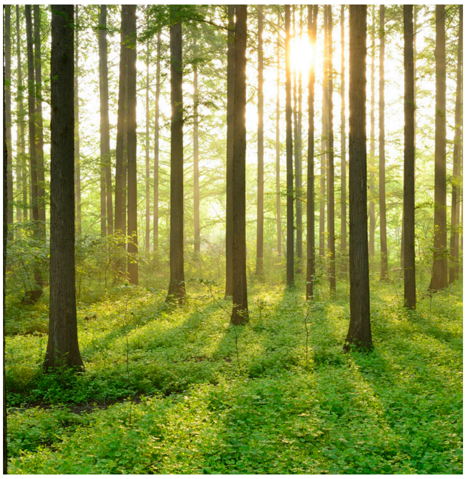
# ACCEPTANCE CRITERIA FOR POLYMERS IN NUCLEAR APPLICATIONS

REPORT 2017:389



NUCLEAR

Energiforsk

# Acceptance Criteria for Polymers in Nuclear Applications

## Results from COMRADE 2016

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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 first 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 Marcus Granlund, Anna Bondesson and Anna Jansson, senior researchers at RISE (Research Institutes of Sweden) and senior researchers Konsta Sipilä, Harri Joki, Tiina Lavonen, Antti Paajanen and Sami Penttilä at VTT Technical Research Centre of Finland.

An advisory group consisting of Annelie Jansson (Forsmark), Erik Jansson (OKG), Henrik Widestrand (Vattenfall), John Rogers (James Walker), Jukka Sovijärvi (STUK), Monika Adsten (Energiforsk), Nicklas Ingvarsson (SSM), Andrew Douglas (James Walker), Ritva Korhonen (Fortum), Stjepan Jagunic (Ringhals) and Timo Kukkola (TVO) are acknowledged for assisting the project team.

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Monika Adsten, Energiforsk

# Sammanfattning


**I COMRADE-projektet genomförs studier på åldring av polymerer som används inom kärnkraftverk. Projektet är indelat i tre arbetspaket som fokuserar på utveckling av tillståndsövervakning och livslängdskriterier, kartläggning och förvärv av komponenter som åldrats i reella miljöer samt en studie i polymera åldringsmekanismer både med hjälp av beräknings- och experimentella metoder .**

**WP1 - Utveckling av tillståndsövervakningsmetoder för polymera komponenter**
Peroxidvulkade EPDM O-ringar och testplattor genomgick accelererad åldring med hjälp av värme (90, 120, 140 ° C) och strålning (29 Gy / h). Den totala tiden i värme var 6 månader och den totala stråldosen var 14-18 kGy. Under behandlingen genomfördes fem utvärderingar. Genom att studera förändringen av materialets egenskaper under åldring ses mycket liten till ingen skillnad mellan det som bestrålats och icke-bestrålats. Vidare kan ses att DSC OITe visar en liknande förändring för både 120 ° C och 140 ° C efter hela åldringen men samtidigt visar kompressionsuppsättningen fortfarande en stor skillnad. Arbetspaketets huvudmål var att korrelera en funktion, i detta fall täthet, till en materialegenskap. Tätheten fallerade för första gången för O-ringen i 140 °C (både bestrålad och ej bestrålad) vid utvärdering 3 och senare vid utvärdering 4. Detta är efter 5 månaders värme och 14-18 kGy total dos. De olika materialegenskaperna har ändrats och till exempel är kompressionen 100%.

**WP2 - Barsebäck förstudie på åldrade polymerer**
För att verifiera modellen i WP1 och tillhandahålla åldrat material från kärnkraftverken undersöktes möjligheten att plocka ut polymera material från det stängda kärnkraftverket Barsebäck. Komponenterna från Barsebäck verkar dock vara svåra att få tag i, så omfattningen för arbetspaketet utvidgades för att täcka de kärnkraftverk som fortfarande är i drift. Baserad på tillgänglighet för olika komponenter i kärnkraftverken kommer lämpliga material att samlas och testas med de metoder som används för WPl och WP3.

**WP3 - Polymer-åldringsmekanismer och effekter inom reaktorinneslutningen**
Polymerers åldring sker vid olika storleksordningar (atomsskala, molekylskala osv.) och vid olika långa reaktionstider (jmf strålningspåverkan med diffusion). För närvarande existerar inte en materialmodell som tar hänsyn till alla storlekar och tider. De nuvarande åldringsmodellerna är semi empiriska och har en begränsad tillämpbarhet. De synergistiska effekterna av strålning och värme studerades experimentellt för materialen EPDM och CSM. Som ett resultat noterades att en ökande temperatur antingen kan hindra eller påskynda nedbrytning, beroende på polymertypen. Från oxidationsprofilmätningar noterades att ToF SIMS verkar vara en lovande metod för att erhålla användbara data (FTIR och DSC testades också). ToF SIMS var känslig för att detektera syrehalten på provytorna och även känslig mot ytjämnhet så att en noggrann provberedning krävs för att få repeterbara resultat. För utvärdering av dosratseffekter identifierades tre olika semi-empiriska modeller som kunde användas för att uppskatta detta.

