ROLE OF PFAS SUBSTANCES IN THE PLASTIC MANUFACTURING PROCESS

Polymeric PFAS substances

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Tämän opinnäytetyön tavoitteena oli tutkia per- ja polyfluoroalkyyliyhdisteiden (PFAS) merkitystä, kuten niiden lähteitä ja mahdollisia vaihtoehtoja muovisissa elintarvikepakkauksissa. Lisäksi pyrittiin tutustumaan esimerkiksi PFAS-yhdisteiden analysointimenetelmiin. Opinnäytetyön toimeksiantajana oli tilaajayritys, joka valmistaa muovikalvoja polymeerisiä PFAS-yhdisteitä sisältävistä raaka-aineista esimerkiksi elintarvikepakkausteollisuuteen. Aihe on tilaajalle merkityksellinen, koska Euroopassa vireillä oleva ehdotus PFAS-yhdisteiden rajoitustoimista käsittää kaikkien PFAS-yhdisteiden kieltämisen, mikä vaikuttaisi käytettäviin raaka-aineisiin. Ehdotettujen rajoitusten voimaantulo merkitsisi sitä, että PFAS-yhdisteitä sisältäville raaka-aineille tulisi olla vaihtoehtoisia raaka-aineita, joiden suorituskyky olisi taattava suuren suorituskyvyn tuotannossa.

Opinnäytetyössä käytetyt tutkimusmenetelmät voidaan jakaa kirjalliseen ja kokeelliseen osaan. Kokeelliseen osaan kuuluivat raaka-ainetoimittajien kysely, muovigranulaattien TOF-analyysi ja tuotekehityksen edustajan haastattelu. Raaka-aineiden toimittajille lähetetyllä kyselylomakkeella (vastausprosentti 90 %) kerättiin lisätietoja muovigranulaattien ja PFAS-yhdisteiden välisestä yhteydestä. Granulaattinäytteiden fluoripitoisuuden määrittämiseen käytettiin ulkopuolisissa laboratorioissa suoritettuja TOF-analyysejä.

Kyselylomakkeen tuloksista tehtiin myönteisiä ja kielteisiä huomioita. TOF-analyysissä selvisi suurta vaihtelua eri raaka-aineiden ja laboratorioiden välillä. Suoritettujen laboratoriotestien perusteella TOF-analyysiä ei voida pitää luotettavana menetelmänä muovigranulaattien PFAS-pitoisuuden määrittämiseksi. Eräs tähän vaikuttanut tekijä oli materiaalinäytteiden pieni määrä. Tuotekehityksen edustajan haastattelussa kävi ilmi, että polymeerin prosessin apuaineella (PPA) on oleellinen vaikutus muovin valmistusprosessiin kuten kalvon laatuun ja tuotantovirtaukseen. Haastattelu vaikutti vahvistavan teoriapohjaa, jonka aukkoihin löydettiin vastauksia. Tulevaisuudessa suositellaan valmiiden muovikalvojen testaamista, jolloin voitaisiin tutkia mahdollisia ekstruusiokoneistosta näytteeseen siirtyviä epäpuhtauksia. Tutkimuksia ehdotetaan myös jatkettavan muovikalvon koeajoilla ilman PPA:ta ja sitä sisältävää metalloseeniä, jotta voidaan tutkia niiden vaikutusta polymeerin virtaukseen, tuotannon tehokkuuteen ja joustavuuteen sekä muovikalvon laatuun.

Avainsanat Alkyyliyhdisteet, haitalliset aineet, ionikromatografia, pakkausteollisuus polymeerikemia
Sivut 37 sivua ja liitteitä 4 sivua

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Degree Programme in Biotechnology and Food Engineering Abstract
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Subject Role of PFAS substances in the plastic manufacturing process
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The aim of this thesis was to study the significance of per- and polyfluoroalkyl substances (PFASs), such as their sources and possible alternatives in plastic food packaging. In addition, efforts were made to clarify, for example, the PFASs testing methods for the packaging materials. The thesis was commissioned by a client company that uses extrusion processes to manufacture plastic films from raw materials containing polymeric PFASs for example for the food packaging industry. The subject was relevant for the company as the pending proposal for PFAS restriction measures in Europe includes the ban of all polymeric PFASs, which would affect the composition of the raw materials used. The entry into force of the proposed restrictions would mean that there should be alternative raw materials for polymeric PFAS-based raw materials. In addition, their performance in high volume manufacturing processes should be guaranteed.

The research methods used in the thesis can be divided into a literature and an experimental part. The experimental part included a survey to raw material suppliers, total organic fluorine (TOF) analysis of granulates and a product development interview. A questionnaire sent to suppliers (the response rate was 90 %) of raw materials collected additional information on the link between granulates and PFASs. TOF analyses carried out in external laboratories were used to determine the fluorine content of granulate samples.

The survey results indicated both positive and negative aspects. The TOF analysis showed large variation between different raw materials and laboratories. Based on the laboratory tests, TOF analysis cannot be considered a reliable method for determining the PFAS content of plastic granulates. One factor affecting this was the small number of material samples. The interview showed that polymer processing aid (PPA) has an essential impact on the plastic manufacturing process, on the extrusion, regarding for example the film quality and production flow. The interview seemed to strengthen the theoretical basis offering answers for the remaining questions. In the future, a larger sample for analysis is proposed to build a more comprehensive response. Testing of finished plastic films is also recommended to investigate possible contaminants transferred from the extrusion machinery to the sample. Moreover, trial production runs without polymer processing aid and metallocene polymers with PPA are recommended to investigate the effect on polymer flow, production efficiency and flexibility, as well as on the quality of the plastic film.

Keywords Alkyl compounds, hazardous substances, ion chromatography, packaging industry, polymer chemistry
Pages 37 pages and appendices 4 pages

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List of abbreviations

ECHA: European Chemicals Agency

EEA: European Economic Are

EPA: U.S. Environmental Protection Agency

HFP: hexafluoropropylene

FPA: Flexible Packaging Association

IC: ion chromatography

ILS: interlaboratory study

MB: masterbatch

mPE: metallocene polyethylene

npPFAS: non-polymeric per- and polyfluoroalkyl substances

pcs: pieces

PFASs: per- and polyfluoroalkyl substances

PFC: characterised alkyl substances

PFOA: perfluorooctanic acid

PFOS: perfluorooctane sulfonate

PFPE: perfluoropolyether

POPs: Persistent Organic Pollutants

PPA: polymer processing aid

pPFASs: polymeric per- and polyfluoroalkyl substances

ppm: parts per million

PTFE: polytetrafluoroethylene

PVF: polyvinyl fluoride

RAC: Committee for Risk Assessment

SEAC: Committee for Socio-Economic Analysis

Tg: glass transition temperature

TOF: total organic fluorine

1 Introduction

1.1 Background of the PFASs

Per- and polyfluoroalkyl substances (PFASs) are a group of industrially manufactured chemicals that were developed in the 1940s. (Eurofins, 2022) Per definition PFASs contain at least one fully perfluorinated methyl- or methylene group. The calculated amount of PFASs and the methods of naming and classifying them vary from source to source, but according to the National Center for Toxicology of EPA, for example, there are more than five thousand chemicals that can be classified as PFASs based on their structure. (EPA, n.d., p. 3-1) Unpublished Annex XV Restriction Report of ECHA is mentioning more than 10.000 different structures. Basic distinction of these structure can be made into non polymeric (nPFASs) and polymeric (pPFASs) which include fluoropolymers. Fluoropolymers are used in many applications, for example for their mechanical strength in industry as well as for their non-stick properties in material coatings that are mostly known as Teflon coatings. Popular fluoropolymers are hexafluoropolymer (HFP), polyvinylidene fluoride (PVF) and their copolymers. PFAS substances are commonly used in the manufacture of thin plastic films or polypropylene and polyethylene. PFASs are also applied in other packaging materials, such as fast-food wrappers, where grease resistance is particularly required.

