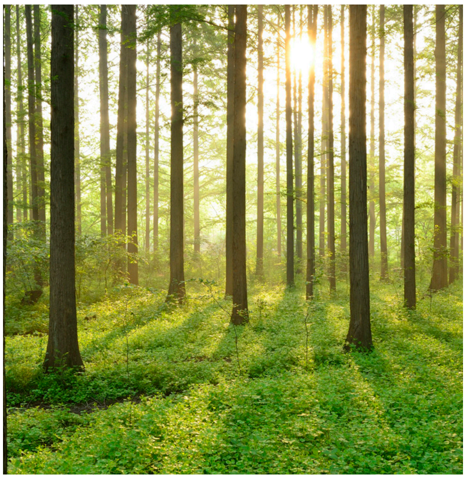
ACCEPTANCE CRITERIA FOR POLYMERS IN NUCLEAR APPLICATONS 2017

REPORT 2018:486



NUCLEAR

COMRADE

Energiforsk

Acceptance Criteria for Polymers in Nuclear Applicatons 2017

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ISBN 978-91-7673-486-5 | © Energiforsk April 2017 | Cover photo: James Walker

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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 second year out of three from 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, Marcus Molander, Johan Sandström and Anna Bondesson, senior researchers at RISE (Research Institutes of Sweden) and senior researchers Konsta Sipilä and Harri Joki at VTT Technical Research Centre of Finland.

An advisory group consisting of Annelie Jansson (Forsmark), Tommy Holm (OKG), Emil Boström (Vattenfall), John Rogers (James Walker), Jukka Sovijärvi (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

I COMRADE-projektet undersöker vi hur polymera material bryts ned vid exponering av låga stråldoser i kombination med accelererad termo-oxidativ åldring. I de flesta publicerade studier är stråldoserna mycket höga för att accelerera nedbrytning av materialen. Vid drift exponeras materialen sällan för så höga doser. Projektet är indelat i tre delar där vi genom experiment undersöker acceptanskriterium för när tätningar bör bytas ut, samt utveckar en matematisk modell för detta. I del två försöker vi hitta material från kärnkraftverk som kan verifiera metoder som ska utvärdera produktens ”end-of-life”. I det sista arbetspaketet undersöks den så kallade doshastighetseffekten.

Som acceptanskriterium för O-ringar har vi valt läckage eftersom en O-ring tätar i t ex rörskarvar och ventiler mm. Sättning mäts och jämförs med läckagetest i en specialdesignad testrigg. Värdena på sättning är väldigt höga innan läckage kan registreras. Vidare verkar strålningen inte påverka det EPDM-gummi som undersöks utan åldring i värme vid förhöjd temperatur har störst effekt.

I det andra arbetspaketet har vi ställt frågor till projektets industrigrupp samt undersökt möjligheter att friklassa material för att undersöka dess egenskaper på lab. Materialet från det nedlagda Barsebäck var svårt att friklassa och har dessutom varit utsatt för okontrollerad omgivningsatmosfär under lång tid. Med anledning av detta har vi valt att gå vidare med material från kärnkraftverk i drift.

EPDM uppvisar en effekt av doshastigheten. Resultaten från Lipalon är mer svåra att tolka och men mer exponering vid låga doshastigheter behövs.

Summary

The COMRADE project investigates degradation of polymer materials exposed to relatively low doses of gamma irradiation and thermo-oxidative ageing at elevated temperatures. In most published studies radiation dose rates are rather high in order to accelerate degradation of the materials. During operation such high doses are not very common. The project is divided into three parts and in part one where acceptance criteria for sealing materials i.e. material properties which indicate when an O-ring should be replaced. A mathematic model for this behavior is also developed. In part two we try to find material used in NPPs and exposed to normal operation conditions. Investigation of these materials should verify methods and models developed in the projects. In the third part the so called dose rate effect is investigated.

For O-rings leakage is chosen as acceptance criteria since sealing in hoses and valves is the use for O-rings. Compression Set is compared to a leakage test performed in a special test rig. Compression Set values of the O-rings are very high before any leakage is observed. Gamma irradiation in this exposure does not seem to affect the EPDM material.

In the second part of the project a questionnaire was sent to the industry group involved in this project asking for possibilities to achieve material from NPPs for studies in the project. Material from the closed plant Barsebäck did not get radiological clearance. Moreover the materials have been exposed to un-controlled environment after close down of the plant. Therefore materials from outages of running plants will be investigated instead.

Part three of the project investigates the dose rate effect in EPDM and Lipalon Cable jacketing material. The samples are exposed to accelerated ageing and irradiation at different dose rates. EPDM show dose rate effects. The results so far are difficult to interpret for Lipalon and more results are needed at low dose rates.

