Development of quality management tools for polymeric components

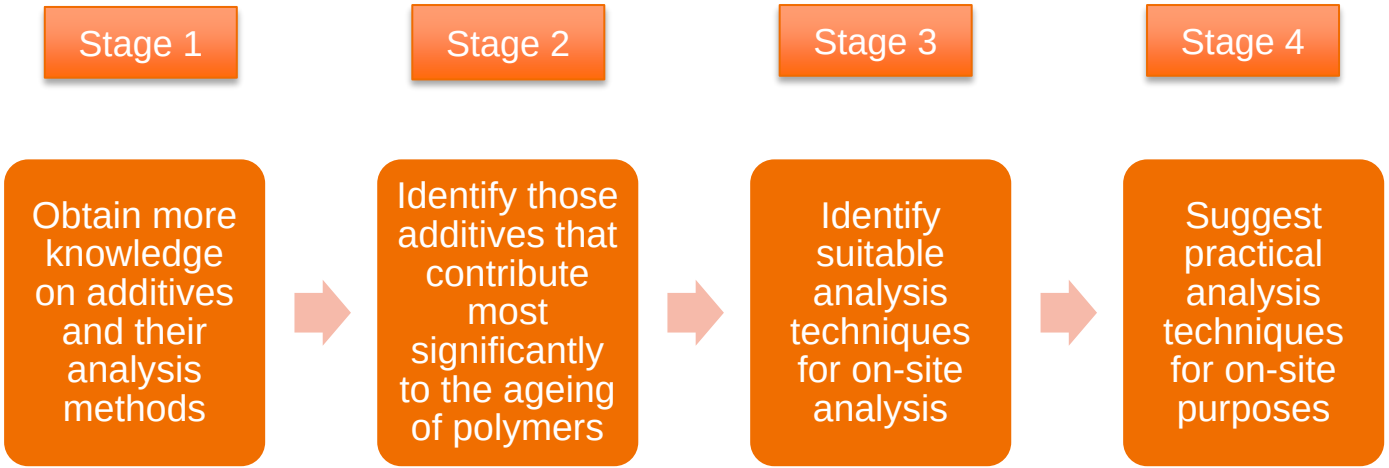
Polymers in nuclear applications 1-2nd December 2021

Konsta Sipilä, Harri Joki

About polymer quality

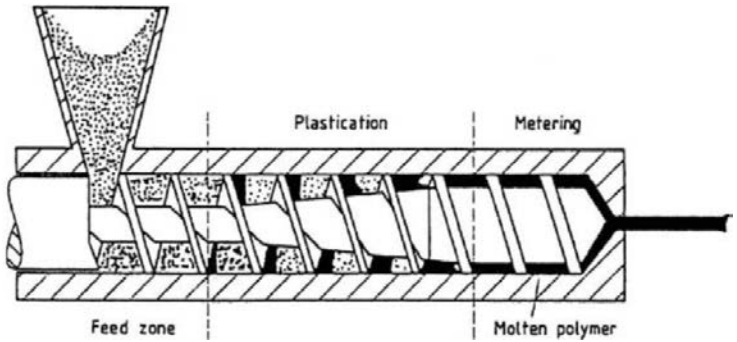
- Polymeric materials are used in several applications in nuclear power plants (NPPs), such as cables and sealing applications due to their electrical insulating and sealing properties.
- Since the compositions of commercially available polymers are not standardized in detail, as e.g. metallic alloys, issues may rise as the manufacturers may change the composition of the originally qualified material
  - Availability issues → subcontractor may have stopped producing some additive or the use of an additive have been restricted due to legislation
- 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.

Processing aids

- Improve the processability of the melt
- The second most consumed additive group is plasticizers
- May diffuse from bulk to the surface and evaporate

Altered property	Additive name	Additive function
Processing	Accelerators	Speed up the cross linking of thermosets.
	Blowing agent	Either in physical or chemical form, blowing agents are dispersed in the polymer melt as gas and causes foamy structure of the processed polymer.
	Heat Stabilizer	The main purpose of heat stabilizers are to prevent degradation of polymer structure at the elevated temperature during its processing phase but they can also function similarly as part of a ready product.
	Lubricants	May have several functions depending on the processing stage, improve melt flow and shear endurance
	Plasticiser	Improve processing characteristics by e.g. decreasing melt viscosity. Plasticisers (or antiplasticiers) can have also an effect to the rigidity of the polymer.
	Processing aids	May have several effects, including improved fusion, melt strength, dispersion and surface quality properties.
	Release agents	Prevents sticking to the processing machinery and mold surface.

Additives affecting mechanical properties

- The fillers are the largest additive group produced with roughly 50% of the total volume of global additive markets

Altered property	Additive name	Additive function
Mechanical	Compatibilisers	Are applied in heterogeneous polymer blends, where the blends are immiscible to each other, to improve the interfacial adhesion.
	Fibre reinforcements	Provide improved strength and toughness.
	Fillers	Typically sized <100 µm particles that have been conventionally used to decrease cost of the product but now days fillers tend to have more functional properties, improving properties related to processing, stiffness, heat distortion temperature, creep, abrasion and tear resistance.
	Impact modifiers	Improve the absorption of impact energy making the polymer thus more resistive towards crack formation and propagation.
	Nucleating agents	Affect to the crystallization rate and thus the morphology of the polymer. May boost transparency or gloss of the final product (in such case may be referred as clarifying agents).

