POLYMER COMPONENTS EXPOSED TO THERMAL-RADIATIVE ENVIRONMENTS 2019

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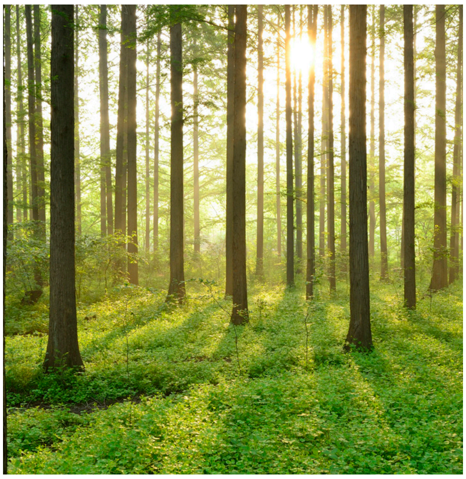

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POLYMERS IN NUCLEAR APPLICATIONS

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Polymer Components Exposed to Thermal-Radiative Environments 2019

Safety criteria and improved ageing management research

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Foreword

Polymeric materials are used in different applications and in different kinds of environment within the nuclear power plants. In many cases, they are an important part of the barriers contributing to nuclear safety.

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

Project leaders are Konsta Sipilä from VTT Technical Research Centre of Finland and Jason Ryan from RISE Research Institutes of Sweden. The activities are financed by the SAFIR program, The Swedish Radiation Safety Authority and Vattenfall, Uniper/Sydkraft Nuclear, TVO, Fortum, Skellefteå Kraft and Karlstads Energi through the Polymers in nuclear applications program.

Sammanfattning

Kärnkraftssäkerhet är en verkligt viktig fråga. Denna rapport sammanfattar första årets planering och kortfattade resultat från projektet ”Safety criteria and improved ageing management research for polymer components exposed to thermal-radiative environments” (SAMPO), som genomförs inom det finska kärnkraftforskningsprogrammet SAFIR.

I projektet genomförs livslängdsuppskattningar för gummikomponenter (t.ex. o-ringar) som används i kärnkraftverk och vilken roll olika tillsatser kan spela i själva materialen. Vidare har litteratursökningsansträngningar genomförts för att hitta icke-förstörande online-övervakning av polymera komponenter, via tekniker som trådlös dielektrisk mätning och datorsimulering.

De första resultaten visar, till exempel, att livslängdsbedömningar kommer vara möjliga och att de korrekt kan beskriva materialens verkliga situation i kärnkraftverk. Detta kan göras genom accelererade tester, eller till och med vid driftstemperaturer via mikrokalorimetri.

Arbetet fortsätter i det fleråriga SAMPO-projekt, som beräknas pågå till och med 2022.

Summary

Nuclear safety is certainly an important issue – this report summaries the first-year plan and brief results of the project Safety criteria and improved ageing management research for polymer components exposed to thermal-radiative environments (SAMPO) carried out within the Finnish nuclear R&D program SAFIR. The reader will be given information about the necessity for the life-time estimation of rubber parts (such as o-rings) used in nuclear power plants (NPP) and the role that additives can play in the materials themselves. Further, the reader will see literature review efforts made towards non-destructive online monitoring of the rubber parts, via such methods as wireless dielectric measurements and computational simulation.

The initial results show, for example, that lifetime predictions will be possible and that they can accurately describe the real-life situation of materials in the NPP. This can be done by ageing materials in the lab using accelerated conditions, or even at operating temperatures via microcalorimetry.

The work will continue in the multi-year SAMPO project, which will be finalized in 2022.

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1 Introduction

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

The project contains three different work packages, which comprise of task with similar topics. The first work package is related to acceptance criterion and safety margin assessment. Here, work is focused on providing improved estimation for lifetimes of critical polymer components, studying the sensitivity of polymer properties to additive content and methods to verify polymer quality and setting up safety margins for O-rings. The second work package focuses on improving ageing management of polymer components. Here within important research topics are online condition monitoring techniques as well as sensitive analysis methods and improving the interpretation of non-destructive testing data. The third work package is solely on international cooperation, improving the knowledge transfer between the research community and industry and following international trends on polymer-based components used in NPPs.

