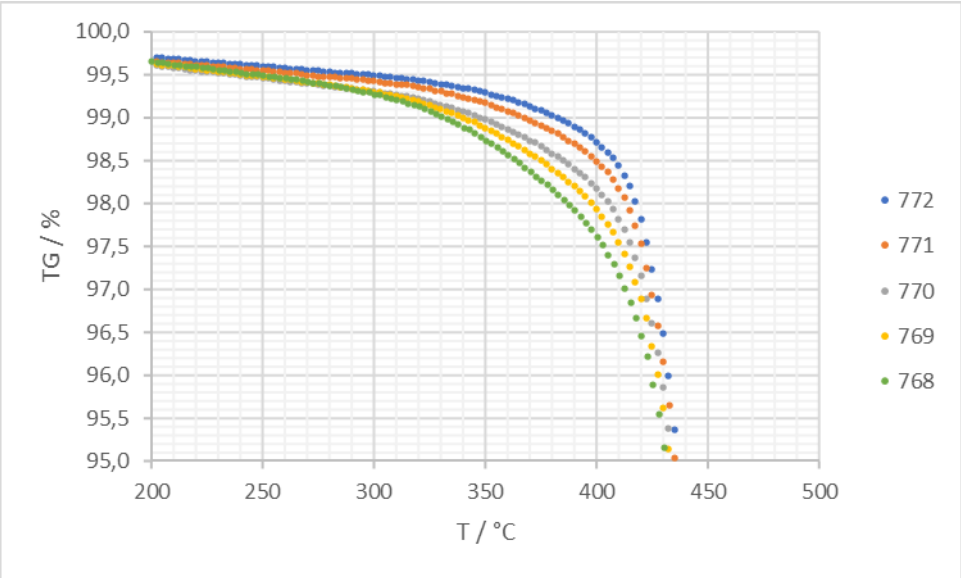
RESEARCH REPORT

VTT-R-00107-22



Sensitivity of DSC and TGA in antioxidant and filler analyses

Authors: Konsta Sipilä and Harri Joki

Confidentiality: Restricted to SAFIR2022 until January 2025

Version: 28.1.2022

VTT

beyond the obvious

Report's title Sensitivity of DSC and TGA in antioxidant and filler analyses	
Customer, contact person, address SAFIR2022	**Order reference**
Project name Safety criteria and improved ageing management research for polymer components exposed to thermal-radiative environments	**Project number/Short name** 129019/SAMPO
Author(s) Konsta Sipilä and Harri Joki	**Pages** 13/
Keywords DSC, TGA, polymer, antioxidant, filler, nuclear power plant, on-site analysis	**Report identification code** VTT-R-00107-22

Summary

Polymers are used in various applications in nuclear power plants, such as cables and sealants, that have safety relevance either during normal power operation or accidental scenarios. Like any other materials in use, polymers also experience ageing in their applications and especially sealants need to be renewed rather often. The polymer-based materials used in such components are not standardized in as high detail as e.g. the metallic alloys, enabling changes in material composition between different batches. To ensure material quality between different material batches, simple on-site analysis methods for such materials are needed. In this report, the development work of two methods measuring the antioxidant performance and filler content is presented. Applicability of oxidative induction time (OIT) and thermogravimetric analysis (TGA) for analysing antioxidant performance and filler amounts in samples with known antioxidant and filler contents were performed. The measured OITs seemed to react to the antioxidant content of the samples and a decreasing trend in OIT could be detected as a function of antioxidant content. However, the absolute OITs were small compared to previously measured values with similar material. Ageing seemed to have an effect on the OIT when the material had a low amount of antioxidant compounded in it. Regarding the TGA measurements, differences in the measured thermographs could be observed on a wider temperature scale ranging from ca. 300°C to 420°C but not from the thermogravimetric weight loss measured after heating up to 800°C. Differences as small as 2 phr in filler content could be extracted. Thermal ageing did not seem to have a significant effect on the measurement results.

Confidentiality	Restricted to SAFIR2022 until January 2025

Espoo 28.1.2022

Written by	**Reviewed by**
Konsta Sipilä Research Scientist	Timo Saario Principal Scientist

VTT's contact address
P.O.Box 1000, FI-02044 VTT

Distribution (customer and VTT)

SAFIR2022 one copy, VTT one copy

Approval

VTT TECHNICAL RESEARCH CENTRE OF FINLAND LTD

Date:	
Signature:	
Name:	Mikko Vepsäläinen
Title:	Research Team Manager

Preface

This work was completed as part of the Finnish Research Programme on Nuclear Power Plant Safety 2019 – 2022 (SAFIR2022) within the SAMPO (Safety criteria and improved ageing management research for polymer components exposed to thermal-radiative environments) project.