Additives affecting chemical properties

- Antioxidants:
  - Primary

  $RH \rightarrow R\cdot + H\cdot$

  - Secondary

  $R\cdot + O_2 \rightarrow ROO\cdot$

  $ROO\cdot + RH \rightarrow ROOH + R\cdot$
- Crosslinking agents

Altered property	Additive name	Additive function
Chemical	Antioxidants	Hinder the degradation processes occurring in the polymer. Primary antioxidants inhibit the chain terminating reactions as secondary antioxidants neutralize hydroperoxides.
	Biocides	Prevent the growth of different kind of organisms, e.g. mould, fungi and bacteria.
	Chain growth regulators	Affect the length of polymer chains.
	Crosslinking agents	Crosslinking agents, e.g. peroxide and silane, are used to form connecting links between polymer chains.
	Flame retardants	Make polymer less flammable by interfering with the combustion reaction by mechanisms based on either gas, char or water formation. Three types of fire retardants exist, halogen-, phosphorous- and metal hydrate based.
	Photostabilizers	Retards the rate of photo-oxidation reaction either by absorbing UV light, quenching the initiated photo-oxidation reaction, binding radicals formed due UV-radiation or reflecting UV radiation from the surface.
	Surfactants	Are applied when emulsions are produced.

Additives affecting surface properties

- Various agents to modify surface properties

Altered property	Additive name	Additive function
Surface	Adhesion promoters	Improve the adhesion properties of the polymers.
	Antifogging agents	Affects the wetting properties of the surface by decreasing surface tension of water resulting in thin film of water rather than individual droplets on a surface.
	Antistatic agents	Reduce the surface resistance of the polymer and thus eliminates electrostatic charges.
	Coupling agents	Inorganic materials that improve the adhesion between polymer and filler materials.
	Slip or Antislip additives	Decrease or increase the friction of the surface.

Additives affecting visual & other properties

- Additives to enhance visual or odour properties
- May have effect to photostability of the polymer

Altered property	Additive name	Additive function
Colour	Dyes	Highly soluble molecules or small clusters that absorb visible light, giving a desired colour or transparency to the final product.
	Pigments	Dispersed crystalline particles, organic or inorganic in nature. The use of organic pigments are considered to give the best results as opaque colours are considered.
Other	Odorants	Generates odour.

Additives and ageing

- 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

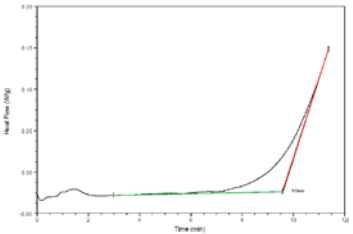
Applicability of polymer additive analysis methods for on-site measurements

- 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

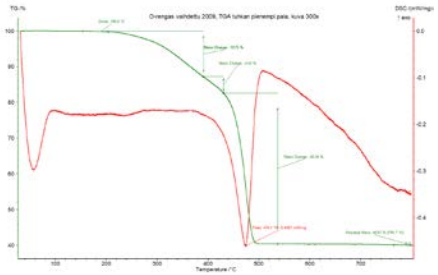
Analysis of antioxidants: DSC

- 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

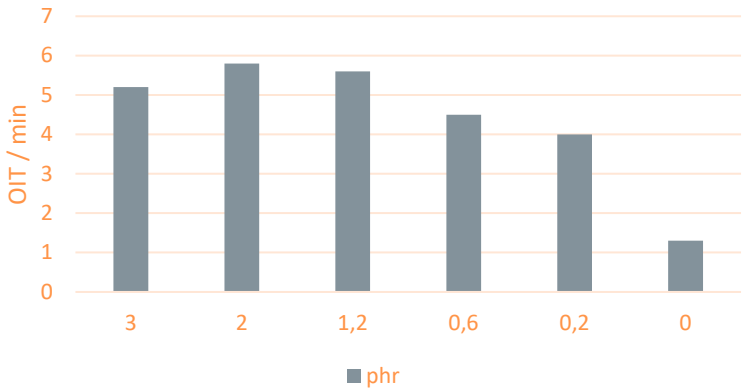
- How small differencies DSC and TGA can measure in materials?
- Special prepared samples by James Walker with various AO and filler content

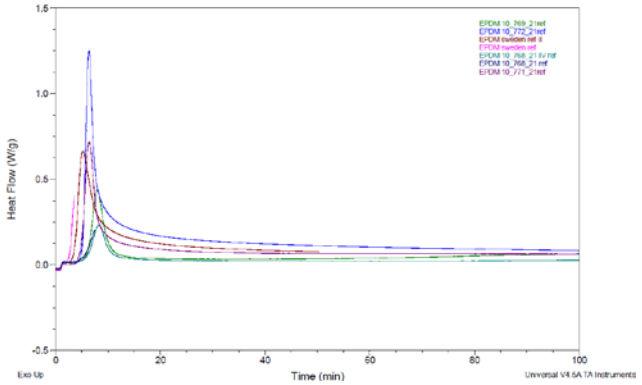
→ Can these methods distinguish these samples from each other?