2 Acceptance criterion and safety margin assessment (WP1)

The objective of WP1 is twofold. The first objective is to evaluate which different factors need to be considered when an acceptance criterion is set for a polymer component. The second objective is to improve safety margin assessment. In this sense, it is important to understand how the material ages in thermal-radiative environments as well as how different additives contribute to the ageing mechanism in order to set the acceptance criterion properly.

2.1 TASK 1.1 - IMPROVED ESTIMATION FOR LIFETIMES OF CRITICAL POLYMER COMPONENTS

In task T1.1 we make use of the results and analyses from the ongoing COMRADE project when suggesting new acceptance criteria and safety margins. Results from laboratory ageing tests and evaluations have been compared to materials obtained from NPPs. Improvements of both test methods and ageing environment is required to set acceptance criteria as well as safety margins. Some polymer components are extremely complicated or impossible to change in operating NPPs and thus their endurance during the whole lifetime of a plant is essential. To be able to make reliable lifetime estimations of components, information on material properties on both materials that have been in use at NPPs and artificially aged materials is extremely valuable. The question of residual lifetime assessment of polymer components in service is often raised. Without sufficient material data and service history of the materials, i.e. temperature, radiation dose, oxygen and moisture content in the atmosphere, this is almost impossible. By studying materials from NPPs available from outages and decommissioned plants that have been in service for at least 40 years, we have a unique possibility to develop material lifetime prediction methods with correlation to materials from real service environment and long-term use. In 2019 the first workshop with Ringhals NPP was held and new important materials, such as valve membranes, were identified. The work package will follow the plan below:

1) Identification of critical components in all plants.

2) Possibility to extraction the components from plants.

3) Estimating their residual and total lifetime.

4) If possible, order samples made from the same material from the supplier.

2.2 TASK 1.2 - SENSITIVITY OF POLYMER PROPERTIES TO ADDITIVE CONTENT AND METHODS TO VERIFY POLYMER QUALITY

Additives are used to improve processability of the polymers as well as their material properties. In task 1.2 the aim is to identify important additives and provide suitable methods for their analysis for on-site purposes. The most important additives in the case NPP cable insulators and sealants would be those, which have an effect to their functional properties and hinder the ageing. In this sense antioxidants, plasticizers (for elastomers) and certain colorants would be relevant, as they are known to contribute to the ageing process. Various methods for additive analysis were exist and they provide various possibilities to examine polymeric materials. Several methods are able to qualitatively and/or quantitatively analyze additives that are important for the polymer material properties and ageing behaviour. However, to be able to use many of the methods with their full capacity, high level of expertise is required. The applicability of the methods for on-site use may be limited due to their complexity in sample preparation phase and high equipment purchase cost. The future work continues screening of the methods in order to recognize which ones would be the most suitable methods for on-site analysis.

2.3 TASK 1.3 - SETTING UP SAFETY MARGINS FOR O-RINGS

Task 1.3 is based on the work performed during 2016-2018 in which O-ring ageing data was produced and their acceptance criteria was determined. The material property "compression set" was compared to leakage in specially designed test rigs where the O-rings sealing performance was tested. Traditionally 50 % compression is set as acceptance criteria for an O-ring, but it is known that significantly higher compression set values, up to 90 %, is enough to provide functionality of an O-ring. In our measurements O-rings with compression set of almost 100 % did not show any leakage. Comparison between in-service components showed that most seals made of FKM and EPDM were still flexible and not deformed (set) after ten years of service. Based on both laboratory tests and observations on O-rings from NPPs, NBR rubber seems to be more sensitive to ageing.

In task 1.3 this work will be continued to be able to set realistic safety margins for O-rings i.e. how well the acceptance criteria are set and safety margin assessment is added. Laboratory conditions are normally static whereas O-rings in service are exposed to thermal fluctuations and vibrations as well as water. Therefore, aged O-rings were leak tested after exposure to simulated thermal and mechanical disturbance in order to set relevant acceptance criteria. From Figure 1 the effect of water exposure to compression set can be seen with EPDM and nitrile O-rings. Ageing in air proved to be more degrading most likely to due to the better availability of oxygen.