Espoo 28.1.2022

Authors

Contents

1. Introduction

Nuclear power plants (NPPs) use polymer materials in several different components such as sealants, cable insulators and jackets due to their sealing and insulating properties. These components are subjected to ageing like any other component used in NPPs. Temperature, ionizing radiation and moisture are considered to be the most important environmental stressors in NPP applications [IAEA, 2012]. It has also been shown that ageing is faster when oxygen is available, compared to a case when ageing is performed in an inert atmosphere [Spång, 1997].

The composition has a significant effect on the polymer's tendency to age. It is also recognized that the quality of the polymer can vary between different material suppliers, or even between different material batches. This may be due to several reasons, but one obvious one is availability issues with additives used in polymer blends. Varying material quality could be problematic in the ageing management perspective and thus practical material quality verification methods would ease recognizing poor materials before their installation.

Within the SAMPO project, the aim is to study the role of different additives and their significance in the ageing process, as well as to provide tools to measure relevant additives in a straightforward manner. The planned progress of the project work is presented in Figure 1. During the first project year, a literature survey was performed where various polymer additives and methods to evaluate them qualitatively and quantitatively were listed [Sipilä, 2020]. It was identified that from ageing perspective antioxidants, plasticizers and certain colorants contributed to the ageing behaviour of the polymer. In addition, it was recognized that fillers were an important additive group since they are commonly used in polymer blends. It can be speculated that increasing the filler amount in a polymer blend can result in lower production costs but also lower product quality.

During the second project year, suitable analysis methods for fillers and antioxidants were identified and small-scale tests were performed to present their applicability [Joki & Sipilä, 2021]. Differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) spectroscopy were used in determining the antioxidant consumption while thermogravimetric analysis (TGA) combined to energy-dispersive X-ray spectroscopy (EDS) was used to analyse the filler content. Oxidation induction time (OIT) measurement results obtained with DSC and the defined carbonyl indexes (CI) with FTIR showed that both methods could clearly distinguish the aged and unaged samples from each other. Based on the filler analysis, it was concluded that combining EDS to the TGA made it possible to accomplish a more detailed analysis of the filler content as it enabled identification of cross-linking agent and processing aids (S and Zn in this context) and thus extracting the mass of those species from the actual carbon black filler content.

As the functionality of OIT and TGA/EDS analyses have been shown, the next step would be estimating their sensitivity in antioxidant and filler analyses, respectively. In this context, the sensitivity means how accurately the measurement methods can measure the additive content in the samples. The sensitivity of the methods needs to be shown before moving to the final stage of the development process, i.e. development of measurement procedures for on-site purposes.

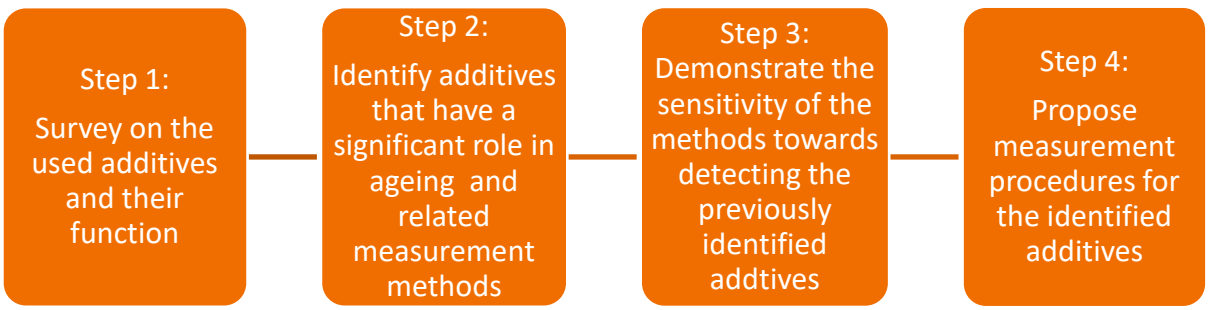


Figure 1. Planned progress for the additive analysis method development.

2. Goal

The goal of the work was to demonstrate the sensitivity of DSC and TGA measurements in measuring antioxidant and filler amounts with custom made EPDM materials having known antioxidant and filler contents.

3. Materials and methods

3.1 Materials

The tested materials were EPDM rubber with a known content of antioxidants and carbon black filler manufactured by James Walker®. The antioxidant and filler content of the EPDM sheets are shown in Table 1. No other information on the composition of the samples was available.