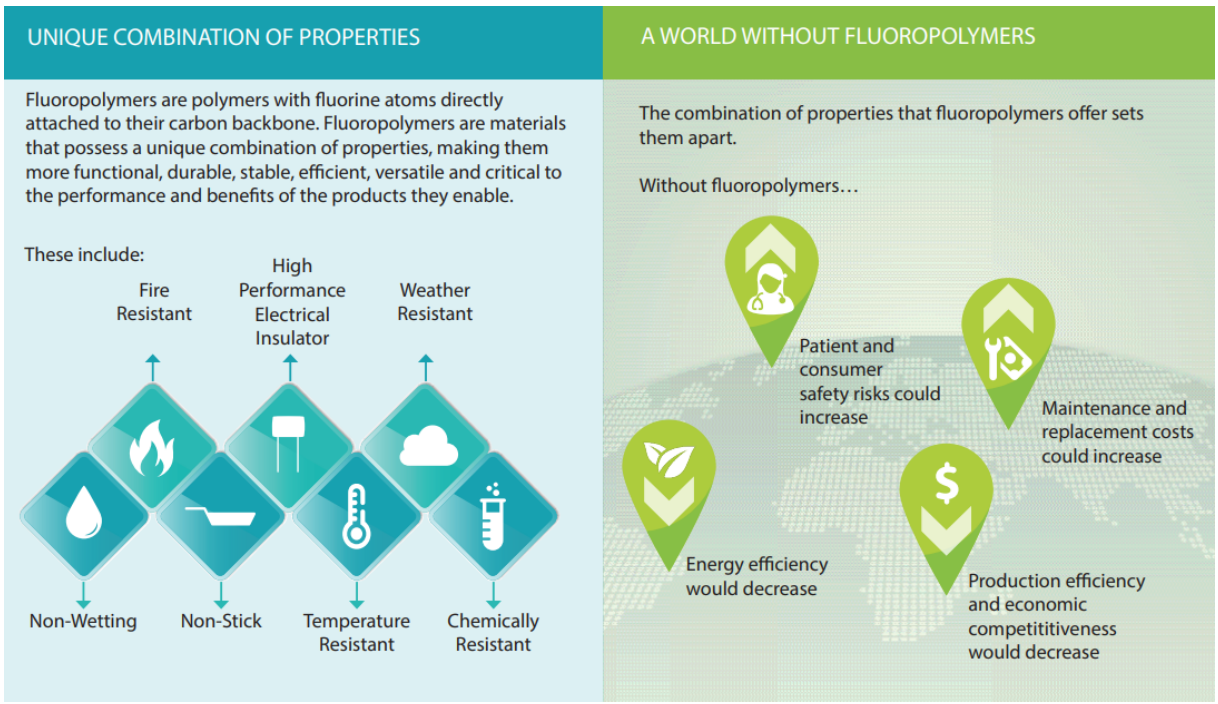
Besides the high bandwidth of positive properties man-made PFASs have also many negative effects, ahead of all persistence in environment. Several sources and extreme resistance carbon-fluor-bonding give them the name *forever chemicals.* Already in 2001, the Stockholm convention was set to monitor and regulate for PFAS globally, starting with two PFASs, or perfluorooctanic acid (PFOA) and perfluorooctane sulfonate (PFOS). (Lein, 2019, p. 2)

The European Chemicals Agency (ECHA) received a request from the German, French, Dutch, Norwegian and Swedish authorities to restrict PFASs on 13th January 2023, one of the most extensive proposed restrictions in the history of the European Union (EU). The proposal, published on 7th of February 2023, considers two options for restrictions: unlimited and time-limited bans. Ban is covering non-polymeric PFASs (npPFASs) as well as polymeric PFASs (pPFASs). For pPFASs a limit of 50 ppm total fluoro content is proposed. These restrictions

have been planned because PFASs can have besides persistence a variety of adverse effects on human health and development. For example, it is possible that npPFASs may reduce immunity of children and increase cholesterol levels, but these have not yet been proven with certainly. (Finnish Food Authority, 2021, p. 120) Only proven negative property of pPFASs is persistence.

Fluoropolymers belonging to the PFASs group have many applications due to their useful properties such as temperature resistance. This brings another perspective to the topic of sustainable development when considering the impact of PFASs on, for example, production efficiency and competitiveness as illustrated in the figure below. (Figure 1)

Figure 1 Properties of fluoropolymers (Fluoropolymer Industry et al., 2018)



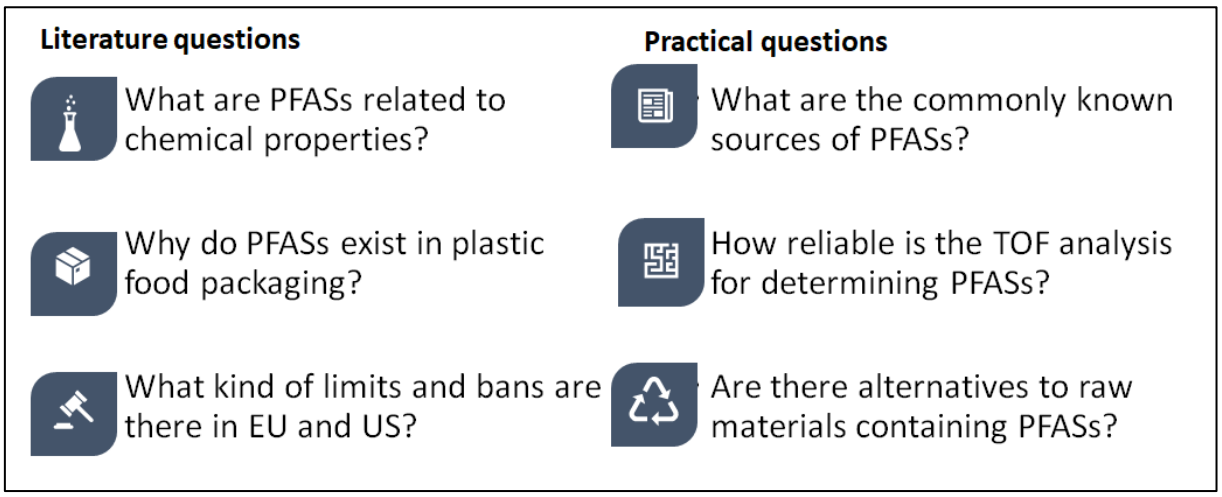
1.2 Background of the thesis

The aim of this thesis was to study the role of PFASs as sources and possible alternatives in the plastic food packaging. Other goals, for example, were to clarify PFASs testing methods for packaging materials. The choice of topic was influenced by factors based on the thesis author's professional background and engineering studies. The thesis was commissioned by a

client company, which uses extrusion processes to manufacture plastic film for example for food packaging industry from raw materials containing pPFASs. The topic is relevant for the company because PFAS restriction proposal of ECHA includes also the ban of pPFASs, and therefore affects the composition of the raw materials. The expected date of entry into force of the proposal is in 2025, and after the transition period of several months for packaging material, alternative raw materials substituting the ones with pPFASs should be available and the performance guaranteed in the high-volume manufacturing process.