# Summary


**In COMRADE project polymer ageing studies are conducted in three different work packages which concentrate on development of condition monitoring methods and related acceptance criteria, mapping and acquisition of components in real ageing environments and study the polymer ageing mechanisms both by the means of computational and experimental methods.**

**WP1 - Development of condition monitoring methods for polymeric components**

Peroxide cured EPDM O-rings and test sheets were aged in sequence using heat (90, 120, 140°C) and radiation (29 Gy/h). Total time of heat 6 months and total dose 14-18 kGy. During the ageing five evaluations were done. By studying the change in material properties little difference between irradiation and non-irradiation can be seen. Furthermore the DSC OITe shows a similar change for both 120 °C and 140°C after 6 months of ageing and 14-18 kGy total dose but at the same time the compression set shows a large difference still. The first goal of the WP 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 and later on at evaluation 4. This is after 5 months of heat and 4 weeks of irradiation. The different material properties have changed and for instance the compression set is 100%.

**WP2 - Barsebäck pre-study on aged polymers**

To verify the model in WP1 and provide materials aged at real conditions for WP3 ageing studies, the possibility to extract polymer materials from the closed down NPP Barsebäck was investigated. 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.

**WP3 - Polymer ageing mechanisms and effects inside NPP containments**

Polymer ageing occurs at different size (atomic level, molecular level and so forth) and time scales. Currently a multi-scale material model that takes account all size and time scales does not exist. The current ageing models are semi-empirical and have limited applicability. The synergistic effects of radiation and heat were experimentally studied with EPDM and CSM. As a result it was noted that increasing temperature can either hinder or accelerate degradation, depending on the polymer type. From oxidation profile measurements it was noted that ToF SIMS seems to be a promising method to obtaining from the three techniques tested (FTIR and DSC being others). ToF SIMS was sensitive to detect oxygen content on the sample surfaces and also sensitive towards surface roughness so careful sample preparation is required. For dose rate effect evaluation, three different semi-empirical models were identified which could be applied for this purpose.

# List of content

# 1 Introduction

Different polymer based materials are widely used in various applications in nuclear power plants and inside containments, e.g. cable jacketing/insulators, sealants, paint coatings, lubricants and greases. As any other material or component, polymers are susceptible to ageing. Elevated temperature, ionizing radiation and moisture are considered to be the most important ageing stressors and they tend to interact with the polymer structure in different ways. In addition to these ageing stressors, properties of polymer blend, e.g. crystallinity degree, amount of fillers and antioxidants, has an effect to the ageing behaviour. Thus the degradation mechanism can be quite complex.

Proper ageing management procedures are based on knowledge on the ageing behaviour and how to set correct requirements for the used polymer components that they will endure their designed lifetime. The ageing behaviour needs to be known when polymer components are qualified. Accelerated ageing is used as part of the artificial ageing of the qualified polymer and the ageing mechanism should be the same as in the real service environment in order to yield in identical ageing conditions. Thus the effects of dose rate and temperature to the ageing mechanism must be known as well as the synergistic effects rising from the simultaneous and/or sequential exposure to ionizing radiation and excess heat.

The requirements that guarantee the proper and safe use of a polymer or any other component are defined as acceptance criteria and they can be used as part of qualification or annual inspections of components. An acceptance criterion for a polymer component is usually a material property that represents the material health, e.g. for cable jacketing materials typical acceptance criterion is 50% of elongation at break and in case of sealants compression set is used. However, the use of such secondary material properties that do not represent the actual functional property of the component (such as tightness of a sealant) must be used with care and excess amount of data should exist which correlates the secondary material property to the actual functional property. In addition destructive measurements cannot be conducted on materials that are already in use. Thus there is a demand for non-destructive techniques that can be used in inspections and qualifications of polymer components as well as defining acceptance criterion for specific component types. These techniques should also provide a possibility to extrapolate the remaining lifetime for components.

COMRADE is developed based on input from a feasibility studies from Energiforsk AB [Granlund et al. 2015] and STUK [Penttilä et al. 2016] and through discussions between VTT, 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 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 containments

The scope of the work packages and the results achieved during the first year of the project are described in the following chapters.

# 2 Development of condition monitoring methods for polymeric components including low dose rate radiation exposure

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 correct O-ring size. 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 was completed in the middle of February.

In task 1.2 Implementation phase, there was a specific question from one of the plants regarding distinguishing between sulphur and peroxide cured 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.

## 2.1 METHODS

The ageing was completed using both radiation and heat. During the ageing samples were taken out to be analysed at 4 evaluation points plus a reference sample. At each evaluation properties tested were oxidation induction temperature (OITe), tensile, hardness and compression set. Fourier Transform Infrared spectroscopy (FTIR) was tested but did not provide any details due to the carbon black filler. Nuclear Magnetic Resonance (NMR) was tested for 3 samples to see if any conclusions could be made. Relaxation was not tested due to the samples being too thin but this will be included in the 2017 test instead.