Table 1. The antioxidant (AO), filler and EPDM content as part per hundred rubber (phr) of the delivered materials.

SAMPLE ID	AO / phr	Filler / phr	EDPM / phr
10/768/21	3	81	100
10/769/21	2	79	100
10/770/21	1,2	69	100
10/771/21	0,6	61	100
10/772/21	0,2	57	100
REF	0	55	100

3.2 DSC

The method used in DSC measurements was the same as in the previous work [Joki & Sipilä, 2021]. The measurement of OIT was performed by using TA instruments DSC 1620 Differential Scanning Calorimeter. A 4 mm diameter sample was stamped out of the EPDM sheet and weighted before inserting it between two aluminium plates. A small hole was pierced in the middle of the aluminium cover and the sample was inserted in the DSC sample chamber. The chamber was filled with nitrogen gas and heated up to 200°C with a constant rate of 20°C/min. When the temperature was reached, it was held constant and the atmosphere was changed from nitrogen to oxygen. The followed heat flow was recorded as a function of time. From the resulting graph, OIT was defined.

3.3 TGA

The TGA was performed with Netzsch STA 449 F1 Jupiter thermogravimetric analyser. In TGA the mass of the sample is measured as its temperature is increased. In this specific case, the temperature ramp was 10°C/min and the system was heated up to 800°C under a nitrogen environment. This would result in vaporizing all volatile species leaving only the assumed filler material to be weighted. A more detailed analysis of the remnants can be conducted by using EDS to extract any elemental species.

3.4 Tensile tests

Tensile tests were performed using Instron 5500K8810/4505H2190 machine with 100 N load cell and pneumatic grips. 50mm/min strain rate was applied in the tests and grip distance was 50 mm. Optical measurement of the cross-head movement was used in the elongation measurement. The samples were prepared from the 1 mm thick sheets according to EN-ISO 37:2005 (type 2). Five individual samples per ageing condition were tested.

4. Results and discussion

4.1 OIT

The OIT curves for the EPDM materials are shown in Figure 2. With each material, one exothermic reaction can be distinguished from the data. There are two repetitions for the reference material since the first test was terminated prematurely. The calculated OITs for each sample are presented in Figure 3. A decreasing trend in OIT as a function of antioxidant content can be observed from the results. However, the absolute values of the OITs seem to be small, especially when compared to results obtained previously with similar material [Sipilä & al. 2017], which seemed to be about a decade larger with the unaged material. With severely aged material the OITs seemed to be of similar magnitude.