List of content

1 BACKGROUND

The COMRADE project is based on input from feasibility studies from Energiforsk AB [Granlund et al. 2015] and STUK [Penttilä et al. 2016] and through discussions between VTT, RISE former 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 a need in gaining a better understanding on how a polymeric component reacts to different levels of low dose ionizing radiation and synergistic effects between thermo-oxidative and radiation degradation was identified. 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
- WP 3: Polymer ageing mechanisms and effects inside NPP (Nuclear Power Plant) containments

The COMRADE project started in 2016 and results from year 1 is already reported. This report focuses on results from experiments performed during 2107.

2 WP1: DEVELOPMENT OF CONDITION MONITORING METHODS FOR POLYMERS

Materials

Peroxide cured Ethylene Propylene Diene Monomer rubber (EPDM) was studied during 2017. EPDMs was chosen based on a request from the Industry team, asking for investigations on EPDM, commonly used in the NPPs. The EPDM studied in 2017 is the same as 2016 but the o-rings have a larger core diameter (5,99 mm) compared to the o-rings from 2016 (3,53 mm). The test sheets for tensile testing had a thickness of 2 mm. The reason to study two different O-ring sizes is to be able to calibrate the computer modelling method for leak tests to different O-ring dimensions.

During 2017 ageing and irradiation of o-ring and tensile test specimen in Viton rubber was started and continues during 2018. Material testing, i.e. tensile testing, compression set and DSC measurements after ageing is not yet started.

Exposure

The samples were exposed to both gamma irradiation and thermo-oxidative ageing at elevated temperatures in heating cabinets according to the scheme below. The exposure started with irradiation followed by three months of ageing and thereafter a second irradiation and finally thermo- oxidative ageing.

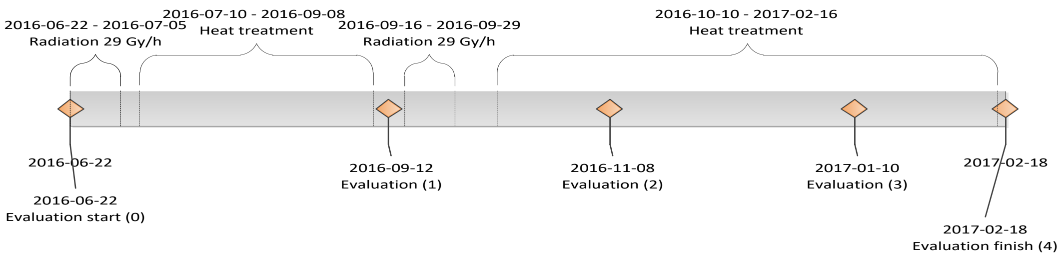

Fig 1: Exposure scheme for radiation and oven ageing.

EPDM was exposed to three different ageing temperatures, 90, 120 and 130 °C. In total the samples were exposed to 6 months of heat treatment and 14-18 kGy total radiation dose. Starting with the radiation before heat treatment is known to cause more degradation of the material. The radiation doses are quite low in order to be more similar to the environment in the NPP than the doses used in qualification of the materials. Still it is significantly higher than during service in the NPP.

A parallel aging without the radiation was done at the temperatures above. In a master thesis work performed during 2017 the samples were exposed to even higher temperatures i.e. 140 and 150 °C.

Testing and evaluation

The samples were evaluates 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.

In compression set tests an O-ring or a cylindric test piece is compressed typically 25% of initial thickness and thereafter exposed to elevated temperatures. Thirty minutes after release of the test piece the thickness is measured again and compression set is calculated and reported in percent of initial thickness.

In this project compression set was measured on the O-rings mounted in the specially designed test rigs shown in figure 2 below. This is not according to standard method but the reason for this was to measure compression and leakage on the same test specimen.

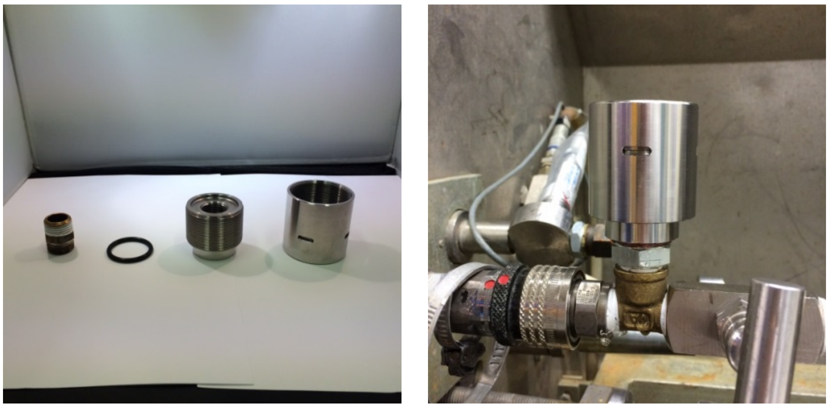

Fig 2: Test rig for leakage tests. To the left test rig before mounting the o-ring and to the right the rig is mounted for leakage test.

