RESEARCH REPORT

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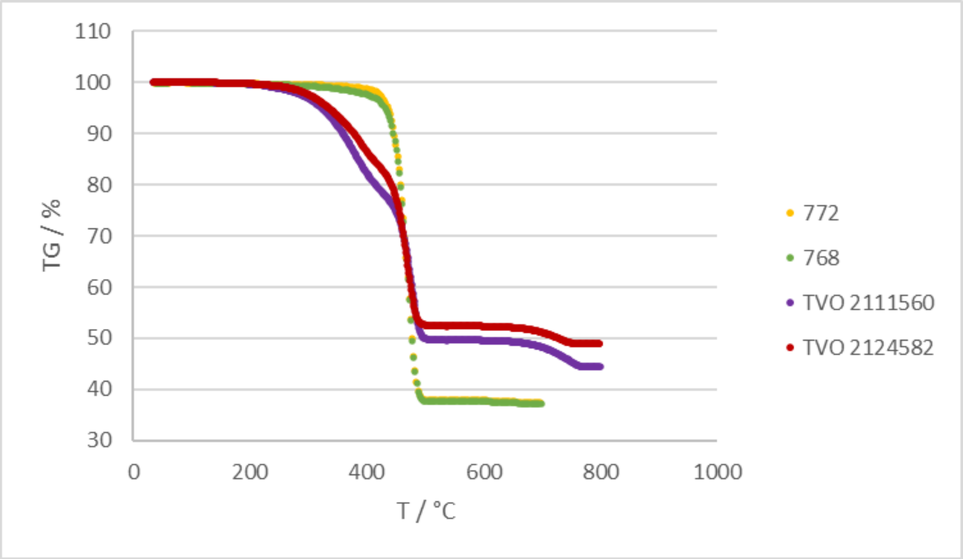

Application of DSC and TGA in quality control of polymer-based components

Authors:	Konsta Sipilä, Harri Joki and Isabella Björkvist
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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. In these applications, polymeric components are subjected to stressors like heat, radiation and moisture, which lead to the ageing of the materials. Polymeric sealants are quite often exchanged to new ones due to their low cost. However, when a new sealant is installed, it's material quality may be different compared to the previous batch. Thus, suitable quality control methods for new sealant batches would be good to be available. In this report, development work with two methods, oxidation induction time (OIT) based on differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) measurements is presented. The OIT measurement seemed to work well with the commercial EPDM quality but provided suspiciously small OIT values with the model materials. It was proposed that the high-end material might contain antioxidant system that is not very well measured with the conventional OIT measurement. The TGA results seemed to show a good capability to detect differences between the commercial and model EPDMs as well as differences between the filler contents in the model materials. Two different temperature ranges in the TGA graph is proposed to distinguish the commercial grade EPDM from the high-end EPDM and small variations between the high-end materials in the composition.

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Written by	**Reviewed by**
Konsta Sipilä Senior Scientist	Aki Toivonen Senior scientist

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

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Date:	
Signature:	Vepsäläinen Mikko 912690851 Digitally signed by Vepsäläinen Mikko 912690851 Date: 2022.12.28 15:16:38 +02'00'
Name:	Mikko Vepsäläinen
Title:	Research Team Leader

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. The Finnish Nuclear Waste Management Fund VYR and VTT are acknowledged for funding this work.

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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. 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.

On the following year, OIT and TGA measurements were further developed to be used for on-site quality analysis of polymeric components at nuclear power plants [Sipilä & Joki, 2022]. 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 as the antioxidant content decreased. The measured OITs decreased due to ageing too, although it took longer ageing times to see an effect when the antioxidant content was higher.

TGA analysis seemed to distinguish the differently filled materials from each other both in unaged and aged conditions at temperatures around 400°C. Figure 1 shows the results from the TGA measurements performed during the previous year. Samples having as small as 2 phr (parts per hundred rubber: grams of filler per 100 grams of rubber or resin) differences in filler content could be distinguished from each other (curves 768 and 769 in Figure 1).

