Quality control methods for polymeric sealants

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SAMPO

WP1 - Acceptance criterion and safety margin assessment

- T1.1 – Improved estimation for lifetimes of critical polymer components
- T1.2 – Sensitivity of polymer properties to additive content and methods to verify polymer quality
- T1.3 – Setting up safety margins for O-rings

WP2 - Improvements in ageing management of polymer components

- T2.1 – Online condition monitoring techniques
- T2.2 – Sensitive analysing techniques
- T2.3 – Improved interpretation of non-destructive testing data
- T2.4 - Sealants applied inside containments

WP3 - International cooperation

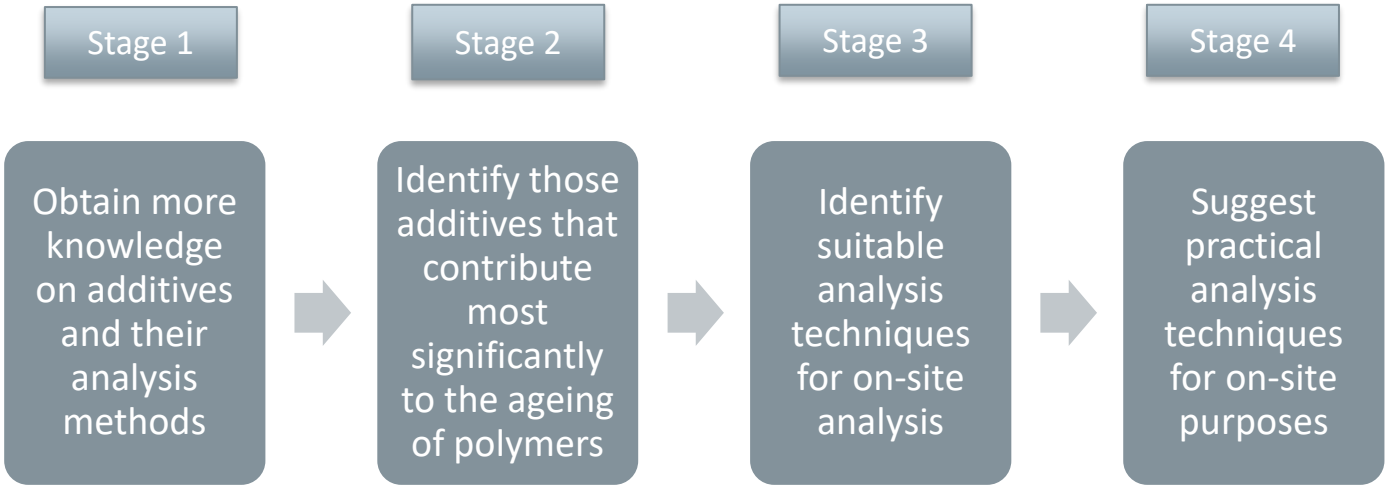
- T3.1 – Polymer ageing in NPP applications – event organization

About polymer quality

- Polymeric materials are used in several applications in nuclear power plants (NPPs), such as cables and sealing applications due to their electrical insulating and sealing properties.
- Standardized composition in polymers vs. metallic alloys
  - Change in the composition of the originally qualified material

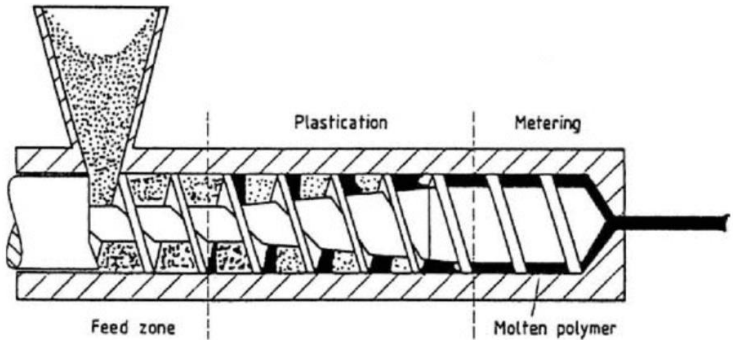
  → Availability issues (limited production of an additive or legislation restrictions)
- This would open a new question whether changing the composition of a polymer affect significantly the quality of the polymer?
  - To answer this, the role of additives in the polymer needs to be understood with a sufficient detail