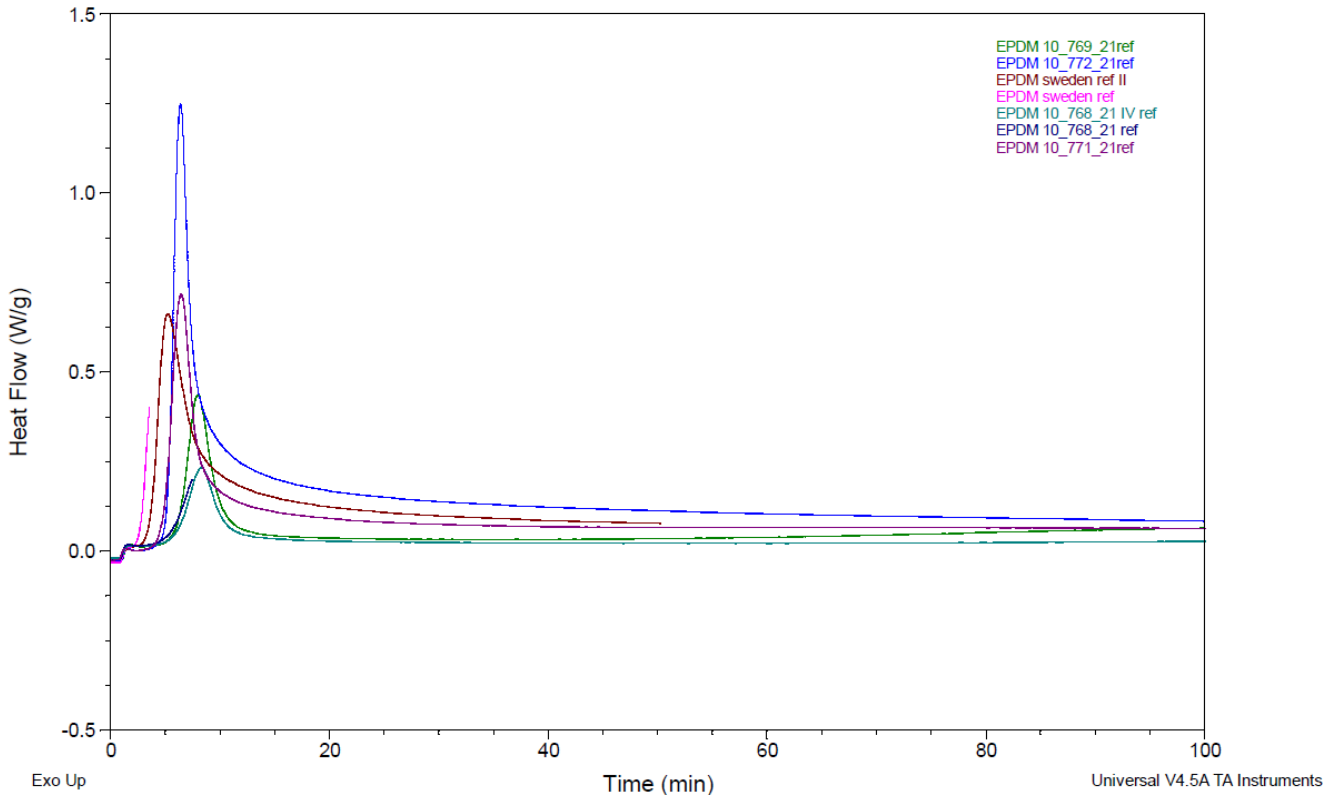


Figure 2. OIT thermographs for the EPDM samples.

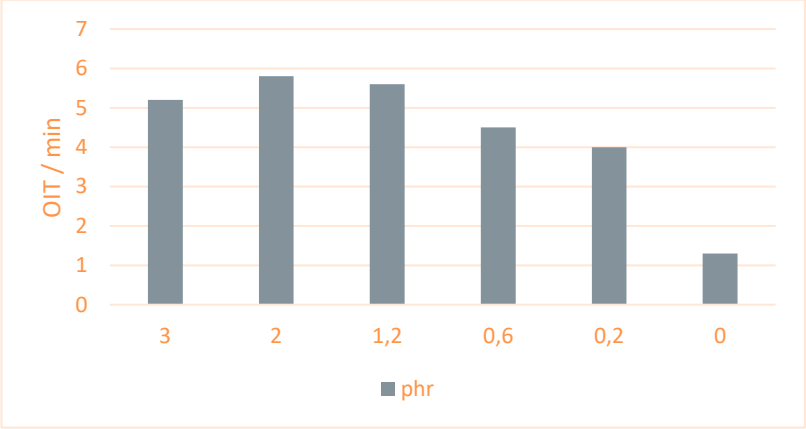


Figure 3. Defined OITs for the EPDM samples tested.

Due to the suspiciously low OITs measured, thermal ageing of the samples 769 and 772 samples was decided to perform in order to see if the antioxidant consumption had an effect on the measured OIT values. The ageing was performed at 130°C in an air atmosphere. OITs and elongation at break values measured for the thermally aged 769 and 772 samples are shown in Figure 4 and Figure 5.

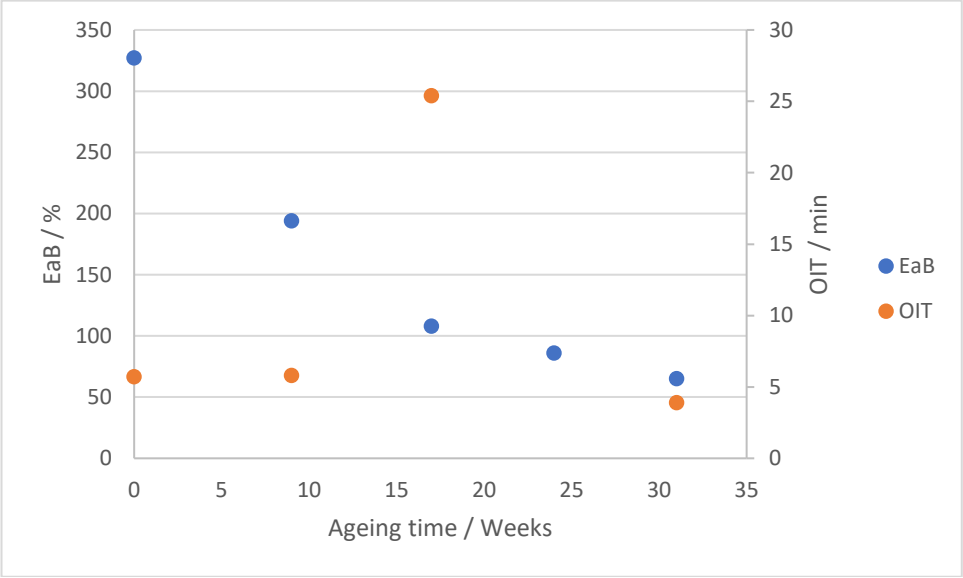


Figure 4. OITs and elongation at break (EaB) values measured for the aged 769 samples.

