
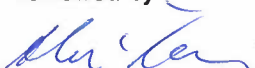


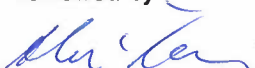


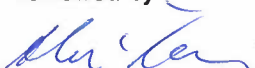



Polymer additives and methods to verify polymer quality

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Summary <p>Within nuclear power plants, polymers are used as part of e.g. cable insulators and sealants. Thus, they may have safety relevance and their use in the designed application should be qualified accordingly. As these polymer components comprise not only of the actual polymer itself, but of several different chemical substances, which are generally referred as additives, so it might be that not only the polymer itself determines its material properties. The polymer formulas are not very commonly fixed and changes in the formulas may occur due to various reasons. This would lead in question whether changing an additive in the polymer blend would require re-qualification. In this literature work, the additives used in polymer blends are listed and their functionality discussed. In addition, different methods that can be used to measure the additives were presented. It was concluded that the amount of the used additives is high and some of the additive groups, e.g. antioxidants, plasticizers (for elastomers) and some of the colorants, were recognized to be important for the polymer component functionality in the ageing perspective. Several different methods were presented that can be used to measure different additives qualitatively and/or quantitatively. However, many of the methods require high level of expertise in order to operate them with full capacity. The future work aims to identify a suitable method for onsite analysis.</p>				
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Preface

This work was completed as part of the SAFIR2022 –research program in SAMPO (Safety criteria and improved ageing management research for polymer components exposed to thermal-radiative environments) project’s Work Package 1 ”Acceptance criterion and safety margin assessment”, Task 1.2 “Sensitivity of polymer properties to additive content and methods to verify polymer quality”.

Espoo 28.1.2020

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1. Introduction

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. In these applications, polymers are exposed to environmental stressors such as heat and ionizing radiation. The environmental stressors cause changes in the polymer structure, which is ultimately observed as changes in macroscopic properties, colour changes, loss in insulating or sealing properties etc. It has been a common practice in the polymer industry to add different additives to the manufactured polymer blends to improve the product performance and extend the lifetime.

Verification ensuring the performance of NPP components or materials that are part of structures or systems and have safety relevance is typically required. For polymer based materials, qualification (in form of experimental results or other kind of documentation) can be used to prove whether a certain polymer type is safe to use in its designed application. The obtained qualification can be valid for a certain component for several years. Since the compositions of commercially available polymers are not standardized in detail, as the e.g. metallic alloys, issues may rise as the manufacturers may change the composition of the originally qualified material. Replacing additive elements are usually due to 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 a quality of an additive used in a previously qualified polymer material would require a re-qualification or not.

In order to estimate the need of re-qualification in such cases, proper indicators need to be recognized and a suitable measurement procedure proposed. The progress of the development process is described in Figure 1. The first step would be figuring out the additives used by the polymer industry and understand their function as part of the final product. The second step would be recognizing the most relevant additives in the ageing point of view. The third step would estimate how their performance is measured with a sufficient accuracy and by using a relatively simple procedure. This report aims to summarize the most common additives used in the polymer industry and techniques that can be used to identify individual additives as well as measure their quantity.

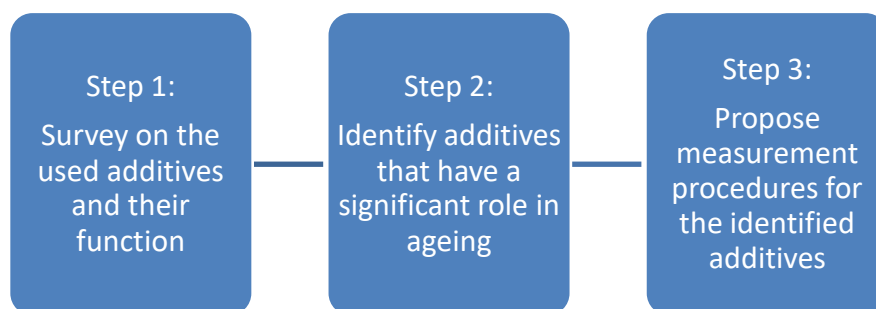


Figure 1. Planned progress for the additive analysis method development.

2. About polymer ageing mechanisms

As stated in Introduction, in a typical NPP environment the primary stressors are considered to be heat and irradiation. In addition, the presence of oxygen has an effect to the ageing process. The ageing mechanism of polymers in NPP environment has been previously discussed in [Paajanen et al. 2017] and a general overview on the fundamental steps of the ageing process are presented in Figure 2. The initial step is launched by ionizing radiation or thermal energy where energy is scattered or absorbed into matter. This causes an excited state in the matter, which is followed by the formation of radical species. These radicals interact with the surrounding matter, which can yield in several phenomena as depicted in Figure 2.

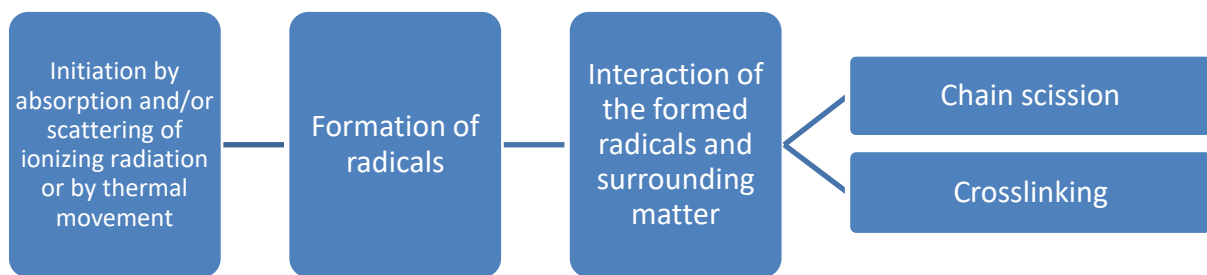


Figure 2. Progress of the degradation process in a polymer.

In Figure 2, the third step is presented as the interaction of the radicals with surrounding material. These radicals can cause directly chain scission or crosslinking, but in the presence of oxygen, additional steps into the degradation phase can be included in the form of oxidation reaction. Molecular oxygen is reactive with the formed radicals (initiated either by thermal movement or by irradiation) and has thus a tendency to enhance the ageing process. Oxidation is initiated by the formed radicals ($R\cdot$) and propagates as radicals react with the molecular oxygen, forming peroxy radicals ($ROO\cdot$). Peroxy radicals further react with the non-radical species (RH), abstracting hydrogen species from it, thus forming hydroperoxide ($ROOH$). The decomposition of hydroperoxide generates additional radicals that continue reacting with non-radical species, which can lead either in termination of the process and/or formation of additional radicals. The schematic cycle for auto-oxidation is presented in Figure 3.