Study plan


Stage 1
Stage 2
Stage 3
Stage 4
Obtain more knowledge on additives and their analysis methods
Identify those additives that contribute most significantly to the ageing of polymers
Identify suitable analysis techniques for on-site analysis
Suggest practical analysis techniques for on-site purposes

Additives

- Plastics are manufactured typically from raw pellets, powder or resin by extrusion and molding processes
- The pellets/powder/resin may already contain the additives or they can be added during the manufacturing phase by using a separate mixing device or in an extruder → the additives are dispersed into the major component (i.e. polymer matrix in molten state) either as dispersed phases, droplets, filaments or agglomerates.
- Additives are used to improve:
  1. Processing of the melt
  2. Mechanical properties
  3. Chemical properties
  4. Surface properties
  5. Visual properties
- There are many, many different additives available!



Rao, N. 2017. Basic Polymer Engineering Data. Hanser Publishers. 245 pp.

Additives and ageing

- Material quality – How well it endures in its designed use
- From the ageing point of view, the most interesting additives include:
  - Antioxidants – prevent oxidation
  - Fillers – relatvie amount vs. the polymer
  - Plasticisers – evaporation
  - Colorants - photostability
- Analysing these additives would provide information on the polymer quality

Analysis methods for additives

- Analysis methods include:
  - Chromatography techniques
  - Luminescence spectroscopy
  - Light scattering techniques
  - Atom absorption spectroscopy
  - Atomic emission spectrometry
  - Infrared spectroscopy
  - Nuclear magnetic resonance
  - Mass spectrometry
  - X-ray spectrometry
  - Electroanalytical methods
  - Elemental analyses
  - Thermogravimetric analysis
  - Differential scanning calorimetry

- Perspectives related to different methods:
  - Sophisticaed methods are able to qualitative and quantitative analysis
  - Amount of expertise rerquired to operate
  - Fluent analysis (sample preparation!)
  - Equipment cost
  - Databases
  - Applicability for on-site measurements

VTT-R-00065-20 Polymer additives and methods to verify polymer quality

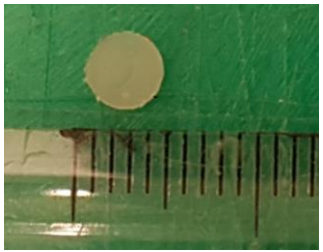
Applicability of polymer additive analysis methods for on-site measurements

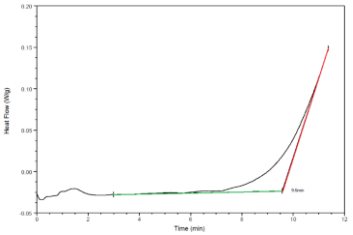
- On-site quality measurement methods should be ”staight forward” → fast and reliable
- Three criteria:
  - Sensitivity
  - Sample preparation
  - Limitations
- Based on the evaluation:
  - DSC, IR, TGA and XRD potential on-site methods

Method	Measured parameters	Sensitivity	Sample preparation	Limitations	On-site applicability
Atom absorption spectroscopy	Absorption	Moderate to high	Dissolved samples required	Only analysis of individual elements	Limited
Atomic emission spectrometry	Emission	High	Dissolved samples required	Skilled operator required, cost of the equipment	Challenging
Differential scanning calorimetry	Heat flow	Moderate to high	Minimal	Applicable to only additives that react under heat	Possible
Electroanalytical methods	Current or potential	Low to moderate	Dissolved samples required	Complex data interpretation, only for electroactive species	Limited
Infrared (IR) spectroscopy	Absorption	High	Depends on sample and measurement type	Dark coloured samples may not be applicable	Possible
Light scattering techniques	Intensity	High	Chromatographic	Impurities (dust), absorption, particle interactions limit applicability	Limited
Luminescence spectroscopy	Luminescence intensity/wavenumber	High	Chromatographic	Only samples that have fluorescence properties	Limited
Mass spectrometry	Mass to charge ratio	High	Dissolved samples required	Skilled operator required, cost of the equipment	Challenging
Nuclear magnetic resonance	Nuclear spins	Low to high	Dissolved samples required	Requires a sufficient amount of sample and skilled operator	Challenging
Thermogravimetry	Weight	Low to high	Minimal	Does not provide detailed information on the sample	Possible
X-ray spectrometry	Scattering (x-rays)	Low to high	Minimal	ppm level concentration required to function, lighter elements cannot be analysed	Possible