The research questions based on literature review covered the chemical identity of pPFASs, elucidating sources and investigating sustainable development perspective. In addition, a review of current and upcoming limits and bans for PFAS includes European Union legislation, but also United States legislation, which has already set bans for products containing PFAS. The restrictions in the market area of one of the main economic partners of European Union. (European Parliament, 2022) These restrictions are expected to have a major impact on the export of goods from the EU region, especially as in this case, the EU legislation has progressed more slowly than the legislation in the US. The research questions based on the functional part of the thesis covered the known sources of PFAS, reliability of TOF analysis and possible alternatives to raw materials containing PFAS as illustrated in the figure below. (Figure 2) The topic was limited to extrusion raw materials called granulates. Other raw material groups like purchased films, liquids like inks and coatings or machinery parts are not covered by this thesis.

Figure 2 Research questions



Both exploratory and guiding research was used in the literature part because the aim was to gather a wide range of literature-based theory from reliable sources to build a comprehensive picture. In line with the guiding research, the aim was to build new perspectives on the top of the facts. Qualitative and quantitative research were used in the experimental part. The qualitative approach, for example, investigated the effect of PFASs on the extrusion process. The thesis is also based on strongly on the literature review and the conclusions done from it, as well as on the responses from suppliers. The quantitative perspective, for example, investigated the concentration of PFASs in the granulates in external laboratories. (Eskelinen & Karsikas, 2012, p. 91). A questionnaire was sent to suppliers of raw materials to gather more information on the link between granulates and PFASs. For example, interviews with the legislators of the United States and several webinars were used to gather information on PFAS-related legislation.

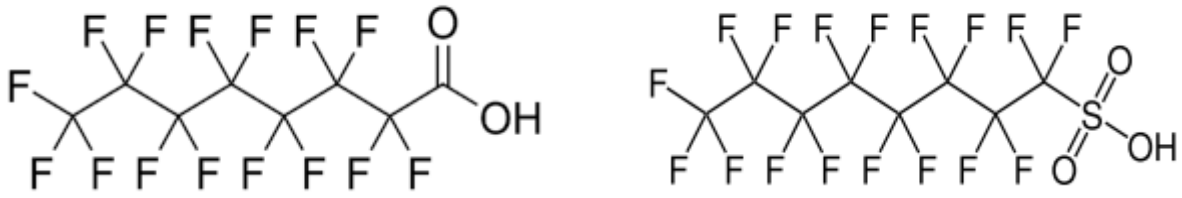
2 Literature part

2.1 Chemistry of PFASs

The name PFAS is a conjunction of the main, substance describing part AS and the prefix PF. AS stands for alkyl substances and PF is the abbreviation for per- and polyfluoro subtances. In the organic chemistry, alkyl substances are in the organic chemistry defined as structures containing an alkyl group, which consists of a chain of hydrogen and carbon atoms with sum formular C_nH_{2n+1}. Adding one more hydrogen it leads to the substance group alkane. Other common functional groups are -OH (alcohols), -COOH (carboxylic acids) or $-SO_3H$ (sulfonic acids). The prefix per- and poly fluorinated characterised alkyl substances, synthetically produced organic compounds, in which the hydrogen atoms have been replaced by fluorine. (Stahl et al., 2011, p. 1) Within perfluorinated alkyl substances all hydrogen atoms of the alkyl group (not the functional group) are fully substitute by fluorine. Polyfluorinated alkyl substances contain still at least one -CH2- or CH3- group in the alkyl rest. The overall property of a molecule can be significantly modified by attaching a fluorine atom to it, as fluorine is the most electronegative of the elements. Fluorine is found in natural inorganic minerals such as fluorite, but fluorinated organic compounds are very unusual. (Sato, n.d.)

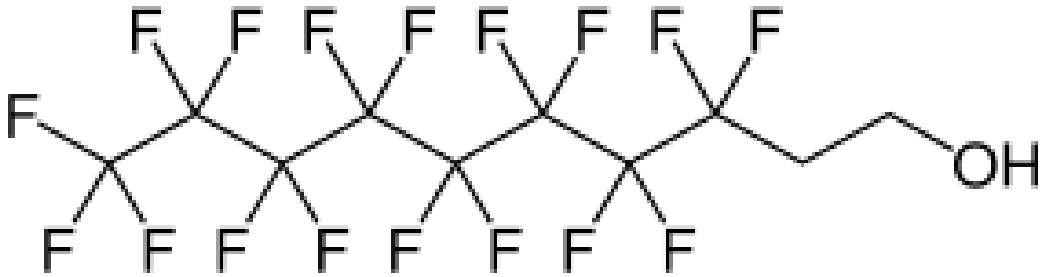
PFAS chemistry was discovered in the late 1930s, and some PFASs have been manufactured since the 1950s. Despite this, PFASs have only been identified in environmental samples in the early 2000s, when PFAS testing was widely available. (Mueller & Schlosser, 2020, p. 2) In 1947, 3M Corporation developed perfluorooctanic acid (PFOA), among other chemical compounds, called C8 because of the eight carbons bonded to fluorine. These compounds are now known as PFAS. (DiGiannantonio, 2022) In addition to PFOA, perfluorooctane sulfonate (PFOS) is one of the most widely used substance of PFAS group. (EPA, 2023) The chemical structures of PFOA and PFOS have been illustrated in the figure below. (Figure 3)

Figure 3 Chemical structure of PFOA (left) and PFOS (right) (EPA, n.d., p. 3-3)



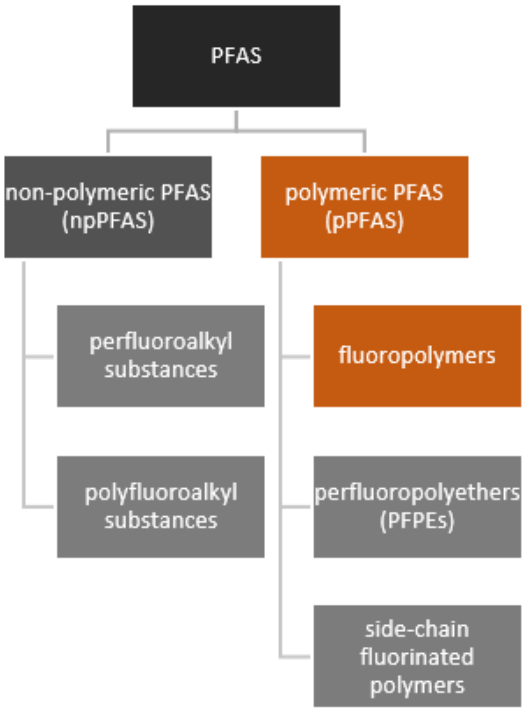
PFASs also include polyfluorinated substances. A typical representative of polyfluorinated substances is 8:2 fluorotelomer alcohol containing eight perfluoro carbon-hydrogen groups and two not fluorinated methylene groups. Chemical structure of 8:2 fluorotelomer alcohol has been illustrated in the figure below. (Figure 4)

Figure 4 Chemical structure of 8:2 fluorotelomer alcohol (EPA, n.d., p. 3-3)



The total group of PFAS can be divided into polymers and non-polymers, which may contain different subgroups as illustrated in the figure below. (EPA, n.d., p. 3-1) (Figure 5)

Figure 5 One way to classify PFASs (adapting from IYRC, 2022)



Polymeric PFASs are large molecules formed from smaller molecules, or monomers, with a regular structure. Non-polymeric PFASs (npPFASs) can be used as raw material or as processing aid in the production of some polymeric PFASs. Subcategories of polymeric PFASs (pPFASs) are perfluoropolyethers (PFPE), side-chain fluorinated polymers and fluoropolymers. (EPA, n.d., p. 3-7) Fluoropolymers used in plastic packaging are described in chapter 2.2.1.

