ARCADA

Harmful substances in Waste of Electrical and Electronic Equipment

With focus on analyzing methods, recycling aspects and legislation

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Abstract:

The increasing use of electrical and electronic equipment's (EEE) causes a massive surge of e-waste. Solutions are needed to put the emphasis on proper disposal and recycling which includes both technological innovations, political good-will and creative legislative regulation. This thesis is a part of the PLASTin project which aim is to develop the recycling of challenging plastic streams such as plastics from WEEE. Brominated flame retardants, chlorinated flame retardants and phthalates are all chemicals associated with being hazardous to the environment and human health. These chemicals are frequently added into electronic equipment's and their removal from the polymer matrices is crucial from a recycling point of view. There are different analyzing methods for identifying the polymer and for detecting additives with, FTIR spectroscopy being one of them and it is used in this thesis for analyzing WEEE samples. Plastics from WEEE can be recovered through mechanical, chemical or thermal recycling. The European Commission has funded different projects to improve the recycling of challenging waste plastics. The WEEE Directive, RoHS Directive and REACH Regulation are legislative tools concerning the production, handling, and recycling of EEE. The source of information is gathered from EU databases, environmental institutions information channels and articles concerning the matter. The empirical part in this thesis was to analyze WEEE samples consisting of ABS, PS, PC/ABS and PP and they were obtained from a Kuusakoski recycling plant. The FTIR spectrometer was well suited for polymer identification. However, there were some indications that the samples could contain harmful substances of some sort, but this could not be determined with the FTIR spectrometer. As a conclusion, some type of elemental analysis should be used as a complementary measure to confirm if the samples contain harmful additives.

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Sammandrag:

Den ökande användningen av elektriska och elektroniska produkter orsakar en massiv ökning av e-avfall. Det behövs lösningar för att lägga tonvikten på korrekt avfallshantering och återvinning, vilket inkluderar tekniska innovationer, politisk välvilja och kreativ lagstiftning. Detta examensarbete är en del av PLASTin-projektet vars syfte är att utveckla återvinningen av utmanande plastströmmar som exempelvis plast från e-avfall. Bromerade flamskyddsmedel, klorerade flamskyddsmedel och ftalater är kemikalier förknippade med att vara farliga för miljön och människans hälsa. Dessa kemikalier tillsätts ofta i elektroniska produkter och deras avlägsnande från polymermatriserna är avgörande ur återvinningssynvinkel sett. Det finns olika analysmetoder för att identifiera polymerer och upptäcka tillsatta kemikalier med, FTIR-spektroskopi är en av dem och den används i detta examensarbete för att analysera e-avfall sampel. Plast från e-avfall kan återvinnas genom mekaniska, kemiska eller termiska återvinnings metoder. Europeiska kommissionen har finansierat olika projekt för att förbättra återvinningen av utmanande plastavfall. WEEE-direktivet, RoHS-direktivet och REACH-förordningen är lagstiftningsverktyg för produktion, hantering och återvinning av elektroniska produkter. Informationen hämtas från EU:s databaser, miljöinstitutionernas informationskanaler och artiklar gällande ärendet. Den empiriska delen i detta examensarbete var att analysera e-avfall prover bestående av ABS, PS, PC/ABS och PP och de erhölls från en Kuusakoski återvinningsanläggning. FTIR-spektrometern var väl lämpad för polymeridentifiering. Det fanns dock vissa indikationer på att samplen kunne innehålla skadliga ämnen av något slag, men detta kunde inte fastställas med FTIR-spektrometern. Sammanfattningsvis kan det konstateras att någon typ av elementaranalys borde användas som en kompletterande åtgärd för att bekräfta om samplen innehåller skadliga kemikalier.

Nyckelord:	Flamskyddsmedel, FTIR spectroskopi, Plast, Återvinning, WEEE, PLASTin projekt
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Abbreviations

ABS	Acrylonitrile Butadiene Styrene
ATR	Attenuated Total Reflectance
BBP	Benzyl Butyl Phthalate
BFR	Brominated Flame Retardant
BrPS	Brominated Polystyrene
BSEF	Bromine Science and Environmental Forum
CFR	Chlorinated Flame Retardant
CENELEC	Comité Européenne de Normalisation Èlectrotechnique
DBP	Dibutyl Phthalate
Deca-BDE	Decabromodiphenyl Ether
DEHP	Di-2-ethylhexyl Phthalate
DIBP	Diisobutyl Phthalate
DP	Dechlorane Plus
ECHA	European Chemicals Agency
ECS	Eddy Current Separator
EEE	Electrical and Electronic Equipment
EFSA	European Food Safety Authority
FTIR	Fourier Transform Infrared spectroscopy
GC-MS	Gas Chromatography-Mass Spectrometry
HBCDD	Hexabromocyclododecane
HIPS	High Impact Polystyrene
LIBS	Laser-Induced Breakdown Spectroscopy
MIR	Mid-Infrared spectroscopy
MIR-T	Mid-Infrared Thermography
NADES	Natural Deep Eutectic Solvents
NIR	Near Infrared spectroscopy
PBB	Polybrominated Biphenyl
PBDE	Polybrominated Diphenyl Ether
PC	Polycarbonate
PFR	Phosphorous Flame Retardant
POP	Persistent Organic Pollutant

PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl Chloride
REACH	Registration, Evaluation, Authorization, and restriction of Chemicals
RoHS	Restrictions of Hazardous Substances
SC	Stockholm Convention
SEM-EDS	Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy
SSS	Sliding Spark Spectroscopy
TBBPA	Tetrabromobisphenol
TCEP	Tris(2-chloroethyl) Phosphate
TCPP	Tris(2-chloro-1-methylethyl) Phosphate
TDCP	Tris[2-chloro-1-(chloromethyl)ethyl] Phosphate
THz	Terahertz spectroscopy
WEEE	Waste of Electrical and Electronic Equipment
XRF	X-ray Fluorescence spectroscopy

1 INTRODUCTION

We live in a world where “wear and tear” is perfectly normal and this attitude has led us towards serious questions about diminishing resources, pollution problems and health issues. This thesis is part of the ALL-IN for Plastic Recycling (PLASTin) project which aim is “to support the plastic industry actors to develop systemic, and environmentally optimized recycling concepts”. To improve the recycling rates of plastic waste, it is required to improve the technological solutions.

The recycling of plastics is an extensive process. The challenges with recycling waste of electrical and electronic equipment’s are the detection and removal of harmful substances that they often contain. The plastic in e-waste must be free from any hazardous substances in order to progress in the recycling process. On that account, the analysis of the plastic waste is a fundamental part towards a circular economy.

Therefore, the purpose of this thesis is to study the different aspects regarding recycling of e-waste and to investigate the suitability of FTIR spectroscopy as an analyzing method for polymer identification and to recognize potential additives in polymer matrices. Furthermore, the legislative aspects of managing WEEE have been taken into consideration mainly from an EU perspective.

1.1 Objectives

The objectives in this thesis are divided in to four categories. The first objective is to investigate the existence of harmful substances in waste of electrical and electronic equipment’s (WEEE) and the challenges concerning them. Secondly, the focus is put on determine different analyzing methods to detect harmful substances in polymers and the recycling of WEEE. The third objective is to find out the legislative boundaries concerning WEEE in Europe. The source of information is gathered from EU databases, environmental institutions information channels and articles concerning the matter. Finally, a small empirical part is made in order to establish the existence of possible harmful substances in samples provided by Kuusakoski and polymer identification of the samples using FTIR spectroscopy as an analyzing method.

2 LITERATURE REVIEW

A lot of research has been made in recent years concerning the impact plastics have on the environment, human well-being, and the depletion of scarce resources. The population growth together with the ever-growing need of electrical and electronic equipment's increases the load of e-waste containing harmful substances ending up in the environment unless more affordable and effective methods are found to enable reuse and recycling of WEEE.

Some hazardous substances that are common in electronic equipment's are brominated flame retardants, chlorinated flame retardants and phthalates and therefore this thesis is focused on these substances.

2.1 Waste Electrical and Electronic Equipment

The amount of electrical and electronic waste produced each year around the world is increasing rapidly. Our society is full of electrical and electronic equipment's which eventually comes to their end and therefore must be disposed in a sustainable way. Electrical and electronic equipment's consists for instance of household appliances, medical devices, monitoring instruments and IT gadgets. These products are usually a mix of a variety of materials and substances, some of which are harmful and causes environmental and health issues if not disposed correctly. To identify various kinds of hazardous substances in these polymers is essential when trying to increase the knowledge in recycling process'. (European Commission 2021)

Figure 1 portrays the amount of electrical and electronic equipment (EEE) that has been put out on the market and the electrical waste that has been collected, treated, recovered, and reused in the EU between the year 2011 to year 2018. The volume of EEE put on the market in the EU has grown from 7,6 million tonnes to 8,7 million tonnes from year 2011 to year 2018. In the same period, the total WEEE recycled and reused improved from 2,6 to 3,2 million tonnes equivalent to an increase of 23,1%. Even though there has been progress in recycling and reusing WEEE, there is room for improvement. (Eurostat 2021)

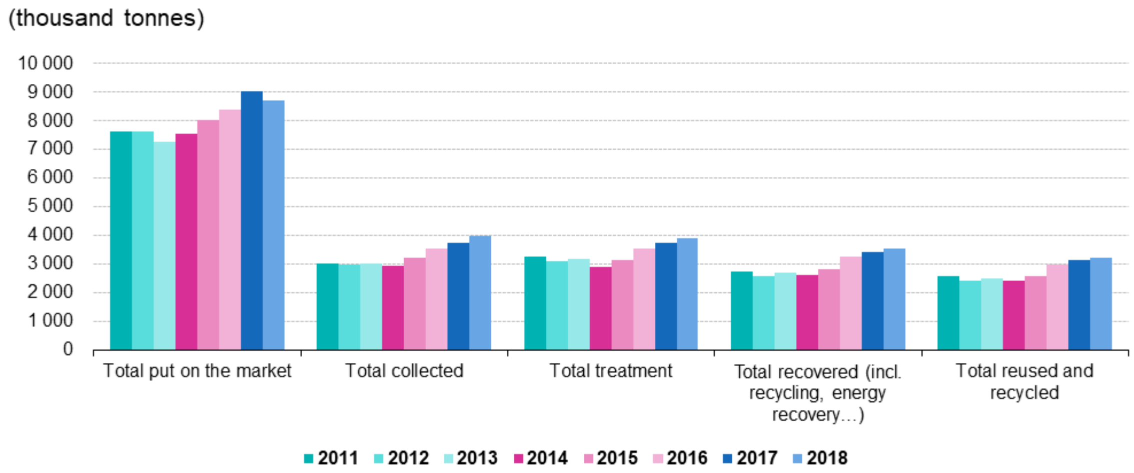

Figure 1. EEE put on market, collected, treated, recovered, and reused in EU 2011-2018 (Eurostat 2021).

The recycling of WEEE is important for various reasons. WEEE can be considered as a valuable source of different raw materials. If these materials are not recovered properly, new raw materials must be extracted and manufactured which eventually results in a remarkable loss of resources and an increase in environmental damage. (F.O. Ongondo et al. 2021)

According to the Bromine Science and Environmental Forum (BSEF) it is estimated that in the EU area the amount of WEEE officially collected is around 1,3 million tonnes every year of which approximately 1 million tonne ends up in recycling facilities but there is still a lapse of 300 kilo tonne in the process. (BSEF 2021)

It is furthermore worth mentioning that by WEEE-cost is meant that those who produce WEEE must participate in financing the collection and the recycling of these products. Though WEEE legislation includes all EU member states it is up to each country to implement the rules in their own way. According to WEEE legislation in the EU, each enterprise involved in the production of WEEE must take the following questions into consideration:

- Which devices must be registered in which categories and quantities?
- What collection and recycling costs will a company be paying?
- In which countries have a business need to be registered?
- What is the take-back obligations for the company?
- What information does the company have to provide? (WEEE Europe 2021).