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 bars 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 an O-ring to see at what pressure leak started. At 10 bar first leak indication was shown and at 30 bar a continuous flow of water came through the leak indicators. The leak indicator can be seen in figure 3 marked by red arrow. After the analysis of the samples they are scrapped.

Differential Scanning Calorimeter (DSC – OITe) test was conducted on samples prepared from the used dumb bells. The tesring procedure followed ISO 11357-6.

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 two samples were available for testing.

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

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.

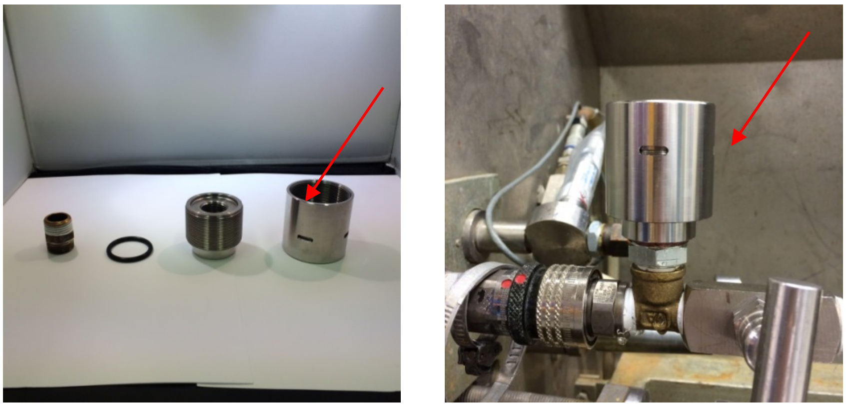


**Figure 1. Test block not mounted to the left and mounted to the right.**

## 2.2 MATERIALS

A 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)
- sheets (4 test pieces 2 x 290 x 290 mm)

## 2.3 ACCELERATED AGEING

The accelerated ageing was done in sequence with radiation – heat – radiation – heat. 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.

The thermo–oxidative ageing was done using 3 different temperatures; 90°C, 120°C, 140°C. The ovens did not have any controlled air flow. A monitoring system was used to monitor the temperature and the curves are available in the project report. The treatment was done according to the following time periods 2 months, 1 month, 2 month, 1 month.

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 the project report. 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 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.

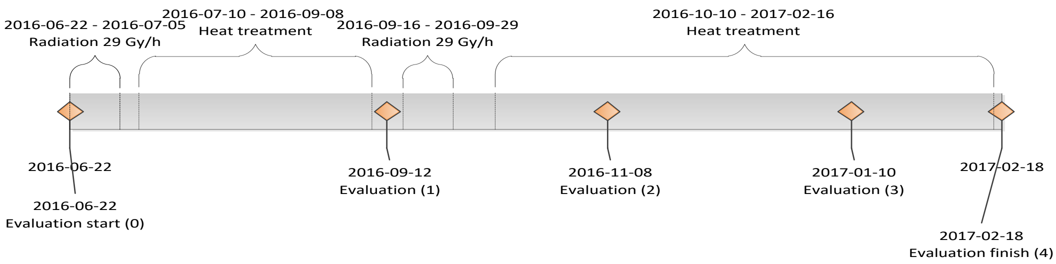
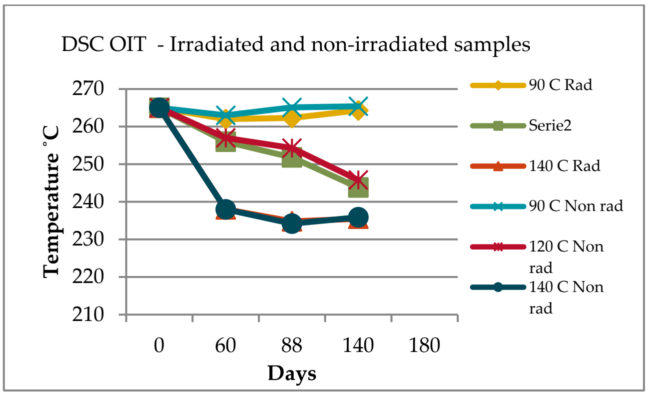



**Figure 2. The time line for ageing process.**

*Results and discussion*

OITe measurement results are presented in Figure 3. As can be seen, there is very little difference between the irradiated and non-irradiated samples. It seems to be the temperature that provides a greater difference to the OITe. Tensile testing results are presented in Figure 4. The results do not show a similar trend as for the compression set. However, a difference between the irradiated and non-irradiated samples is difficult to distinguish. There is very little difference between the irradiated and not irradiated samples as can be seen from Figure 5. Compression set measurement results are presented in Figure 6. 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. There is very little difference between the irradiated and not irradiated samples.