The presented ageing mechanisms are applicable to various polymer backbone structures, but does not take into account how degradation of additives will affect the macroscopic properties. It has been suggested that in NPP environments the loss plasticizers, defluorination and dechlorination are relevant ageing mechanisms for some polymer types [Burnay, 2018]. The loss of plasticizers commonly concerns PVC but may be relevant for elastomers as well. If the attachment between the polymer chain and the plasticizer is not sufficient, plasticizers can migrate, evaporate or be extracted by fluids from the polymer matrix. This would yield in degradation of mechanical properties [Wei et al. 2019]. Defluorination on the other hand may concern fluorine containing elastomers such as Viton.

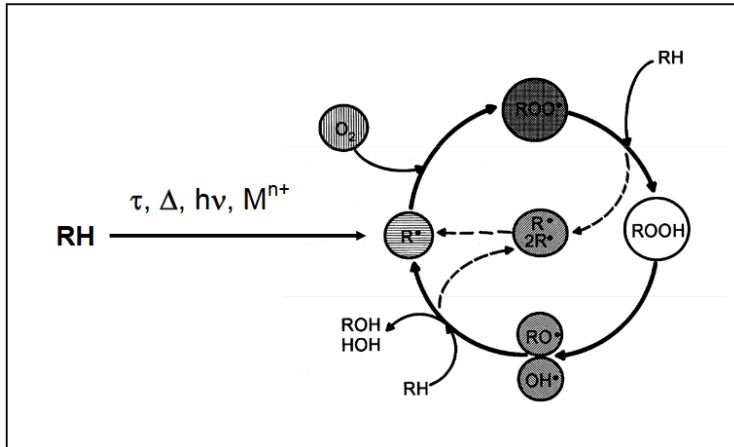


Figure 3. Schematic illustration on the auto-oxidation reaction. [Affolter, 1999]

3. Additives used in polymer blends

The number of various additives used in plastics is high, one estimate being over 13 000 [Ash et al. 1995]. Their function is to improve the properties of the polymer in its designed use and optimize the production process. In this report, additives are categorized based on the property they primarily affect (processing, chemical, surface, mechanical or colour), although there can be several properties that one additive can contribute to.

3.1 Manufacturing process

Plastics are manufactured typically from raw pellets, powder or resin by extrusion and moulding processes. Depending on the type of the plastic, manufacturing process may involve heating and solidifying the product to its final shape (thermoplastics and thermoplastic elastomers) or synthesizing process, such as crosslinking (thermosets and elastomers). In Figure 4, a schematic cross section from a screw extrusion equipment is shown. The raw material is added in the base of the rotating screw. Heating will melt the raw material as it pushed forward by the rotating screw and the melt is homogenized. At the other end of the screw melt is forced through a die.

Additives are mixed in the polymer by using a separate mixing device or in an extruder (as in Figure 4) to obtain homogeneous distribution of added substances. The additives are dispersed into the major component (i.e. polymer matrix in molten state) either as dispersed phases, droplets, filaments or agglomerates. The mixed melt can be transformed in pellet form and dried, or if an extruder is used as a mixing device, the melt can be further processed by extruding or moulding (in case of thermoplastics). Pellets can be further refined into finer form, such as powder if, e.g. sintering and coatings are produced. Compounding of thermosetting materials includes also similar mixing process in melt state and in addition, a pre-polymerization process of the mixed resin in order to obtain the required viscosity before the melt is transformed into pellets.

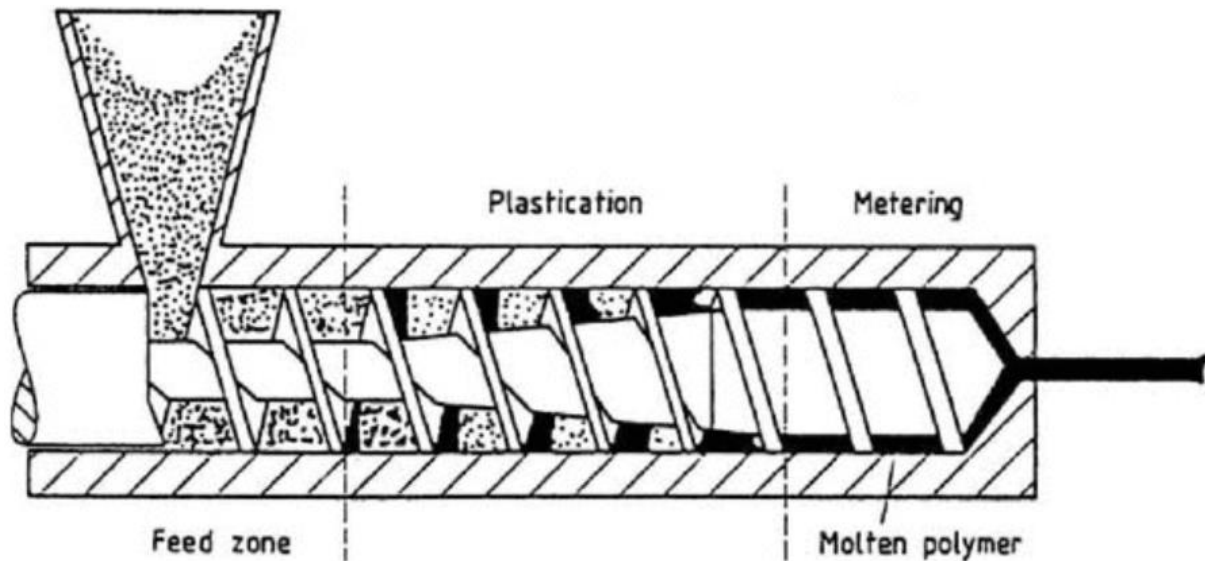


Figure 4. A Schematic cross section on a screw extruder. [Rao, 2017]

The manufacturing process can be rather complicated when the rheological, mechanical and transport properties of the melt are considered. These properties have an effect to the final product and fluency of the manufacturing process. Several methods can be used to improve the processability of the melt, including adjustment of temperature, pressure and other manufacturing equipment related parameters. Processing aids have similar function and may be added into the melt to improve the processability and quality of the final product.

3.2 Processing aids

Some of the processing aids are added to obtain a certain type structure for the end product, e.g., blowing agents are used in manufacturing foamy structures. Lubricants and plasticizers can be applied to improve processability by improving the melt viscosity and decreasing friction between metal walls and the melt. Typical lubricants include fatty acid esters, -amides and -diamides and various waxes. Their use is mainly for PVC but also for PS, ABS and polyolefins.