The amount of WEEE produced per year has been annually increasing all over the globe. If we for instance look upon the growing Asian market the demand for electrical gadgets is still on the rise. Instead of large family complex, the one or two person households has emerged and that means that the need for personal electronic equipment's has also increased. It is impossible to deny people their right to use modern technology and from this perspective, the emphasis must be put on the responsible production process', recycling and safe disposal of the waste it causes.

Though the EU area is on the top of the list of countries that has a responsible grip on WEEE recycling and disposal mechanism there are still issues that must be noticed. One problem is the mismanagement of e-waste ending up in criminal network. Many electronic equipment's consists of precious metals such as gold, copper, indium or palladium of which indium and palladium are considered as critical raw materials. These valuable metals are collected, and the rest is dumped for instance in oceans and landfills regardless of toxic contents (Marino 2021). Then there are also the dubious transactions with "donations" and "second-hand business" between the EU and third world countries. In this case the good intentions are heavily contradicted despite the regulations and legislative frameworks (Noticias Asociados 2016).

2.2 Additives in plastics from electrical and electronic equipment

The plastics in electrical and electronic equipment usually contain different kinds of additives. The additives are added to the material to improve different characteristics of it. According to Sormunen et. al. you can easily claim that the average amount of additives in plastics constitutes of around 7% by weight (wt%) (Sormunen et. al. 2022). Additives can be categorized in to four main groups:

- Functional additives
    - Flame retardants (0.7-25 wt% for BFRs and 0.7-3 wt% for HBCD), stabilisers (0.05-3 wt%), plasticisers (10-70 wt%), slip agents (0.1-3 wt%), lubricants (0.1-3 wt%) curing agents (0.1-2 wt%), biocides (0.001-1 wt%) and antistatic agents (0.1-1 wt%)

- Colourants
    - Soluble (0.25-5 wt%), organic pigments (0.001-2.5 wt%) and inorganic pigments (0.01-10 wt%)
- Fillers (up to 50 wt%)
- Reinforcement agents (15-30 wt%). (Hahladakis et.al. 2018)

Table 1. Table of the function of different types of additives. (British Plastic Federation 2022)

Type of additive	**Function**
Flame retardants	Prevents ignition and the spreading of flames in plastic materials.
Stabilisers	Prevents decomposition during processing.
Plasticisers	Makes the plastic material softer and flexible.
Lubricants	External lubricants prevent damage to the plastic and mould during processing, internal lubricants improve the melt flow and processability of the plastic material.
Antistatic agents	Prevents the build-up of static electric charge in the plastic material.
Pigments	Tiny particles that create a particular colour in plastic materials.
Fillers	Improves the strength and lowers the costs of the plastic material, increases the bulk of the plastic.
Reinforcements	Improves tensile strength, flexural strength and stiffness of the plastic material.

Table 1 above briefly describes the function of different additives. This thesis focuses on three different additives: brominated flame retardants, chlorinated flame retardants and phthalates. The BFRs are the most commonly used flame retardant and therefore an obvious option. Other not as frequently used flame retardants are CFRs and that is why they are included in this thesis. The last chemical group investigated are phthalates because they are not flame retardants but are often added to plastic materials.

2.2.1 Brominated Flame Retardants

Bromine is the third halogen of the periodic table. It is a red-brown liquid that can be found in soluble salts from salt lakes and seawaters. According to the Bromine Science and Environmental Forum, the production of bromine is estimated to be around 500 000 tons annually worldwide and the majority of it is used within fire safety. (BSEF 2021)

Brominated flame retardants (BFRs) characterise a comprehensive group of chemicals that are added to polymeric components to improve the fire resistance. BFRs can be categorized in to three groups: additive BFRs, reactive BFRs and oligomeric and polymeric BFRs. In table 2 these categories are briefly described and examples of BFRs from each category are given. (Haarman et al. 2020)

Table 2. Table of the categories of BFRs. (Haarman et al. 2020)

Category	Description	Example of BFR
Additive BFRs	Physically blended but not chemically bound to the polymer	Hexabromocyclododecane (HBCDD)
Reactive BFRs	Chemically bound to the polymer structure	Tetrabromobisphenol A (TBBPA)
Oligomeric and polymeric BFRs	The atoms are incorporated directly to the polymeric structure	Brominated polystyrene (BrPS)

According to European Food Safety Authority (EFSA) BFRs can be classified into five main classes. The polybrominated diphenyl ethers (PBDEs) that are used in plastics, textiles, and electronic castings, the hexabromocyclododecanes (HBCDDs) that are used in thermal insulations, the tetrabromobisphenol A (TBBPA) and other phenols that are used in thermoplastics such as televisions, the polybrominated biphenyls (PBBs) that are used in consumer appliances and plastic foams and lastly the other brominated flame retardants. (EFSA 2021)

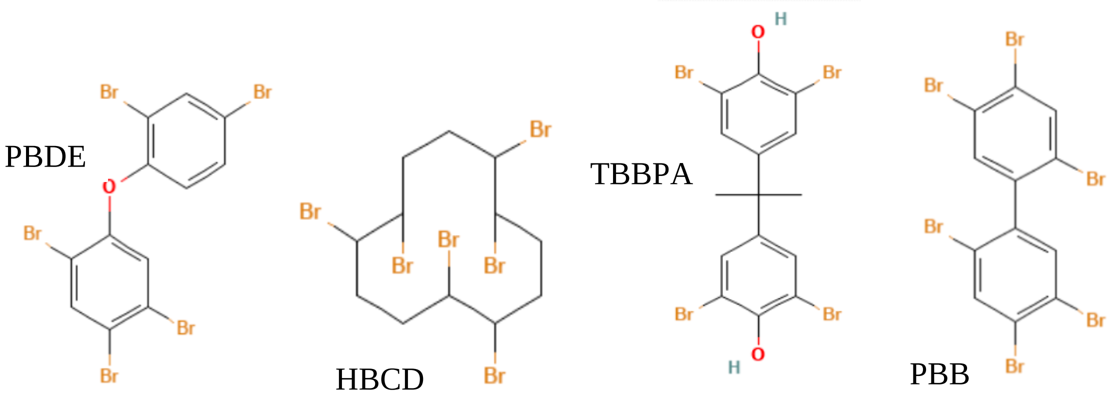

Figure 2. Chemical structure of PBDE, HBCD, TBBPA and PBB. (PubChem 2022)

Charitopoulou et. al. states that there are around 75 different BFRs and PBDE, HBCD, TBBPA and PBB being the most common ones. PBDE and PBB are however not manufactured anymore due to their serious toxicity. TBBPA makes up of over 50% of the BFR volume in total. (Charitopoulou et. al. 2021) Figure 2 above shows the chemical structure of PBDE, HBCD, TBBPA and PBB. (PubChem 2022)

The problem with BFRs is that even though they can save a life due to increased fire safety when added to e.g., a product because of its high melting temperature, they can cause severe damage to the environment and the human health. As reported by Ma et. al. BFRs are bioaccumulative substances and they are known to also contaminate food chains and eventually affect the human health. (Ma et. al. 2016 p. 436)

2.2.2 Chlorinated Flame Retardants

Chlorinated flame retardants (CFRs) are not used as widely as BFRs. CFRs have emerged when restrictions around BFRs have come into existence. Examples of CFRs are tris(2-chloroethyl) phosphate (TCEP), tris(2-chloro-1-methylethyl) phosphate (TCPP) and tris[2-chloro-1-(chloromethyl)ethyl] phosphate (TDCP). Table 3 summarize the use and characteristics of these CFRs as well as their hazard classification. (ECHA 2021) Figure 3 below shows the chemical structure of TCEP, TCPP and TDCP. (PubChem 2022)

Table 3. Hazard classification and use of TCEP, TCPP and TDCP (ECHA 2021)

Name	Use of substance	Hazard classification
TCEP	- binding agents, coatings, adhesives - food storage containers, construction and building materials	- toxic to aquatic life and reproduction, suspected to be carcinogenic
TCPP	- toys, mobile phones, clothing - construction, isolation materials, adhesives, sealants, and coatings	- harmful when swallowed - precautionary measures when handling this substance
TDCP	- polymers and semiconductors - used to manufacture machinery, vehicles, and furniture	- toxic to marine life - suspected to cause cancer

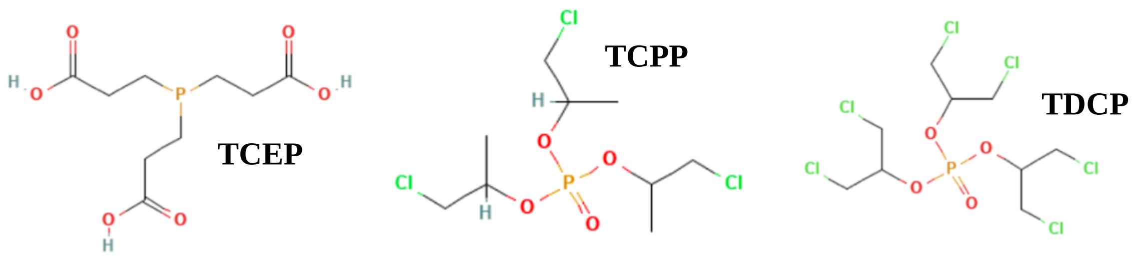

Figure 3. Chemical structure of TCEP, TCPP and TDCP. (PubChem 2022)

After the Stockholm Convention (SC) on Persistent Organic Pollutants (POPs), that is a global environmental agreement, came into existence it became necessary to find replacements for the restricted chemicals. This led to the increased use of e.g. Dechlorane Plus (DP). (Schuster et. al. 2021)

Hansen et. al. say that DP, which is a chlorinated flame retardant, has emerged as a replacement for the most common flame retardant deca-BDE that became regulated after POPs regulation. DP has been manufactured since the 1960s and is produced annually up to 6000 tonnes per year globally. It is mostly used in thermoplastics such as polyethylene and polypropylene in electronic equipment's. (Hansen et. al. 2020)

2.2.3 Phthalate esters

Electrical and electronic equipment usually contains other harmful substances beside flame retardants. Phthalate esters are a class of chemicals frequently used as additives such as plasticizers in a broad spectrum of products e.g. textiles, furniture, toys, food packaging materials and EEE. Phthalate esters are colourless and sticky liquids that can transfer from the product to the environment since they are not chemically bonded to the product they are added to. (Araki et. al. 2020, Gao et. al. 2016)

The usage of phthalate esters has played a key role in plastic manufacturing since the 1930s. The production of these chemicals grew from almost 2 million tonnes in 1975 to more than 8 million tonnes in 2011. According to Bamai et. al. phthalates can be classified as semi-volatile organic compounds and the most commonly used phthalate is the di-2-ethylhexyl phthalate (DEHP). In the European Union one-third of the phthalates produced is the DEHP. (Bamai et. al. 2014, Gao et. al. 2016)

The exposure to phthalates from diverse types of products in the environment have been proven to be hazardous for the human health. Studies have shown that exposure to these chemicals can cause insulin resistance, pregnancy loss and breast cancer. It has not been discovered until recently that the exposure to phthalates together with e.g., phosphorous flame retardants (PFRs) may be harmful and cause health issues such as asthma, inflammation, and allergies. (Araki et. al. 2020, Wang et. al. 2021)

Regulations around the use of phthalates in toys and food packages containing PVC became active in the late 1990s. The regulations did not however apply to building and interior materials which is unfortunate due to the fact that phthalates can leak out from the material they are added to over time. Not until as late as 2020, the European Commission has been able to come up with restrictions concerning the use of the phthalates DEHP, BBP, DBP and DIBP in consumer products. This amendment is a part of the REACH Regulation that will be further discussed in the text. (Bamai et. al. 2014, European Commission 2021) Figure 4 below shows the chemical structure of DEHP, BBP, DBP and DIBP. (PubChem 2022)