2.2 Usage of PFASs in food contact materials

Food contact materials (FCM) include not only packaging materials but also cutlery, as well as machines used in the food industry or at home, such as the coffee machine. Materials in direct contact with food include for example paper, plastic, and coatings. (RIVM, 2018, p. 23) In kitchen utensil coatings, which are classified as food contact materials, PFASs are mainly used

as monomers from which a core chain of fluoropolymers is built upon curing. A daily example is the coating of frying pans, which is usually polytetrafluoroethylene (PTFE) or Teflon.

Coatings can also use PFASs as so-called polymer processing aids, which are processing aids added to the polymer. Although these auxiliaries are added to the polymer, they are not intended to act a role in the final product. As surfactants, the auxiliaries are not part of the polymer chain. Paper and board coatings differ from fluoropolymer coatings for kitchen utensils so that in paper and board coatings the fluoropolymers function as an additive. Additives are therefore substances that are supposed to be present in the final product for chemical or physical properties such as oil repellents. (RIVM, 2018, p. 14)

Concentrations of PFAS in FCM vary between different countries due, for example, to differences in packaging composition and local and national legislation. In general, migration of PFASs is usually due to factors such as the duration of contact and the nature of PFASs and the food. (Barhoumi et al., 2022, p. 10) Research data on the presence of PFASs in FCM such as plastics is relatively scarce. To gain further knowledge, it would be essential to investigate the migration of PFASs into food and the factors affecting sorption in microplastics. This information would allow an understanding of the migration on PFASs from FCM and other multi-purpose materials to organisms such as humans. (Barhoumi et al., 2022, p. 2)

Studies on the transfer of PFASs from FCM to food have used various food simulants such as ethanol and oil, and foodstuffs such as cereals and milk. The aim of the experiments is to determine the concentrations of PFASs migrated into food when packaging materials are placed in simulants and/or food for different periods of time and at different temperatures. (Barhoumi et al., 2022, p. 3) Several studies have found that a combination of heating and, for example, emulsifiers, increases the migration of short-chain PFASs. In contrast, the migration of precursors is more affected by the presence of fatty foods than by the migration of PFAA precursors. (Zabaleta et al., 2020, pp. 3-4, 8)

The available literature suggests that the migration of PFASs into microplastics is influenced by the physicochemical properties of PFASs, such as chain length and functional groups, as well as by the properties of the microplastics, such as charge and size, and solution chemistry,

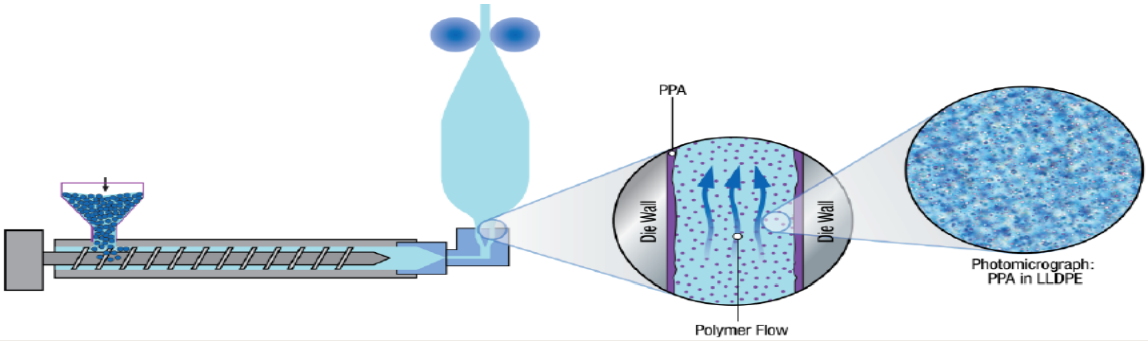
such as ionic strength and pH value. (Barhoumi et al., 2022, p. 4) Physical properties, such as crystallinity, and chemical properties, such as polarity, of microplastics have proven to be crucial factors in sorption processes. Polymers can be either crystalline or amorphous. The glass transition temperature (Tg) indicates the temperature at which an amorphous polymer can become, for example glassy. This parameter is a key factor influencing the adsorption capacity. (Barhoumi et al., 2022, p. 8)

2.2.1 Presence of fluoropolymer in extrusion processing aids

Extrusion is a method of moulding plastics in which the raw material plastic granulates, are melted, homogenised, and extruded at high temperature in a continuous process. The plastic mass is dispensed through a die and the mass is fed into rolls or cured to the desired shape. Melt pressure is one of the most essential parameters affecting product quality in the extrusion process.

The polymer processing aids (PPAs) are used, for example, to reduce the melt pressure and to make the manufacturing process more efficient. (Rifra, n.d.) PPA ensures uniform polymer flow in the extrusion process by producing a thin coating on the surface of die walls, as illustrated in the figure below. (Figure 6)

Figure 6 PPA improves polymer flow (Irrgang & Kirchner, personal information, 16.1.2023)

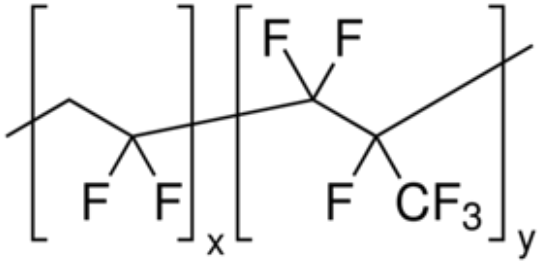


PPAs can be part of the composition of raw materials to enhance their performance in extrusion, such as in certain metallocene polyethylene (mPE) granulates. Also, polymer processing aids can be added separately during the extrusion, as PPA masterbatches.

PFASs in general are good surfactants, i.e., they reduce the surface tension of liquids (Spanoudi, 2022), and these properties are used for polymer processing aids. PPAs based on fluoropolymers are commonly used in the production of polyolefins, as their use as a processing additive is approved by Commission Regulation (EU) 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food. Polyolefins is the collective name for polyethylene (PE) and polypropylene (PP) plastics, which are used in a wide range of plastic materials.