Plasticizers not just improve the processability of the polymer product, but have also an effect to the rigidity of the final product as well as the glass transition and melting temperatures. Plasticizers are the second most used additive group and are commonly used as part of PVC products but can be applied to with other semicrystalline polymers as well. The used plasticizers can be divided in phthalates (dioctyl-, diisononyl-, diisodecyl- and di-n-buthyl phthalates) and non-phthalates (adipates, benzoates, phosphates, polyesters and trimellitates). From these diisodecyl- and di-n-buthyl phthalates, adipates, phosphates and polyesters can be also used with other polymers than PVC.

Heat stabilizers are applied in order to prevent the degrading effects of the elevated processing temperature while release agents, such as PTFE, wax, metal soaps and silicone, prevent the melt adhering on to process equipment or mould surfaces. For thermosetting polymers, accelerators are used to accelerate crosslinking process. Summary for the additives used in improving processing properties is shown in Table 1.

Table 1. Summary on the additives used to improve processability of polymers.

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.
	Plasticizer	Improve processing characteristics by e.g. decreasing melt viscosity. Plasticizers (or anti-plasticizers) can have also an effect to the rigidity of the polymer.
	Release agents	Prevents sticking to the processing machinery and mould surfaces.

3.3 Chemical additives

Modifying polymers' chemical properties has been shown to improve their applicability significantly in several fields of industry. For example, application of flame retardants has made possible to use polymers as part of structures and electronics. Their function is based on hindering the combustion process either by 1) diluting combusting substance with non-combusting substance 2) gas release 3) cooling 4) chemically interfere the combustion reaction 5) charring and 6) crosslinking. ISO 1043-4 classifies fire retardants in nine different categories. The most common ones include halogen-, phosphorous- and metal hydrate based fire retardants.

Another significant additive in this category is antioxidants. They protect the polymer from the effects of ageing by reacting with the radicals formed within it and thus hinder degradation processes, such as oxidation. Antioxidants can be divided based on their function to primary and secondary antioxidants. Primary antioxidants are phenols, amines and aromatic amines, which contain reactive hydrogen atoms that can neutralize radicals. Secondary antioxidants, such as organic phosphites, phosphonites and thioesters, hinder oxidation reaction by reacting with hydroperoxides. For elastomers different antioxidants can be used, e.g., substituted phenols and bisphenols. Typical amount of antioxidants vary from 0.05 to 1.0 wt%. Photostabilizers (substituted benzophenones, salicylic acid esters and carbon black, to name few) act like antioxidants and are specially designed to hinder the photo-oxidation process. [Baur et al. 2019]

Chain growth regulators and crosslinking agents can be used to modify the length of the polymer chains and crosslinking density, respectively. Biocides are applied when growth of organisms is prevented. In the production of emulsions, surfactants are used to obtain the

desired structure. Table 2 summarizes the used additives that have effects on chemical properties.

Table 2. Summary of the additives used in altering polymers' chemical properties.

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 the combustion reaction by mechanisms based on either gas, char or water formation.
	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.

3.4 Additives used to improve mechanical properties

Several additives can be used to increase the mechanical properties of polymers. Reinforcing fibres, e.g. glass, aramid or carbon fibre, generally improve tensile strength and Young's modulus of the polymer. They can be included in the polymer with different lengths or in mats. Some synthetic fibres can be used as impact modifiers, which make the polymer more resistant towards external impacts.

The crystallinity degree governs widely the properties of semicrystalline polymers. Nucleating agents have an influence to the crystallization process by increasing the melting temperatures of the crystals, their growth rate and content. They have also an effect to the size of the crystalline regions. Typical nucleating agents are inorganic fillers, salts of carboxylic acids, sodium organophosphates, dibenzylidene sorbitols, waxes and certain ionomers.

Compatibilizers are applied when the final product is manufactured from two (or more) different components that are immiscible to each other. They are typically block copolymers, which are miscible to the components that constituents the blend. As the compatibilizers are miscible into the applied components, they improve the adhesion of these components and increases the stability of the polymer.

Fillers have been traditionally mixed into to the polymer blends to decrease cost but they can have some functional properties as well. They are the most produced additives, with roughly 50% of the total volume of global polymer additive markets. Fillers come in many sizes but typically they are applied in particle sizes smaller than 100 μm . Depending on the filler type,

they can improve processability, stiffness and impact resistance properties as well as electrical conductivity. It has been suggested that the added components may be referred as fillers if their total concentrations exceed 5% of all of the used components in the blend, in order to extinct them from functional additives [Baur et al. 2019]. The most common filler materials include calcium carbonate, carbon black, kaolin, talcum (i.e. magnesium silicate), mica, silica and wollastonite.

Table 3. Summary of the additives used in altering polymers' mechanical properties.

Altered property	Additive name	Additive function
Mechanical	Compatibilizers	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).

3.5 Additives to improve surface properties

The surface properties of the polymer can be modified in many ways. Plastic materials typically tend to develop a static charge on to their surfaces, which causes sticking phenomenon or even spark formation. Antiblocking agents can alter the electrostatic charge on the surface by affecting the surface roughness (inorganic antiblocking agents, e.g., calcium and magnesium based salts) or by migrating from the bulk to the surface (organic antiblocking agents are typically different kind of amides) [Zilles, 2016]. Antistatic inhibitors decrease the surface resistivity so that formation of static charges decrease and thus susceptibility for spark formation becomes smaller. Antistatic agents can be internal or external. The internal ones can be similar to those used as antiblocking agents (fatty acid esters and amides) and they function also by migrating to the surfaces. The external antistatic agents consists of ammonium salts and they are applied by dipping a ready product in the salt solution and dried. [Baur et al. 2019]

Antifogging agents are used typically by the packing industry as the condensation of moisture on the package surfaces is wanted to be avoided. For example, ethoxylated fatty acid esters are used to modify the surface tension, thus preventing formation of water droplets on the surfaces. [Subramanian, 2013]

Coupling agents are added in the polymer blend to improve the adhesion between filler particles and the polymer matrix. They are basically molecules where one end is able to react with the polymer chain and other end with the filler, thus forming a bond between the two [Kutz, 2011]. Coupling agents are inorganic in nature, e.g. silane, titanate or zirconia. The additives used to alter surface properties are summarized in Table 4.

Table 4. Summary of the additives used in altering surface properties of polymers.

Altered property	Additive name	Additive function
Surface	Antiblocking agents	Prevent sticking of surfaces to each other.
	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.