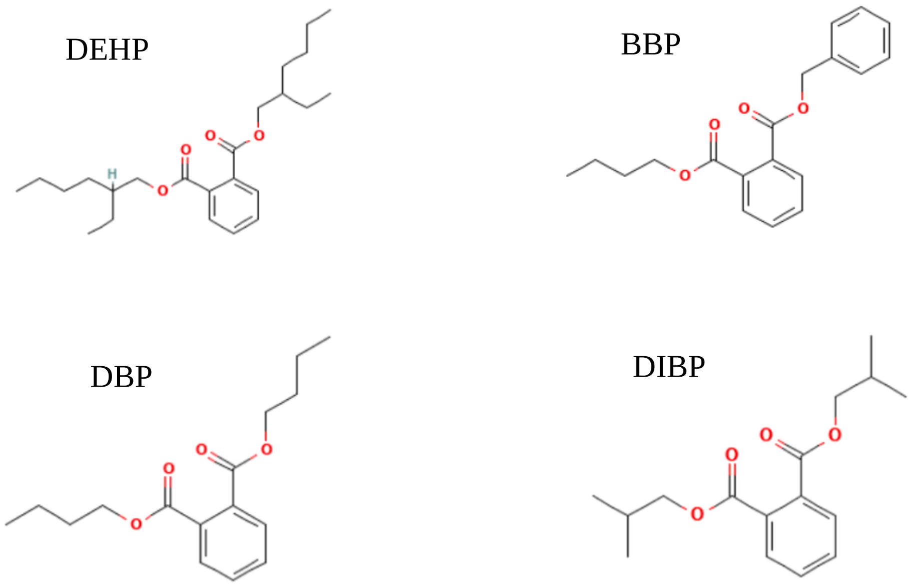

Figure 4. Chemical structure of DEHP, BBP, DBP and DIBP. (PubChem 2022)

2.3 Analyzing methods

The identification of polymers and hazardous substances in WEEE is a crucial part of the recycling process. There are several different methods and instruments to do this with. According to Kolias, analysing methods that can be used for this type of identification are for instance Fourier transform infrared spectroscopy (FTIR), near infrared spectroscopy (NIR), mid infrared pyrolysis spectroscopy (MIR), sliding spark spectroscopy (SSS), X-ray fluorescence spectroscopy (XRF), laser induced thermal impulse response (TIR), laser induced breakdown spectroscopy (LIBS) and gas chromatography – mass spectrometry (GC – MS). (Kolias 2016, p. 20-21)
Another technique that has been recently used by Sormunen et. al. in a study is Raman spectroscopy for detecting different flame retardants in polypropylene with successful results. (Sormunen et. al. 2022)

In this study FTIR is used for polymer identification most because of the availability of this instrument. Therefore, the FTIR is described in chapter 3.1 and the remaining analysing methods are described briefly within this chapter. There are many different analysing methods and here are some of them discussed due to the fact that they are all suitable for identification of flame retardants such as BFRs.

For a while it was thought that it would have been possible to use XRF as an analysing method to determine the elemental composition and the concentration of possible additives in the samples. There were discussions with another laboratory that had the XRF analyser if the samples could have been analysed with it, but it turned out to be too expensive. This set back partially limited the results in this thesis. And by the time it became clear that this is not an option it was too late to find another method that could provide the required information.

2.3.1 NIR

Near Infrared spectroscopy can be used for quantitative analysis, qualitative analysis and process control. It uses the near-infrared region of the sample's electromagnetic spectrum. NIR works in the spectral range of 700-2500 nm, it is a fast method for polymer identification, and it is non-destructive to the sample. The NIR radiations penetrates deep with many wavelengths or frequencies into the sample which means that pre-treatment for the sample is not necessary. O-H, C-H and N-H bond vibrations results specifically in NIR absorbance bands. One disadvantage with NIR is that it does not detect any black samples. It is also known that the NIR produces typically broad bands which means that the spectra can be more complex interpret compared to FTIR spectra. However, NIR can penetrate deeper into a sample than FTIR and it is not affected by fluorescence. Even if NIR is not as chemically specific compared to FTIR or Raman, it is suitable for analysing bulk material with almost no sample preparation. According to Freegard, NIR is capable to detect BFRs in a sample but with limitations. Freegard also states that NIR is a very popular method used in automated plastic sorting and that there are NIR sorting systems that can identify different additives to ppm (parts per million) levels. (Kolias 2016, p. 23, Freegard 2006, p. 61, 64, Thermo Fisher Scientific 2022)

2.3.2 MIR

Mid-infrared spectroscopy belongs to the vibrational spectroscopy techniques. MIR can through the interaction of molecules with electromagnetic radiation identify different chemicals in a sample. It operates in the mid-infrared region, that is 400-4000 cm^{-1}. Molecular vibrations caused by molecular absorbance of mid-infrared light can be classified in different functional groups. The peaks in a MIR spectrum are very specific to the measured sample. Unlike NIR, this technique can be used to measure and characterize plastics containing carbon black. The C-H, O-H, N-H and O-C molecular groups contributes with their fundamental vibrations to the MIR spectral features. The MIR instrument consists of four main parts: light source, splitter, detector and optics. The sampling technique of this analyzing method can be classified as reflection and transmission. In transmission measurement, where the sample has a detector placed behind it and is illumined by a light source, the sample should be somewhat transparent. With a thin specimen it is possible to obtain a 'straightforward' spectrum, improved signal-to-noise ratio, decreased distortion of spectra, and the specific correlation between molecule structure and spectral feature. In reflection measurement, that is suitable for thick samples, the detector and the light source are both placed on the same side to record the signal reflected. The reflection measurement spectra contain absorption, reflection, refraction, scattering and other processes. (CBRNE Tech Index 2022, Becker et. al. 2017, Türker-Kaya et. al. 2017)

2.3.3 SSS

Sliding Spark spectroscopy uses thermal vaporization and a chain of high-current sliding sparks on a small area of the sample surface. The advantages of SSS are that it is non-destructive and fast, and it is possible to identify additives in the sample with this method. The downside with SSS is that the sample that is measured must be pressed against the sensor and is therefore not suitable for automation in a sorting facility. Lowest detection limit for bromine containing flame retardants with this analysing method is 0.1%. SSS is for instance used in WEEE dismantling plants and within other fields to determine if the plastic contain halogens. This analysing method can distinguish if the sample contains BFRs or is almost free from BFR components. When combining NIR and SSS, this dual-function equipment is able to determine different polymer types and have potential to separate different polymers at WEEE dismantling and recycling facilities during the dismantling stage. Only limitation for this dual-function method are the black plastics that the NIR cannot distinguish. (Kolias 2016, p. 23, UNEP 2017)

2.3.4 LIBS

Laser Induced Breakdown spectroscopy is a simple analysing method that uses laser to ablate the sample surface in order to determine the elemental structures of the sample. The laser will form plasma on the surface that consists of atoms and ions that are electronically excited. The atoms in the plasma have characteristic wavelengths of light, and they are individual for every element. (Thermo Fischer Scientific Inc. 2022) LIBS is also suited for analyzing samples in liquid or gas form. This analyzing method is sensitive to every element and can detect flame retardants in a sample. The sample preparation for this analyzing method is minimal and it is easily adapted for automated monitoring. The LIBS technique can be used to determine alloy compositions, the manufacturer origin through monitoring trace components and for molecular analysis of an unknown substance. According to Noll et. al., LIBS can be used for inline automated process' of inverse production lines of end-of-life products. (Freegard et. al. 2006, p. 62, 64)

2.3.5 GC - MS

Gas Chromatography – Mass Spectrometry is an analysing method that can separate, identify and quantify mixtures of chemicals. It is suitable for analysing solid, gas and liquid samples. A sample that is analysed using GC-MS has to be thermally stable and adequately volatile. Additionally, the sample may require to be chemically modified before analysis in order to extinguish any absorption effects which could influence the quality of the data. Some samples may have to undergo some type of wet chemical treatment before proceeding to GC-MS analysis. First the sample is vaporized into the gas phase and the different components are separated. Each compound will then elute from the column at varying times based on the boiling point and the polarity. There are two existing methods for ion production which are electron ionisation and chemical ionisation, and electron ionisation being the most common one. Then the mass spectrometer fragments the ionized components, and the ions are separated depending on their mass-to-charge ratio. The last step is ion detection and analysis. (Thermo Fischer Scientific Inc. 2022)

2.3.6 Raman spectroscopy

Raman spectroscopy can be used for identifying different chemicals and the amount of them that are present in a sample. A Raman spectrum can provide both qualitative and quantitative information. Raman spectroscopy, which belongs to vibrational spectroscopy, is focused on inelastic scattering of photons. This is called Raman scattering and it is typically a weak phenomenon. However, it has a good spatial resolution combined with a wide spectral range. This analysing method captures the difference in the molecular vibrations and produces a fingerprint specific to each chemical. In a Raman spectrum the nonpolar bonds show especially intensive bands, and they are C=C, N=N, O-O, S-S and P-P. Raman is suitable for analysing solids, liquids or powders and it is non-destructive to the sample. The disadvantages with this analysing method are the interference emerging from fluorescence, the weak signal strength and the high laser power resulting in possible heating of samples of colour. But this can be minimised through choosing the laser wavelength that is in the NIR range. One limitation with Raman spectroscopy is that it is not common to have a complete, comprehensive spectral library. Additionally, the commercial libraries that are available focuses on virgin plastics which could have an impact on the results. (Sormunen et. al. 2022, Zeiss 2022, Oxford Instruments 2022, Nava et. al. 2021)

2.4 The recycling of WEEE

Recycling is an especially important part of sustainable thinking and therefore much effort is put to issues concerning recycling of various materials and products. Waste management systems find waste of electrical and electronic equipment to be an extensive issue in most parts of the world. This is due to the fact that the harmful substances that are often added to electrical and electronic equipment need intricate and high-quality treatments in order to progress in the recycling process. Additionally, this part of the recycling process is yet more critical for the plastic segment of the e-waste. For instance acrylonitrile butadiene styrene (ABS), high impact polystyrene (HIPS), polycarbonate and ABS blends (PC+ABS) are thermoplastic polymers that are associated with technical difficulties related to the recovery of resources. These polymers cannot be resourcefully treated by mechanical recycling because they usually contain heavy metals and flame retardants such as BFRs. (Ardolino et. al. 2021)

The European Commission has established a financial instrument called the Horizon 2020. This programme strives to support and fund research and innovation within science and societal challenges. All EU member states are accessed to apply for funding from the Horizon 2020 programme. NONTOX Project 2020, REMADYL Project 2021 and CREAToR 2021 are projects that are financed by the Horizon 2020 programme. Their main focus is around the challenging waste plastics and to develop and improve the recycling of it. (Ardolino et. al. 2021)

Recycling of plastics has become even more important due to the fact that plastic has become an unavoidable material in electrical and electronic equipment's and furthermore both the collecting targets and quality aspects have increased. The NONTOX projects focus is on the recovery of plastics from for instance WEEE including harmful substances such as flame retardants. Another goal is to spread knowledge in pre-treatment and collecting of plastic waste from its hazardous stuff. A new method called CreaSolv has been introduced by Fraunhofer IVV research team together with CreaCycle GmbH and the master idea is that you by this method can treat mixed plastic waste and as the final product gain high-quality reusable plastic material. The process consists of reusable solvent treatment and the final product is sustainable in the sense that the recycled plastic is of high purity standard. Figure 2 visualizes the CreaSolv process. (NONTOX Project 2021)

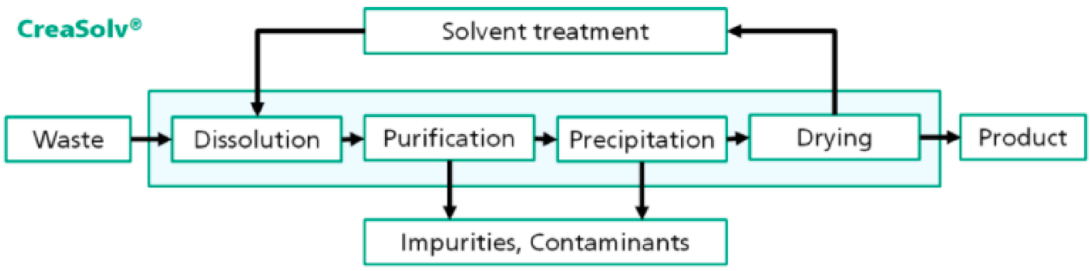

Figure 5. CreaSolv waste treatment process (NONTOX Project 2021)