The test rigs with O-rings inside were exposed both to heat and irradiation according to fig 1. 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.

Tensile testing was performed on dumb bell shaped test pieces also exposed to the ageing scheme presented above. Stress and elongation at break were measured. In DSC (Differential Scanning Calorimetry) a small sample piece typically10 mg of the material was heated at a constant rate in oxygen atmosphere. Thermal changes in the material such as melting, glass transition or oxidation is registered by the instrument. In these experiments oxidation is measured as the onset point where exothermic reaction or degradation of the material starts, OIT (Oxidation Induction Temperature). OIT may be used as an indirect measure of the stability of a material which is dependent on the antioxidants added to protect the material from oxidation.

Test results

Figure 3 below illustrates the compression set results for the 5,99 mm O-rings tested during 2017 as a function of exposure time.

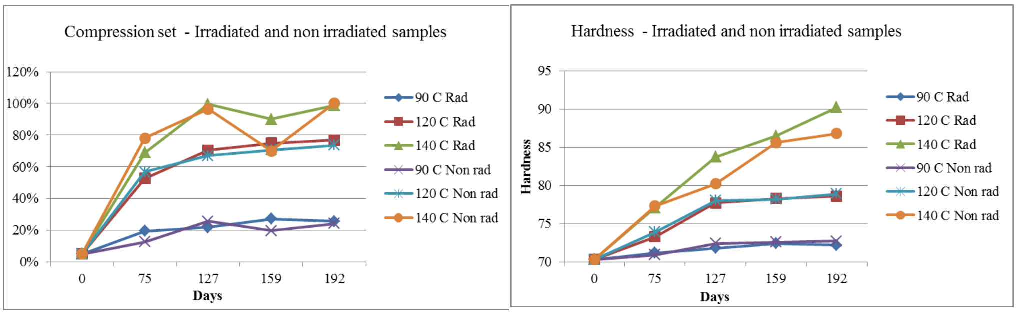

Figure 3: Compression Set after different ageing and irradiation exposure.

The main conclusion is that the radiation does not seem to affect the materials at doses used in this experiment. Elevated temperature causes the main part of the degradation. EPDM is known to be radiation resistant and the studied material is a high quality material, compression set remains stable at 20% at 90°C. At 120°C and 140°C compression set increases significantly after the first ageing step and this effect is probably a combination of physical ageing and thermo-oxidative ageing.

Leakage is observed only for the samples exposed to 140°C after 127 days or longer exposure where maximal compression set around 100% is measured.

Hardness tests results correspond quite well to the compression set results. At higher temperatures, 120 and 140°C the increase is significant, around 10 IRHD whereas at 90°C the increase is only a few hardness degrees. As for the Compression Set the radiation does not seem to affect the hardness of the material.

Also the results from tensile testing show that higher ageing temperature has strong impact on the material properties. Both elongation and tensile strength decreases significantly more at 140°C exposure temperature.

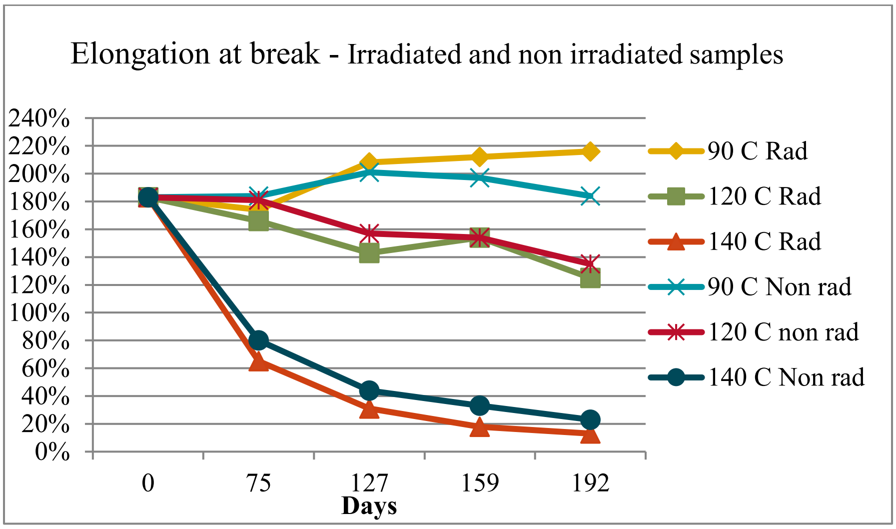

Fig 4: Elongation at break plotted versus ageing time.

In order to function during long service antioxidants are added to polymer materials. Antioxidants function in different ways but usually they are consumed as they protect the material from degradation. As the antioxidants are consumed, the Oxidation Induction Time (OIT) decreases.