3.6 Colorants

Different colorants are used to alter the visual properties of the polymers and their functionality is based on their capability to selectively absorb light. The used colorants may be divided into dyes and pigments of which the use of pigments is more common. Inorganic pigments are more common than organic ones. The most common inorganic pigments are titanium oxide followed by carbon black. Various metal compounds are used as well. The most important organic pigments are azo- or polycyclic pigments, which cover very wide range of different colours.

Some colorants have an effect to the photostability of the polymer. Colorants may either enhance or hinder the ageing induced by UV light. Some organic red- and yellow-based colorants and some inorganic pigments can decrease the polymer stability against UV induced ageing while others can protect the base polymer by absorbing UV radiation. Examples on these kind of colorants include phthalocyanine blue and green as well as rutile titanium oxide. However, high amount of absorbed energy will lead in increased temperature of the polymer, which can cause an increase in another degradation mode, thermal oxidation. [Subramanian, 2013]

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.

3.7 Discussion on additives

The previous sections showed that there are several purposes why additives are used in polymeric products. The question remains that which ones of the presented additive groups are such that if an individual additive is changed to another, will it have a significant effect to the polymer properties? For example, if antioxidant A is changed to antioxidant B, it should be verified whether the change affects significantly to the ageing behaviour.

In NPP environment, cable insulators and various sealants can be considered to be the most significant applications where polymers are used. It is important they maintain their functional properties (insulation and tightness, respectively) during the normal service conditions, and depending on their safety relevance, also during a design basis event. Thus, cables and sealants must remain in sufficient condition throughout their service life. All polymer based components tend to lose their functional properties as a result of ageing. Thus in addition to those additives, which adjust polymer functional properties, the additives used in hindering the ageing effects become important. For both sealants and cables, antioxidants are used to hinder the effects of ageing. Colorants can be considered to be a relevant additive group to some extent, as they may have a role in the oxidation of the polymer. For elastomers, plasticizers are an important additive group as they are prone to migrate and thus have an effect to sealant properties. Furthermore, when elastomers are considered, the used crosslinking agent may be relevant for the applicability of the component (sulphur vs. peroxide). Fillers should be inert in the sense that they would have an effect to the functionality of the component. However, it should be noted that increasing the amount of fillers and respectively decreasing the polymer ingredient probably would have an effect to the functional properties. What comes to the other additives, their role in the ageing of polymers could not be directly presented here based on the studied literature.

4. Techniques to measure additives

A vast number of techniques has been developed to identify and analyse composition of polymeric products. Their applicability to analyse different additives vary in some extent and there is no single universal technique, which can identify all additives in every polymer type. Before the actual analysis, samples must be obtained and prepared, which can be an essential part of the analysis process. In addition, after the analysis the results are interpreted. There are some requirements for the analysis methods that they can be considered to be suitable for industrial purposes. An ideal technique would fulfil the following criteria:

- Qualitative
- Quantitative
- Reliable
- Sensitive
- Applicable

Ability to identify particular additives and measure their specific amount would be the most essential requirements for the additive analysis techniques. However, techniques may be limited to be either qualitative or quantitative only and still have feasible applications as is shown in the later chapters. Reliability of the techniques can be related to the maturity of the technology that the measurement techniques is based on as well as to their ability to produce accurate measurement results. Sensitivity can be defined based on the lower detection limit of the technique. One general definition for the sensitivity is given by [Bart 2005] that the

sensitivity should be 0.01 wt% or less. In this case, the term applicability covers various properties that enables fluent and comfortable use of the technique. These include relatively simple sample preparation requirements, short analysis time, reasonable training requirements and low purchasing and running cost of the equipment.

In the following sections, different techniques are introduced. The sample preparation phase is considered to be important when polymer additive analyses are conducted. Thus, the next section presents and discusses chromatography, a technique that is widely integrated as part of additive analysis, to make the sample preparation and analysis phases more fluent.

4.1 Chromatography techniques

The sample preparation phase is an essential phase during the whole analysis process. It has been estimated that in industrial laboratories, the sample preparation phase takes about ten times more time by average than the actual analysis [Bart, 2005]. Sample preparation methods are numerous but most of them include some sort of extraction step.

Chromatography is a common technique that is applied in the sample preparation phase of polymer additive analysis.

Approximately 50% of the industrial analyses comprise of chromatographic analyses [Bart, 2005]. It is a technique that separates individual components from one sample. Usually the separation is conducted by exposing the static sample to mobile phase or carrier, which separates a desired component from the sample. This would make the extracted component ready for analysis. It is common that chromatographs are integrated as part of the analysis equipment. Generally, two types of chromatography techniques are identified: gas chromatography (GC) and liquid chromatography (LC).

In LC, the used mobile phase is in liquid form. The mobile phase is pumped through a sample injection point (where sample can be injected as a solution or dissolved in the mobile phase) and chromatographic column, where reactions with the column packing material cause separation of various phases in the flowing mixture. At the output end of the column, a detector is installed which analyses a certain sample property depending on the detector type. Data acquisition and analysis systems are used in data handling. Various types of liquid chromatography techniques exists but currently the most dominant LC method is high-performance (or high pressure) LC. The applied detectors can measure wavelengths of ultraviolet or visible light, fluorescence, electrochemistry, scattering or refracting of light or conductivity. Applicability of the method is very good as it can be virtually used on any organic compound.

GC deviates from LC in sense that the mobile phase is gaseous. The injected sample is usually in liquid form so sample preparation in some extent is required. The injected liquid is heated until vaporized and mixed with the mobile phase. The mixture reacts with the column packing material and different components are separated based on their differences in boiling points. The most common detector used in GC is flame ionization detector (FID), which can detect the ions formed in the combustion process of organic materials and correlate the measurement result to specific compound based on the concentrated amount of ions. GC is applicable to detect volatile components, such as waxes, alcohols, fatty acids and their esters, plasticizers, antioxidants, stabilizers, surfactants and vulcanization accelerators.

4.2 Luminescence spectroscopy

Luminescence is a phenomenon where the excited state of an atom or molecule relaxes and simultaneously emits energy in the form of light. Luminescence spectroscopy is based on exploiting this phenomenon. The equipment itself is comprised of a source, excitation

monochromator, sampling area, emission monochromator and detector. The source produces the energy required for excitation, usually being a light source (a special lamp or a laser). The produced light travels through excitation monochromator to sample and further through emission monochromator to detector. The two monochromators can be used to filter the wavelengths of the applied light. Finally, fluorescence detector records the signal. These detectors are considered to be simple, highly sensitive and reliable. The obtained data is displayed as a function of fluorescence excitation and wavelength.