The legacy substances are a big challenge for improving the collection of plastic material in order to by recycling find its way back into the circular economy. The REMADYL project has the ambition to recycle hazardous additives such as phthalates from PVC and DEHP being the most common one. One obstacle has been the economic issues which are targeted by the REMADYL project. The rejuvenating process is based on modern technology that combines extractive extrusion and new solvents and melt filtration. Behind the project are several actors in the polymer industry in Europe. (REMADYL Project 2021)

The third EU funded project mentioned is the CREAToR project which is based on both cost-benefit, recycling, and removal of harmful substances in WEEE. The CREAToR project is a consortium from seven European countries and six large enterprises. Their focus is on recycling secondary raw materials and in that sense fits well into the concept of circular economy. After collection, the waste is treated by using LIBS technology (laser-induced breakdown spectroscopy) that sorts the polymers. BFRs are removed from the polymers by extractive extrusion using supercritical CO_2 and NADES (natural deep eutectic solvents) ionic liquids. The goal is that the purification process has lowered the hazardous BFR content to 0,1 wt %. (CREAToR Project 2021)

Due to the fact that WEEE can contain different kinds of hazardous metals, such as lead and mercury there are of course a risk for those who manages the recycling. If the WEEE materials are crushed or graded there can be high amounts of dust in the air and if a person comes into dermal contact with hazardous metals, it can of course lead to exposure. Attention have been paid towards workers safety and many steps in the recycling process has been automated. There are also safety regulations for the working spaces for instance concerning ventilation. Although flame retardants are to be found in WEEE and processing workers are exposed to these additives, there have not been found any reliable evidence that the amount of these substances causes health issues for the workers. (Searl & Crawford 2012)

2.4.1 Recycling methods

WEEE plastics can be recovered in two ways, either by material recovery or energy recovery. Material recovery is done through mechanical recycling or chemical recycling, also called feedstock recycling. Energy recovery can be done by thermal recycling which can include e.g. gasification and combustion. (Ma et. al. 2016 p. 436)

Mechanical recycling is a type of primary and secondary recycling that reprocess' the plastic waste into secondary raw materials that are further used in the production of new products. The pre-treatment process for mechanical recycling of

WEEE is inevitable and it consists of a number of separate phases. Maisel et. al. defines these steps to be collection, pre-sorting, manual dismantling, pre-shredding, manual sorting, metal separation, shredding, metal separation and shredding once more, sorting and end-processing (Maisel et. al. 2020 p. 3). Additionally, it is important to identify and subtract any harmful substances such as flame retardants from the plastic polymer before mechanical recycling. This type of recycling is suitable for homogenous plastics only, heterogenous plastics must be separated for this recycling method. (Delva et. al. 2018 p. 199, Ma et. al. 2016 p. 435)

In chemical recycling the plastic polymer is transformed back into its individual monomers resulting in a lower molecular weight. This can be done in numerous ways, for example pyrolysis which is a common technique used in this type of recycling. Chemical recycling uses different solvents and reagents to create chemical reactions, and through that convert the plastic waste into fuels and chemical feedstock that can be used to produce new products. Chemical recycling is considered to have big advantages both from an economical and environmental perspective. This recycling method is usually divided into two main techniques that are called solvolysis and thermolysis. Solvolysis uses different solvents, either with or without initiators and catalysts, to dissolve the plastic polymer. Thermolysis, that can consist of processes' such as pyrolysis, gasification, and hydrogenation, treats the polymer with heat together in an inert atmosphere. (Charitopoulou et. al. 2020 p.8, Ma et.al. 2016, p. 435)

According to Ma et. al., energy recovery is a form of recycling where the plastic waste is used as alternative fuel for energy production (Ma et. al. 2016, p. 435). This can be done through incineration in a boiler or in some other industrial equipment (Charitopoulou et. al. 2020). There are howerver some disadvantages if it is done incorrectly and that includes hazardous substances leaking in to the environment and damaging it (Ma et. al. 2016, p. 435).

2.4.2 Sorting technologies

The purpose of the different technologies that sort plastic waste, is to make sure a subsequent high-quality recycling is laid up, where there is only a single polymer output and at the same time reduces the amount of non-target plastic polymers. The sorting process has the aim to remove all non-plastic impurities and all plastic polymers that contains harmful substances such as flame retardants. The sorting can be done in an automated or a manual way. (Maisel et. al. 2020)

The manual sorting process is done through separating the plastic waste by hand into separate bins or suitable conveyor belts. This type of sorting technology is usually used in countries where the labor costs are on the lower side and the mass flow is small. In the automated sorting process the plastic parts are separated based on their physical properties at plastic recycling facilities. The most common automated sorting technologies are sensor-based sorting, magnetic sorting, electrostatic sorting, density sorting and flotation. Density based sorting includes technologies such as different sink/float methods, wet and dry jig separation, hydro cyclone, and centrifugal sorting. Sensor-based sorting separates the plastic particles with detection technologies such as X-ray fluorescence (XRF), near-infrared spectroscopy (NIR), mid-infrared spectroscopy (MIR), Fourier transfer infrared spectroscopy (FTIR), mid-infrared thermography (MIR-T), laser-induced breakdown spectroscopy (LIBS) and terahertz spectroscopy (THz). Ferrous metals (e.g. steel, cast, iron, and titanium) are separated with a magnetic separator and non-ferrous metals are sorted with an eddy current separator (ECS). (Maisel et. al. 2020)

2.5 Legislation and environmental demands

One challenge when talking about WEEE legislation is the gap between ecological and economic costs. In the EU rules on treating WEEE, it is said that all the electrical and electronic gadgets contain a wide range of materials of which some are hazardous. If measurements in safe collecting is not taken the results will be environmental pollution and health problems. Recycling is also important because many electronic equipment contains rare and vulnerable resources. (European commission 2021)

The EU has collected information from member states in 2018 about the amount of WEEE per year per inhabitant and found out that the average amount was 8,9 kg per inhabitant. Figure 6 represents the amount of WEEE per inhabitant in kilograms in each European country during 2018. (Eurostat 2021)

Figure 6. Waste electrical and electronic equipment collected in 2018 (Eurostat 2021)

WEEE Forum was founded in 2002 by six European countries and has since grown to a non-profit-seeking multinational centre of competence in know-how concerning the use, disposal, logistics and reuse of electronic waste. This organisation arranges happenings, webinars, and information banks in order to share information and knowledge in the matter. Though founded in Europe this organisation has the goal to cover all the continents in a common struggle against pollution throughout WEEE. (WEEE Forum 2021)

2.5.1 WEEE Directive

An important way to handle environmental issues concerning WEEE is through legislative measures. There are different channels through which it is possible to monitor the problems concerning recycling, waste disposal and reuse. The European Union has as a target to involve every member country in the fight against inappropriate handling of WEEE for instance through the WEEE Directive. The WEEE Directive became effective in 2003 but it was revised in 2012. The remade Directive took effect in August 2012 with a transitional period of six years, until August 2018. In the Directive (2012/19/EU) in recital 6, it is said the “key purpose is to contribute to sustainable production and consumption by, as a first priority, the prevention of WEEE and, in addition, by the reuse, recycling and other forms of recovery of such wastes.” (EUR-Lex 2012)

The development of common standards is crucial for the unity approach and therefore the European Commission has created CENELEC (Comité Européenne de Normalisation Électrotechnique) standards for collection, transport, and treatment of e-waste. The CENELEC standards are a part of the implementation of the WEEE directive. The directive includes the following electrical and electronic equipment: lightning equipment, video display, photovoltaic panels, temperature exchange equipment, household appliances, electrical toys, IT, and telecommunication equipment. (European Commission 2021, EUR-Lex 2012)

2.5.2 RoHS Directive

Since 2003 EU has specific rules concerning Restrictions of Hazardous Substances in electrical and electronic equipment (RoHS). The amount of WEEE has grown almost potentially since 2003 and the aim to limit the use of substances that can cause both environmental and health related issues is important. In WEEE is to be found for instance lead, mercury, and cadmium, which are a major concern for the health of species. (European Commission 2021)

Though the RoHS directive includes all European member countries at the same time, there are exemption procedure that delays the implementation of the rules to full extent. Things that have an impact on the restriction of use of RoHS are for instance:

- suitable substitution for a substance
- socioeconomical issues concerning the substitute
- potential health, environment, and consumer safety issues of the substitute

It is said that every cloud has its silver lining and concerning RoHS there are many to be found, for instance:

- a cleaner and healthier environment
- avoid depletion of scarce resources
- creation of new jobs and professions such as designers, chemists, engineers and so forth

Every regulation must be followed up and evaluated and so will also RoHS eventually. A big question is finding sustainable substitutes that fulfil all the environmental and health related concerns. Then there is also the big question about money; how to compensate for possible costs when the substances used today are transitioned into new chemicals. (European Commission 2021)

2.5.3 REACH Regulation

Then there is also the EU regulation called REACH (EC 1907/2006) which came into force in June 2007. REACH is the abbreviation of Registration, Evaluation, Authorisation, and restriction of Chemicals. The purpose of this regulation is to minimise the health risks of chemicals but at the same time provide the business opportunity for chemical industry. The REACH regulation covers all chemical substances and the majority of companies within different sectors in the EU and is influenced by this regulation. The REACH regulation works as a tool for the European Chemicals Agency (ECHA) to collect data about different chemicals and substances that are produced, imported, or sold in the EU. To register a substance it is required to submit a report to ECHA where the risks are identified and a description of how they will be managed.

3 MATERIALS AND METHODS

The analyzing method used to identify and confirm the polymer samples is the Thermo Scientific Nicolet iS5 FTIR spectrometer equipped with an iD7 ATR accessory at Arcada University of Applied Science chemistry laboratory.

The only sample preparation needed for the analyze is to clean the surface with Isopropyl alcohol and laboratory tissues. All the samples were in an appropriate size and form and did not need any reshaping. After the surface is cleaned the sample is put directly on to the ATR crystal on the FTIR and a spectrum is obtained. The OMNIC software is used for data analysis.

Figure 7. The plastic samples used in the experiment.

The samples analyzed in this study originate from a Kuusakoski recycling plant. The only information available of the samples is that they were sorted to the category with low bromine content and are presumably suited for material recycling. The FTIR analysis is done to validate that the material is what it is claimed to be and detect possible additives.

In the beginning it was thought that the benchmarking of the analytical method would be done through using WEEE samples that would contain known amounts of BFRs, CFRs and phthalates. This was done by scanning old EEE products in hope of that some of these products would contain BFRs, CFRs and phthalates. However, this did not work out. Then I considered to acquire own FTIR spectra of BFRs, CFRs and phthalates by measuring reference compounds. This would have been done with getting the chemicals that were investigated through a chemical supplier. I called a few companies located in Finland if they would have some of the required chemicals in order to get reference spectrums. There were some companies that I never got in touch with and those who I spoke with, Telko and Avient for example, but they could not help me with this. When it became clear that this is not an option either, I thought about using XRF as an elemental analyzing method. As previously stated, this was not possible either. All of the above took several months to figure out and by the time it became clear that the last alternative is not an option either I just had to scan the samples with the FTIR and try to determine if the samples contain any of these substances through investigating their spectrums without any reference spectrums.