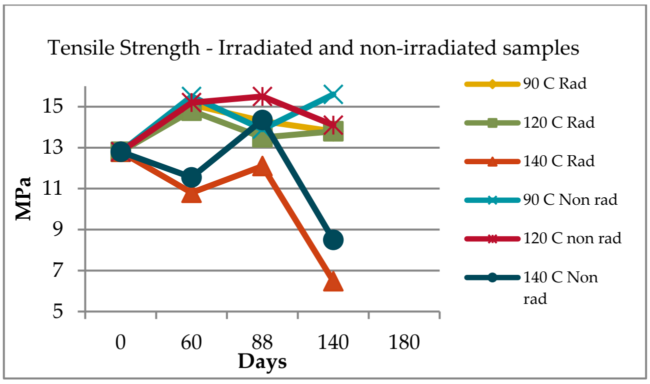
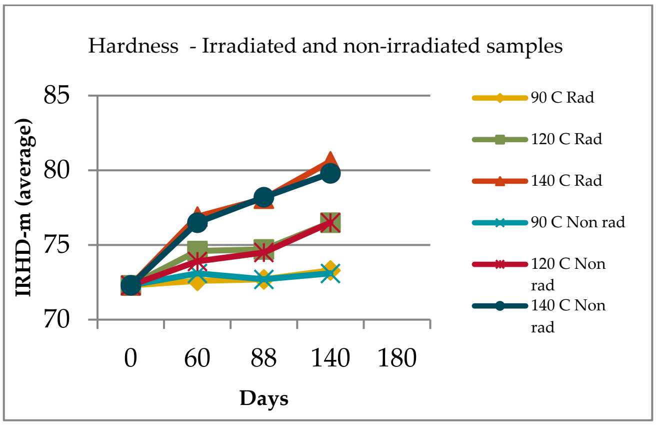




**Figure 3 and 4. DSC OITe and Tensile strength for irradiated and non-irradiated samples.**



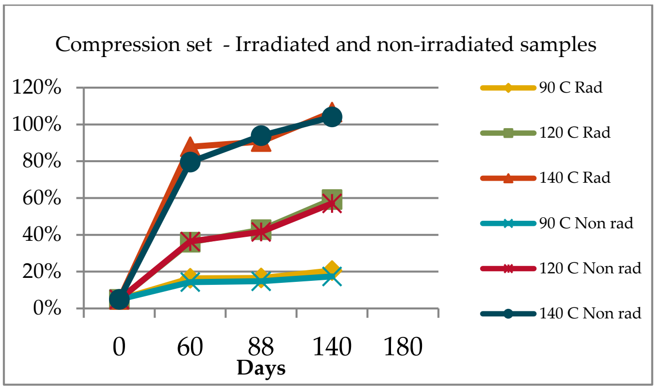




**Figure 5 and 6. Hardness and compression set for irradiated and non-irradiated samples.**

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 – OITe (235,9°C). 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 a 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. Based on the current ageing treatments, the end of life criteria defined as different material properties are shown in Table 1.

**Table 1. 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 |
| DSC – OITe | 235,9°C | 265°C |

End of life is defined as when the O-ring stops to function. 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.

No experimental test has been done using material from a power plant. 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 modelling 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 Arrhenius diagram plotted in the project report 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.

# 3 Survey on polymeric materials available for ageing studies from Barsebäck plant under decommissioning

Acquiring aged components from real service conditions and studying their material properties could provide more detailed information on degradation mechanisms and kinetics occurring in real service conditions. This information would be valuable when accelerated ageing treatments that aim to simulate the real ageing conditions are validated. The available materials can be used to verify the O-ring condition monitoring method developed in COMRADE-project (WP1) and degradation process studies (WP3).

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. More feasible way to obtain used materials from properly documented service environments would be acquiring materials from running plants during annual take outs. For this purpose a questionnaire is introduced to NPP polymer material experts (via COMRADE industry group) to obtain data on different polymers available to study. The questionnaire will compile the materials that interesting for industry and the project team, materials available from different Nordic NPPs and their service history. This work will be continued within COMRADE-project during year 2017.

# 4 Polymer ageing mechanisms and effects inside NPP containments

The ageing environment for polymers within the containments of NPPs is rather complicated. During normal service of NPP the temperature within the containment can be tens of degrees beyond room temperature. Also radiation levels can vary from less than mGy/h to Gy/h. [Penttilä, 2016] So called hot spots with elevated temperature and higher dose rates are located in the vicinity of steam generator tubing or in process valves. Thus polymer components are subjected to various stressors such as heat, radiation and moisture. In the both cases of thermal and radiation ageing, oxidation is considered to be the most common and dominating degradation mechanism. [Bartonicek & al] Oxidation of polymers is due to polymer radicals that are formed by thermal or radiation energy. These radicals react with oxygen forming peroxy radical which further reacts with the polymer chain forming hydroperoxide and polymer radicals. Hydroperoxide thermally decomposes to species that cause chain scission. Under radiation oxygen diffusion can be thus detrimental for polymers in room temperature and it is accelerated by increased temperature. The further complicating factor is diffusion-limited oxidation which has an effect to the oxidation behaviour of polymers. [Celina & al]

In Work Package 3 the effects of radiation and heat on polymer degradation are evaluated. Relevant issues that are under interest and have an effect to practical applications include use of modelling tools in simulating polymer ageing mechanism and possible development of predictive ageing methods based on computational material science, ageing effects and procedures in simulated accidental conditions, diffusion limited oxidation and dose rate effect.