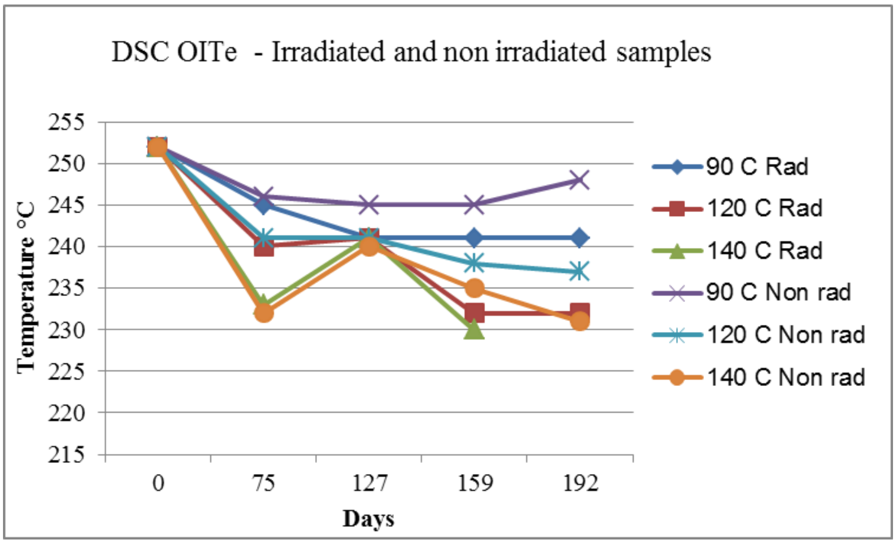

Fig 5: OIT as a function of ageing time. OIT values at 127 days of ageing at 140°C deviate from the others and the deviation has to be investigated further.

3 WP 1: MODELLING

As a part of WP 1 Finite Element (FE) simulations describing the behavior of EPDM rubber sealing rings behave over time are performed. The particular aim of this part of the COMRADE project is the development of simulation methods that can be used to evaluate test methods of aged seal and how they perform in service i.e. provide leak tightness. A major challenge for the simulations is to find an appropriate material model for the rubber materials and how to calibrate it to experiments. Here is a material model proposed that can include effects like creep, permanent set, and temperature dependence. Calibration of material models for relaxation tests on EPDM rubber is performed and presented with good results. Further modelling to include more effects in the material and to simulate leak and tightness of seals are proposed.

An issue with rubber materials is their creep behavior i.e. they deform over time and can also retain a permanent deformation – permanent set. This can reduce the sealing function since the compressive force on the seal reduces which can cause penetration of the pressurized fluid to be contained by the seal. A further complication in nuclear power applications is elevated temperatures and radiation levels which can accelerate or initiate degradation like creep in polymers like rubbers.

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 rubber becomes the major difficulty to address here.

An O-ring in a normal application is subjected to compressive strain of moderate magnitude (stretch 0.5 or engineering strain -50 %). In such conditions where the strains are compressive together with moderate shear strains.

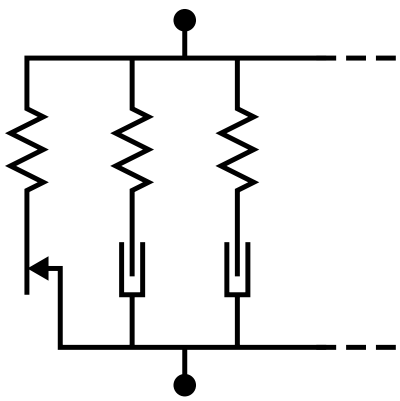

Figure 6: Rheological network with multiple chains where the springs model hyper-elasticity, dash-pots model viscoelasticity and one slider models plasticity.

The specific behavior of material models is determined by the parameters in the model. In an engineering application, the parameters are calibrated to the materials in use. The process of calibration takes place by adjusting the parameters, so the response of the model matches a test with a material sample. When the material model is complex, advanced methods for fitting the parameters to test data are usually needed. The method for this fitting is referred to as an optimization and is typically conducted so an error measure between test data and predicted values from simulation is minimized. The optimization is described in more detail in RISE Report 6P01138-01A.