Hexafluoropropylene is a reactive chemical used, for example, in the production of fluoropolymers. Its known applications include co-monomer in the manufacture of thermoplastics and vinylidene fluoride. (Ecetoc, 2005, p. 10) The chemical structure of copolymer of vinylidene fluoride (x) and hexafluoropropylene (y) are illustrated in the figure below. (Figure 7)

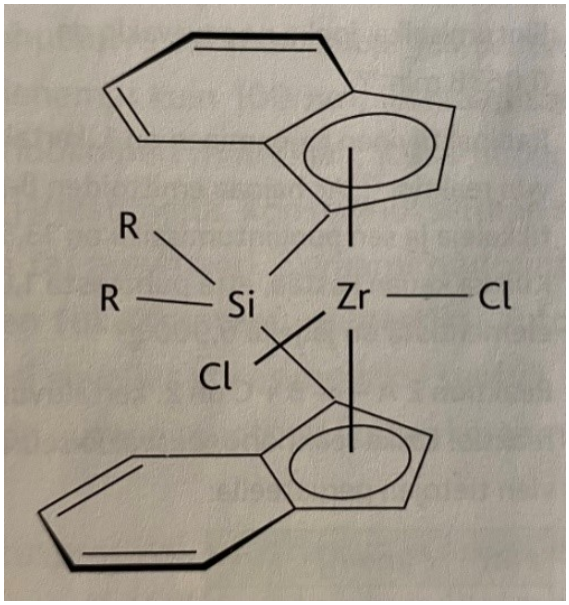
Figure 7 Copolymer of vinylidene fluoride (x) and hexafluoropropylene (y) (Merck, n.d.)



Metallocene polyethylene (mPE)

Metallocene polyethylene (mPE) belongs to the polymers that are manufactured by using a metallocene catalyst. The structure and properties of the polymer can be influenced by modifying the well-known structure of the metallocene catalyst. (Hänninen et al., 2019, p. 280) The nucleus of metallocene contains an active metallic centre to which two C_5-rings are bonded. Hundreds of different metallocenes can be produced by modifying groups of rings. (Hänninen et al., 2019, p. 281) The figure below shows an example of a silicified metallocene, where R is the alkyl group. (Figure 8, p. 10)

Figure 8 Metallocene with silicon bridge (Hänninen et al., 2019, p. 281)



A single pathway directs the monomers to the metal atom, contributing to the formation of structurally homogenous polymers. The above events, for example, result in increased stiffness and strength of polymers. (Ponomareva & Likhacheva, 2001, p. 8) The metallocene catalyst results in a significantly narrower molecular weight distribution, which creates a higher melting temperature polymer. (Shamiri et al., 2014, p. 5078) The rheological properties of metallocene plastics, such as viscosity, can be controlled by a PPA, and therefore the fluoropolymer may end up in the metallocene plastic. (Liu et al., 2005, p. 1824)

Masterbatches

Masterbatches (MBs) are concentrated additive granulates. MBs are manufactured by concentrating or adding a desired additive to a compatible carrier polymer. The amount of the additive in masterbatches is typically 5-70 %, and the amount of masterbatch in final product is around 500-5000 ppm. MBs have multiple functions depending on the used additive type. For instance, antiblock and slip additives prevent undesirable friction and stickiness of the final product, plastic film, while masterbatch granulates are also used simply to add colour. Masterbatch PPAs (MB PPAs), as the name implies, contain polymer processing aids.

2.3 Legislation

2.3.1 Europe

Regulation of persistent chemicals started with Stockholm Convention on Persistent Organic Pollutants as a global treaty to protect human health and the environment from chemicals. They remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and wildlife, and have harmful impacts on human health or on the environment. (Stockholm Convention, n.d.) In 2009, first PFAS substance PFOS was restricted by the convention. In 2020 PFOA followed and is forbidden globally besides a few exceptions. (ECHA, n.d.-a; ECHA, n.d.-b)

Since Stockholm convention has got no legally binding character the content was transferred in EU into the POPs Regulation (EU) 2019/1021. In June 2022, beside PFOA and PFOS, perfluorohexanesulfonic acid (PFHxS) with its salts and compounds, was included in the POPs Regulation and is expected to enter into force at the end of 2023. In addition, the inserting of long-chain perfluorinated carboxylic acids (C9-21 PFCAs) to the POPs Regulation for global phase-out is under consideration. (ECHA, n.d.-c; ECHA, n.d.-d)

The Commission Regulation of 7th December 2022 specifies the maximum permitted levels of perfluorinated alkyl compounds (PFOS, PFOA, PFNA, PFHxS) in certain foodstuffs. (Commission Regulation (EU) maximum levels of perfluorinated alkyl compounds in certain foodstuffs 2388/2022)

Other restrictive measures on PFASs pending in Europe include:

- the RMOA of the United Kingdom (Risk Management Options Analysis of PFASs) and the Government's Chemical Strategy (Spanoudi, 2022)
- proposal of Norway to restrict PFHxS acid, its salts, and related substances
- proposal of Germany to limit undefluorohexanoic acid (PFHxA), its salts and related substances. (ECHA, n.d.-d)

More restrictive measures on PFASs are planned based on the Sustainable Chemicals Strategy of the European Commission, published on 14th October in 2020, which underlines that chemicals are essential to society and that a robust framework is needed to make EU legislation more coherent and robust. Consequently, in January 2023, the European Chemicals Agency (ECHA) received a proposal from Denmark, the Netherlands, Germany, Sweden, and Norway for restrictions on the whole group of PFASs. The proposal is one of the widest restriction proposals in Europe and is based on issues such as the impact of PFASs on human health and the environment, and emissions from the life-cycle stages of PFASs. (ECHA, n.d.-a) The proposal foresees a transitional period of 18 months from entry into force and two exceptional transitional periods of five years and 12 years. (Keller&Heckman, 2023) Acceptable limit of total organic fluorine will be 50 ppm. The figure below illustrates the steps of the restriction process. (Figure 9)

Figure 9 Timeline of the restriction proposal (Marquez-Camacho, 2023)

In February, the proposal was published on the website of ECHA, containing information related to the risks of the PFASs, available information on alternatives, the rationale for EU-wide action, as well as an analysis of the socio-economic impacts. (Marquez-Camacho, 2023) In March, the scientific committees for Risk Assessment (RAC) and Socio-Economic Analysis (SEAC) met to verify that the proposal fulfil the legal requirements of the REACH regulation. (ECHA, n.d.-b) This was followed by a six-month consultation period during which anyone with knowledge of the PFASs can give their views. Facts on risks, socio-economic perspectives, and alternative substances, among others, are considered particularly relevant. (ECHA, n.d.-e)

The next step is the evaluation of RAC and SEAC, where the first one mentioned gives its opinion on whether the proposal can be considered a reasonable risk to the environment and human health. The second mentioned committee is responsible for giving its opinion on the socio-economic impact of the proposed restriction. The opinions are published and sent to the European Commission after approval by the committees. The decision to implement the restrictions is taken by the European Commission and its member states in the REACH committee. (Marquez-Camacho, 2023) At the writing state of this thesis, the proposed restrictions process is continuing, so more exact information is not available at the moment. The committees may need more time to finalise their opinions, due to the challenging nature of the proposal. Normally, the opinions of RAC and SEAC are completed within a year of the start of the scientific assessment. (ECHA, n.d.-b). In addition, the proposal is demanding for all industrial sectors. Especially fluoropolymer industry association is preparing contradiction opinion during the consultation phase to enforce the exemption of fluoropolymers of the proposal. (PlasticsEurope, 2023)

2.3.2 The United States

By July 2022, six states had passed legislation to regulate the appropriate use of PFASs in flexible food packaging. These laws were due to enter into force between the end of 2022 and the beginning of 2024. However, these laws were not intended to prohibit the total use of PFASs. According to the Flexible Packaging Association (FPA), fluorinated polymer processing aid (PPA), can be considered as part of the production of sustainable packaging, for example by improving material flow. The association will continue to work to ensure that the importance of fluorinated additives is recognised in legislation by excluding them from packaging regulations. (FPA, n.d.)