Analysis of antioxidants: DSC

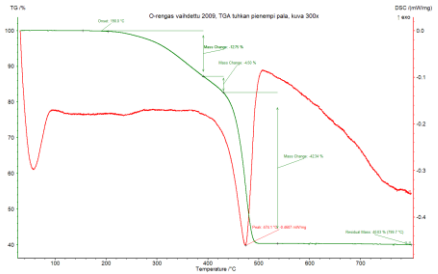
- Small sample, typical weight ca. 10 mg, inserted in between two aluminium plates
- Sample heated up to 200°C with a constant rate in N_2 atmosphere
- The reached temperature is held constant and the atmosphere changes from nitrogen to oxygen
- The heat flow is recorded during this stage and the major exothermic reaction correlated with oxidation of the base polymer is identified from the graph
- The time elapsed until the start of this exothermic reaction is defined as oxidation induction time (OIT)
- OIT is thought to correlate with antioxidant content – longer OIT, more antioxidants present/better AO performance





Analysis of fillers: TGA

- Small sample size, 10-20 mg
- In TGA the mass of the sample is measured as the temperature is increased, e.g. up to 800°C
- The principle is to vaporize all volatile species and measure the weight change (and released heat)
- More detailed analysis of the remnants can be conducted by using EDS
- Based on the results the filler content can be estimated



Resolution of DSC and TGA

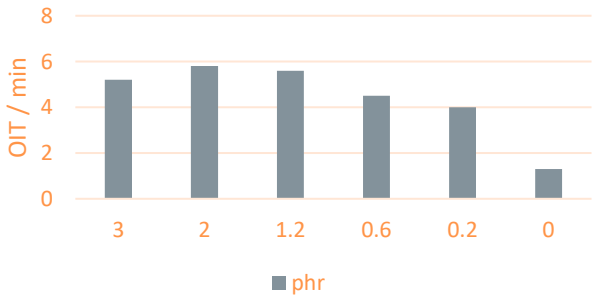
- How small differencies DSC and TGA can measure in materials?
- Special prepared samples by James Walker with various AO and filler content

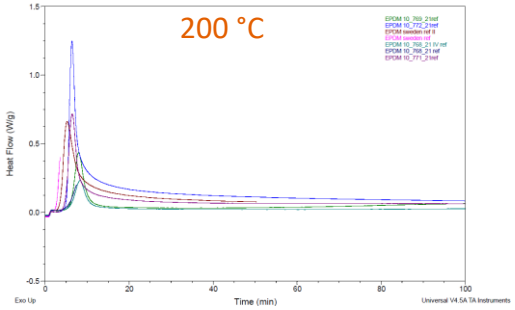
→ Can these methods distinguish these samples from each other?

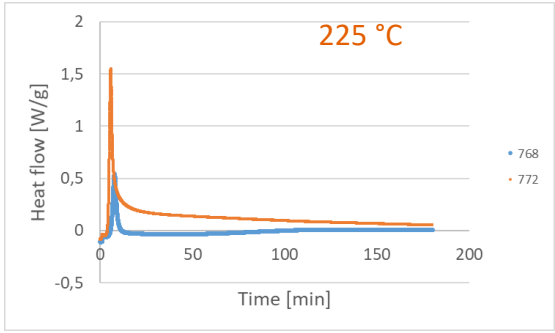
SAMPLE ID	AO/phr	Fillers/phr	EDPM/phr
10/768/21	3	81	100
10/769/21	2	79	100
10/770/21	1,2	69	100
10/771/21	0,6	61	100
10/772/21	0,2	57	100
REF	0	55	100

Resolution of DSC

- First round of measurements completed
- When AO above 1,2 phr, no clear trend in OIT
- Below 1,2 phr, decreasing trend in OIT can be seen
- Low OIT values?
- Possibilities to get differences between the samples by adjusting the measurement procedure?
  - At higher test temperature (225 °C vs. 200 °C) still no additional peaks