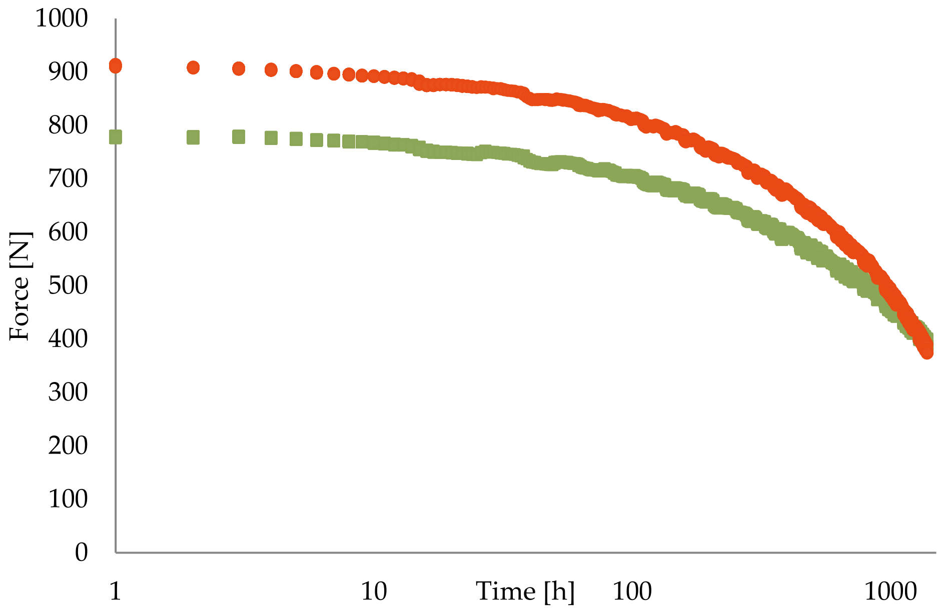

Figure 7: Relaxation test data on two specimens.

The material-model calibration is performed for a test resembling a seal. In such a test the stress and strain in the material cannot be calculated directly. Instead, and as previously discussed, the specimen is modelled with a FE model that handles the complicated deformation. The resulting quantities, total compressive displacement and compressive force, are then available from the FE calculation and can then be compared to the experiments. The FE software package Abaqus/Standard version 2018 [Dessault Systèmes Abaqus 2018 Documentation 2018] is used for simulations.

Some first attempts for calibration of the preliminary test data and the rheological network model presented in RISE report 6P01138-01 A. The results in this report are more of relaxation type and since the plasticity behavior is best evaluated by including compression set data, the elastic-plastic chain is not included, see fig 6.

Two material models are tried by performing a calibration for each of them. One material model with a single visco-elastic chain and one material model with two visco-elastic chains.

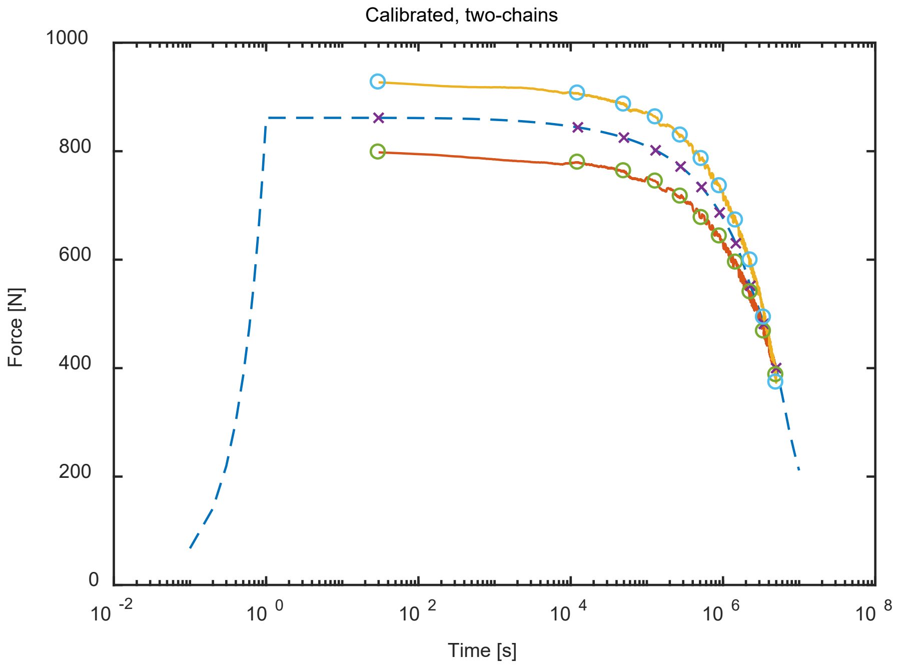

Fig 8: Relaxation forces from the tests (solid lines) and the simulation (dashed line) with the two-chain material model and calibrated material parameters. The circles are evaluation points from the testing data and the x-markers are evaluation points from the simulations.

The modelling work continues during 2018.

4 WP 2 MATERIAL FROM NPP

The goal of WP2 is to identify polymers that could be available for research purposes from Barsebäck NPP or currently running NPPs participating in this project via industry group meetings. Also polymer service conditions are of interest as well as procedures related to moving polymer components out from the plant. The pre-study survey on Barsebäck materials was conducted in 2016 and compilation of the data from currently running NPPs in 2017.