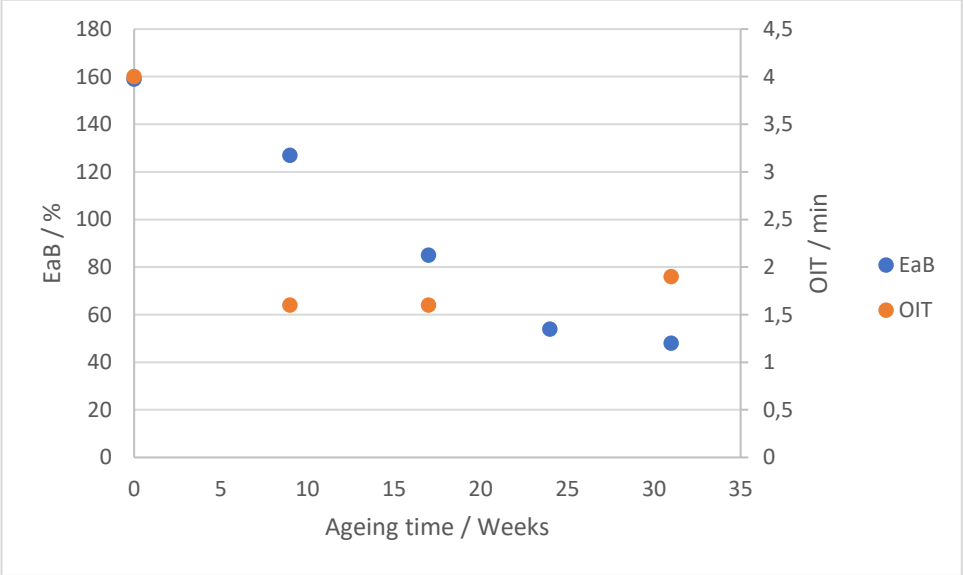


Figure 5. OITs and elongation at break (EaB) values were measured for the aged 772 samples.

From the EaB values it can be seen that the sample 769 degrades as a function of ageing. However, the OIT measurement results are not as straightforward. After 17 weeks of ageing the OIT suddenly increases to 25 min. This measurement point obviously should be re-measured and it can be left out from the analysis for now. The final measurement point at 31 weeks shows some decrease in OIT. This is somewhat different from the previous experience, where the OIT decreased tens of minutes from the initial value when the samples were severely aged [Sipilä et al, 2017]. Another interesting point arising from Figure 5 is that the EaB value decreases already after 9 weeks of ageing. This would indicate that the antioxidants do not fully protect the polymer backbone from oxidation. This would mean either hindered reaction of the antioxidants with the forming radicals or almost full consumption of the antioxidant. The low absolute OIT values indicate the latter, but the measurements performed here are not complete enough to make a certain conclusion. Measuring the carbonyl index from the aged samples might give insight into how severely the polymer backbone has oxidized in this case.

Figure 5 shows a bit different behaviour for 772. In the beginning, the OIT is larger (4 min) compared to the aged values (below 2 min). Such behaviour would be expected as the antioxidants are consumed as the material is aged. Due to the low amount of antioxidants in 772, a rather fast decrease in OIT was expected and also observed. Nevertheless, further analysis is required to explain the low OIT values measured. Here again, measuring the carbonyl index should give indications on the formation of oxidation products and thus the severity of ageing as a function of ageing.

4.2 TGA

TGA results for the EPDM samples are shown in Figure 6. At first sight, it seems that no significant differences could be observed between the samples. The thermogravimetric weight loss seems to behave similarly throughout the temperature range and at the end of the test, the weight losses were very close to each other, as can be seen from Figure 7. The final weight loss is actually 0.22 % higher with the sample having the least amount of fillers in it compared to the most filled material. This was an unexpected result and indicates that the thermogravimetric weight loss after heating the sample up to 800°C can not be used in detecting the differences in filler contents.

However, the curves differ slightly around 400°C and this area in the thermographs was examined in more detail. Magnification of the data around this section of the curve is shown in Figure 8. From this figure, the difference in weight loss becomes evident in a temperature range from roughly 300°C to 420°C. The differences between the curves seem to be at the maximum around 400°C, so this

temperature was chosen as the temperature at which the weight loss between the samples was compared. Here the weight loss increases as the filler content increases (the same behaviour applies to the whole beforehand mentioned temperature range). The difference in weight loss at 400°C between the most and the least filled materials is 1.1%.