3.1 FTIR spectroscopy

Fourier transform infrared (FTIR) spectroscopy uses infrared radiation to collect spectral data. The FTIR spectrometer measures the amount of light that is absorbed in a sample at each wavelength at the same time and reports the intensity of each frequency. Figure 8 shows the basic components of the FTIR spectrometer, which are the source, interferometer, sample, detector, and computer. The FTIR spectrometer applies a beam of infrared radiation to the sample material followed by a beam splitter that parts the beam on to two mirrors, a fixed and a moving one. The beams are then reflected back from the two mirrors to the beam splitter where they recombine and go to a detector. This produces an interferogram which refers to the signal that is created as a function based pathlength changes between the two beams. The distance and frequency have the capacity of being exchanges equivalently by the Fourier transformation. (Thermo Fischer Scientific Inc. 2021, Kolias 2016)

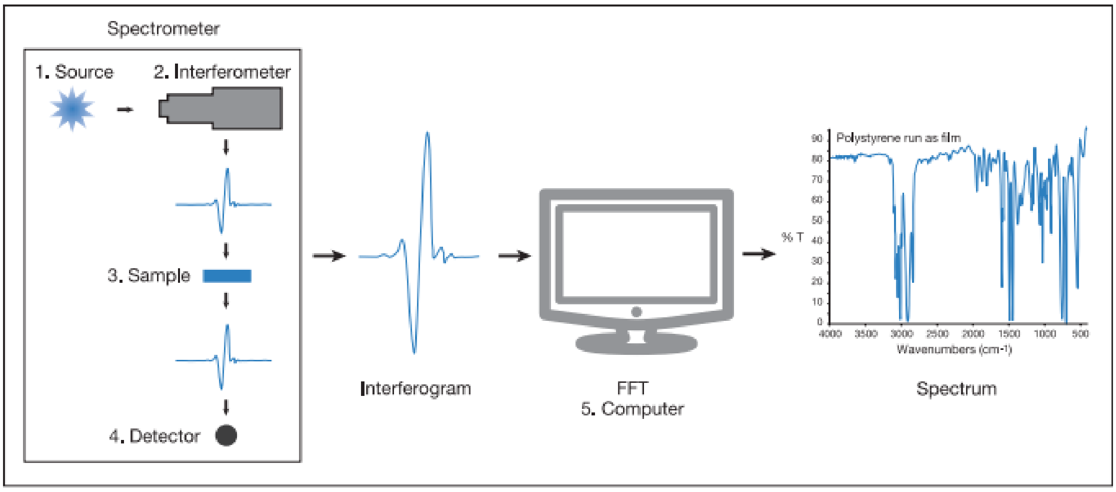

Figure 8. Visualization of the FTIR analysis (Thermo Fischer Scientific Inc. 2021)

The term 'Fourier transform' refers to the mathematical function that changes the function of time to a function of frequency. The generic form of the Fourier transform equation is $F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt$, in which t stands for the time and i is the square root of -1. (Anon 2020)

FTIR spectroscopy can be used to measure different solids, liquids, and gases. The main advantages with FTIR spectroscopy are that it is a reliable method for analyzing and non-destructive on the material. It measures all the frequencies at once rapidly and has an improved sensitivity due to its detectors. The major disadvantage with this instrument is that the result is easily impacted by any surface impurities and the sample that is being measured should be as flat as possible. (Kolias 2016)

Attenuated Total Reflectance (ATR) is a technique used together with the FTIR to analyze solid and liquid samples. When the internally reflected infrared beam encounters the sample, changes can occur. The ATR accessory measures these changes. The infrared beam reflects on an optically dense crystal that has a high refractive index at a specific angle. The evanescent wave that is created through the internal reflection extends beyond the crystals surface into the sample that is in contact with the crystal. The evanescent wave will lose energy where the sample absorbs energy in the specific regions of the infrared spectrum. The spectrometer will then measure the radiation and then plot it as a function of wavelength. This delivers information about the characteristic absorption spectrum of the sample. (Thermo Fischer Scientific, 2021)

For a successful analysis with the FTIR and the ATR accessory there are two requirements to fulfill. First, the sample must be directly in contact with the ATR crystal. Secondly, the crystal that is used must have a significantly higher refractive index than the sample or else the light would be transmitted instead of reflected in the crystal. Crystals that are suitable for the ATR technique is e.g. Zinc Selenide and Germanium. (Kolias 2016)

According to Thermo Fischer Scientific the ATR is best suited for analyzing thick or strongly absorbing samples and homogeneous solid samples. Other solid samples that are ideal to analyze with the ATR are laminates, paints, plastics, rubbers, coatings, natural powders, and solids that can be ground into powder. Liquid samples that ATR can analyze are free-flowing aqueous solutions, viscous liquids, coatings and biological materials. (Thermo Fischer Scientific 2021)

4 RESULTS

The results obtained from the FTIR spectrometer are described in table 4. The table shows the sample, the polymer and the match (%) with the software library to the respective polymer sample. It can be noted that the majority of the samples have a match of around 90% or above which is proclaimed to be an adequate match considering polymer identification. The slightly lower match percentages of PC/ABS samples are presumably since they are blends and/or a lack of reference spectrums in the software library. It could also indicate that the surface on this sample is scratched and in poor condition on a microscopic level and impacts the analysis through this.

Table 4. Table over the FTIR spectroscopy results of each sample from each polymer group and the library match for the respective sample.

Sample	Polymer	Library match (%)
1.1	ABS	93,92%
1.2	ABS	94,66%
1.3	ABS	85,42%
2.1	PS	93,74%
2.2	PS	96,57%
2.3	PS	91,61%
3.1	PC/ABS	84,76%
3.2	PC/ABS	83,53%
3.3	PC/ABS	85,79%
4.1	PP	95,91%
4.2	PP	85,07%
4.3	PP	95,79%

4.1 FTIR spectrums

The following figures shows the FTIR absorbance spectrums of one sample from each polymer group. For the interpretation of these spectrums the publication ‘Plastic Testing and Characterization’ by Naranjo et. al. is used. In all the figures below the x-axis represents the wavenumber of absorbance and the y-axis represents the frequency of the transmitted light from the sample.

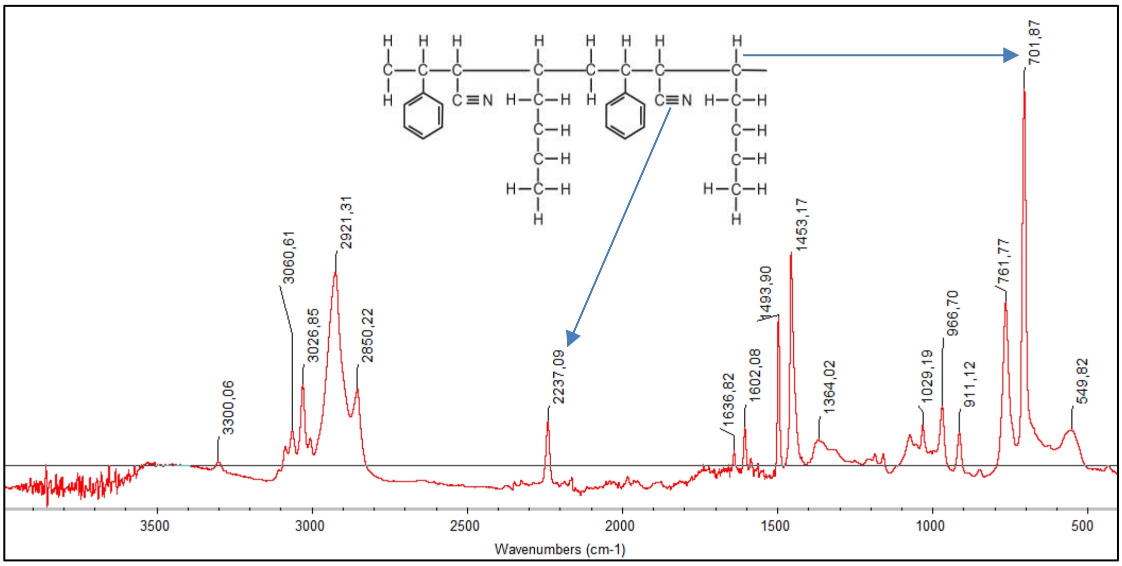

Figure 9. FTIR spectrum and molecular structure of ABS, sample 1.1.

According to Naranjo et. al. the characteristic absorption peaks for ABS are around 2260, 970, 760 and 700 (cm^{-1}) (Naranjo 2008). In figure 9, the peak at 2237,09 cm^{-1} indicates the triple C≡N bond and the peak at 701,87 cm^{-1} indicates a single C-H bond, even though it is in the region that is a bit problematic to interpret. With a match of 93,93% to the software library and the presence of all four characteristic absorption peaks it can be stated that the polymer is ABS.

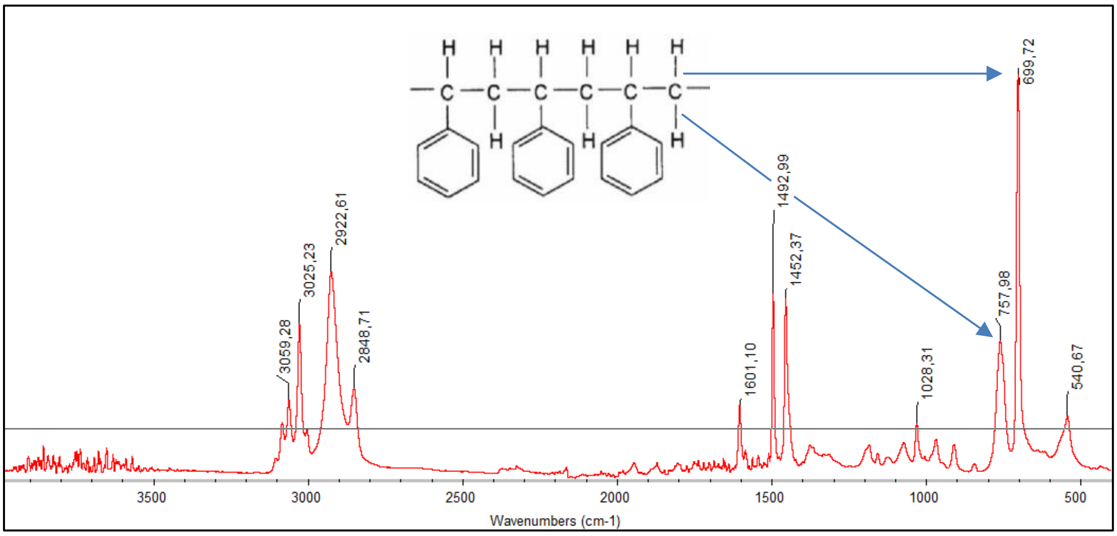

Figure 10. FTIR spectrum and molecular structure of PS, sample 2.2.

The characteristic peaks for PS are at 760 and 700 (cm^{-1}) (Naranjo 2008). Figure 10 shows the vibration in PS sample 2.2 at both 757,98 cm^{-1} and 699,72 cm^{-1}, which represents these characteristic peaks. Both peaks are single C-H bonds. This sample has a match of 96,03% to the software library and it can be determined that the sample is PS.