Several applications for fluorescence spectroscopy has been listed by [Bart, 2005]. Good qualities of the technique include very high sensitivity and specificity. It can be considered also as non-destructive. However, the technique is limited to study such additives that have fluorescent properties. Such additives include UV absorbers, optical brighteners, phenolic and aromatic amine antioxidants. In addition, the technique has limited capability to conduct quantitative analysis.

4.3 Light scattering techniques

Light scattering techniques are based on the interaction of an electromagnetic field with matter. When the wavelength of electromagnetic radiation is at the same scale as the heterogeneity of the matter, scattering phenomenon according to refraction and reflection laws can be observed. Polymer solutions include natural fluctuations in density and concentration, which are revealed by scattering phenomenon. Light scattering techniques can be divided in static or dynamic. In static light scattering (SLS) a light source (usually laser) is used in order to apply beam of electromagnetic radiation on the studied sample. Interaction with the sample causes scattering of the radiation and excitation. This excitation causes re-emission of the radiation, but at different intensity. From the intensity of the scattered radiation molecular weight and other information on the polymer can be extracted. In dynamic light scattering (DLS), similar light source is used as in SLS, which applies a beam of light on the sample via a filter. The light is scattered from the sample and goes through a second filter, forming a scattering image called "speckle pattern". The form of the speckle pattern depends on the fluctuations of the scattered light intensity. By analyzing speckle patterns, information on the size distribution of the particles in the sample can be obtained as well as information on diffusion properties.

Both SLS and DLS can be applied to various types of samples, but expertise on sample preparation as well as in data interpretation is needed. General limitations related to light scattering include dust, light absorption and particle interactions. Dust in the samples may lead erroneous spectrum as the dust particles have typically different scattering behaviour than the studied sample. Absorption behaviour affect the measurement system in two major ways: by heating locally sample system causing changes in particle diffusion and causing unusual dynamic processes [Schärfl, 2007]. Undesired particle interactions may rise if the studied sample is not dilute enough and, especially in case of SLS, it can have effect into the measurement result.

4.4 Atom absorption spectroscopy

Atom absorption spectroscopy (AAS) is based on absorption of light at specific wavelength. The relatively simple principle of AAS is presented in Figure 5. A light source (e.g. a cathode lamp) emits light to the burner system where the sample is fed. In the burner system, a high temperature is applied to generate free atoms. The light beam travels through the space where the atoms are located and some of the light is absorbed by the atoms. The concentration and type of the atom affect to the absorption behaviour. After the absorption, the applied light beam travels through a monochromator, which allows the selected

wavelengths to travel further to the detector. The absorption behaviour is plotted as function of absorbance and wavelength and from this plot, individual elements can be identified.

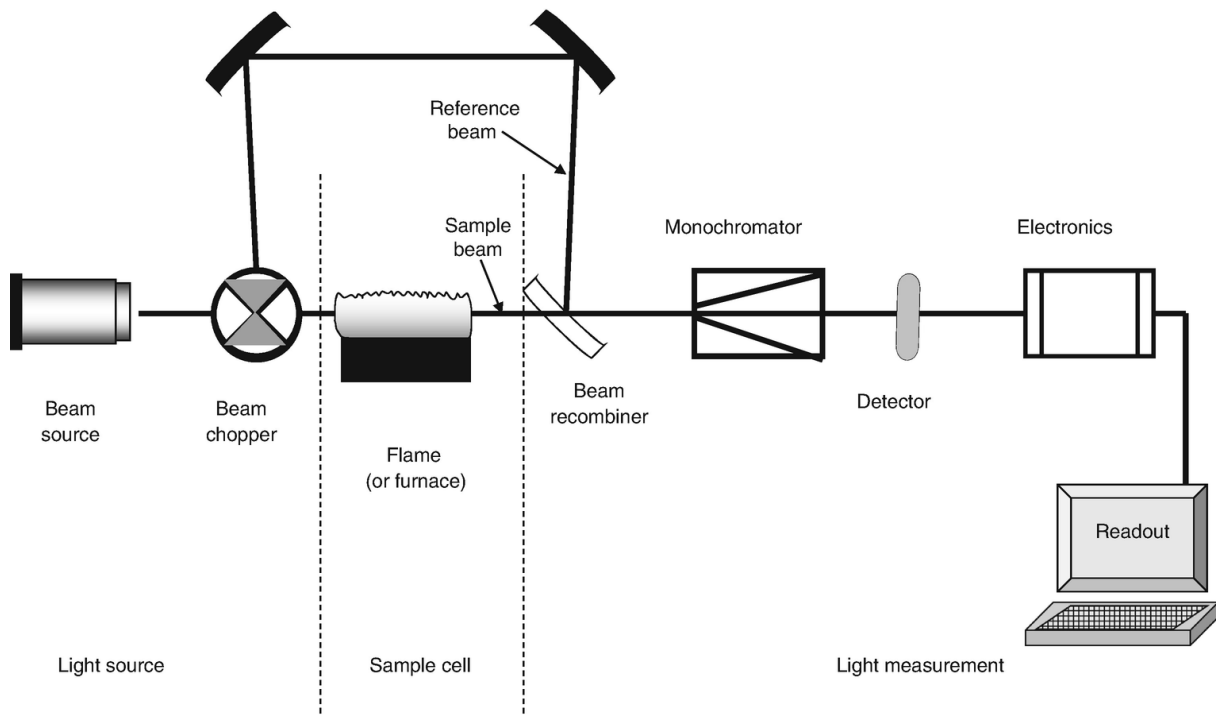


Figure 5. Schematic illustration on AAS equipment. [Beaty & Kerber, 1993]

AAS has high detection ability for fairly high amount of elements. It has not been very actively used in polymer additive analysis. Some analysis of PVC stabilizing systems has been conducted, heavy metal analyses in food packages, toys and consumer goods. Also, calcium and zinc stearates have been analysed in polyethylene, as they have been used as surfactants and release agents, respectively. In case of synthetic fibres, residues of catalysts, stabilizers, flame retardants (Sb containing) and antibacterials can be analyzed. However, it should be noted that AAS is limited to analyse individual elements and no organic compounds are possible to be analyzed which limits the applicability of the method.

4.5 Atomic emission spectrometry

Atomic emission spectrometry (AES) is very similar to AAS. In AES, instead of measuring absorption of the electromagnetic radiation applied, the emission of radiation from atoms in excited states is measured. [Yeung et al. 2017] Flame or plasma is used to induce the excited state in the studied atoms of the sample and as the excited state is discharged, the resulting radiation is filtered, detected and recorded. Thus in AES external source for excitation is not required as in AAS.