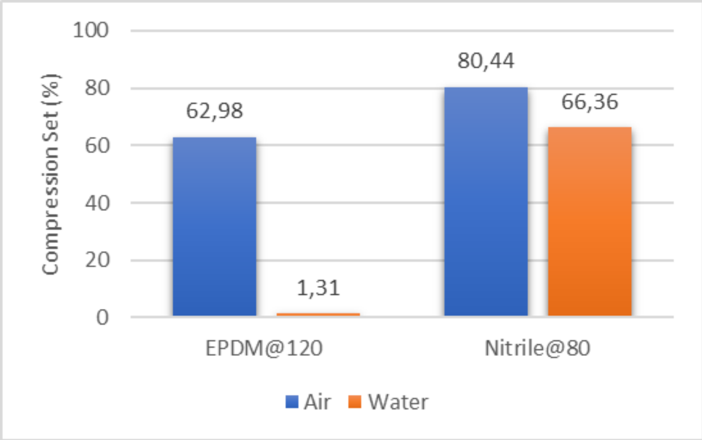

Figure 1. Comparison of the compression set of rubbers aged in air and water. EPDM and nitrile rubber samples were aged for half year at 120 and 80 °C, respectively.

Stress relaxation tests have also been used in the ongoing project in order to evaluate the O-ring material. This method is similar to compression set, but instead of dimension changes, the sealing force of the rubber or O-ring is measured. Test data is recorded online and the specimen are exposed to heat during the measurement, i.e. ageing and measurements are performed simultaneously.

3 Improvements in ageing management of polymer components (WP2)

The objective in WP2 is to provide improvements to ageing management in order to enhance the long term and safe use of the plants. The most suitable way to do this is to provide techniques that can be used to measure component condition non-destructively. For practical reasons, these techniques are typically non-destructive or require very small piece of sample material. One key issue developing novel non-destructive condition monitoring techniques is to understand how the non-destructively measured material parameter relates to polymer condition and its ageing. Such correlations are of interest in this research, combined with the objective to develop techniques for on-site measurements.

3.1 TASK 2.1 - ONLINE CONDITION MONITORING TECHNIQUES

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

If ageing of the materials leads to e.g. cracking or inhomogeneities in the materials these could possibly be detected by designing a method utilizing partial discharge. State of the art measurements of impedance are not ready for products, only for test samples. The research question is how to design specific measurements methods and test samples sizes that are suitable for aging tests. The electric properties will be correlated to relevant material properties such as elongation, compression set and tightness etc. before and after ageing in order to verify the methodology.

3.2 TASK 2.2 - SENSITIVE ANALYSING TECHNIQUES

In task 2.2 we will look at a sensitive technique i.e. MC to be able to measure material deterioration/ageing at temperatures, as close as possible to the temperature experienced by the material in NPPs. MC like DSC (Differential Scanning Calorimetry) can register oxidation exotherms or any exothermic chemical and physical changes. The DSC used to study reactive materials can have a detection limit of about 50 μW using 1 mg sample mass. Microcalorimeter can have the detection limit of about 20 μW using 1 – 10 g sample mass. The specific sensitivity is thus 103 times higher than DSC. This also means that microcalorimeters can detect the reactions at about 100 K lower than the DSC. Small sample sizes allow studies on materials such as coatings, adhesives and seals. Using newer techniques, measurements can be performed over a shorter period and at lower temperatures in comparison to the conventional oven tests. Polymers used in NPPs are usually very durable and hence traditional lifetime prediction measurements are very time consuming. Therefore, a sensitive technique able to detect degradation in an early stage is required.

The aim within task 2.2 is to verify the use of this MC as a condition monitoring technique as well as lifetime prediction for cables and other polymeric materials. This is conducted with a series of sensitivity studies, coupled with other techniques (e.g. detailed chemical analysis of the rubber before and after the trials) which can be used for the validation of the technique. According to the results obtained in 2019, activation energy values for EPDM sample material could be estimated from the measured specific integrated heat.