## 4.1 MODELLING TOOLS FOR THE SYNERGISTIC EFFECTS OF RADIATION AND HEAT

A literature survey was completed in 2016 on the synergistic effects of temperature and radiation in polymer ageing, and on possible ways of considering them in the lifetime prediction of nuclear power plant components. The following topics were looked into in more detail: the proposed mechanisms behind the synergistic effects, material modelling methods feasible for studying ageing and an overview of previous research related to the topic.

The mechanisms underlying combined thermal and radiation ageing can be exceedingly complex, involving various chemical and physical processes across multiple structural and time scales. Probably due to this, practical lifetime prediction methods are semi-empirical and based on accelerated ageing experiments. Methods applicable to combined thermal and radiation ageing include the superposition of time-dependent data method, and the superposition of dose-to-equivalent-damage data method. The semi-empirical methods are limited in their predictive capability, as they cannot address possible changes in the dominant ageing mechanisms. For this reason, anomalous ageing phenomena such as the reverse temperature effect can render their predictions useless.

Mechanistic details of both thermal and radiation ageing can be addressed with the theoretical tools of computational materials science, as can be seen from Figure 7. For example, electronic structure calculations can be used to assess the feasibility of proposed reaction paths, and to predict the associated kinetics. At the other end of the spectrum, finite element analysis can be used to study how ageing-induced microstructural changes translate into the degradation of mechanical properties. Nevertheless, there remains a formidable gap between the present multi-scale materials modelling capabilities and practical lifetime prediction. Bridging the gap is clearly beyond the resources available in the context of the SAFIR2018 programme. However, modelling focused on a particular synergistic mechanism or some other relevant detail of the ageing process is feasible.

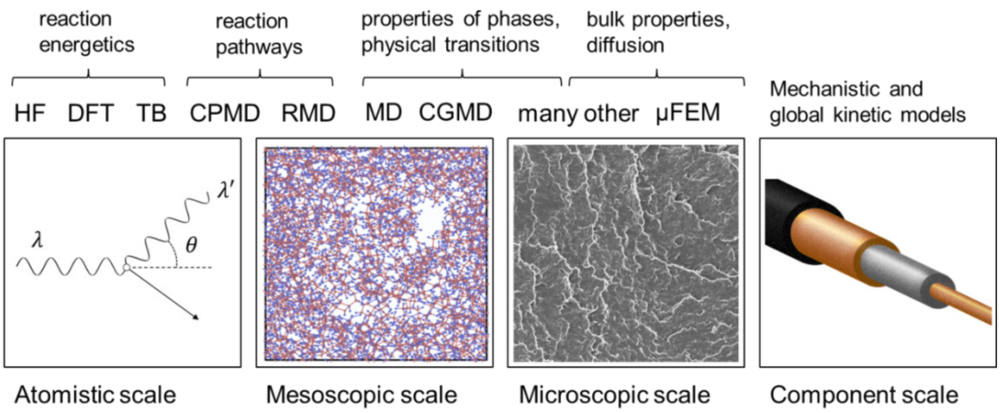



**Figure 7. Scales and processes of thermal and radiation ageing coupled with numerical modelling methods. Abbreviations for the following modelling techniques: HF = Hartree-Fock method, DFT = Density-functional theory, TB = Tight-binding method, CPMD = Car-Parrinello molecular dynamics, RMD = Reactive molecular dynamics, MD = Classical molecular dynamics, CGMD = Coarse-grained molecular dynamics, FEM = Finite element method.**

## 4.2 POLYMER AGEING DURING DBA

During a DBA polymer components will be exposed to high temperatures and dose rates. It is not clear that which stressor causes greater amount of degradation to the polymer, and does the exposure to these two stressors yield in any synergistic effects? In order to clarify this, two commonly used rubber compounds peroxide vulcanized EPDM and CSM (tradename Lipalon) rubber cable jacketing materials were artificially aged thermally and irradiated by using gamma radiation. Total of nine different absorbed dose and temperature combination were used as ageing environment where the "worst" case was defined to be similar to those conditions present during a DBA i.e. dose rate 390 Gy/h, absorbed dose 228 kGy and temperature of 125°C. The aged samples were studied by tensile testing, hardness measurements and DSC analysis.

Tensile strength was not thought to be a good indicator for material degradation for these materials since it was not effected very strongly by the ageing treatments, except slightly after exposure to the most aggressive ageing environments. Similar observations were made in the case of hardness. A sufficient amount of degradation needs to be generated before hardness could be used as a degradation indicator. Elongation at break was clearly better criteria to evaluate the degradation of the materials. DSC analysis was considered to be sensitive in ageing detection when EPDM samples were studied and the results were aligned with the elongation at break results. However, the small sample size which was analysed could could yield in some uncertainty in the results due to heterogeneities in sample structure and more accurate results would require several analyses. In case of CSM samples DSC is not applicable when detection of ageing is considered.

