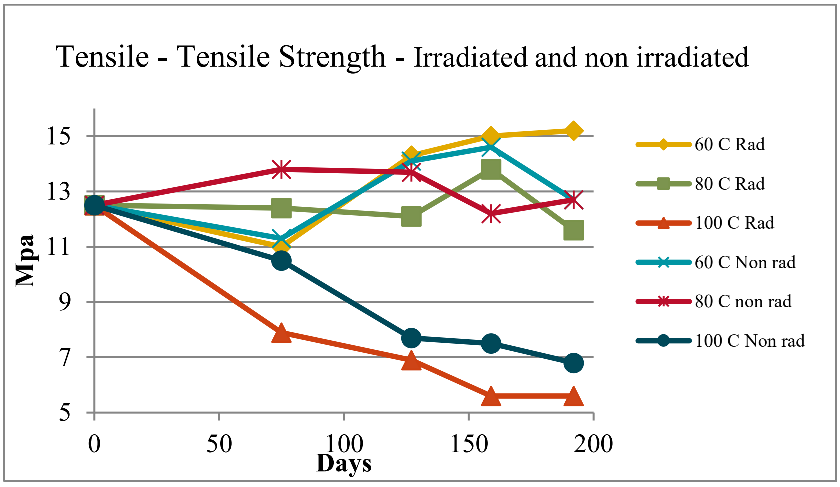

Figure 19: Stress at break plotted vs ageing time.

5.3.3 Hardness

Hardness results correlates very well with the compression set results. The gamma radiation does not seem to have any effect on the hardness, see fig 20.

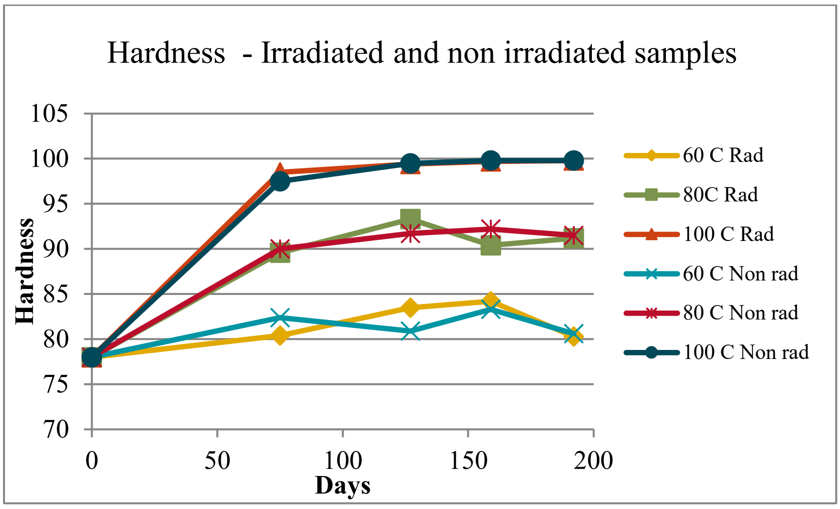

Figure 20: Hardness results for Nitrile rubber.

The initial increase of the hardness was quite pronounced after the first ageing and then leveled out after further ageing. Some plate-out was also observed on the samples and loss of additives such as plasticizer may explain the increased hardness. Thermogravimetric analysis, where a sample is heated, and the weight registered by a very sensitive scale and the weight is plotted vs temperature was used to investigate this. Weight decrease was indicated starting at approximately 150°C. See thermogram below.