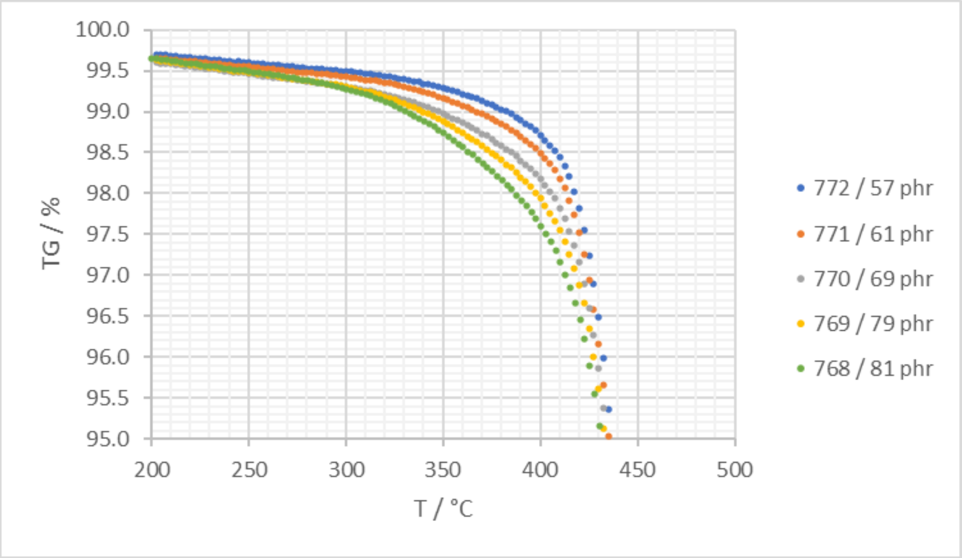

Figure 1. Magnification on the thermographs for the studied EPDM samples having various filler contents.

This work aims to develop these two methods further to be ready to be used at on-site measurements. More detailed analysis of the OIT curves obtained by DSC measurements is performed to ensure that the obtained OITs really correlate with antioxidant consumption. TGA results seemed promising but further data is required to estimate the scatter of the individual measurements. Finally, measurement procedures are listed in a simplified manner.

2. Goal

The goal of the work is to study the applicability of DSC and TGA methods as on-site quality monitoring tools for polymeric components used in nuclear power plants.

3. Experimental methods

This section gives a detailed instruction on how to perform DSC and TGA measurements on-site. The procedure with both methods is comprised of three parts: sample preparation, measurement, and data analysis.

3.1 DSC

The principle of OIT measurement is rather simple, the sample is heated in an inert atmosphere to a desired temperature and the atmosphere is changed to oxidizing. The released heat flow in this oxidizing atmosphere and constant temperature is measured as function of time. DSC equipment are commercially available from several manufacturers and most of the equipment are able to perform the required analysis sequence.

3.1.1 Sample preparation

A proper sized cutting or puncher tool is used on the sample to cut or stamp out suitable size sample. The sample weight should be about 10 mg, but slightly larger sample amount, e.g. 20 mg, do not complicate the measurement procedure. 10 mg sample stamped out of a 1 mm XLPE sheet would usually correspond smaller than 5 mm diameter circular sample. The sample is weighed and inserted between two small aluminium plates and a needle is used to pierce the upper aluminium plate.

3.1.2 Measurement procedure

The sample is now inserted into the measurement chamber. The chamber is filled with nitrogen gas. The chamber is heated up to 200°C with a constant rate of 20°C/min. When the temperature is reached, the atmosphere is switched to oxygen. The heat flow will be recorded as function of time and plotted on a graph. Duration of the recording can be optimized when measuring a lot of similar type of samples, but if there is no previous knowledge what the OIT could be, duration of 240 minutes could be applied.

3.1.3 Data analysis

An example on the obtained isothermal DSC curve is shown in Figure 2. The baseline of the curve is determined by fitting a horizontal curve (green curve in Figure 2) on the data where the heat flow is constant. The heat flow starts to increase the same time as the oxidation process starts in the polymer. Another line is fitted to this part of the curve (red curve in Figure 2). The cross section of these two lines is defined as onset for oxidation and the OIT value is defined by this point. However, it should be noted that for some antioxidant systems it seems that OIT is not suitable method and further studies would be required to confirm the actual cause behind this limitation.