Compared to AAS, AES has better detection limits. On the other hand, the equipment cost is higher. Depending on the excitation source used, AES has some applications in polymer additive analysis. When arc or charge discharges are used as excitation sources, Cl-containing applications are possible, e.g. identification of PVC, Cl-containing fire retardants and chlorinated polyethylene. In case of pigments and fillers, the technique has been used for qualitative analysis. Applicability in metal containing halogens and fire retardants (presumably non-chloride containing) has been also speculated. When plasma is used as excitation source (ICP-AES), more applications for polymer additive analysis is reported.

Elemental analysis of lubricating oils is well advanced as there is a dedicated ICP-AES standard for this purpose (ASTM D4951). Generally, ICP-AES has been used in similar manner as AAS, determine metals (as part of thermal stabilizers and catalyst residues) and residues of sulphur (curing agent).

4.6 Infrared spectroscopy

Infrared (IR) spectroscopy is based on exposing the studied sample on infrared rays and measuring the absorbed energy at specific frequencies. The absorption of IR radiation is governed by the molecule structure of the sample. To be more exact, IR radiation interactions with molecules are due to changes in molecular dipoles. These changes can be due to certain movements between atoms and chemical bonds. The movement can cause stretching or bending of the bond. Depending on the type of the movement, the bond variation can be either symmetric or asymmetric in nature. The variations of the bond length and the relative movement of atoms are generally referred as vibrations. Each of these different vibrations produces an absorption signal. Since there are various possibilities for different atoms to move and vary bond length within a molecule, a band of signals is produced. These signal bands can be correlated with the characteristic functional groups present in polymer chains, thus making possible to fingerprint whole molecules. [Saldivar-Guerra et al. 2013]

The used equipment is a spectrometer, which uses Fourier transform (FT) in the data analysis and is usually referred as FTIR. IR source generates the IR radiation, which passes through an interferometer and sample before entering the detector. In the modern equipment, the obtained signal is amplified and filtered before converted and analysed with FT. As a result, an IR spectrum is produced (see Figure 6), where transmittance (how much IR radiation is passed through the sample) is plotted versus the wavenumber (unit directly proportional to frequency and energy of an electromagnetic wave). Figure 6 shows an IR spectrum for high density polyethylene. The different signal bands can be correlated to symmetric and asymmetric stretching of methyl and methylene groups (A), symmetrical bending of methyl (B) and methylene (C) and stretching of the methylene groups in the polymer backbone (D).

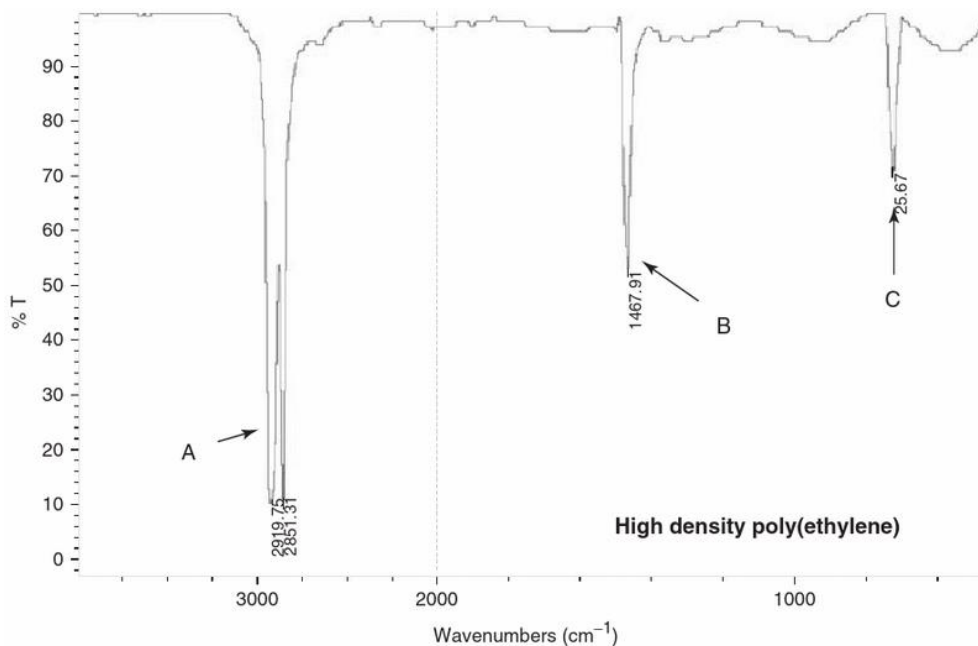


Figure 6. An example FTIR data presented for high density polyethylene. [Saldivar-Guerra et al. 2013]

FTIR can be used in qualitative and quantitative analyses for wide range of additives. The qualitative analysis is based on identifying the characteristic wavelength range for each chemical bond. As these characteristics are quite different among additives, FTIR is a good tool for qualitative identification. Saldivar-Guerra et al. has listed the most common chemical bonds and their wavelength ranges [Saldivar-Guerra et al. 2013]. Quantitative analysis is possible when concentration of the analyte is known. The unknown concentrates can be analysed if a calibration curve is available.

FTIR is a convenient method to analyze solid, liquid or gaseous samples. It can be considered to have a good ability to identify individual functional groups from the polymer backbone and sufficient sensitivity since it can detect absorption bands with weak intensity. Data on the signal bands of base polymers seem to be reasonably well available from open literature making their identification relatively simple (as exemplified in Figure 6). However, to be applied in identification of different additives, expertise is required when identifying the signal bands correlating with additives.

4.7 Nuclear magnetic resonance NMR

NMR is based on obtaining information on the magnetic properties of nuclei. A basic physical property of nuclei is that they carry electrical charge. Depending on the nucleus type, the charge may or may not spin around the nuclear axis inducing a magnetic dipole along the axis. The spinning charges can be described with spin numbers, which describe the angular momentum of the spinning charge. When these spins are exposed to external magnetic fields and energy transmitted at radio frequencies (RF) to the sample, the energy levels of the spins may be affected by the absorption of the transmitted energy. This phenomenon is called magnetic resonance.

Figure 7 shows a schematic illustration on the NMR equipment. The sample tube is inserted in a detector coil where it is rotated around the tube's axis. Magnets are used to generate the external magnetic field. Radio frequency (RF) coil is used to transmit (and detect if only one coil is used) RFs on the detector coil. When the system is at resonance state, RF radiation is absorbed into the sample. Detector coil receives the resulting signal, which is then amplified and recorded as a spectrum.