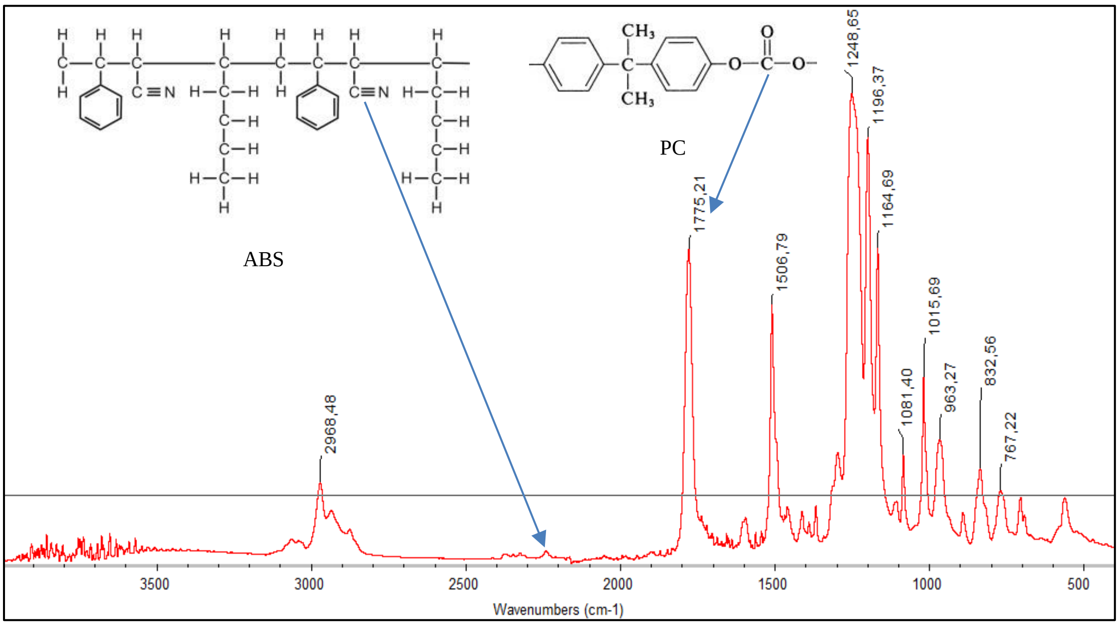

Figure 11. FTIR spectrum and molecular structure of PC/ABS blend, sample 3.1.

Figure 11 visualizes the FTIR spectrum of the PC/ABS sample 3.1. The characteristic absorbance peaks for PC are 1775, 1235 and 830 (cm^{-1}) and for ABS they are 2260, 970, 760 and 700 (cm^{-1}) as previously stated (Naranjo 2008). The presence of both PC and ABS can be seen when compared to the characteristic absorbance peaks of these polymers. The peaks that prove this are e.g. the little peak around 2260 cm^{-1} that indicates the triple C≡N bond from the ABS and the peak at 1775,21 cm^{-1} that implies the double C=O bond from the PC. This sample has a match of 92,10% to the software library which also confirms that the sample is a PC/ABS blend.

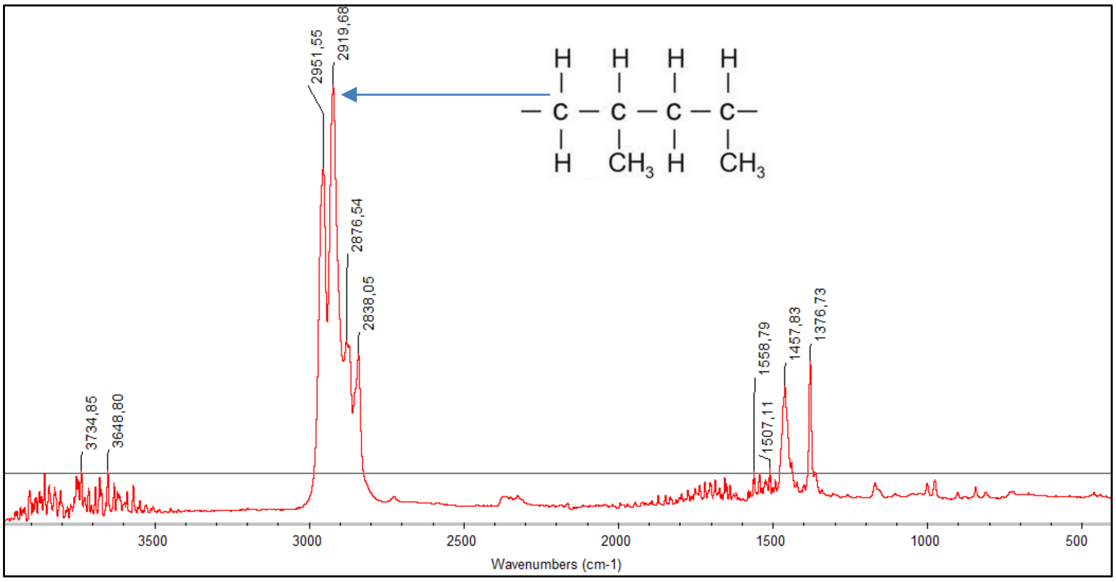

Figure 12. FTIR spectrum and molecular structure of PP, sample 4.1.

Naranjo et. al. state that the characteristic absorbance peaks for PP are 2950, 2920, 1470, 1380, 1160 and 970 (cm^{-1}) (Naranjo 2008). All these characteristic absorbance peaks can be seen in figure 12 for PP sample 4.1. For example, the peak at 2919,68 cm^{-1} refers to a single C-H bond. This sample has a match of 95,91% to the software library.

4.1.1 Subtraction from spectrums

One sample spectrum from each polymer group is individually subtracted from its highest library match spectrum. The subtraction is done to detect any deviating peaks that could indicate that the sample contains e.g., additives of some sort. In the following four figures, one sample from each polymer group is subtracted and analyzed. The purple spectrum represents the sample, the green spectrum represents the highest match from the software library to the respective sample and the red spectrum represents the two spectrums subtracted.

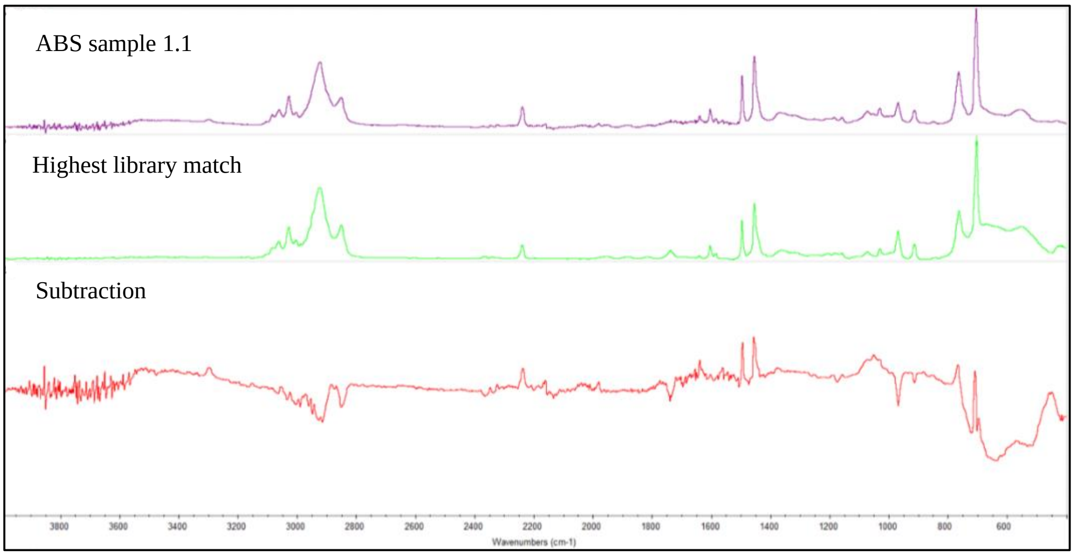

Figure 13. ABS sample 1.1 subtracted from its highest match from the software library.

In the ABS sample 1.1 in figure 13, there is a deviating peak at 3300 cm^{-1} that is not present in the highest library match spectrum. In the region between 1500-2200 cm^{-1} there are some small abnormalities which could be explained like noise, but it can also point in other direction.

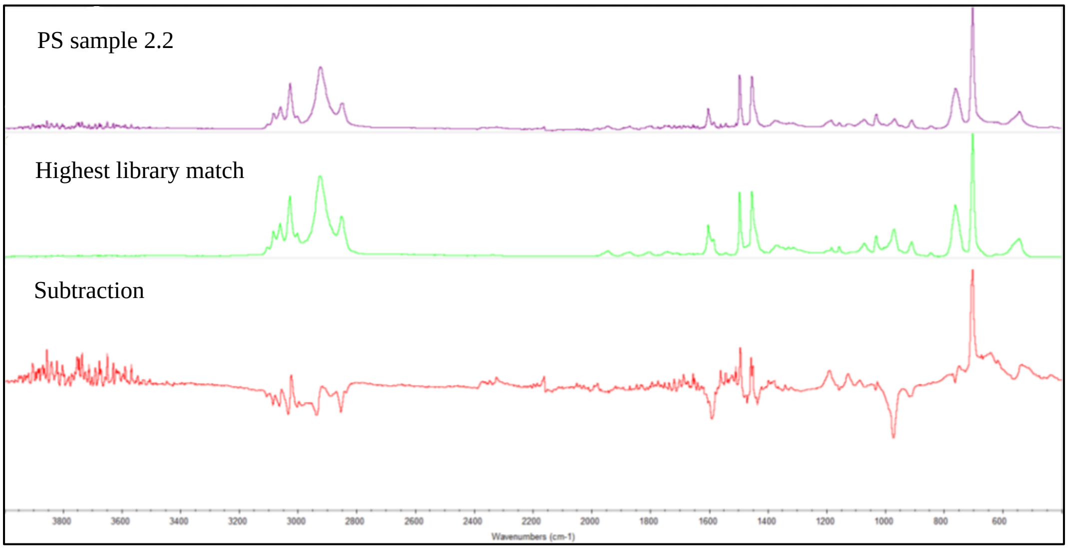

Figure 14. PS sample 2.2 subtracted from its highest match from the software library.

In the PS sample 2.2 in figure 14, there are deviating peaks at 2150 cm^{-1}, 1550 cm^{-1} and 1100 cm^{-1}. Some deviation can be noted in the region between 1650-2100 cm^{-1} which could indicate an additive of some sort or noise.

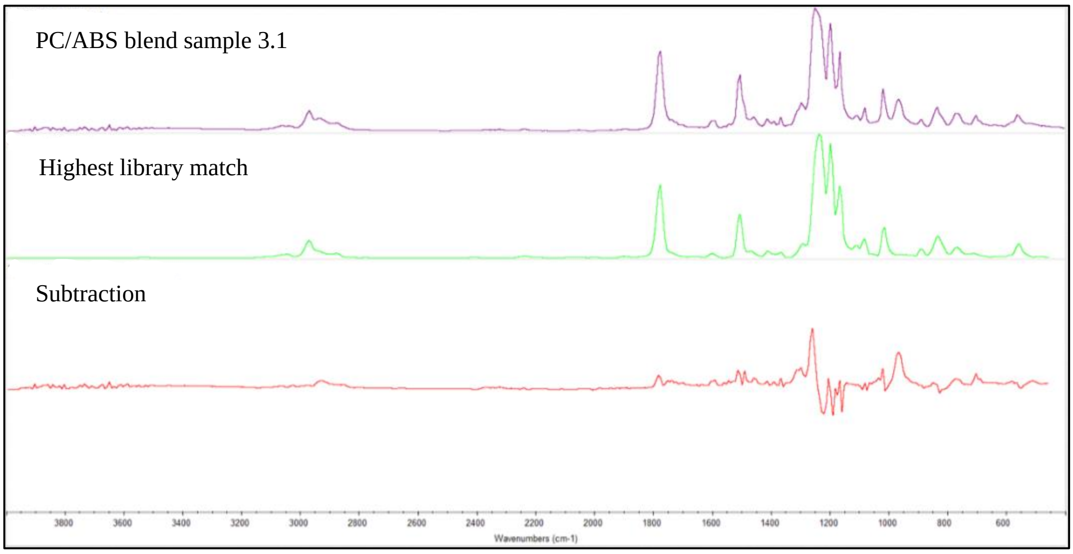

Figure 15. PC/ABS blend sample 3.1 subtracted from its highest match from the software library.

In the PC/ABS blend sample 3.1 in figure 15, there are deviating peaks at around 2900 cm^{-1}, 1400 cm^{-1}, 900 cm^{-1} and 700 cm^{-1} which again could indicate that the sample can contain an additive of some sort.