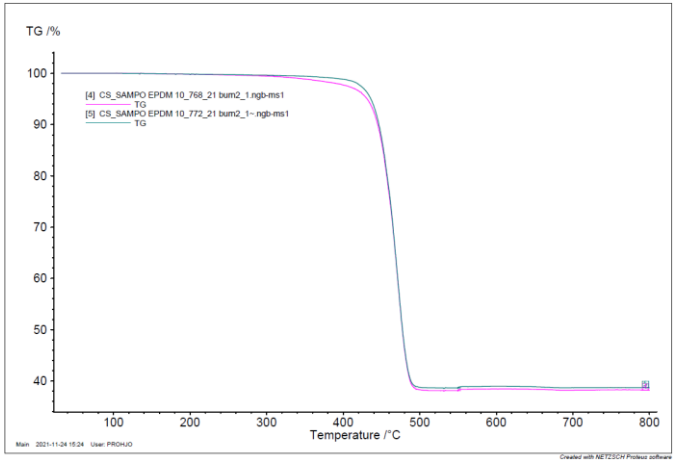


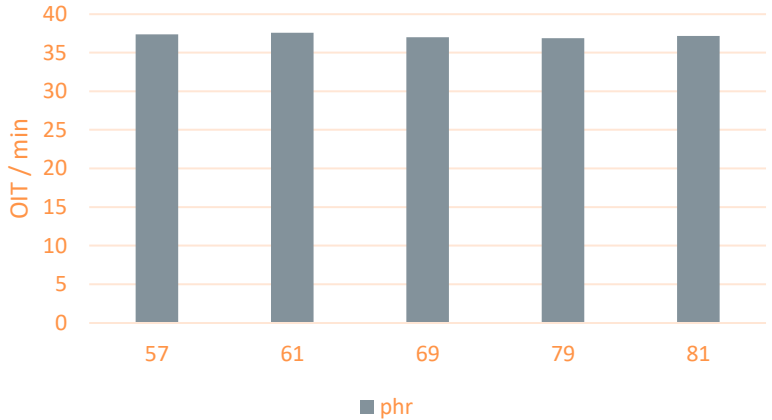




Resolution of TGA

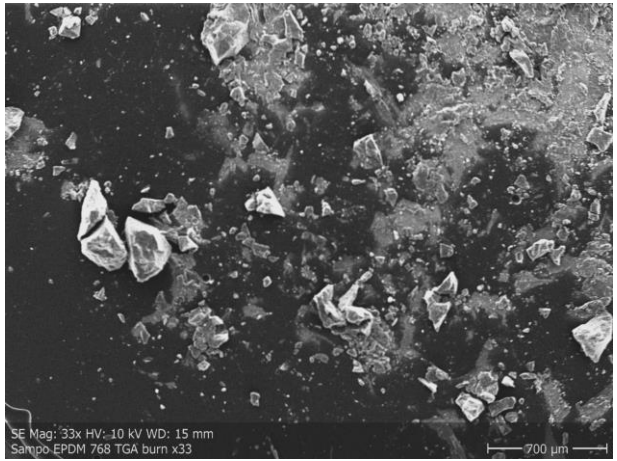
- No significant changes in the residual mass
- Thermographs similar shape with higher and lower filler content
  - Slight difference in the ”lower” temperature region

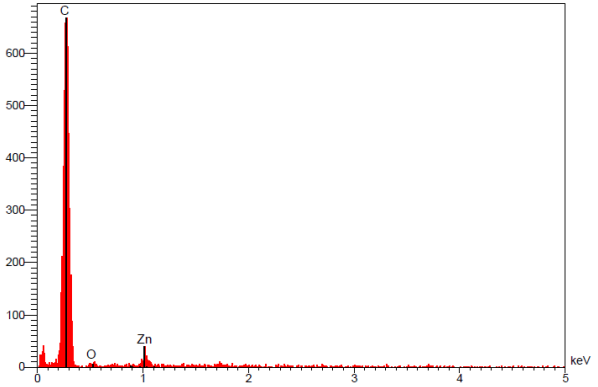




Resolution of TGA

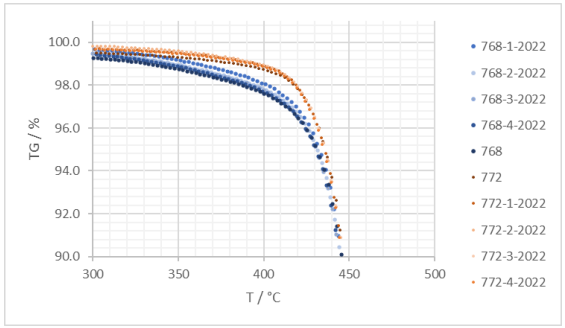
- Additional EDS analysis on 81 phr sample
- Mostly C, small amounts of Zn and O