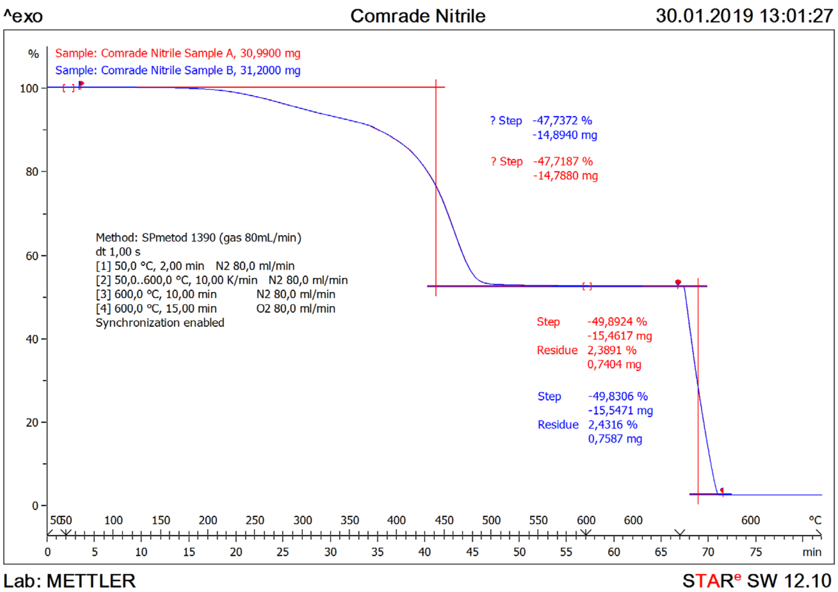

Figure 21: Thermogram for Nitrile rubber. Weight losses are detected at 150-450°C and at 600°C. At 600°C the rubber polymer is pyrolyses. The residue is inorganic filler.

6 Naturally aged materials (WP 2)

The aim of this work package is to study materials undergone aging in operating and shut down power plants. This includes Barsebäck but also materials from outages in still operating power plants in the Nordic countries. This includes a pre-study to identify the polymeric components available for studies and analyses. This work package is summarized in this report, all data and results are found in RISE Report 2019:14[8].

In this section we try to compare artificially aged materials studied in WP1 with materials that have been in operation in a nuclear power plant.

6.1 INTERVIEWS AND QUESTIONNAIRE

Two persons were interviewed regarding polymers from Barsebäck NPP. Lars-Uno Berg, head of business operations at Barsebäck Kraft AB and his colleague Lars Appelgren. Barsebäck plant did not have the ability to give radiological clearance in situ so an external authorized regulator must be engaged, and it was not certain that the materials or equipment that had been inside the enclosure could be given radiological clearance at all. Another aspect against using materials from Barsebäck was that after the outtake of the reactors the materials have been stored for many years in non-controlled environment, i.e. different temperatures and atmosphere.

Based on the result of the Barsebäck interviews a questionnaire was sent to different running plants in order to obtain polymer components from running plants during outtakes. The questionnaire was introduced to NPP polymer material experts via COMRADE industry group, to obtain data on different polymers available to study, service history material data etc. The questionnaire which compiles the materials of interest for the industry and the project team, materials available from different Nordic NPPs and their service history, is found in a RISE research report[7].

One of the product groups pointed out in the questionnaire as important to study, was O-rings of EPDM, Nitrile, Silicone and Viton and those were also studied in the COMRADE project work package 1.

6.2 LABORTATORY TESTS

Some of the old collected samples were tested in the laboratory. Because of the limited number of components and material, only measurements that required small samples were possible to perform. The amount of material also limited the possibilities to perform accelerated ageing tests.

Several O-rings were collected at Ringhals NPP (full information in RISE report[7]) and a rubber membrane from OKG NPP (Oskarshamn). They had been in use for between 3 and 12 years at different temperatures. After removal they have been stored for 1 year.

[8] RISE Report 2019:14 ISBN 978-91-88-907-38-7

Energiforsk

Some of the used O-rings supplied by Ringhals were tested regarding hardness and visual properties. For damaged used O-rings hardness values were high starting from 90 IRHD. The artificially aged O-rings started to leak at very high values of hardness, around 90 IRDH for EPDM, and 100 IRHD for Nitrile Rubber. The FKM rings did not leak at all. Since the hardness data from laboratory test and discarded samples correspond very well the conclusion is that the laboratory methods are quite useful for determining status of polymeric materials and perform accelerated ageing.

Figure 22: Damaged EPDM O-ring (from Ringhals) after service at 50°C for 6 years.

Most of the used FKM O-rings seemed to be in good condition according to visual inspection. Hardness measured on FKM (Viton) O-rings had typically values around 70 and were in good condition which correspond to the laboratory tests.

The condition of the investigated Nitrile O-rings varied. Those with hardness around 70 IRHD were flexible and those with hardness above 90 IRHD were brittle and often damaged. Most of the Nitrile O-rings had been in service for 12 years but probably some of them had been replaced.

Figure 23: Hard and brittle NBR O-ring (from Ringhals, service conditions unknown).

The rubber sheet from OKG is approximately 35-40 years old and was installed when the power plant was built. It is a part of an EPDM or Neoprene joint seal installed between buildings. Usage temperature has been 20-22°C, 60 % relative humidity and negligible radiation.