Based on the elongation at break results obtained with EPDM samples, it can be stated that moderate increase (ca. 75-125°C) in temperature during exposure to ionizing radiation hinders the degradation process, as shown in Figure 8. In addition, plane thermal ageing (equivalent to the thermal ageing component during simultaneous ageing) did not result in any changes in elongation at break. The observations made are opposite to what have been previously reported in literature [Ito 2007, Placek et al. 2008]. It was thus speculated that base polymer in the studies is the same but the different additives used can vary significantly between different EPDM blends which could have an effect to the nature and magnitude of the synergistic degradation yielding from exposure to heat and gamma radiation.

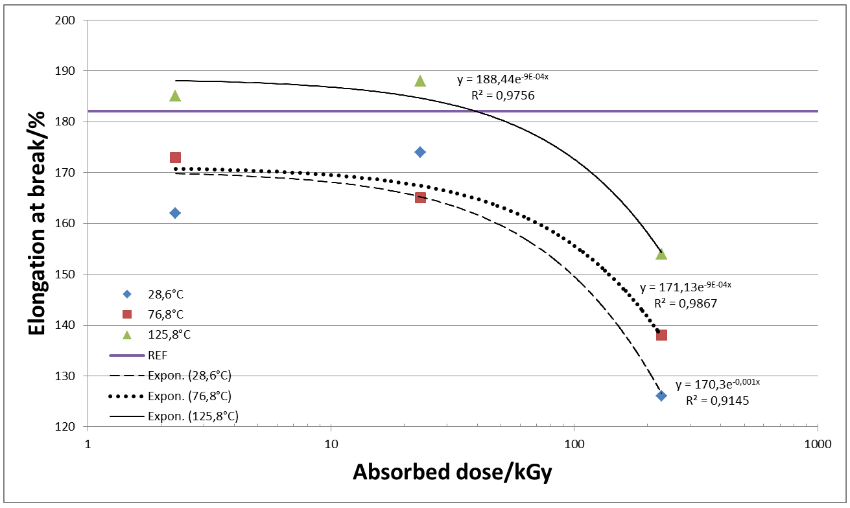



**Figure 8. Elongation at break as function of absorbed dose for EPDM. Results obtained experimentally at 28,6°C are marked as blue diamonds, 76,8°C red squares and 125,8°C green triangles. Purple line indicates results obtained with reference samples. The fitted exponent functions are plotted as dashed, dotted and solid curves at temperatures of 28,6°C, 76,8°C and 125,8°C, respectively.**

CSM (Lipalon) seemed to be more susceptible to both irradiation and thermally induced ageing and only small synergistic effects rising from simultaneous exposure to radiation and heat could be observed. Thermal ageing at 125°C resulted in clear decrease in elongation at break. Only slightly larger decrease was observed at 125°C when irradiation was conducted simultaneously. Simultaneous exposure to increasing temperature with irradiation resulted in increasing degradation as can be seen from Figure 9. This behaviour was opposite to what was observed on EPDM samples.

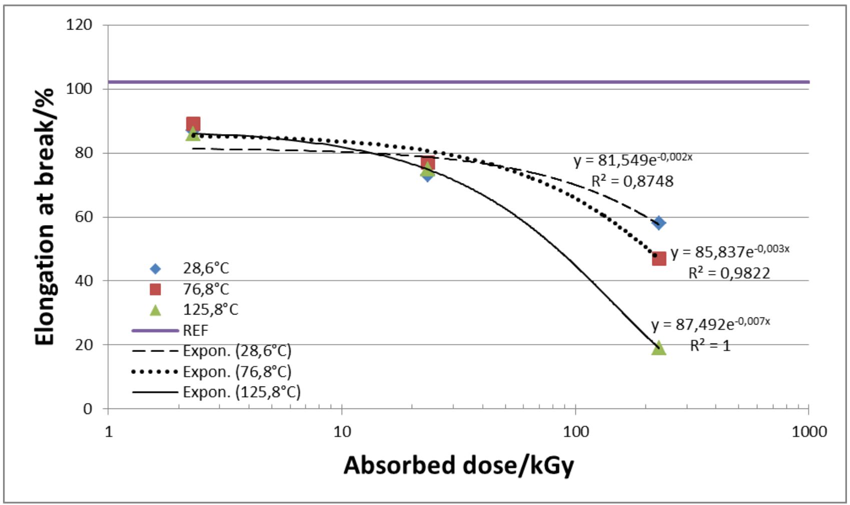



**Figure 9. Elongation at break as function of absorbed dose for Lipalon. Results obtained experimentally at 28,6°C are marked as blue diamonds, 76,8°C red squares and 125,8°C green triangles. Purple line indicates results obtained with reference samples. The fitted exponent functions are plotted as dashed, dotted and solid curves at temperatures of 28,6°C, 76,8°C and 125,8°C, respectively.**