The material acquisition from Barsebäck was considered to be challenging so the scope was expanded to cover the NPPs still in use e.g. outtakes or containments that has been/will be closed down. From the candidate materials given by the NPPs, suitable materials will be collected and tested by the methods used for WP1 and WP3. The test results will be used to verify the model in WP1 and provide materials aged at real conditions for WP3 ageing studies.

Two material experts related to Barsebäck polymer components were interviewed in order to clarify whether the used components could be taken out from the plant for ageing studies. The polymer components available for ageing study and which service conditions are well documented are few in numbers. Also radiological clearances and the related precautions to working with decontaminated materials yield in complicated and costly material acquisition. A more feasible way to obtain used materials from properly documented service environments would be acquiring materials from running plants during annual take outs.

A questionnaire was sent out to investigate the polymeric materials possibly obtained from the participating NPPs and properties of the materials were filled in by NPP material experts. According to the questionnaire there are some EPDM O-rings available for testing that are similar to those materials tested in WP1 and WP3.

At the COMRADE workshop in September 2017, O-rings were pointed out as a feasible first choice for testing. The obtaining and testing of the O-rings will be done during 2018.

5 WP3: DOSE RATE EFFECT ON EPDM AND LIPALON CALBE JACKETING

This work package is performed by VTT in Finland and some of the results from 2017 are presented here. Full report "Dose rate effect study on EPDM and Lipalon cable jacketing materials VTT-R-01052-18 is published by VTT.

Dose rate effect is a phenomenon where the damage caused to a polymer due to ionizing radiation is depending on the dose rate used during the irradiation. The degradation kinetics is such that lower dose rates cause more damage to the polymer than higher dose rates. This may pose a threat when accelerated ageing of polymers are conducted and the ageing is supposed to be equivalent to the condition that the component would be after experiencing the real service environment over many years. In order to study the existence of dose rate effect on EPDM rubber and Lipalon cable jacketing experimental data was gathered in irradiation environment and a semi-empirical power law model was applied. It was noted that radiation resistivity of EPDM was rather high which impaired quality of the obtained DED (Dose to Equivalent Damage) values. In case of Lipalon it seemed that there is a dose rate effect over the dose rate range studied but in order to confirm this observation, more data on lower dose rate range would be required. Overall, it should be stated that confirming the homogenous oxidation of the irradiated samples would increase the reliability of the extraction of the DED parameters. ToF SIMS technique seemed to be sensitive in detecting ageing products but uncertainty remains how e.g. impurities of the surface affect the normalized measurement signal.

Exposure

The ageing of samples was conducted by subjecting them to high dose gamma radiation. The used dose rates and absorbed total doses are shown in Table 1. The irradiation treatments having the dose rate ≥ 0,36 kGy/h were conducted at ROZA irradiation facility in ÚJV Řež, Czech Republic. The low dose rate irradiations (0,06 kGy/h) were conducted at VTT's gammacell. Both facilities use 60Co as gamma radiation source. The deviation between the absorbed dose and target dose was ±10%. Same deviation applies to target and measured dose rates.

Table 1. Target doses and dose rates compared to total absorbed doses and dose rates during irradiation ageing. ToF SIMS samples marked with an asterisk.

Ageing condition #	Target dose/kGy	Target dose rate/kGy/h
1*	1000	6
2	1000	2
3*	1000	1
4	600	2
5	600	1
6	600	0,6
7	400	2
8	400	1
9	400	0,6
10*	200	2
11	200	1
12	200	0,6
13*	200	0,36
14*	200	0,06
15*	40	2
16	40	1
17	40	0,6
18*	40	0,36
19*	40	0,06

The mechanical tests were performed at VTT but with the same methods as at RISE.

Results EPDM

The elongation of break values decrease until absorbed dose of 400 kGy is reached and after that, the general trend seems to be that no significant changes in elongation of break can be observed, with the exception of the samples irradiated with dose rate of 1 kGy/h. There are no significant changes in tensile strength values as function of absorbed dose. Decrease in elongation of break combined with constant tensile strength values as function of increasing absorbed dose indicate embrittlement of the material.