Figure 23: Rubber membrane from OKG (Oskarshamn)

Table 4 Rubber membrane (OKG)

Tensile strength MPa	Elongation at break %	Tensile strength at 50% elongation MPa	Tensile strength at 100% elongation MPa	Height mm	Hardness m-Shore A
5,87	177	3,20	4,18	3,85	80,2

Initially the hardness was 60 Shore at the studied samples was 80 Shore. No values of initial tensile properties were available.

6.2.1 Conclusion

The main conclusion for this work package is that to be able to study materials from a closed Nuclear Power Plant it is important to plan for this already before closure.

Also, extraction of components from outtakes at running plants need a lot of planning in advance. By using the experience from this project, we would specify component for studies more carefully:

- Type of component, for example O-ring, what dimension.
- Amount of material/component needed.
- Specify relevant tests in advance.
- Decide if additional accelerated ageing should be performed. For example, ten O-rings of minimum core diameter is needed for hardness and tensile testing and one ageing cycle. In this project we asked for any type of material and tests were performed depending on type and amount of materials achieved.

7 Modelling of leakage

The particular aim of the modelling work is the development of simulation methods that can be used to evaluate test methods of aged seals e.g. compression set and how they perform in service i.e. provide leak tightness. The developed methods should both be models that are of direct use and lay a basis for more advanced development on both numerical simulation techniques and materials modelling. The full report on the modelling work is found in RISE report 2019:19[9]

Seals are typically made of a rubber material and in this project EPDM in the form of O-rings was studied. An issue with rubber materials is their creep behavior i.e. they deform over time at constant load and can also retain a permanent deformation – permanent set. This can reduce the sealing function since the compressive force on the seal decreases which can cause penetration of the pressurized fluid to be contained by the seal.

7.1 METHOD

The simulation is performed with finite element (FE) modelling. The advantage of FE modelling is that complex geometry and material behavior can be handled. In this case the complicated behavior of the rubber becomes the major difficulty to address here.

It is shown how the relaxation tests can be used together with simulations to calibrate rubber material behavior in seal applications. The visco-elastic (creep) behavior is the most important in this respect. The creep model that was shown to be most suitable is the Bergstrom-Boyce model. When compared to the strain-hardening model from the previous report, the Bergstrom-Boyce model has better efficiency and more stability which allows for larger time increments in the simulations. The material model can also include a plasticity part in the rheological network. Since only one type of relaxation test is used there is not enough data to distinguish the plasticity from the creep and elasticity leading to that plasticity is not included in the model. A possible way to include and calibrate a plasticity part could be to also use the compression set test data. Here it is chosen not to use the compression set in this way. Instead this data is used in a validation process. A validation process here means that the calibration is done without the validation data. The validation data is instead used to test if the calibrated model can match results from the different validation test. The result is thus a more credible material model.

The effect of temperature is included with calibration of relaxation tests at different temperatures. It would have been possible to also perform a thorough calibration to this data. The resources in this project do not allow this. Instead, a simple observation is made on how much relaxation roughly occurs. With this observation the activation energy in Arrhenius equation can be determined. This modelling of the temperature effect is also validated with the compression test data. In the

[9] RISE Report 2019:19 ”Simulation of rubber materials for seals in nuclear power plants” Johan Sandström, www.ri.se

validation, the match between the test and simulated results is reasonably good when considering the rather crude and simple way the temperature effects calibration is performed. Furthermore, the Arrhenius equation is derived for one well defined chemical reaction while creep in rubbers is a complex process. Considering also this, the thermo-effects modelling seems good. This successful use of the Arrhenius equation for more complex effects is an experience that is often seen in various applications. Although not attempted here, it could also be possible to use the Arrhenius equation for ionizing radiation together with temperature.

The material models are used in a leak and tightness simulation attempt. This work is not fully completed. Although such simulations were successfully used in work such as[10], it does not work to full extent here. Numerical difficulties occur that prevent the simulations to be used to simulate leakage with confidence. From the leak and tightness simulations performed here it is shown that the increased creep for higher ageing temperatures seems to have a detrimental effect on the tightness, although one cannot assure or quantify the effect.