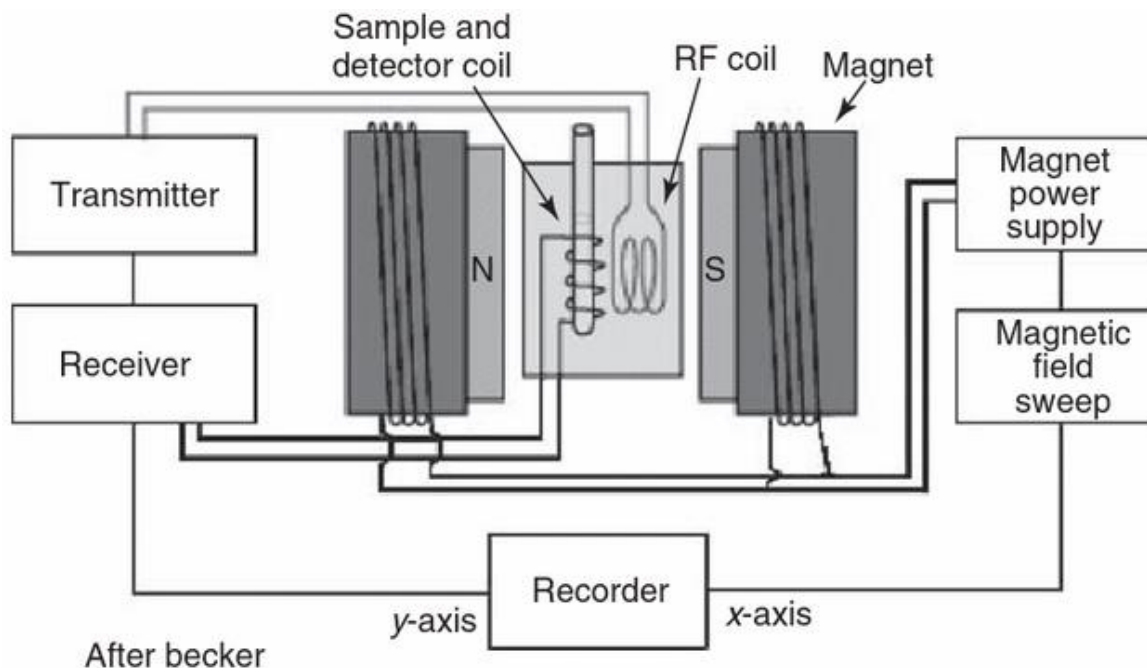


Figure 7. Schematic illustration on NMR equipment. [Saldivar-Guerra et al. 2013]

The magnetic field of the atomic electrons oppose the externally applied magnetic field. The produced effective magnetic field thus differs from the applied field. The magnitude how much the shift is from the applied field is defined as chemical shift. NMR data is presented by using this chemical shift. This chemical shift can be correlated to the electrical properties of the surrounding atoms and molecules thus making possible the identification of functional groups. Other studied properties from the recorded spectrum are peak multiplicity and intensity, line shape and width and time dependency of intensity. Peak multiplicity gives information on the adjacent atoms while peak intensity is characteristic to the number of nuclei detected, which can be informative as molecular structures are considered. Line shape and width as well as the time dependency of intensity are related to the molecular dynamics and magnetic properties of the spins.

Generally, NMR can produce a lot of information on polymer properties based on the behaviour of substances subjected to a magnetic field. However, high level of expertise is required in order to adequately understand the physics related to magnetic resonance and interpretation of the analysis results. NMR spectroscopy is most useful as qualitative analysis of pure compounds are considered. Thus, a sample preparation procedure is needed. Signal intensities can be used to determine molecular structures in polymers.

4.8 Mass spectrometry

Mass spectrometers are instruments that turn neutral molecules into ions in gaseous phase and analyse the mass-to-charge ratio of the gaseous ions. As a result, a spectrum comprising of mass lines is produced of which the location and intensity of the mass lines are analyzed.

The basic principle of a mass spectrometer is shown in Figure 8. A mass spectrometer can be considered to comprise of a sample inlet, source for ion production, mass analyzer and ion detector. Depending on the complexity of the sample, sample preparation procedure may be needed. During ionization, charged particles are extracted from the sample. This can be conducted in several manners. Generally, hard and soft ionization can be distinguished, the difference being that in hard ionization the high amount of residual energy affects the fragmentation of the molecules significantly more compared to soft ionization. Examples of

hard and soft ionizations are electron ionization and chemical ionization, respectively. The most applicable ionization method depends on the sample type and the used detector. The beam of ions produced during ionization, which is directed into a mass analyser where the ions are analyzed according to their mass-to-charge ratio. The function of mass analyzers are based on the use of static/dynamic and magnetic/electric fields. The basic principle is that the ions comprising the beam can be affected by the applied external fields in that extent that the ions having different mass-to-charge ratios can be separated accordingly. Finally, the ions travel to detector, which records the induced charge or current.

Mass spectrometry is very convenient tool for polymer additive analysis as it can produce both qualitative and quantitative information out of wide range of samples. The quantitative analysis often requires highly skilled operator. The obtained qualitative information includes molecular weight distribution, formula and structure. The method is considered to be sensitive as well as reliable, and it can be used to analyze substances with unknown composition. Mass spectrometry can be used for fingerprinting purposes. However, this would require quite an extensive amount of analysis data. Disadvantages of the method include the amount of expertise required for running the equipment and analyzing the results, especially when quantitative information is to be obtained. The purchase cost for the equipment is also high.

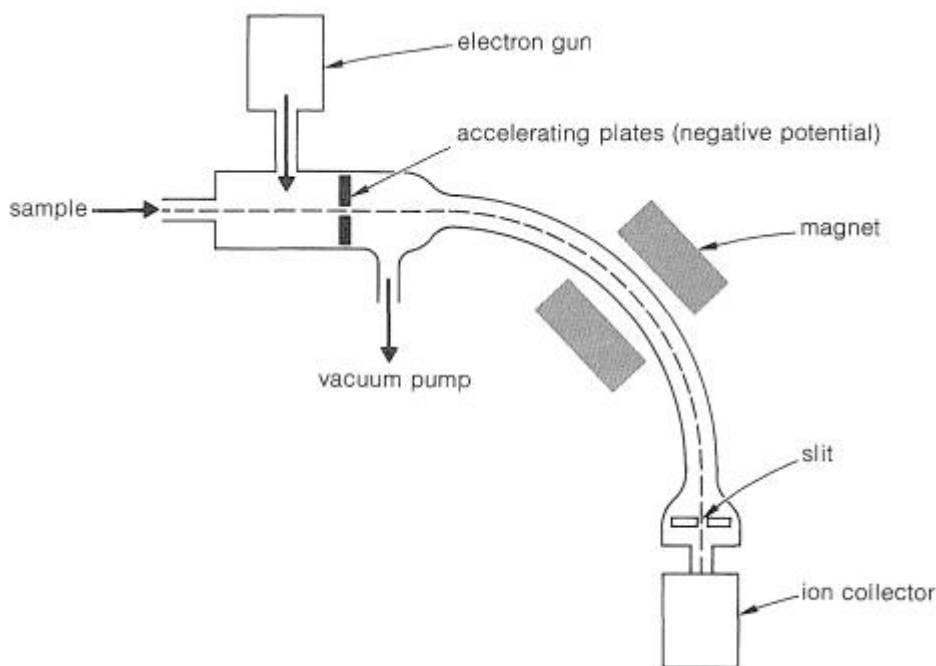


Figure 8. The basic functioning principle of a mass spectrometer. [Roberts and Caserio, 1977]