Safer States is a coalition of various American environmental health unions and organizations dedicated to building a healthier world. (Safer States, n.d.) The coalition published its *Analysis of State Legislation Addressing Toxic Chemicals and Materials* of 2023 where state-specific legislation on toxic materials and chemicals has been analysed. Some main points of analysis are:

- minimum 16 stages are considering restrictions on PFASs, for example their applications, apart from inevitable situations as well as actions on food packaging (Safer States, 2023)

- minimum 22 states are considering actions to remove harmful plastics and harmful chemicals from plastics (Safer States, 2023)

- minimum 11 stages are considering actions to ban PFASs from food contact materials such as packaging. (Safer States, 2023, p. 6)

Especially the laws of two US national states should be highlighted. From 1st January in 2023, the State of California banned the use of PFASs in plant fibre-based food packaging that contains or has been deliberately added to 100 ppm as defined by total organic fluorine (TOF). (Rackl et al., 2021) In addition, the State of Rhode Island was meant to ban manufacturing, sale, and distribution of PFAS-based food packaging in the state from 1st January in 2023. The ban includes food packaging with intentionally added PFASs, which also include polymer processing aid (PPA). (FPA, n.d.)

2.4 Analysing methods of PFASs

For example, knowing where to find PFASs is one factor that makes it difficult to limit their use. The testing of materials is important to find out where PFASs are used, and to study the amount of different concentration levels. Some methods can be used for many different applications. Among others, the TOF analysis according to standard EN 15408:2011 can be used for both recycled fuels and plastic granulates. However, the lack of standardised PFAS test methods makes it hard to compare results between laboratories and studies. (CFE, 2020)

2.4.1 Total organic fluorine (TOF)

TOF analysis can be used to determine the total PFAS. This analysis also reveals the organic fluorine content, which is related to the presence of PFAS in the sample, as packaging company Constantia explains about PFAS analysis methods in a meeting. As mentioned at the

beginning of Chapter 3.3, TOF analysis can be performed according to a standard EN 15408:2011 that includes methods for the determination of total fluorine (F), but also sulphur (S), chlorine (Cl) and bromine (Br) content. The fluorine content of solid samples is determined after combustion in an oxygen atmosphere. (EN 15408:2011, p. 4) The preparation of the sample extracts leaves only the organofluorine compounds, the majority of which are PFASs. This is achieved by removal of inorganic fluorine compounds, followed by combustion of the extracts at temperatures above plus 1000 °C and determination of the mineralised fluorine by ion chromatography. (Bureau Veritas, 2021) Reaction products of the combustion process such as halides including fluorine contribute environmentally detrimental emissions and corrosion. (EN 15408:2011, p. 4) The reaction products are then dissolved or absorbed in the absorption solution. (EN 15408:2011, p. 6) According to standard, this method can be used for fluorine at concentrations above 0.015 g/kg. (EN 15408:2011, p. 5)

The total organic fluorine in an absorption solution can be determined by ion chromatography (IC) in the TOF analysis. (Bureau Veritas, 2021) IC is developed at DOW Chemical Company for the determination of ionic analytes in solutions of different compositions. (Small et al., 1975, p. 1801) In this method, the separation of ions in the solution composition is carried out according to the ion exchange affinities and reactions typical of each ion type. (Fritz, 2005, p. 8)

The result of the TOF analysis is the individual component levels in aqueous samples in hectograms per litre (µg/l) and in solid samples in hectograms per kilogram (µg/kg). The total concentration of PFASs is represented by the concentration determined in the sample when the organic fluorine corresponds to PFASs.

2.4.2 Other methods

Another possible method for determining the concentration of PFASs is the TOP Assay where the oxidation reaction is based on a hydroxyl radical that converts the starting materials to perfluoroalkyl acids (PFAAs). The maximum amount of PFAS precipitates in the sample can be estimated from the increase in PFASs measured after oxidation compared to pre-oxidation concentrations. (Eurofins, 2019) The Top Assay can also be recommended for the plastics

industry, as the method is suitable for the analysis of complex samples. The weakness of the analysis is its oversimplification, that is it does not allow the detection of individual compounds present in the sample. (Pace, n.d.)

2.5 Sustainability of PFASs

Sustainable development is about social change, both locally and globally, with the aim of ensuring that future generations have adequate living conditions. Sustainable development requires that decisions and actions consider the economy, the environment, and people in a balanced way. Sustainable development can be divided into ecological, economic, and social sustainability. The objectives of ecological sustainability include preserving the integrity of ecosystems and acting in accordance with the precautionary principle. (Ministry of the Environment, n.d.) An example of ecological sustainability of Finland efforts is the PFASs in the Vantaa River, funded by the Ministry of the Environment, which was implemented between 1st May 2020 and 30th October 2021. The short-term objective of the project was to investigate the spatial and temporal distribution of PFASs and the role of different emission sources in the Vantaa River basin. A long-term goal was set, for example, to ensure a safe source of raw water for local needs. (Junttila et al., 2021, p. 8)

Economic sustainability is the basis for a sustainable economy that seeks to safeguard the essential functions of society. Economic sustainability can be seen as the starting point for social sustainability. For example, The Cost of Inaction, a socio-economic analysis carried out by the Brussel-based company Milieu Consulting, assesses the environmental and health impacts of PFASs and their associated costs. According to the results of the analysis, the costs are estimated to be between 2.8 billion euros and 4.6 billion euros per year in the Nordic countries between 52 billion euros and 84 billion euros in the EEA countries. (Goldenman et al., 2019)

2.5.1 Connection of pPFASs with humans and the environment

PFASs degrade very slowly in the environment due to their persistent carbon-fluorine bond, which is why they are also known as “forever chemicals”. Their environmental degradation,

toxicity and absorption into humans are affected by structural differences between PFASs. The most widely used and studied PFAS are the non-polymeric perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). (EPA, 2023) PFASs are used in a wide range of industrial products, for example because of their grease, dirt, and water repellence. Some of the most common applications have been Teflon pans, ski wax, fire-fighting foams, and floor waxes. (Eurofins, 2022; Saavalainen, 2023; THL, 2022)