## 4.3 SYNERGY EFFECTS BETWEEN RADIATION AND HEAT AND OXIDATION DEPTH

The focus of this subtask is on evaluating applicability of different techniques on measuring the oxidation profile created on EPDM samples during accelerated ageing. These techniques include differential scanning calorimetry (DSC), time of flight secondary ion mass spectroscopy analysis (ToF SIMS) and Fourier transmission electron microscopy (FTIR). Obtaining homogenous ageing is required when polymer components are artificially aged to correspond the ageing condition that they will reach after normal service conditions (low dose rate and temperature). These different analytical techniques that could be used in oxidation profile measurements are required to use properly in order to distinguish homogenous vs. heterogeneous ageing from each other after accelerated ageing treatments.

The studied material was sulphur and peroxide cured EPDM rubber and it was aged to three different conditions: thermally aged, gamma radiated and simultaneously (peroxide cured EPDM sequentially) thermally and gamma radiated. The overall condition of samples was evaluated by tensile testing (i.e. tensile strength, elongation at break and modulus at 100% strain). The aim was to study ageing induced oxidation from surface towards the bulk with each technique.

Based on the results obtained with ToF-SIMS, it can clearly detect the oxidation occurring in the vicinity of surfaces of the aged samples. An example of formed two dimension oxidation graph is shown in Figure 10. The carbon black filler did not disturb the analyses. Based on the results alone no clear correlation to the material condition (i.e. material properties measured in tensile testing) could be drawn. The obtained oxidation profile thicknesses seemed to vary when repetition measurements were conducted. During repetition measurement the analysis spot changes which would indicate that material is oxidised quite heterogeneously or the material itself would be heterogeneous (at least at the analysis range ca. 0,1μm). Also the effect of uneven cross section surfaces contributes to the measured intensities. However, improvements in sample cross section surfaces and increasing the number of analysed samples is considered to lead to more reliable evaluation of the oxidation profile thicknesses.

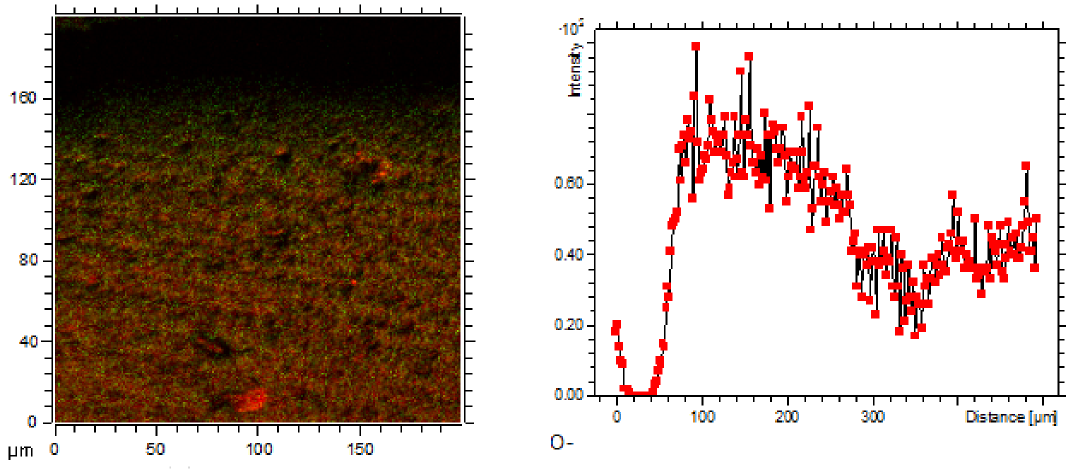



**Figure 10. On left, two dimension quantitative oxidation graph obtained with sample irradiated and exposed to thermal ageing with even cross section surface. Surface is on top and oxygen illustrated as green colour. On right measured oxidation profile where profile thickness ca. 240 µm.**

FTIR measurements were conducted on rubber samples that contained clay instead of carbon black. The samples that contained carbon black could not be analysed due to the absorbed infrared light used by the technique. According to the results no oxidation products were found in the surface or bulk material that were expected. However, changes in absorption bands were observed due to the ageing treatments. More detailed analysis of these founding's would require data on the ingredients of the studied EPDM blend (which was not available). FTIR method seems to be sensitive to detect different compounds from surfaces and also bulk, when sample preparation is conducted with care.

DSC analyses were conducted on peroxide cured samples. Exothermic behaviour was recorded as a function of time and OITs were defined on each sample. The technique was sensitive to detect changes in polymer structure/constituent. However, the more detail evaluation of the exothermic peaks recorded would require detailed data on the ingredients of the EPDM blend. Also the resolution of technique in formation of oxidation profile is limited to the thicknesses of samples prepared. During sample preparation it was noted that thinner samples than 200 μm are challenging to prepare limiting thus the analysed areas/spots along the profile to 200 μm thick, at the best. This is considerably greater than in case of ToF SIMS.