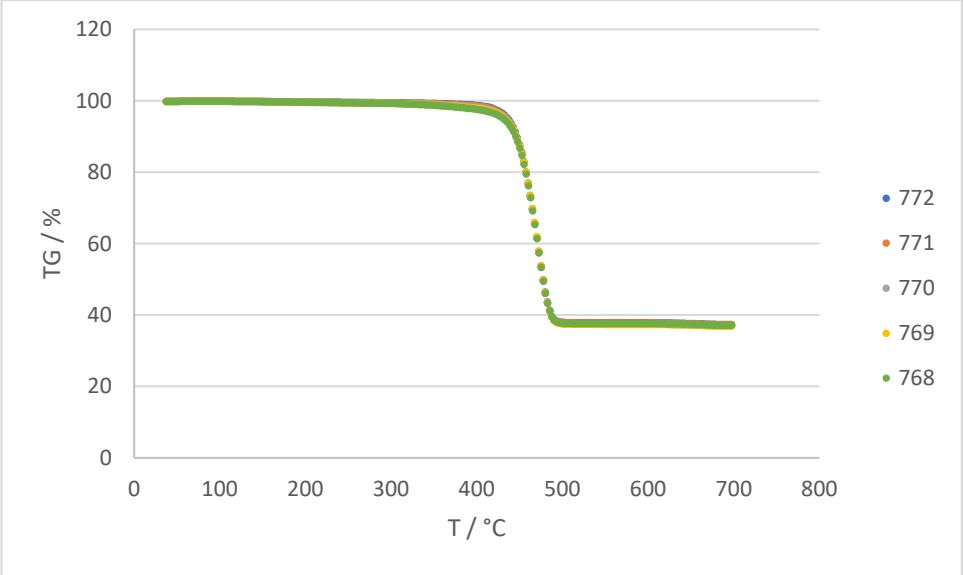


Figure 6. Thermographs for the studied EPDM samples.

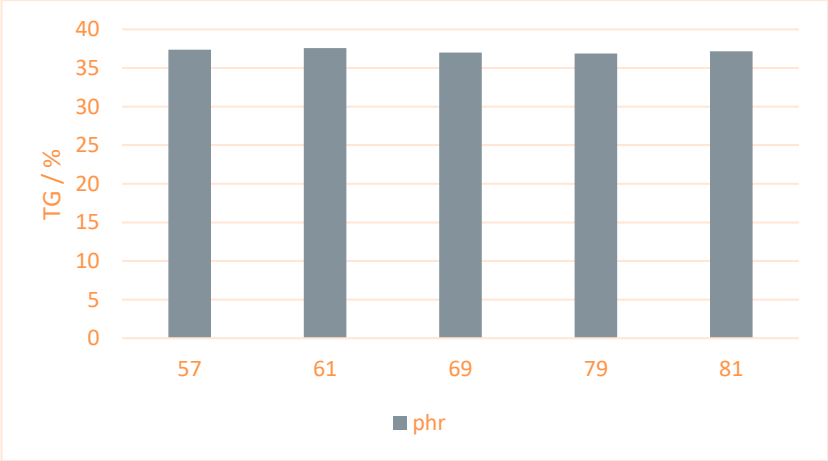


Figure 7. Thermogravimetric weight loss after heating the samples up to 800°C as function of filler content (phr).