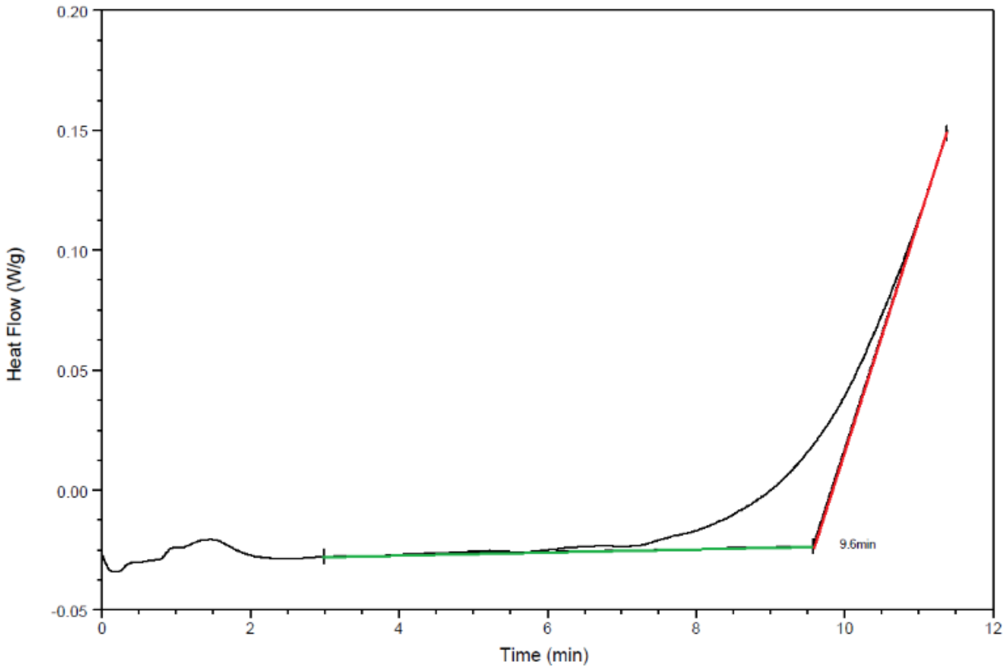

Figure 2. An example DSC curve on EPDM sample aged at 100°C for 40 weeks and definition of OIT.

3.2 TGA

TGA method has a rather simple operation principle. The sample is heated up and the weight of the sample is monitored as the temperature increases. The weight decreases as the volatile species are removed from the sample due to the increased temperature. TGA equipment is commercially available from several manufacturers.

3.2.1 Sample preparation

A sharp knife is required to cut a small piece of sample. Sample mass of 15 mg is sufficient but larger sample, e.g., 35 mg, do not affect the measurement significantly.

3.2.2 Measurement procedure

The sample is inserted in the sample chamber and nitrogen atmosphere is applied. The heating will start with the rate of 10 °C/min until the temperature of 800 °C is reached. The weight of the sample is recorded constantly during the test. In some equipment also the released heat can be measured simultaneously to provide additional information.

3.2.3 Data analysis

The measured data should be compared to a reference sample, previously shown to endure in the chosen application. The comparison should be performed first at the temperature range around 600 °C to see significant changes in residual weight. If there are no significant differences in the remaining weights around this temperature, then the lower temperature range around 400°C should checked if there are any significant variations in the remaining weight.

4. Results and discussion

In this section the applicability of DSC and TGA measurements for on-site quality analyses are evaluated. The evaluation is based on the results obtained earlier in SAMPO project, new measurement results obtained in 2022 and data available from open literature.

4.1 DSC

The earlier measured OIT results with samples containing different amounts of antioxidants are shown in Figure 3. From the figure, it can be seen that the OIT decreases as the antioxidant amount decreases. However, at higher antioxidant concentrations, no significant changes in the measured OIT could be observed. To evaluate the applicability of the method for on-site analysis, the resolution of the method and the absolute magnitude of the measured OIT was further investigated.

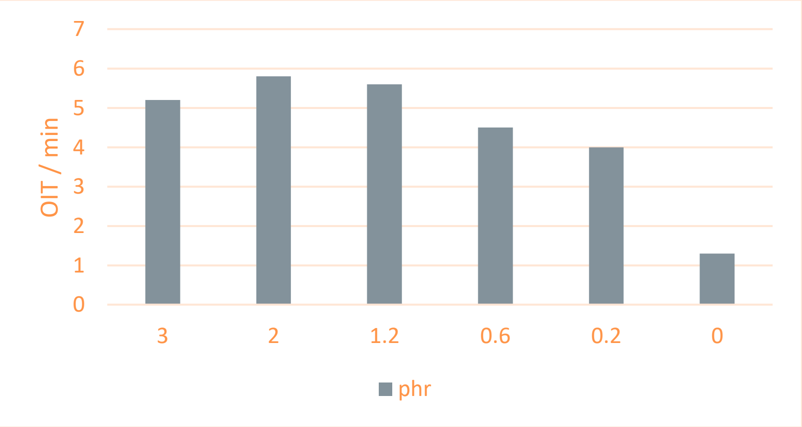

Figure 3 OIT measurement results obtained with EPDM samples as function of antioxidant concentration (phr = part per hundred rubber).

Two additional OIT tests were performed with different test parameters compared to the previous tests with samples containing high and low antioxidant concentrations. A longer testing time up to 180 min and 25 °C higher test temperature was applied (being now 225 °C) to detect any additional peaks in the data. The results are shown in Figure 4 and Figure 5. In Figure 4, only one exothermic peak is observed, despite the high isothermal temperature. The absence of other exothermic peaks is assumed to further indicate that the observed peak in the data is indeed correlating with the oxidation of the polymer matrix.