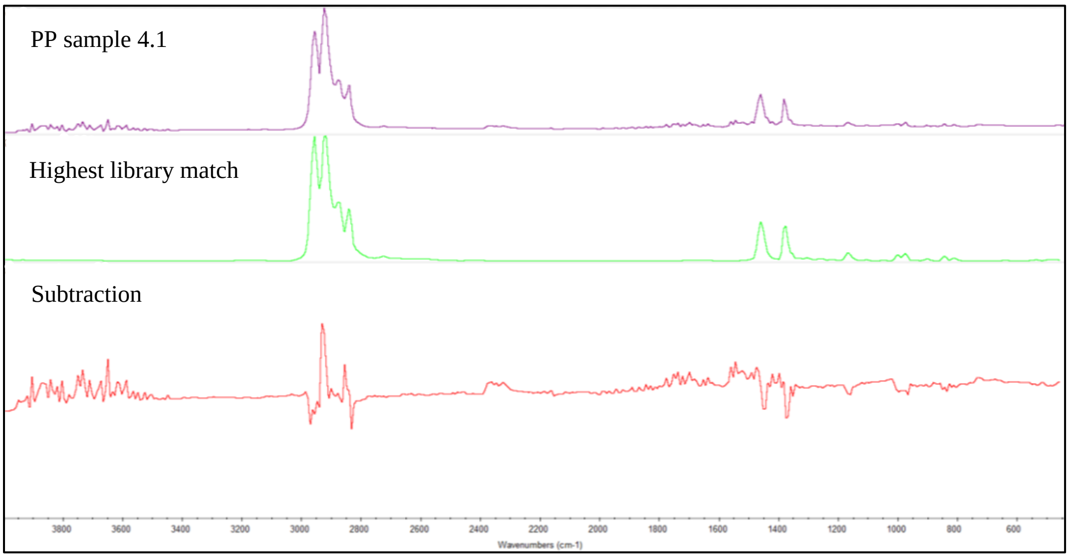

Figure 16. PP sample 4.1 subtracted from its highest match from the software library.

In the PP sample 4.1 in figure 16, some divergence can be noted in the region between 2100-2400 cm^{-1}. This could be due to noise caused by poor surface condition of the sample.

It can be stated that all the four samples above have deviating peaks. However, it is unclear if these peaks indicates that the samples (1) actually do contain any of the substances investigated and if so, how much, (2) if the deviating peaks are just noise or (3) if these peaks do not mean anything due to that the highest library match often refers to a pure sample, meaning that it have never been processed before and it is in its purest form, and when comparing the highest library match spectrum to the sample spectrum it does not really mean anything.

5 DISCUSSION

One of the objectives for this thesis was to establish that the samples consist of given materials. According to the FTIR analysis all the samples were as claimed to be. The subtraction of the spectrums shows that each sample that was subtracted had differing peaks. The FTIR spectroscopy is a well-suited analysing method for polymer identification as it is a fast and non-destructive method. However, the deviant peaks that were found with the subtraction is yet to be determined if they are some sort of flame retardant or some other harmful substance. This is partly due to the fact that the FTIR software spectrum library, that was accessible in this study, was not sufficient enough. Another issue with analysing an unknown additive in a sample with the FTIR spectrometer is that the quantity of the additive is unidentified. The FTIR spectrometer is known for not being capable to detect tiny amounts of an additive in a sample and therefore the samples in this study could also contain substances that are not visible in their spectrums. Additionally, these samples were categorised to contain low amounts of bromine which could also indicate that there were not any major deviating peaks when subtracting the spectrums.

The findings in this thesis are a small part of a bigger concept in order to find economically profitable solutions that also preserves scarce resources. Additional ambitions are to compensate existing hazardous substances in WEEE and to promote circular economy. Further studies in this field could be of interest for different actors such as for producers and/or consumers, for the industrial sector and to support legislative aspirations.

The lack of resources has limited the achievements of this thesis. These deliverables are a part of an extensive process. As individual research object the next step would be to investigate these samples further with some sort of elemental analysis such as XRF or SEM-EDS analysis. But when considering this in a broader perspective this would be included in a multi professional interdisciplinary research study.

6 CONCLUSION

The aim of this thesis was to (1) Investigate the existence of harmful substances in WEEE, (2) Determine different analysing methods to detect harmful substances in polymers and the recycling of WEEE, (3) Find out the legislative boundaries considering WEEE in Europe and (4) Use FTIR spectroscopy for polymer identification and to establish the existence of possible harmful substances in the samples.

As a conclusion, it can be stated that harmful substances are added in EEE in order to improve different characteristics of the polymer matrices. BFRs, CFRs and phthalates are all common additives and as such harmful substances for the environment and human health if not recycled and disposed properly.

The first step in the recycling process is polymer identification and the detection of additives. This can be done by e.g. FTIR, XRF, LIBS and Raman spectroscopy. The recycling of WEEE is an intricate process due to the additives that it often contains and the removal of them. The plastics in WEEE can be recovered by material or energy recovery. Depending on the aim of the recovery, different recycling methods are used such as mechanical, chemical or thermal recycling. Although flame retardants are to be found in WEEE and processing workers are exposed to these additives, there have not been found any reliable evidence that the amount of these substances causes health issues for the workers. The issue arises when these products are not disposed correctly.

There are a lot of legislative points of views that must be taken into consideration when dealing with WEEE. The WEEE Directive, RoHS Directive and REACH Regulation all have the aim to make the production, consumption and recycling of EEE as safe as possible.

FTIR spectroscopy was used to identify the samples obtained from a Kuusakoski recycling plant. The results showed that all the samples were the supposed polymer. However, the subtraction of the spectrums showed deviating peaks in all the analysed samples. It is still unclear if these peaks are caused by some harmful substances, such as

BFRs. This is due to the limitation of the analysing method used. To clarify the peaks, the research should have been completed with elemental analysis of some sort.

Finally, we all share the same planet and therefore we also share the problems and the responsibilities. Both the consumer and the producer must be involved if we are going towards sustainability and recycling. On a global scale this must be a joint venture concerning politicians, enterprises, social networks and individuals. Although EU has approached these problems through legislation, that cannot be said for all the other countries in the world. Poverty, lack of experience and know-how, social issues, human rights and so forth are all questions risen when talking about higher immaterial values connected to our further existence on this planet.

7 SWEDISH EXTENDED ABSTRACT

Det här examensarbete är en del av ’ALL-IN for Plastic Recycling’ (PLASTin) projektet vars syfte är att utveckla återvinningen av utmanande plastströmmar som exempelvis plast från e-avfall. Återvinningen av plast är en omfattande process. Utmaningarna med att återvinna avfall från elektiska och elektroniska produkter är identifieringen och avlägsnandet av skadliga ämnen som dessa produkter ofta innehåller. Plasten i e-avfall måste vara fri från alla skadliga ämnen för att komma vidare i återvinningsprocessen.

Målet med det här examensarbete är att (1) Undersöka förekomsten av skadliga ämnen i e-avfall, (2) Redogöra för olika analysmetoder för att upptäcka skadliga ämnen i polymerer och återvinningen av e-avfall, (3) Ta reda på lagstiftningen gällande e-avfall i Europa och (4) Använda FTIR-spektroskopi för polymeridentifiering och för att fastställa förekomsten av möjliga skadliga ämnen i samplen.

Mängden elektriskt och elektroniskt avfall som produceras varje år runt om i världen ökar snabbt. Dessa produkter består till exempel av hushållsapparater, medicinsk utrustning, övervakningsinstrument och IT-prylar och är vanligtvis en blandning av en mängd olika material och ämnen, varav vissa är skadliga och förorsakar miljö- och hälsoproblem om de inte återvinns på rätt sätt. Att identifiera olika typer av skadliga ämnen i dessa polymerer är viktigt då man försöker öka kunskapen gällande återvinningsprocessen.

Bromerade flamskyddsmedel, klorerade flamskyddsmedel och ftalater är kemikalier som förknippas med faror för miljön och människans hälsa. Identifieringen av skadliga ämnen som dessa, är en viktig del av återvinningsprocessen och det finns flera olika metoder och instrument att göra det här med. FTIR, NIR, MIR, SSS, XRF, LIBS, GC-MS och Raman-spektroskopi är alla lämpliga analysmetoder för att identifiera kemikalier såsom bromerade flamskyddsmedel.

Plast från e-avfall kan återvinnas på två olika sätt, antingen genom materialåtervinning eller energiåtervinning. Materialåtervinning sker genom mekanisk återvinning eller kemisk återvinning (råmaterialåtervinning). Energiåtervinning kan ske genom termisk återvinning som kan omfatta exempelvis förgasning eller förbränning. Sorteringen av e-avfall kan göras på ett automatiserat eller manuellt sätt. Sorteringsprocessens syfte är att avlägsna alla icke-plastiska föroreningar och polymerer som innehåller skadliga ämnen.

En utmaning då man talar om lagstiftningen kring e-avfall är klyftan mellan ekologiska och ekonomiska kostnader. WEEE-direktivet, RoHS-direktivet och REACH-förordningen är lagstiftningsverktyg för produktion, hantering och återvinning av elektroniska produkter. Varje regelverk måste följas upp och utvärderas. En stor fråga är att hitta hållbara substitut som uppfyller alla miljö- och hälsorelaterade problem. Dessutom är det också den stora frågan om pengar; hur kan man kompensera för eventuella kostnader när de ämnen som används idag byts ut mot nya kemikalier.

I den empiriska delen analyserades e-avfall sampel som sändes från Tammerfors universitet och som härstammar från en Kuusakoski-återvinningsanläggning. FTIR-spektroskopi användes för att identifiera och bekräfta att polymersamplen var det material som de påstods att vara och enligt FTIR-analysen var alla samplen det. Subtraktionen av spektrumen visar dock att varje sampel som subtraherades hade avvikande toppar. Det är ännu osäkert ifall dessa avvikande toppar beror på någon form av flamskyddsmedel eller något annat skadligt ämne. Det här beror delvis på att FTIR-programvaruspektrumbiblioteket som var tillgängligt i denna studie inte var tillräcklig. Ett annat problem med att analysera en okänd tillsats i ett sampel med FTIR-spektrometern är att mängden av tillsatsen är oidentifierad. FTIR-spektrometern är känd för att inte kunna upptäcka små mängder av en tillsats i ett sampel. Därför kan samplen i denna studie även innehålla ämnen som inte är synliga i deras spektrum.

Resultaten i det här slutarbete är en liten del av ett större koncept för att hitta ekonomiskt lönsamma lösningar som samtidigt bevarar de knappa resurserna. Ytterligare ambitioner är att kompensera de befintliga farliga ämnena i e-avfall och främja cirkulär ekonomi. Dessutom kan studier inom detta område vara av intresse för olika aktörer, såsom för producenter och/eller konsumenter, för industrisektorn och för att stödja lagstiftningsambitioner.

Bristen på resurser har begränsat resultaten av denna avhandling. Dessa delresultat är en del av en omfattande process. Som enskilt forskningsobjekt skulle nästa steg vara att undersöka dessa sampel ytterligare med någon sorts elementaranalys som exempelvis XRF eller SEM-EDS-analys. Men när man betraktar det här i ett bredare perspektiv skulle det inkluderas i en multiprofessionell tvärvetenskaplig forskningsstudie.

Slutligen delar vi alla på samma planet och därför delar vi också problemen och ansvaret. Både konsumenten och producenten måste vara med om vi ska mot hållbarhet och återvinning. På en global skala måste det här vara ett gemensamt försök som berör politiker, företag, sociala nätverk och individer. Även om EU har närmat sig dessa problem genom lagstiftning, kan det inte sägas om alla länder i världen. Fattigdom, brist på erfarenhet och kunnande, sociala frågor, mänskliga rättigheter och så vidare är alla frågor som uppstår när man talar om högre immateriella värden kopplande till vår fortsatta existens på denna planet.

REFERENCES

Anon, 2020. *How an FTIR Spectrometer Operates.* [Online] Available at: https://chem.libretexts.org/@go/page/1844 [Accessed: September 2021].

Araki A., Bamai Y.A., Bastiaensen M., Van den Eede N., Kawai T., Tsuboi T., Miyashita C., Itoh S., Goudarzi H., Konno S., Covaci A. & Kishi R., 2020. Combined exposure to phthalate esters and phosphate flame retardants and plasticizers and their associations with wheeze and allergy symptoms among school children. *Environmental Research*, volume 183. [Online] Available at: https://www.sciencedirect.com/science/article/pii/S0013935120301043 [Accessed: October 2021].