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

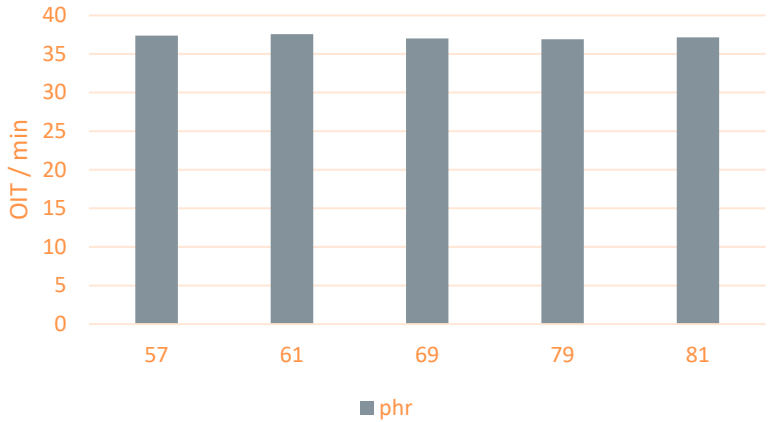
- First round of measurements completed
- When AO above 1,2 phr, no clear trend in OIT
- Below 1,2 phr, decreasing trend in OIT can be seen
- Possibilities to get differences between the samples by adjusting the measurement procedure

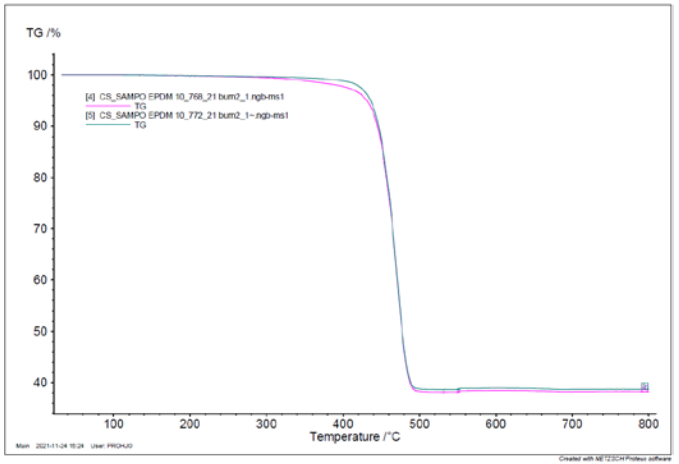




Resolution of TGA

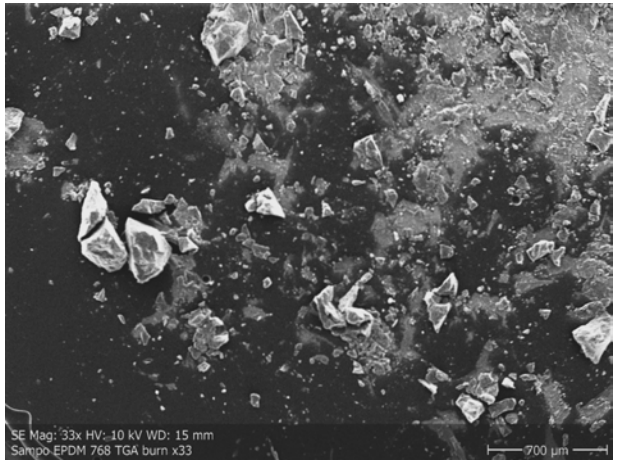
- No significant changes in the residual mass
- Thermographs similar shape with higher and lower filler content
  - Slight difference in the ”lower” temperature region

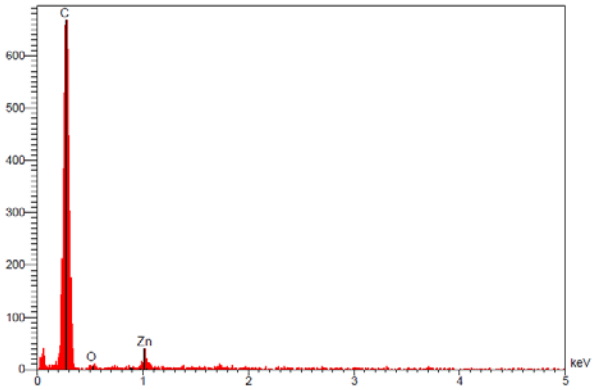




Resolution of TGA

- 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

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 → further optimization of the analysis process is still needed
- Based on the TGA results obtained so far, residual mass did not correlate with the filler content, further analysis is required to confirm whether the method can be used in filler analysis

beyond

the obvious

Konsta.sipila@vtt.fi