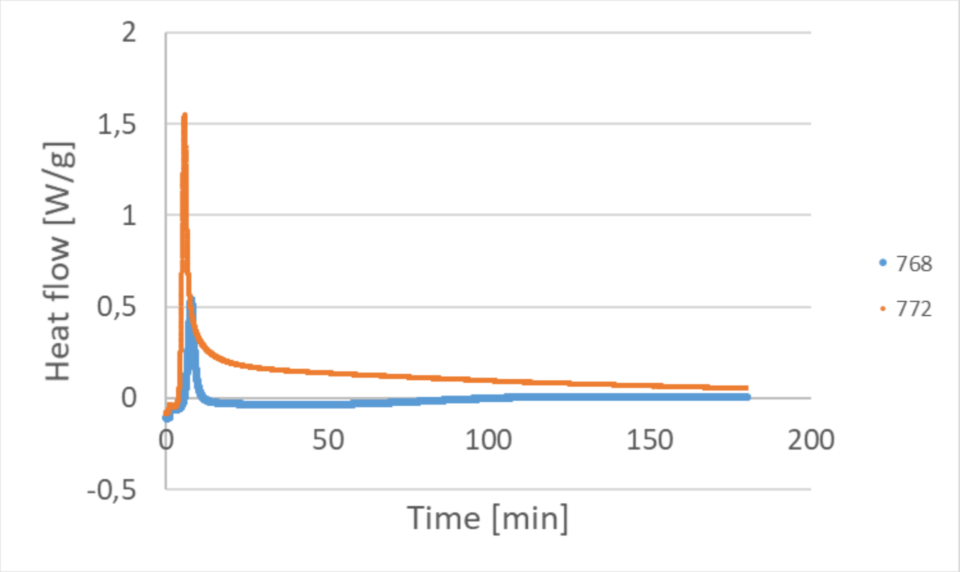

Figure 4 OIT measurements performed at isothermal temperature of 225 °C for sample containing antioxidants 3 phr and 0.2 phr (768 and 772, respectively).

Figure 5 shows the characteristics of the peaks in more detail. OIT is determined by the intersection of the slope of the curves (green and red lines) and the baseline (black horizontal line). The analysis gives OITs of 6.0 min and 4.4 min for the samples containing 3 phr and 0.2 phr antioxidants, respectively. Compared to the OIT values measured earlier at 200 °C there is a small increase in both OIT values. This is somewhat contradictory what has been reported earlier for EPDM materials in [Mason & Reynolds, 1998]. Based on their studies, the OIT decreased with roughly a factor of 2 when the isothermal temperature was risen by 10 °C.

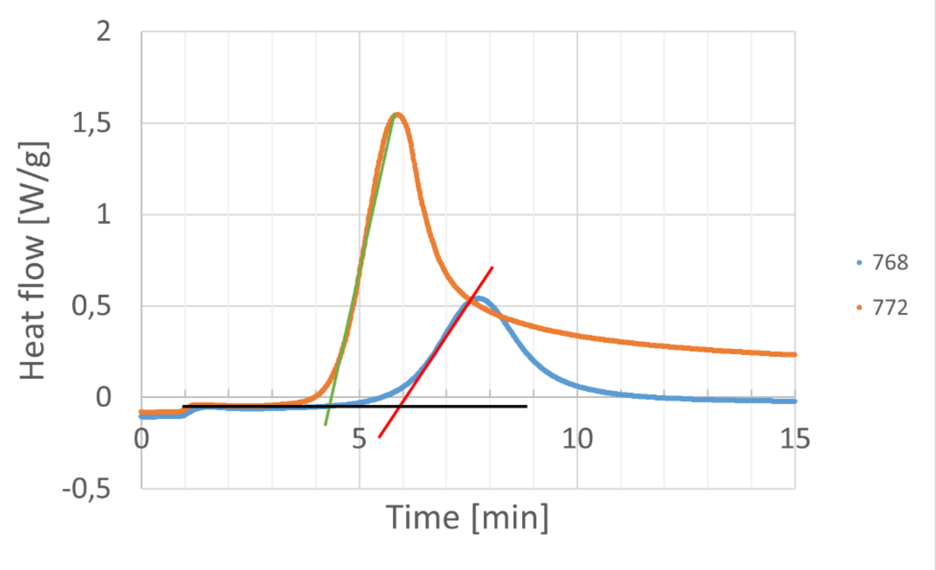

Figure 5 Close up figure from Figure 3.