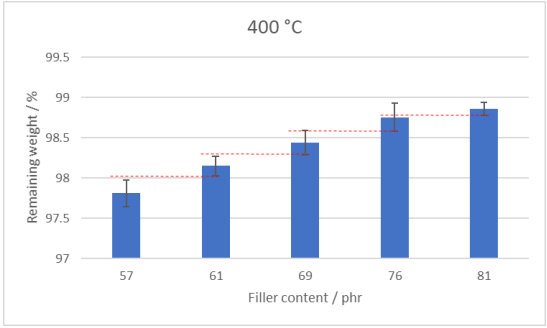


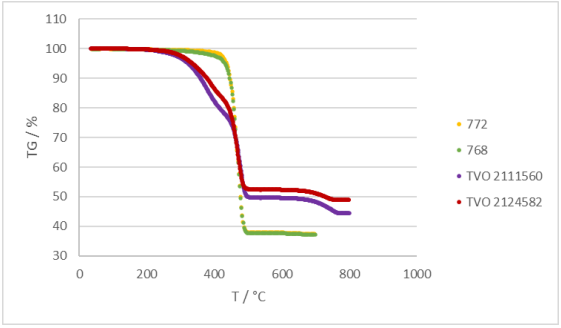


Elt	XRay	Int	Error	K	Kratio	W%	A%	ZAF	Formula	Ox%	Cat#
C	Ka	36.3	1.6141	0.9596	0.8105	93.66	97.78	0.8625		0.00	0.00
O	Ka	0.4	1.6141	0.0051	0.0043	1.70	1.33	0.2517		0.00	0.00
Zn	La	1.4	1.6141	0.0353	0.0298	4.64	0.89	0.6424		0.00	0.00
				1.0000	0.8446	100.00	100.00			0.00	0.00

Resolution of TGA



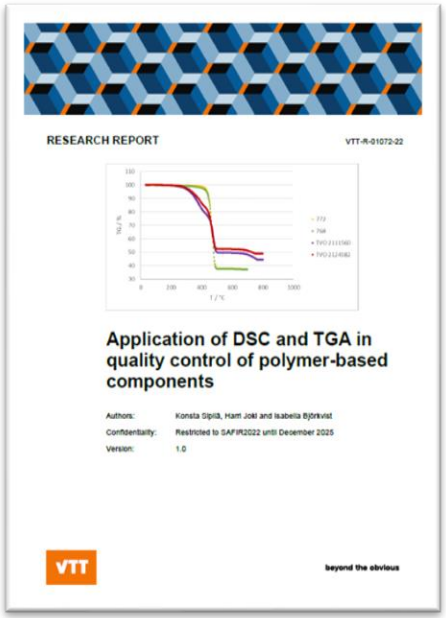




- Repetition measurements 5x – high- and low-filled materials
- Remaining weight at 400 °C all compositions – different compositions can be distinguished from each other quite well
- Comparison to commercial EPDM grade – two temperature regions

DSC and TGA procedures

- Listed in SAMPO deliverable report
  - Sample preparation
  - Measurement procedure
  - Data analysis


RESEARCH REPORT

VTT-R-01072-22

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

Authors: Konsta Sipilä, Harri Joki and Isabella Björkvist

Confidentiality: Restricted to SAFIR2022 until December 2025

Version: 1.0

VTT

beyond the obvious

Summary

- There are numerous additives that can be used to modify polymer properties
- From the quality and ageing perspective, interesting additives include antioxidants, plasticizers, fillers and some colorants
- Several additive analysis methods are available, many require laborious sample preparation and have limited on-site applicability
- DSC and TGA were suggested to be used as potential methods to analyse antioxidant and filler content of polymers
- Results indicate that DSC could distinguish difference when AO content was less than 1,2 phr → Low OIT values?
- In TGA analysis two temperature ranges can be used to compare the performance of the material

Thank You!