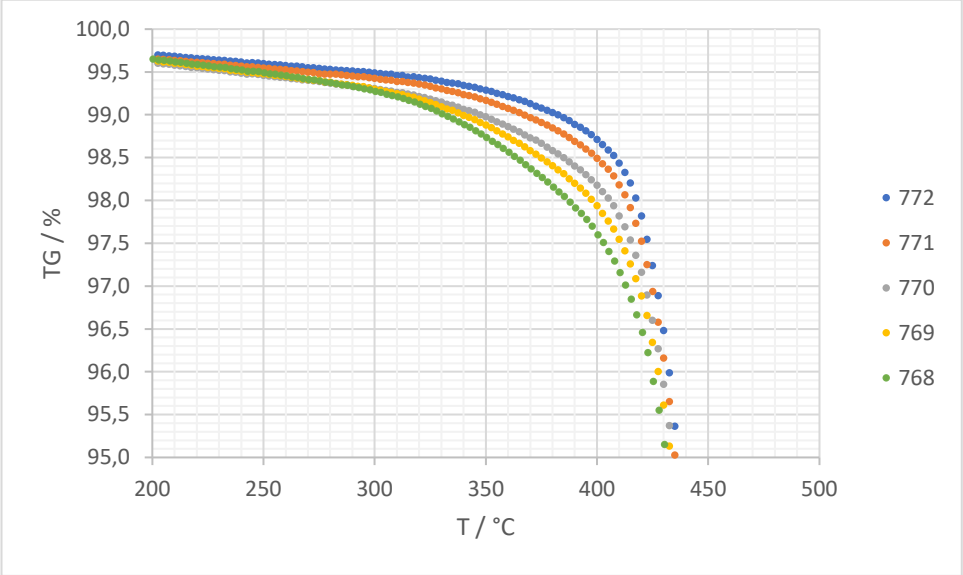


Figure 8. Magnification on the thermographs for the studied EPDM samples.

The same measurements were repeated with aged samples. The results after 9 and 17 weeks of ageing at 130°C are shown in Figure 9 and Figure 10, respectively. The curves obtained with the aged samples differ at lower temperatures. With aged samples, the curves are almost horizontal below 250°C, while with the unaged samples the curves are linear but slightly decreasing around the temperature of 250°C. This behaviour is explained by the evaporation of species that are easily vaporized. Such species have already been removed from the aged samples during the ageing treatment. The ageing does not seem to have an effect on distinguishing the differences between the curves around 400°C. After 9 and 17 weeks of ageing, the difference in weight loss between the least and the most filled materials were 0.8% and 0.9%, respectively. Thus, it seems that TGA can detect differences in filler content at least as low as 2 phr (the difference between 772 and 771 materials) with unaged and aged materials. However, the scatter of the results needs to be verified with additional measurements.

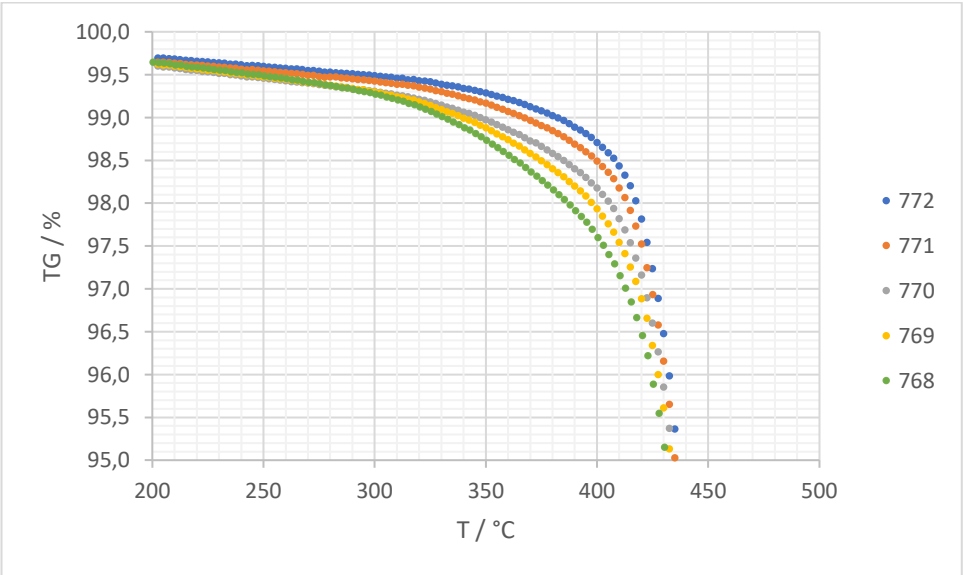


Figure 9. Magnification on the thermographs for the studied EPDM samples aged at 130°C for 9 weeks.