4.9 X-ray spectrometry

X-ray analysis is based on scattering of x-rays interacting with electrons of an atom. Different analysis techniques can be used to obtain data on the different interaction mechanisms. Fluorescence, particle induced emission, absorption and diffraction are phenomena that each have their dedicated technique: x-ray fluorescence spectrometry (XRF), particle-induced x-ray emission spectrometry (PIXE), x-ray absorption spectrometry (XAS) and x-ray diffraction spectroscopy (XRD), respectively. From these XRF and XRD are the most distinguished methods in polymer additive analysis.

XRF has been used to detect flame retardant elements and analyzing the source of supply of mineral fillers (their elemental composition is tied to the geographical location of the mineral). In addition, characterization of pigments, analyses of secondary antioxidants that have P or S in their composition as well as lubricating oils, tracer elements (may be added by manufacturer to “fingerprint” material), processing aids and metallic compounds (e.g. Cd, Pb, Zn used in pigments, Cd used in stabilizers and Zn used in lubricants) have been conducted. XRF has been applied also in plastic waste sorting applications.

XRD can be used to detect inorganic fillers, polymer-clay nanocomposites, UV absorbers in coatings, melamine-based fire retardants, organic and inorganic pigments. In structural analysis, XRD has been applied to antioxidants, flame retardants, plasticizers, fillers, pigments and dyes. XRD has been combined to other techniques, such as XRD, in mineral filler studies.

PIXE has been applied in analysis of metallic elements from orthopaedic implant systems and polymer foils as well as pigments.

XAS has been applied in analysis of Zn (in zinc stearates and antiwear additives), certain dyes in cotton and cellophane substrates and catalyst studies. It may be applied also for studying ultrathin polymerized films.

4.10 Electroanalytical methods

Electroanalytical methods are applied in the measurement of the electrochemical properties of the sample. Properties such potential, current, resistance, capacitance or combination of these is measured. Electroanalytical methods are not that widely used as the measurement data is affected by the electrochemical complexity of the samples, i.e. distinguishing the electrochemical signal rising from a certain reaction involving an additive under interest is easily interfered by other simultaneously occurring electrochemical reactions. Electrochemical analysis methods have some advantages related to practical and inexpensive measurement equipment, ability to determine low level analytes, well automated measurement procedures with high speed and the methods ignore interference rising from certain sample properties related to turbidity, colour or suspension.

Polarography is a method, which determines a potential difference forming between two measurement electrodes exposed to a sample solution. The formed potential difference can be related to the activity of the species in the solution according to Nernst equation. The method has been applied in control of foodstuffs (i.e. drinks), Br-based flame retardants, heat stabilizers used in PVC and processing aids of fluoropolymers. As part of chromatographic processes, polarography can be used to monitor the selected ions or pH.

Voltammetric methods study the oxidation-reduction reactions occurring on a surface of a metal electrode. The potential of the working electrode is adjusted versus a constant built reference electrode with certain scan rate and over a potential range. The resulting current flow between the working and counter electrodes is recorded. From the resulting potential-current diagram, concentrations of different chemical species can be estimated as the resulting current is directly proportional to the concentration of electroactive species. Voltammetry has been previously applied in determining different type of antioxidants (e.g. phenolic and amino-based), several PVC specific additives and inorganic pigments from art artefacts.

In coulometric analysis, the charge of the electrochemical system is recorded at constant current or potential. The charge is originating from an oxidation-reduction reaction between a certain reagent and the analyte. As the electrochemical properties of the reagent and

analysis are known, the measured charge can be correlated to the mass of analyte. Coulometry is applied in coulometric titrations where the moisture of the samples can be estimated even at ppm levels.

4.11 Elemental analyses

In principle, elemental analysis methods can be used to identify individual elements in the studied sample. These can be organic or inorganic in nature, though the organic ones typically require multi-element analytic techniques to be properly identified. Table 5 presents the most common elements that the applied additives comprise of.

Combustion analysis is a traditional method that is based on removing carbon as CO₂ and hydrogen as H₂O. Combustion analysis can be conducted in either open or closed system. In open system, the sample is heated in elevated temperature (typically 400-800°C) in open atmosphere or under controlled gas flow until organic constituents are removed and a solid ash is formed. In closed system, the combustion is conducted under controlled conditions and typically with a catalyst. The combustion can be carried out with several different techniques (applying e.g. oxygen, CO₂, oxidizing agent or pyro-hydrolysis). The formed ash can analysed as such or further treated with e.g. acid to remove organic material, and analysed with a suitable technique (e.g. spectrometry methods, neutron activation analysis, fluorescence methods, voltammetry).

Table 5. The most common elements present in additives used in commercial polymers. Reproduced from [Bart, 2005].

Element	Corresponding additive
Al	Talc, catalyst residue, flame retardant
As	Biocide
B	Flame retardant, smoke suppressant
Br, Cl	Flame retardant
Ca	Stearate processing aid, filler, heat stabilizer
Cr	Pigment, catalyst residue
Cu	Pigment, biocide
F	Processing aids
Hg	Biocide
Mg	Talc, flame retardant
Mo	Smoke suppressant
P	Phosphite stabilizer, plasticizer, flame retardant
S	Vulcanizing agent, dye, biocide
Sb	Flame retardant, biocide

Se	Pigment
Si	Silica, filler, catalyst, residue
Sn	Flame retardant, pigment, stabilizer, biocide
Ti	Pigment, catalyst residue
Zn	Stearate processing aid, heat stabilizer, pigment, smoke suppressant, biocide

5. Conclusions

This literature survey compiles information on the used additives in polymer blends and presents different methods that can be used to analyze them. Additives are used to improve processability of the polymers as well as their material properties. 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 presented and their applicability to analyze different additives discussed. Several of the presented 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 future work continues screening of the methods in order to recognize which ones would be the most suitable methods for on-site analysis.

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