## 4.4 EVALUATION OF DAMAGE CAUSED BY DOSE RATE EFFECT TO POLYMER COMPONENTS USED WITHIN CONTAINMENTS

This subtask concentrates on the irradiation based degradation of polymers and more precisely on methods that can be used in evaluation of dose rate effect as function of dose rate i.e. predicting from experimental data whether equivalent absorbed dose at lower dose rates causes more degradation in polymer than the corresponding equivalent absorbed dose at higher dose rates. These kinds of models could provide cheaper and more practical way to approach the existence of dose rate effect on certain polymer grades than time consuming low dose rate irradiation experiments. Applicable method would ease the recognition of the existence and severity of the dose rate effect so it could be taken into account when polymer component lifetime is predicted during qualification.

Ionizing radiation induces excited states in atoms that form the polymer structure and these unstable radicals will react with the surrounding material. This will ultimately lead to changes in polymer chain structure (e.g. chain scission) and degradation of macroscopic material properties will be observed. Dose rate effect is apparent phenomenon on many polymer grades that has effect on the amount of degradation that the polymer is experiencing in ionizing radiation environments. The phenomenon yields either from physical or chemical aspects. At high dose rates diffusion limited oxidation (DLO) effects become evident cause for dose rate effect and at low dose rates more complex chemical reactions determine the magnitude of dose rate effect. Very large dose rates are used during the accelerated ageing in many of the current qualification processes due to the high cost of the irradiation treatments. This would yield in neglecting the additional degradation rising from the dose rate effect in cases when the irradiation treatment should simulate the ageing during the designed service life or even DBA.

There are few semi-empirical methods that can be used in predicting the magnitude of degradation caused by the dose rate effect. Power law method and the two methods based on superposition are shown to function in the dose rate effect modelling on many polymer grades excluding those which have tendencies towards complex dose rate effects. For these materials sufficiently working method to predict dose rate effect behaviour in the vicinity of thermal transient temperatures is currently lacking. However, the use of these methods requires additional experimental data obtained in ionizing radiation and thermal environments which is costly. Thus using already existing experimental data could be used in estimation of dose rate effects. This would be possible in case of CSPE where differences in degradation data between different material manufacturers are remarkably low when the data is superposed and dose rate effects evaluated.

# 5 Conclusions

COMRADE was established to provide better understanding on different polymer ageing, qualification and ageing management issues. Project consists of three different work packages that concentrate on condition monitoring techniques, mapping suitable components for ageing studies and studying ageing mechanisms and effects inside NPP containments, both experimentally and by using computational methods. The work continues until the end of the current programme and after one year of project work, following conclusions/observations could be drawn:

- By artificially ageing EPDM O-rings and testing them with a certain sequence, an acceptance criteria based on the functionality of the O-rings could be suggested.
- Peroxide cured EPDM grade can be distinguished from sulphur cured grade by using XRF.
- Material acquisition from closed down Barsebäck NPP can be tedious and the documentation of polymer components seems insufficient for the purpose of ageing studies. Thus material acquisition from running plants would seem to be more reasonable.
- There remains a formidable gap between the present multi-scale materials modelling capabilities and practical lifetime prediction and bridging this gap would require greater resources than currently available. Thus more limited and still relevant ageing phenomena can be dealt in modelling point of view, such as the reverse temperature effect on semi-crystalline polymers.
- Synergistic effects yielding from heat and ionizing radiation can be either beneficial or detrimental for polymers, depending on the polymer type. The mechanism behind synergy needs to be studied in more detail.
- Applicability of three different techniques, which were used to study the oxidation in the vicinity of surfaces of artificially aged samples, was evaluated. ToF SIMS seemed to be the most promising technique with good sensitivity and resolution. In future work more attention should be drawn to sample preparation, in order to avoid erroneous measurement signals yielding from surface roughness.
- Some semi-empirical models for predicting ageing behaviour based on experimental data exists. The application of these models to predict effects of ionizing radiation at relatively low dose rates is possible if suitable artificial ageing data is available.

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# ACCEPTANCE CRITERIA FOR POLYMERS IN NUCLEAR APPLICATIONS

Polymeric materials are widely used in nuclear power plants. In this COMRADE project polymer ageing studies are conducted. A correlation, between the function of an O-ring and the material properties when the end of life criteria is reached, has been identified. Different material properties have shown better or worse correlation to the end of life of the function. Almost no difference in change in material properties between radiated and non-irradiated has been identified.

The synergistic effects of radiation and heat were experimentally studied with EPDM and CSM. As a result, it was noted that increasing temperature can either hinder or accelerate degradation, depending on the polymer type. From oxidation profile measurements, it was noted that ToF SIMS seems to be a promising method to obtaining from the three techniques tested (FTIR and DSC being others). For dose rate effect evaluation, three different semi-empirical models were identified which could be applied for this purpose.

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