In order to compare the OITs measured with the model materials, two different commercial EPDM qualities with unknown composition (previously obtained from TVO) were measured. The results are shown in Figure 6. For both commercial type of EPDMs OITs could be determined and it seems that the obtained values are roughly 20-times greater than was obtained with the model materials.

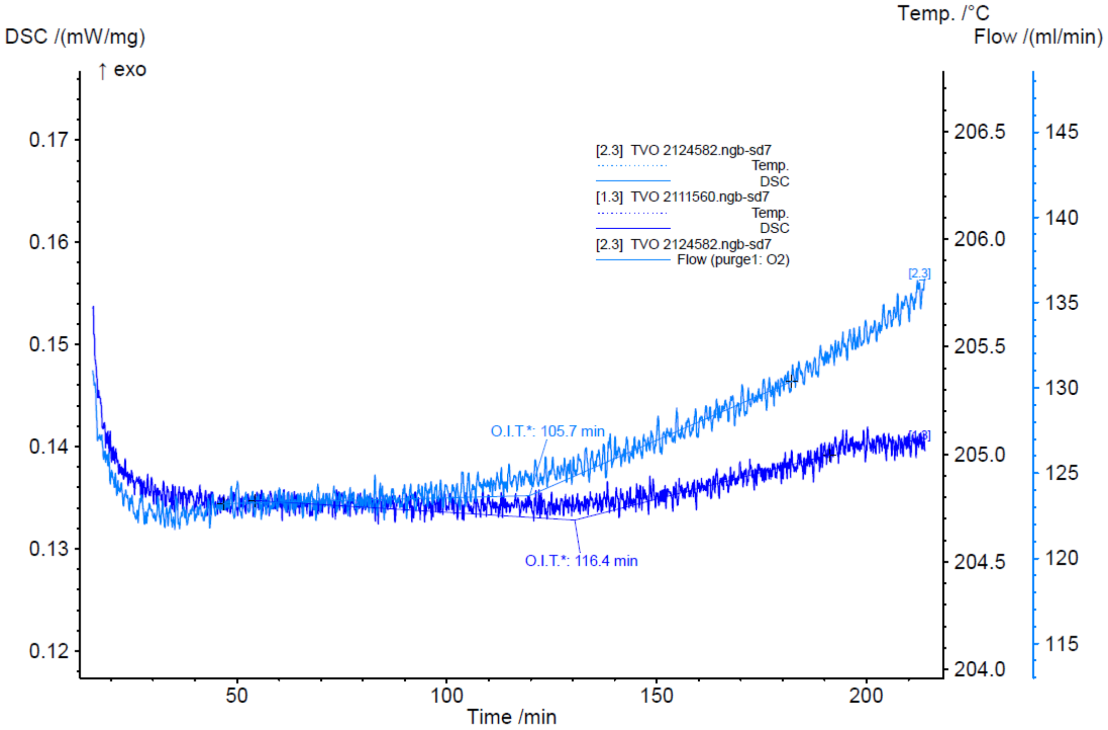

Figure 6. OIT measurement for the commercial grade EPDMs.

4.2 TGA

It was previously shown that the increased filler content causes faster mass loss in the temperature range of ca. 250 - 430°C (see Figure 1). This observation led to the conclusion that it is possible to extract a temperature range in TGA measurement which is affected by the filler content. The work was continued by performing five repetitive measurements to each sample type. This would enable to analyse the scatter between the measurements. In addition to these repetition measurements, the commercial quality EPDMs were measured and the obtained TGA curves were compared to the ones obtained with the model materials.

The comparison between high and low filler containing model materials is visualized in Figure 7. The five repetitions performed with each model material can be clearly distinguished from each other at this temperature range and no overlapping between the two model materials exist. The following Figure 8 visualizes the similar difference between the two highly filled materials. It can be stated that the 769 sample seems to generally have a higher TG % rate at this temperature range, but some overlapping in the measurements can be observed. Thus, distinguishing these two samples from each other is not as evident.

To analyse how well the different model materials can be distinguished from each other, standard deviation calculations were performed for the weight data at 400°C. In Figure 9 the average values and the standard deviations from the five individual measurements for each model material having different filler content is shown. Based on the average remaining weight values, it seems that the remaining weight increases as the filler content increase, which was already observed in Figure 1 too. Horizontal dashed red lines point out how well the adjacent samples can be distinguished from each other. The overlap is expected when the dashed line crosses the adjacent error bar and it is observed with the highly filled materials 768 and 769. Otherwise only minor or no overlap is observed. This would indicate that the TGA method indeed is capable to distinguish two different filler contents from each other with a reasonable resolution when the samples are not highly filled.