Ardolino F., Cardamone G.F. & Arena U., 2021. How to enhance the environmental sustainability of WEEE plastics management: An LCA study. *Waste management*, volume 135, pages 347-359. [Online] Available at: https://www-sciencedirect-com.ezproxy.arcada.fi:2443/science/article/pii/S0956053X21005109#b0050 [Accessed: November 2021].

Bamai Y.A., Araki A., Kawai T., Tsuboi T., Saito I., Yoshioka E., Kanazawa A., Tajima S., Shi C., Tamakoshi A. & Kishi R., 2014. Associations of phthalate concentrations in floor dust and multi-surface dust with the interior materials in Japanese dwellings. *Science of The Total Environment*, volumes 468–469, pages 147-157. [Online] Available at: https://www-sciencedirect-com.ezproxy.arcada.fi:2443/science/article/pii/S0048969713008917 [Accessed: October 2021].

Becker W., Sachsenheimer K. & Klemenz M., 2017. Detection of Black Plastics in the Middle Infrared Spectrum (MIR) Using Photon Up-Conversion Technique for Polymer Recycling Purposes. *Polymers*, *9*, 435. [Online] Available at: https://doi.org/10.3390/polym9090435 [Accessed: May 2022].

British Plastic federation, 2022, BPF. *Plastics Additives.* [Online] Available at: https://www.bpf.co.uk/plastipedia/additives/Default.aspx [Accessed: May 2022].

Bromine Science and Environmental Forum (BSEF) 2021. *Bromine Science and Environmental Forum.* [Online] Available at: https://www.bsef.com/ [Accessed: September 2021].

CBRNE Tech Index, 2022. *Mid-infrared spectroscopy (MIR).* [Online] Available at: https://cbrnetechindex.com/Explosives-Detection/Technology-ED/Molecular-Spectroscopy-ED-T/Mid-infrared-Spectroscopy-ED-MS [Accessed: March 2022].

Charitopoulou, M.A., Kalogiannis, K.G., Lappas, A.A. & Achilias D.S., 2021. Novel trends in the thermo-chemical recycling of plastics from WEEE containing brominated flame retardants. *Environmental Science and Pollution Research*. [Online] Available at: https://link-springer-com.ezproxy.arcada.fi:2443/article/10.1007/s11356-020-09932-5#Bib1 [Accessed: November 2021].

CREAToR Project, 2021. CREAToR. [Online] Available at: https://creatorproject.eu/ [Accessed: November 2021].

Delva L., Hubo S., Cardon L. & Ragaert K., 2018. On the role of flame retardants in mechanical recycling of solid plastic waste. *Waste Management*, volume 82, pages 198-206. [Online] Available at: https://www-sciencedirect-com.ezproxy.arcada.fi:2443/science/article/pii/S0956053X18306494 [Accessed: November 2021].

ECHA, 2021. *European Chemical Agency*. [Online] Available at: https://echa.europa.eu/fi/substance-information/-/substanceinfo/100.003.744 [Accessed: October 2021].

EUR-Lex, 2012. *Directive 2012/19/ EU of the European Parliament and of the Council of 4 July 2012 on waste electrical and electronic equipment (WEEE)*. [Online] Available at: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32012L0019 [Accessed: September 2021].

Eurostat, 2021. *Eurostat Statistics Explained.* [Online] Available at: https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Waste_statistics_-_electrical_and_electronic_equipment [Accessed: October 2021].

European Commission, 2021. *European Commission, Environment.* [Online] Available at: https://ec.europa.eu/environment/index_en [Accessed: September 2021].

European Food Safety Agency (EFSA), 2021. *Brominated flame retardants.* [Online] Available at: https://www.efsa.europa.eu/en/topics/topic/brominated-flame-retardants [Accessed: October 2021].

Freegard K., Tan G. & Morton R., 2006. Develop a process to separate brominated flame retardants from WEEE polymers, Final report. [Online] Available at: https://polymerandfire.files.wordpress.com/2015/04/brominatedwithappendices-3712.pdf [Accessed: March 2022].

Gao D-W. & Wen Z-D., 2016. Phthalate esters in the environment: A critical review of their occurrence, biodegradation, and removal during wastewater treatment processes. *Science of The Total Environment*, volume 541, pages 986-1001. [Online] Available at: https://www-sciencedirect-com.ezproxy.arcada.fi:2443/science/article/pii/S0048969715308093 [Accessed: October 2021].

Haarman A., Magalini F. & Courtois J., 2020. Study on the impacts of Brominated Flame Retardants on the Recycling of WEEE plastics in Europe. *BSEF*. [Online] Available at: https://www.bsef.com/wp-content/uploads/2020/11/Study-on-the-impact-of-Brominated-Flame-Retardants-BFRs-on-WEEE-plastics-recycling-by-Sofies-Nov-2020-1.pdf [Accessed: October 2021].

Hahladakis J.N., Velis, C.A., Weber R., Iacovidou E. & Purnell P, 2018. An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling. *Journal of Hazardous Materials*, volume 344, pages 179-199. [Online] Available at: https://doi.org/10.1016/j.jhazmat.2017.10.014 [Accessed: May 2022].

Hansen K.M., Fauser P., Vorkamp K., Christensen J.H., 2020. Global emissions of Dechlorane Plus. *Science of The Total Environment*, volume 742. [Online] Available at: https://www-sciencedirect-com.ezproxy.arcada.fi:2443/science/article/pii/S0048969720341991 [Accessed: October 2021].

Kolias K.W., 2016. Identification of polymers and flame retardants in sWEEE: personal computers and microwave ovens by FTIR. *University of Natural Resources and Life Sciences Department of Water – Atmosphere – Environment Institute of Waste Management.* [Online] Available at: https://forschung.boku.ac.at/fis/suchen.hochschulschriften_info?sprache_in=en&menue_id_in=107&id_in=&hochschulschrift_id_in=13832 [Accessed: February 2022]

Ma C., Yu J., Wang B., Song Z., Xiang J., Hu S., Su S. & Sun L., 2016. Chemical recycling of brominated flame retarded plastics from e-waste for clean fuels production: A review. *Renewable and Sustainable Energy Reviews*, volume 61, pages 433-450. [Online] Available at: https://www-sciencedirect-com.ezproxy.arcada.fi:2443/science/article/pii/S1364032116300375 [Accessed: October 2021].

Maisel F., Chancerel P., Dimitrova G., Emmerich J., Nissen N.F. & Schneider-Ramelow M., 2020. Preparing WEEE plastics for recycling – How optimal particle sizes in pre-processing can improve the separation efficiency of high quality plastics. *Resources, Conservation and Recycling*, volume 154. [Online] Available at: https://www-sciencedirect-com.ezproxy.arcada.fi:2443/science/article/pii/S0921344919305257#bib0050 [Accessed: November 2021].

Marino G., 2021. WEEE: illegal trade of electronic waste must be stopped to achieve EU goals. *Renewable matter*. [Onine] Available at: https://www.renewablematter.eu/articles/article/weee-illegal-trade-of-electronic-waste-must-be-stopped-to-achieve-eu-goals [Accessed: November 2021].

Naranjo A., Roldán-Alzate A., Sierra J. & Osswald T., 2008. Plastics Testing and Characterization: Industrial Applications. *Carl Hanser Verlag, Hanser Gardner publications cop.*, pages 7-28.

Nava, V., Frezzotti, M. L. & Leoni, B., 2021. Raman Spectroscopy for the Analysis of Microplastics in Aquatic Systems, *Applied Spectroscopy*, 75(11), pp. 1341–1357. [Online] Available at: https://doi.org/10.1177/00037028211043119 [Accessed: May 2022].

Noll, R., Fricke-Begemann, C. & Schreckenberg, F., 2021. Laser-induced breakdown spectroscopy as enabling key methodology for inverse production of end-of-life electronics. *Spectrochimica Acta Part B: Atomic Spectroscopy*, volume 181. [Online] Available at: https://doi.org/10.1016/j.sab.2021.106213 [Accessed: May 2022].

NONTOX Project, 2021. NONTOX Project. [Online] Available at: http://nontox-project.eu/ [Accessed: November 2021].

Noticias Asociados, 2016. The challenges of the management of WEEE in Europe. *Instituto Tecnológico de la Energía*. [Online] Available at: http://www.ite.es/en/los-desafios-la-gestion-raee-europa/ [Accessed: December 2021].

Ongondo F.O., Williams I.D. & Cherrett T.J., 2010. How are WEEE doing? A global review of the management of electrical and electronic waste. *Waste Management*, volume 31, issue 4, 2011. [Online] Available at: https://www-sciencedirect-com.ezproxy.arcada.fi:2443/science/article/pii/S0956053X10005659 [Accessed: September 2021].

Oxford Instruments https://raman.oxinst.com/learning/view/article/raman-knowledge-base?gclid=EAIaIQobChMIr9CpicLo9wIV8BJ7Ch3yLAdiEAAYASAAEgKsXfD_BwE

PubChem, 2022. National Institutes of Health (NIH). [Online] Available at: https://pubchem.ncbi.nlm.nih.gov/ [Accessed: May 2022].

REMADYL Project, 2021. Remadyl. [Online] Available at: https://www.remadyl.eu/ [Accessed: November 2021].

Schuster J.K., Harner T. & Sverko E., 2021. Dechlorane Plus in the Global Atmosphere. *Environmental Science & Technology Letters*, volume 8, page 39-45. [Online] Available at: https://pubs.acs.org/doi/10.1021/acs.estlett.0c00758 [Accessed: October 2021].

Searl, A. & Crawford, J., 2012. Review of health risks for workers in the waste and recycling industry. *Institute of Occupational Medicine.* [Online] Available at: https://www.blmlaw.com/images/uploaded/news/File/Review_of_Health_Risks_for_workers_in_the_Waste_and_Recycling_Industry1%20(2).pdf [Accessed: May 2022].

Sormunen T., Uusitalo S., Lindström H., Immonen K., Mannila J., Paaso J. & Järvinen S., 2022. Towards recycling of challenging waste fractions: Identifying flame retardants in plastics with optical spectroscopic techniques. *Waste management & research.* [Online] Available at: https://doi.org/10.1177%2F0734242X221084053 [Accessed: March 2022].

UNEP, 2017. Guidance on best available techniques and best environmental practices for the recycling and waste disposal of articles containing polybrominated diphenyl ethers (PBDEs) listed under the Stockholm convention. [Online] Available at: http://chm.pops.int/Implementation/NIPs/Guidance/GuidanceonBATBEPfortherecyclingofPBDEs/tabid/3172/Default.aspx [Accessed: May 2022].

Thermo Fisher Scientific Inc., 2021. Thermo Scientific. [Online] Available at: https://www.thermofisher.com/fi/en/home.html [Accessed: September 2021].

Türker-Kaya, S., & Huck, C.W., 2017. A Review of Mid-Infrared and Near-Infrared Imaging: Principles, Concepts and Applications in Plant Tissue Analysis. *Molecules*, 22 (1), 168. [Online] Available at: https://doi.org/10.3390/molecules22010168 [Accessed: May 2022].

Wang, Y. & Haifeng Q., 2021. Phthalates and Their Impacts on Human Health. *Healthcare (Basel, Switzerland)* volume 9(5) 603. [Online] Available at: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC8157593/ [Accessed: November 2021].

WEEE Europe, 2021. Why WEEE? *WEEE Europe.* [Online] Available at: https://www.weee-europe.com/22-1-Why-WEEE.html [Accessed: November 2021].

WEEE Forum, 2021. *WEEE Forum Organisation.* [Online] Available at: https://weee-forum.org/ [Accessed: October 2021].

Zeiss, 2022. Zeiss Spectroscopy. [Online] Available at: https://www.zeiss.com/spectroscopy/solutions-applications.html [Accessed: May 2022].