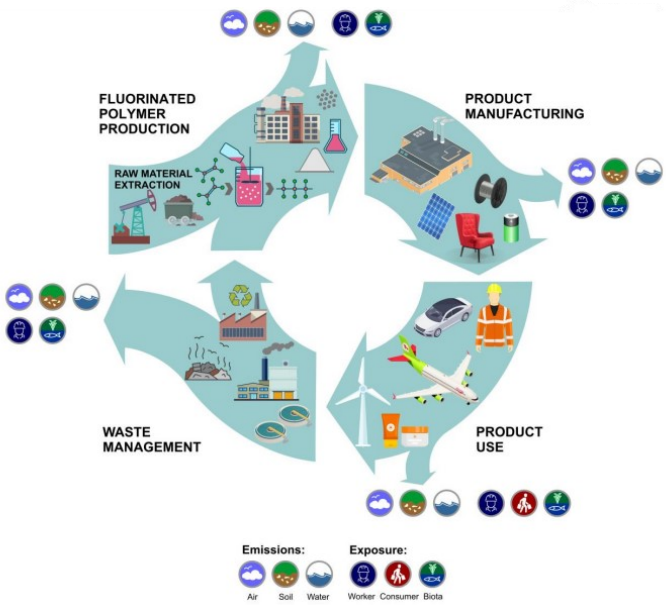
Although plastic that ends up in the environment may contain contaminants, almost no attention has been paid to studying the impact of, for example, plastic type, time, and the degree of adsorption of contaminants. A study commissioned by the University of Illinois and the Annis Water Resources Institute investigated the interaction of PFASs and microplastics under field and laboratory conditions. The field experiment investigated the migration of PFASs from different grades of microplastics in a lake environment. The study found that three plastic materials (PE, PP, PET) adsorb PFASs in the aquatic environment. In the field, the materials were found to have a higher adsorption capacity than under laboratory conditions. (Scott et al., 2021, p. 1)

From a sustainable development perspective, it is possible that without limiting PFASs, future challenges will include a lack of clean water and declining fish stocks. This in turn would lead, for example, to the depletion of livelihoods of fishermen. PFASs have been found to be harmful to human health, which means that unrestricted use in the future could lead to an increase in human illnesses, which in turn can lead to health service overload and labour sufficiency issues. Another effect might be an increase in climate change because PFASs production is associated with strong greenhouse gas emissions. (Perkins, 2021; Perkins, 2023)

Humans can be exposed to PFASs through many different routes, such as the environment and consumer products, but also through packaging materials and process equipment in food processes. (Finnish Food Authority, 2021, p. 33, 55; Finnish Food Authority, 2023; THL, 2022) From an environmental perspective, PFASs can enter wastewater treatment plants from sources such as domestic and industrial sources. The wide range of uses of PFASs contributes to their release into drains and the environment. (Nacwa, 2022, pp. 1–2) Their life cycle can be thought of as starting with the production of PFAS polymers such as PTFE (Teflon). The next

step in the life cycle is the use of a product containing a PFAS such as a Teflon pan, after which the product is disposed of and ends up in waste treatment. During these life cycle stages, PFAS emissions are released into the environment as illustrated in the figure 10 on text page. (Figure 10) According to ECHA, 75,000 tonnes of PFASs were emitted in 2020 from PFAS production and use alone, without considering waste treatment, as there is insufficiently accurate data available. By ECHA, over the next thirty years, 4.4 million tonnes can be expected to be released into the environment if emissions are not addressed. (ECHA, n.d.-a)

Figure 10 PFASs cycle (EEA, 2021)



The production of some fluoropolymers can be linked to the use of PFASs as polymer processing aids. Some fluoropolymers (for example granular PTFE) produced by suspension polymerization do not require the use of PFASs-based polymer processing aids. In contrast, other fluoropolymers (like fine powder PTFE) are produced by emulsion polymerization using PFAS-based polymer processing aids. (Lohmann et al., 2020, pp. 12820-12821)

During the synthesis of fluoropolymers, the residues of oligomers, polymers and smaller polymers are formed because of incomplete polymerization, and they are known to have a maximum of approximately 100 monomer units. (Lohmann et al., 2020, pp. 12822) For example, it is these by-products that can be released into the air during processing, as they are not bound to the polymers. (Newton et al., 2017, pp. 2, 7) However, more research is

needed on airborne fluoropolymer emissions, that is oligomers and particles. (Lohmann et al., 2020, pp. 12823) The study found that the migration of PFASs was higher in the controlled field than in the laboratory experiment with only plastic and water present. This suggests that the migration of PFASs in microplastics is strongly influenced by the presence of inorganic and/or organic matter in the environment, which in turn may threaten aquatic biota. (Scott et al., 2021, p. 1)

Fluoropolymers make it also possible to achieve energy savings and support recycling. Among other things, fluoropolymers enable to promote product sustainability, thereby extending the life cycle of products, saving resources, and preventing the generation of excess waste. For example, fluoropolymer sealants are used in many industrial sectors to prevent leakage. (PFP, n.d.-a)

It should be noted that fluoropolymers are stable and of high molecular weight, which means that they are unable to penetrate biological membranes, which means that the potential for environmental and human exposure can be considered low. Fluoropolymers are not long-chain PFASs like PFOA or PFOS, nor do they have the potential to transform into these types of substances in the environment. (PFP, n.d.-b)

3 Practical part: Methods and materials

The practical part of the thesis can be divided into three parts, namely a survey for raw material suppliers, testing of raw materials and product development interview with the subscriber company. The survey to suppliers was to find out their awareness of the pending PFASs proposed restriction, as well as the possible connection of PFASs to raw materials. The aim of the survey was to contribute to answering the research question on possible sources of PFASs. The purpose of the testing of the raw materials was to determine their fluorine content to find out whether they contain fluoropolymers that belong to the PFASs group. The experimental part also included a discussion with the product development department of the subscriber company to further clarify the role and connection between PPA, mPE and MB as well as future perspective of using PPAs.

3.1 Survey

The survey was a three-page questionnaire that was created and sent to suppliers to determine their awareness of the ongoing PFASs restriction acts in US and Europe, as well as the content of PFASs in their products. Data collection started by collecting information from the purchasing department of subscriber company on all materials for 2022. The target set was limited to polyolefin-based materials. This delimitation was further reduced by purchased materials, or more than five tonnes for main types (the others being trials and test materials) and more than half tonnes for masterbatches and other functional materials. The data basis for questionnaires consisted of 26 suppliers and 185 materials.

In addition, the survey response was used to examine the consistency between the states of suppliers and the results of the TOF analysis of the granulates. The questions asked in the questionnaire were:

1. Awareness of EU-wide PFAS restriction proposal and of the new US state PFAS regulations
2. Presence of fluorine-based substances in product supplied to subscriber company
3. Details of substances defined as PFAS, like chemical identity and concentration
4. PFAS removal plan

The entire questionnaire can be found in Appendix 1.

3.2 Laboratory tests

3.2.1 Materials

The testing of raw materials was started with the searching of polymer processing aid (PPA) and metallocene polyethylene (mPE) samples from warehouse of local plant. This was done using the factory system of subscriber company called SAP, which shows, among other things, the number of raw materials in stock. After that, what PPA and mPE raw materials could be found in different batches. This was done to compare the same raw material from different

suppliers, as well as the result variation of the batches of the same material and the result variation between three different laboratories.

Normally, the factory stock of the thesis commissioner consists of different raw material batches. In general, raw materials are used based on a FIFO method (first in, first out), and according to customer orders. On the other hand, the availability of raw materials also varies, which in turn affects the number of batches in stock. Therefore, alternative raw materials are also important to ensure continuity of production. Granulate samples were collected in separate Minigrip bags marked with the sample material number, name, batch number and date as illustrated in the figure below. (Figure 11)

Figure 11 Part of the samples collected

The PPA and metallocene samples found in the stock were listed as shown on the table below. (Table 1, p. 22) Because more detailed information of the materials, such as name and batch number, are not allowed to be published, code names were invented for them in this thesis. That was done by combining the material name and the batch number, for example mPE1:Batch1 and mPE2:Batch2.