Additional EDS analysis was performed to samples 768 and 772 after the TGA test and the results are shown in Table 1. In addition to oxygen, only three different elements were identified in the ash. The highly filled sample 768 contains slightly more Si and Zn and slightly less Ca than the less filled material 772.

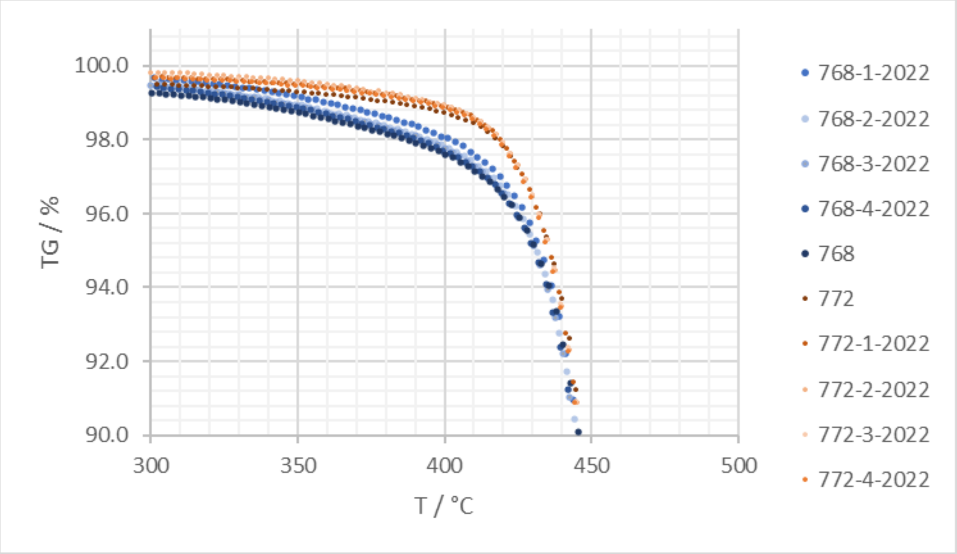

Figure 7. Repetition TGA measurements for samples 768 and 772.

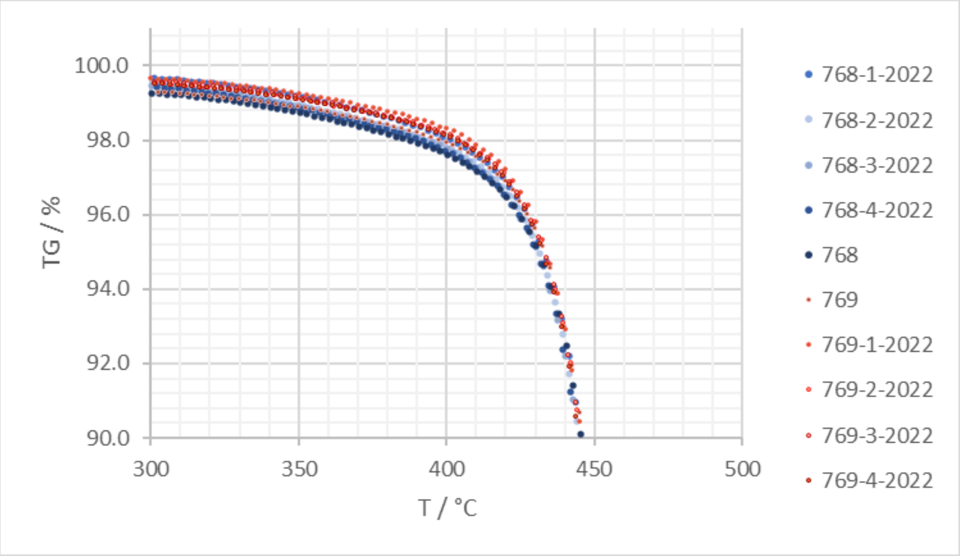

Figure 8. Repetition TGA measurements for samples 768 and 769.

The TGA comparison of the two model materials to the two commercial grade EPDMs are shown in Figure 10. The TGA curves of the commercial materials differ from the ones of the model materials. Between temperature range of 280 to 450°C the weight loss is faster with the commercial materials. This is the temperature range where the extenders (mineral oils) and polymer are being consumed. This indicates that the commercial EPDMs start to degrade earlier, despite their initial higher OIT value compared to the model materials.

After 450°C, the commercial materials reach a plateau after which the slight weight loss increases a bit more as the temperature reaches 800°C. At the plateau all extenders and polymer are consumed and the slight weight loss in the very end could be due to the consumption of $CaCO_3$ (Ca is used as e.g. processing aid).