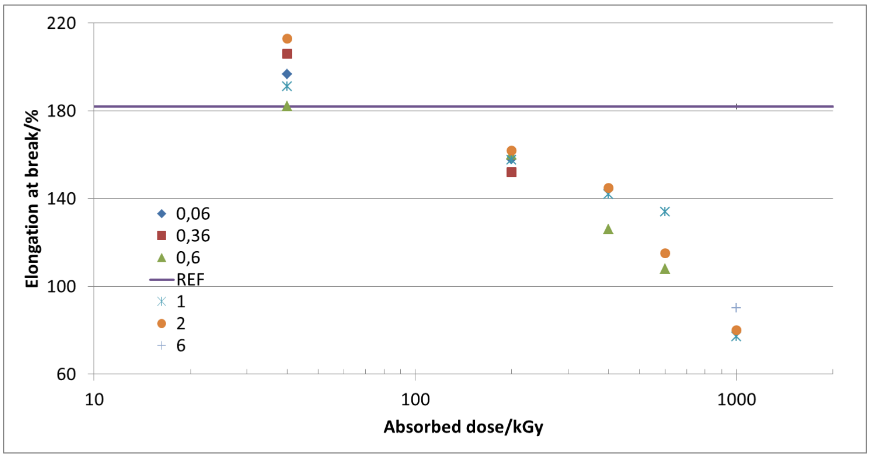

Fig 9: Elongation-at-break of EPDM at different dose rates as function of absorbed dose.

Both elongation-at-break and tensile strength decrease as the absorbed dose increases. No clear indications between different dose rates can be extracted from the data presented in this form. In order to predict existence of the dose rate effect, extraction of DED values (the dose at which the end-point criterion is met) was conducted according to the power law model [IEC TS-61244-2]. In this case, the typical 50% absolute elongation of break end-point value is not used since it was not simply reached during ageing. Also by defining multiple end-point criteria, the sensitivity of the power law model can be examined. The end-point criterion is defined as the relation of measured and initial elongation of break, e/e_0. DED values can be extracted when the end-point criteria at different dose rates are plotted versus the absorbed dose, as shown in Fig 9. While extracting the data, the linear function was fitted to the experimental data and it was used to extrapolate the low end-point criteria.

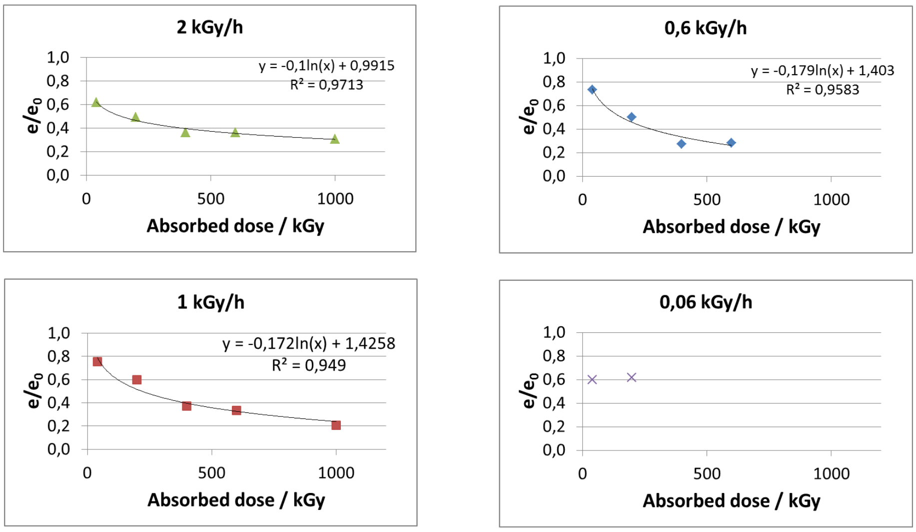

Fig 10: Extraction of end-point criteria from experimental data.

The surface and bulk oxidation of EPDM was studied by using ToF- SIMS. ToF-SIMS seemed to be very sensitive technique in detecting oxidation products in the samples but identifying artefacts from the normalized signals still causes uncertainty to the measurement results. The results are shown in Figure 11 below. The signals are normalized to the total amount of two fragments (CH and C2H) which exist both on the surface and in the bulk material.

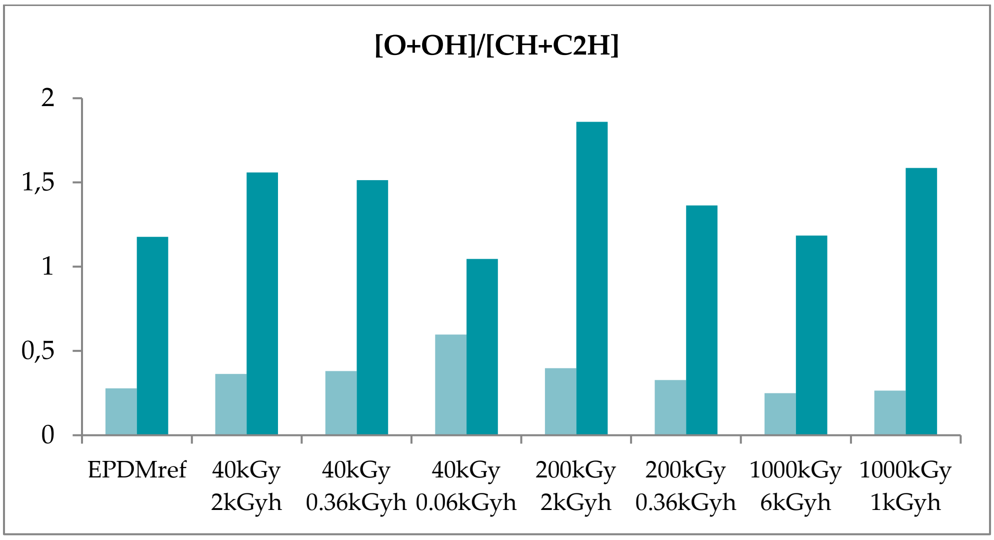

Fig 11: The light blue bars show total oxygen content in the bulk material and the dark blue bars the surface material. The surface seems to contain higher concentration of oxygen containing reaction groups.