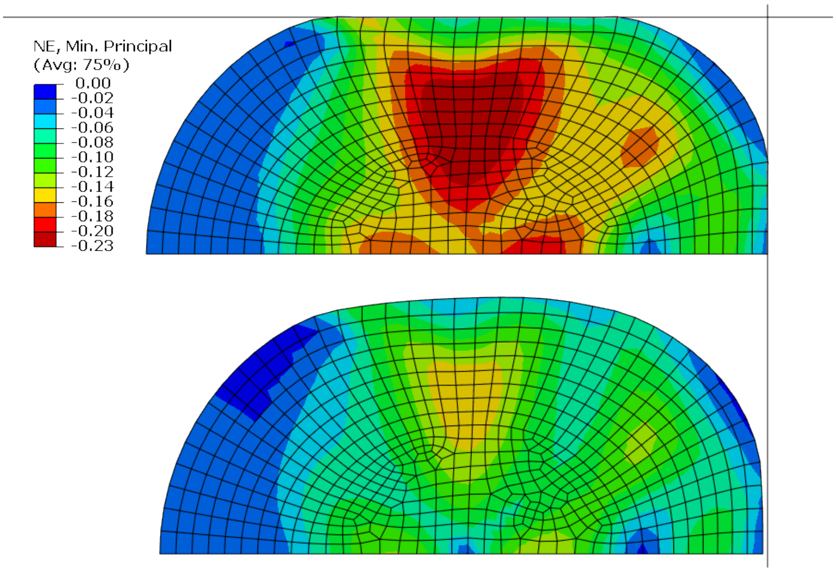

Figure 24: FE simulation results at end of ageing for 60 days in compression, immediately before release of compression (upper) and 1000 seconds after the release (lower). The color contour is minimum principal (compressive) strain. Temperature is 140 °C. The lines are rigid bodies representing the permanent set fixture.

[10] **Sällström, Jan Henrik, Sandström, Johan och Sällberg, Sven-Erik.** *Täthet hos flänsförband mellan stora polyetenrör och ventiler – experimentell och numerisk studie.* Bromma : Svenskt Vatten Utveckling, 2016. Rapportnr: 2016-17 .

Further work that can improve and build on the findings in this report is:

- More detailed calibration and modelling of temperature and ionizing radiation effects
- Use of O-rings also in the calibration stage instead of flat specimens. This would be better as the deformed state then better matches the reality. Currently, the used coefficient of maximum friction has some uncertainty. The effect of this would have less impact for O-rings specimens compared to flat specimens.
- Use of more chains in the rheological network to get better accuracy in the calibrations

Another possibility could also be to use radically more advanced material modelling in the FE-simulation framework when such modelling becomes available. An example is to use molecular dynamics as a creep law. Such work is also part of the COMRADE project. This would allow to explicitly include e.g. temperature, radiation and other chemical degradation effects.

8 Conclusions

The following conclusions were made in the project:

- End of life criteria measured by comparing function to material properties and investigating old components indicate the components has longer service life than requirements set.
- The radiation dose used in the experiments does not have any significant effect on the material properties.
- Material qualities for sealings may be checked by stress relaxation tests. This method also tends to give relevant data for activation energy calculations.
- Hardness measurements on components used in NPP correspond to those hardness results achieved from the samples at end-of-life as determined by leakage.
- For conditioning monitoring the use of dummies and hot spots in the NPP is valuable tools.
- The FEM model shows possibilities to model leakage at different temperatures, geometries and ageing times. The model needs to be developed further.

ACCEPTANCE CRITERIA FOR POLYMERS IN NUCLEAR APPLICATONS 2018

Polymeric materials are widely used in the nuclear sector, from small components like O-rings that are regularly exchanged to complex components that are rarely exchanged. In the COMRADE project on acceptance criteria for polymers in nuclear applications, several ageing related issues in NPP environment were studied. Acceptance criterion for O-rings are set, real components are used in ageing studies and combined effects of radiation and heat and dose rate effect are investigated.

As a result, several end-of-life criteria were suggested for EPDM O-rings based on the functional property of the O-ring. FE-simulations were conducted to estimate how O-rings endured in a realistic environment. Feasible ways to acquire polymeric materials from running plants and plants under decommissioning were evaluated. MD simulations were applied in explaining the mechanisms governing the reverse temperature effect. As part of studying the synergistic effects of radiation and heat, two different kind of behavior were observed with EPDM and Lipalon cable jacket material in combined high temperature-radiation environments. Furthermore, it was shown that the used sequence in ageing treatments do matter in the case of EPDM. Finally the use of semi-empirical models were estimated in the use of predicting dose rate effect and it seems that they require a lot of experimental data to provide reliable predictions.

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