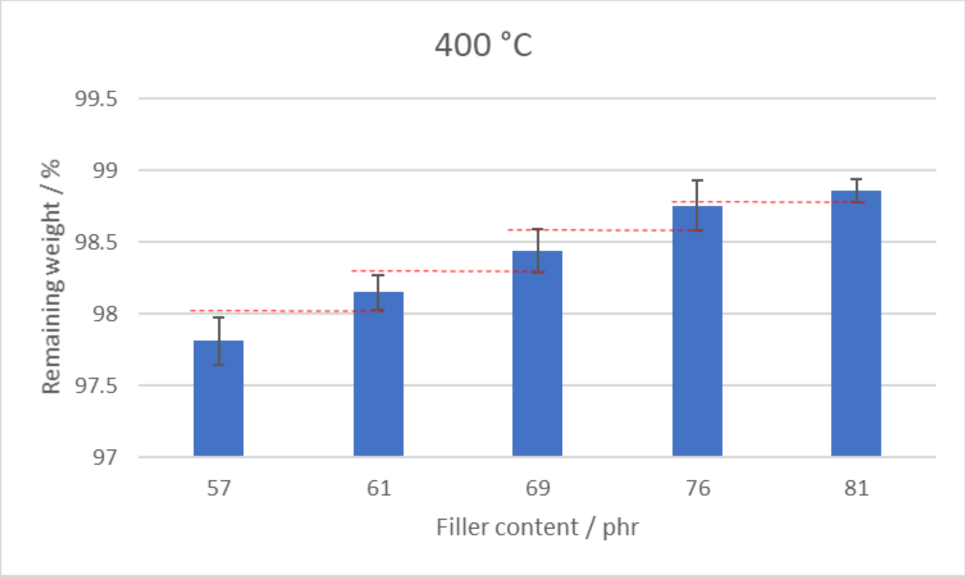

Figure 9. Remaining weight of the samples at 400°C. Error bars represent the standard deviation and horizontal dashed lines drawn parallel to the error bar bottom values.

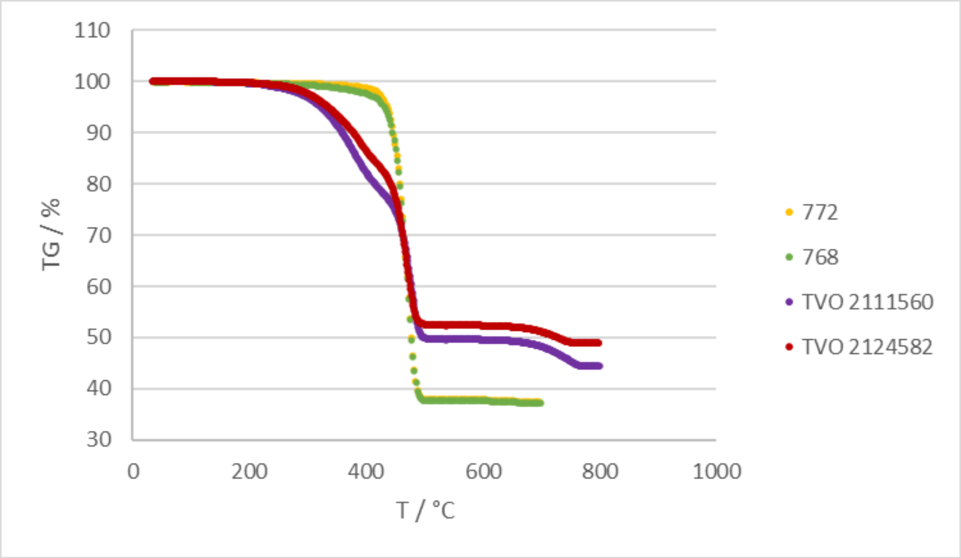

Figure 10. TGA curves for two model materials and two commercial grade EDPMs.

Table 1. EDS analysis results for samples 768 and 772. Elemental composition in weight-%-.

Sample	**Si**	**Ca**	**Zn**
768	4.10	12.33	83.57
772	3.89	13.89	82.22

The model materials studied are considered to represent a high-quality product. The measured TGAs indicate this too as the commercial qualities had a clearly higher residual weight values around the temperature of 600°C indicating a higher non-volatile additive content. Thus, it seems that there are two separate temperature ranges which should be interpreted when filler content is analysed. The lower temperature range is roughly from 280 to 450°C, where high-end product differs from commercial grade product. The higher temperature range is around 600°C, which correlates with the non-volatile additive content. The commercial quality product seems to deviate from the high-quality product in both temperature ranges. Differences between high-quality products can be distinguished at the identified lower temperature range.