However, there is a risk of over-estimating the ion concentration on the surface due to handling and contamination on the surface and insufficient cleaning of the samples, the so called yield effect.

As for the other results (tensile testing, hardness etc.) no significant correlation of oxidation and dose rate effect can be seen. Generally the oxygen content is clearly lower in bulk, expect in the case of 40 kGy/0,06 kGy/h where the difference between bulk and surface is less than a half. This kind of behavior would be expected as the dose rate is decreased and oxygen has time to diffuse further into the bulk before being radicalized by ionizing radiation. When dose rates 2, 0,36 and 0,06 kGy/h are compared, 0,06 kGy/h shows the lowest oxygen content on the surface and this might indicate the formation of crosslinks instead of formation of oxygen containing degradation products at higher doses of gamma radiation. In order to verify this, samples irradiated with 0,06 kGy/h and higher absorbed doses should be analyzed.

Lipalon material

The CSM cable jacket material (tradename Hypalon, cable tradename Lipalon) was provided from storage of the Finnish nuclear power company TVO.

In case of Lipalon the dose rate had and an effect to the DED values but more experimental data from low dose rate irradiations would be required in order to confirm this observation. Overall, it should be stated that the used dose rates during the irradiations were relatively high and homogeneity of oxidation could not be confirmed which would ease the examination of the data quality.

Results from tensile testing, elongation at break plotted versus absorbed dose illustrates the results from this material.

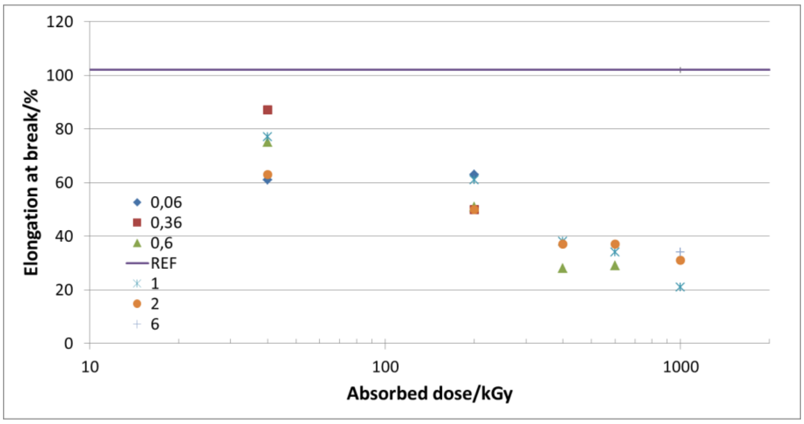

Fig 12. Elongation of break of Lipalon at different dose rates as function of absorbed dose.

The elongation of break values decrease until absorbed dose of 400 kGy is reached and after that, the general trend seems to be that no significant changes in elongation of break can be observed, with the exception of the samples irradiated with dose rate of 1 kGy/h. There are no significant changes in tensile strength values as function of absorbed dose.

6 WORKSHOPS AT NPPs

At this point three workshops at the NPPs are finalized, two in Sweden and one in Finland. At the workshops the COMRADE project is presented followed by a workshop where each plant has presented some polymeric materials where severe degradation has occurred. Based on these examples we discussed probable reasons for the damage and how to prevent this in the future.

7 Plans for 2018

During 2018 testing proceeds according to the research plan in the application for 2018.

In addition to the plan we will perform some tests to separate physical ageing effects from chemical degradation at high ageing temperature 120 and 140 °C. A short compression set test at elevated temperature will verify if post curing of the material occurs.

ACCEPTANCE CRITERIA FOR POLYMERS IN NUCLEAR APPLICATONS 2017

Different polymer-based materials are widely used in various applications in nuclear power plants and inside containments, such as cable jacketing/insulators, sealants, paint coatings, lubricants and greases.

As any other material or component, polymers are susceptible to ageing. This report summarizes the results from the second year out of three from the COMRADE project focused on thermal- and radiation induced ageing of polymeric materials. Two ageing test series were performed on EPDM material, showing that high ageing temperatures causes high levels of compression set and hardness which correspond to leakage.

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