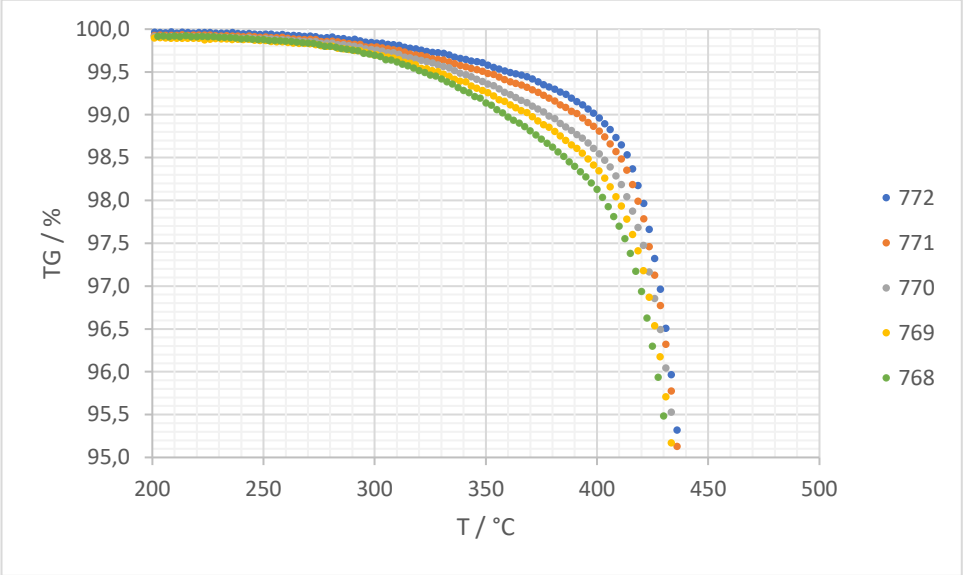


Figure 10. Magnification on the thermographs for the studied EPDM samples aged at 130°C for 17 weeks.

An additional EDS analysis was performed on one 768 sample to confirm the composition of the ash after the TGA experiment. The results are summarized in *Figure 11*. EDS analysis revealed that most of the ash was carbon. There was a small amount of oxygen and Zn in the analysed ash. Zn is not a filler material but most likely a processing aid used during the manufacturing of the compound.

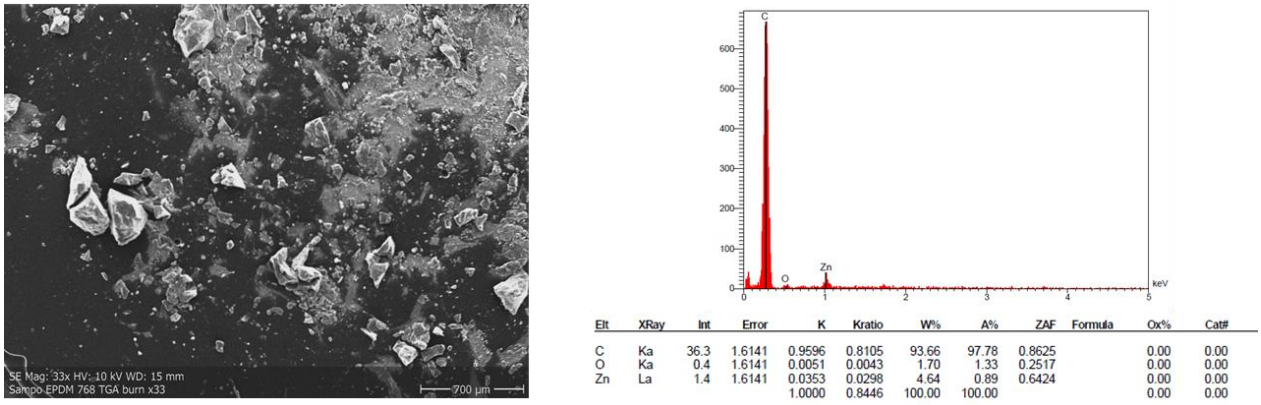


Figure 11. SEM image (left side) and EDS spectrum (right side) from the ash of the 768 sample.

5. Conclusions

OIT and TGA measurements were further developed to be used for on-site quality analysis of polymeric components at nuclear power plants. The ability of the methods to measure known antioxidant and filler amounts in EPDM samples with the known composition of these ingredients was evaluated. OIT measurements provided lower OIT values than previously measured with similar material. However, the OIT values seemed to decrease with decreasing antioxidant content. The measured OITs decreased due to ageing, although it took longer ageing times to see an effect when the antioxidant content was higher. Further measurements of the carbonyl index might provide insights into the low measured absolute OIT values and the ageing effects observed. TGA analysis seemed to distinguish the differently filled materials from each other both in unaged and aged conditions at temperatures around 400°C.

Samples having as small as 2 phr differences in filler content could be distinguished from each other. Repetition measurements would be still required to evaluate the scattering of individual measurements.

References

Joki, H. and Sipilä, K. 2021. Identifying suitable methods for on-site polymer quality verification. VTT-R-00072-21. 14 pp.

Sipilä, K., Joki, H., Jansson, A. and Wogelred L. 2017. Oxidation of EPDM: oxidation depth measurements and effects on material properties. VTT-R-01190-17. 21 pp.

Sipilä K. 2020. Polymer additives and methods to verify polymer quality. VTT Research report VTT-R-00065-20. 23 pp.

Spång. 1997. Aging of Electrical Components in Nuclear Power Plants – Relationships Between Mechanical and Chemical Degradation After Artificial Aging and Dielectric Behaviour During LOCA. SKI Report 97:40. 118 pp.