4.3 Applicability of the methods for on-site analysis

4.3.1 DSC

The results obtained with OIT measurement seemed to be contradictive. The model materials showed a decreasing trend in OIT with decreasing antioxidant concentration, which was expected. In addition, the earlier work showed that the OIT decreased with the sample containing 0.2 phr antioxidant to approximately to half after 9 weeks of ageing at 130°C, which was expected too [Sipilä & Joki, 2022]. On the other hand, the highly concentrated sample containing 2.0 phr antioxidant did not show any decrease in OIT until after 31 weeks of ageing [Sipilä & Joki, 2022]. This was a bit surprising as the antioxidant consumption was expected to be linear and might indicate that something else than measurable antioxidant content (with OIT) is consumed in the material in the beginning of the ageing.

Additional observations that support the complexity of OIT measurement with the model materials are summarized below:

- The obtained OITs for highly antioxidant concentrated samples resulted in OITs of only some minutes, conventionally indicating very low antioxidant concentrations.
- The commercial materials resulted in approximately 20-times greater OIT values compared to the model materials, although in TGA test their degradation is observed to proceed at clearly lower temperatures.
- The increase of the testing time and temperature did not result in any additional exothermic peaks in the model material measurement data, indicating that the polymer degradation really is initiated after a short exposure period of some minutes.
- The increase of testing temperature resulted in slightly higher OIT values which was opposite what would have been expected based on the earlier literature [Mason & Reynolds, 1998].
- The high antioxidant concentration did not yield in slower decrease of mechanical properties [Sipilä & Joki, 2022], which would contradict the idea of applying antioxidants as protective measure versus degradation of the actual polymer.

Thus, it might be that the antioxidant system applied in these model materials is either:

1. Too complex to be measured with conventional OIT method or
2. Too effective that extensively long time periods (which are not practical) would be required to measure it or
3. There is no antioxidant at all in the model materials which are able to protect the polymer from ageing at elevated temperature of 130°C.

Further analyses would be required to distinguish the exact reason why the OIT magnitude obtained with the model materials deviated from the ones obtained with the commercial qualities. An additional FTIR analysis of the model samples could be performed to detect oxidation products from the material but combining such analysis to the on-site procedure would further complicate the procedure itself too much. Additional work to understanding the antioxidant behaviour would be required to make kinetic predictions on their consumption and first efforts regarding it have already been performed [Vaari 2022].

Based on the results obtained, only indicative measurements with OIT could be recommended for on-site condition monitoring where a reference value from an earlier measurement with known and suitable material is available and comparison is performed against it. However, very low initial OIT values should be still treated with caution.

4.3.2 TGA

Unlike for OIT measurement, for TGA the results seem promising and the method can be suggested to be used as a quality monitoring method for on-site purposes. Although it is not possible to provide an exact acceptance criterion for materials which filler content is suitable for each purpose due to the vast range of applications, variations between material batches can be evaluated based on the measurement. Three separate temperature regions from the TGA curves can be distinguished where variations between the samples could be searched. Between 280 to 450°C the role of mineral oils is visible and after 600°C differences in filler content can be extracted. If the TGA curves seem to be similar at general level, smaller deviations in filler content can be seen around 400°C. A reference curve with known good material is recommended to be measured and comparison at the previous temperature ranges suggested.

5. Conclusions

Quality control techniques for polymeric components, such as sealants, were developed to qualify poor material quality from good. Two methods, OIT and TGA measurements were applied for antioxidant and filler analyses, respectively. Instructions on how to perform the measurements were included in the report.

OIT measurement seems to function with the commercial grade EPDM sealant material. However, with the model material the measured OITs seemed to be suspiciously low despite the initial differences could be extracted between the model materials with OIT measurement. It is suspected that the applied antioxidant system is not very well suited for the conventional OIT measurement or extensively long testing times are required. More detailed understanding regarding the antioxidant behaviour is required in order to explain the differences observed with the two EPDM qualities and to provide a more reliable on-site measurement procedure.

TGA seems to distinguish well the model materials from the commercial grade materials. Three different temperature ranges were presented which could be used to distinguish quality differences between the materials. At high temperature range (around 600 °C) large differences in filler content can be observed. At temperature ranges around 400 °C, small differences in filler content can be seen when high-end materials are measured. Between 280 to 450°C the evaporation of mineral oils can be evaluated. No universal acceptance criterion could be suggested for TGA measurements due to the vast number of applications for these materials but when a good reference material is available for comparison, the suggested temperature areas in TGA curve can be used in verification of the polymer quality.

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