3.3 TASK 2.3 - IMPROVED INTERPRETATION OF NON-DESTRUCTIVE TESTING DATA

In task T2.3 the goal is to develop computational methods to assist in interpreting non-destructive testing data for polymeric NPP components. Molecular dynamics simulations can be applied in correlating the ageing effects in material to non-destructively measured material parameters. For example, ultrasonic technique seems to be well compatible with MD simulations. MD simulations has shown that the parameters required for sound velocity calculation, i.e. Young's modulus, Poisson's ratio and density values, could be extracted for PE and XLPE by mimicking standardized tensile test, as shown in Figure 2. However, there seems to be discrepancy between the computationally predicted and literature values. This may be due to the sensitivity of the sound velocity to certain parameters, such as the Poisson's ratio. The future work will focus on examining the inconsistency between the calculated and in the literature reported sound velocity values and providing data how ageing affects to the sound velocity values.

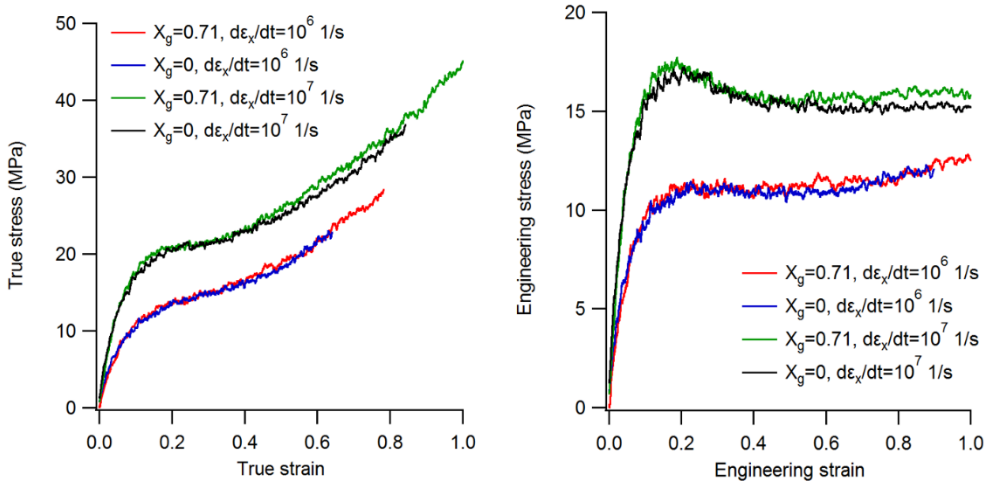

Figure 2. Simulated stress-strain curves for the PE (blue and black curves) and XLPE (red and green curves) systems. Xg stands for gel fraction, and dεx/dt for strain rate in x direction.

4 International cooperation (WP3)

Within WP3 international cooperation is promoted. This is accomplished by organizing and participating meetings and educational events with nuclear power industry members, researchers and regulators. The aim is to gain synergistic advantages from a large Nordic consortium in research activities, nuclear safety issues and improved plant efficiency.

5 Deliverables

- Workshop with NPPs choose material from closed NPPs and/or from outages. Find suitable reference materials.
- Report on polymer additive analysis techniques and condition indicators
- Report suggesting safety margins for O-rings based on the COMRADE project and complementary studies during 2019. Suggestions for further tests and improvement
- Report on available monitoring techniques based on literature, studies of other industrial sectors and initial laboratory tests
- Report on applicability of microcalorimetry on condition monitoring and first results
- Review on NDTs detecting ageing induced changes in polymer structures
- Workshop on polymer ageing in NPP applications

Keywords

Nuclear safety, o-ring, rubber, power plant, microcalorimetry, online monitoring, additive

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Life-time estimation of rubber parts is shown to be a viable study via both accelerated ageing at higher temperatures and sensitive monitoring of degradation at operating temperatures.

Online wireless monitoring is shown to have potential and will be investigated thoroughly. Lastly, and importantly, the involved Nordic power plants have demonstrated great interest in the study and its continuation.

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