Table 1 Table of granulate sampled collected for TOF analysis

Plant	Material number in SAP	Code name	Code batch	Amount (kg)	Supplier
plant code	material number in SAP	mPE1	Batch 1	quantity in stock	name of supplier
			Batch 2	quantity in stock	
			Batch 3	quantity in stock	
plant code	material number in SAP	mPE2	Batch 1	quantity in stock	name of supplier
			Batch 2	quantity in stock	
			Batch 3	quantity in stock	
			Batch 4	quantity in stock	
plant code	material number in SAP	mPE3	Batch 1	quantity in stock	name of supplier
plant code	material number in SAP	MB1	Batch 1	quantity in stock	name of supplier
			Batch 2	quantity in stock	
			Batch 3	quantity in stock	

The choice of the raw materials to be sent for the TOF analysis was influenced by the volume of the raw material and its significance for extrusion within the sample Metallocene 2 (mPE2). Sample Metallocene 1 (mPE1) was chosen to represent the reference sample because according to its supplier mPE1 is PPA free. Metallocene 3 (mPE3) was chosen because it was available from stock and had a relatively high PPA content. Masterbatch PPA 1 (MB1) was chosen to represent the PPA raw material because it is one of the most essential material used in the factory's extrusion process of its plastic film recipes.

3.2.2 Laboratories and methods

The TOF analysis could not be performed in laboratory of plant, so external laboratories had to be contacted. The work started by identifying laboratories carrying out the TOF analysis. The factors influencing the laboratory selections were the costs and accessibility of the TOF analysis. Since beginning 2023, laboratory A offered the TOF analysis with expectable price and detection limit, which should be maximum 20 % below the proposed legal limit or 50 ppm. Most samples were sent to this lab. Shortly after the publication of the proposal, other laboratories were building up suitable methods and lowered their detection limit. In spring 2023, laboratory B was available. After recognising high difference between laboratories A and B, laboratory C was chosen as a third laboratory. Communication with the laboratories was sometimes quite slow, and it took two to four weeks to receive the results of the laboratory tests.

The TOF analysis was used to analyse the granulate samples, as it allows the fluorine content of the granulates to be determined. The analysis of the samples was carried out using a robin round test, also known as an interlaboratory study (ILS), that is an experimental method with aims to determine the reproducibility of a process. It involves running tests several times and then using statistical analysis to assess the variability of the results. (Attia, 2022) The process can be a measurement method such as TOF analysis in this work. (Moylan et al., 2016)

Before sending samples to laboratories, a customer form had to be sent for the details of company to be entered into their client system. The samples were then sent in Minigrip bags, tightly packed in a cardboard box, to laboratories A and B. The sample bags were clearly labelled with the sample information, or material and batch number, name, and sample number, such as one or two. A quotation form and a sample list with careful listing of the samples and their details were also printed with the consignments. Samples were sent three times within two months. The choice of raw materials to be sent was influenced by available batches and previous results.

Later it was decided to send a sample of the materials mPE1, mPE2 and MB1 to laboratory C, because there was a significant variation between the results of laboratories A and B. The samples were tested in the company's own laboratory facilities, except for laboratory A, where samples were analysed in the laboratory of the subcontractor. Laboratory C was the only laboratory that did not use grinding as a pre-treatment method.

Laboratories reported the fluorine content of samples in mg/kg of raw material or as a percentage, when the measurement limit is 0.001 % or above. It was known that one percent equals 10,000 mg/kg, so the percentage value was converted to parts per million (ppm) by multiplying by 10,000 mg/kg. At the end, the ppm-values of all samples were compiled on the same table. In addition, the name of the laboratory, the date of sample sending and the date of receipt of the result were recorded. Table 2 on next page illustrates the basic idea of result table. This made it possible to follow the progress of the analysis of the samples. Because more detailed information of the materials, such as name and batch number, were not allow published, so code names were invented for them in this thesis.

Table 2 Model of the result table

Material number in SAP	Code name	Code batch	Plant	Laboratory	Report Nr.	Sample sent	Result arrived	TOF result (ppm)

3.3 Product development interview

The interview was conducted as a thematic interview, with the topic chosen in advance focusing on the function of polymer processing aids (PPA) in film extrusion. In addition, from a product development perspective, there was a desire to discuss PPA substitution and possible alternatives. The interview also had the characteristics of an open interview, as it was conducted in a conversational style. In addition, the aim was to confirm and refine the previously collected literature, which still had some gaps, that is, questions left unanswered. (Eskelinen & Karsikas, 2012, p. 86) The interview questions were:

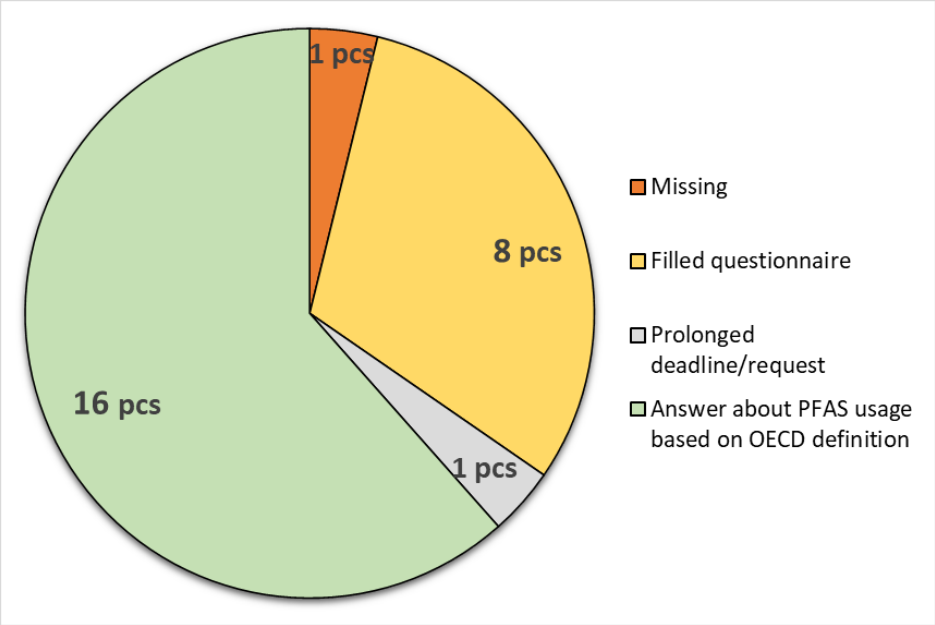
1. What is the role of PPA in the functioning of extrusion?
2. Can PPA be somehow replaced, or the manufacturing even run without it?
3. What is the connection between metallocene and PPA?
4. What is the function of the masterbatches in the extrusion process?

4 Results

4.1 Survey

Almost all, 90 %, of the suppliers (24 of 26) sent in their answers. At the time of writing this thesis, one supplier had not responded at all, and one supplier had asked for a longer response time. The figure below categorises the supplier responses. (Figure 12, p. 25)

Figure 12 Categorised survey responses of the suppliers (pcs = number of responses)



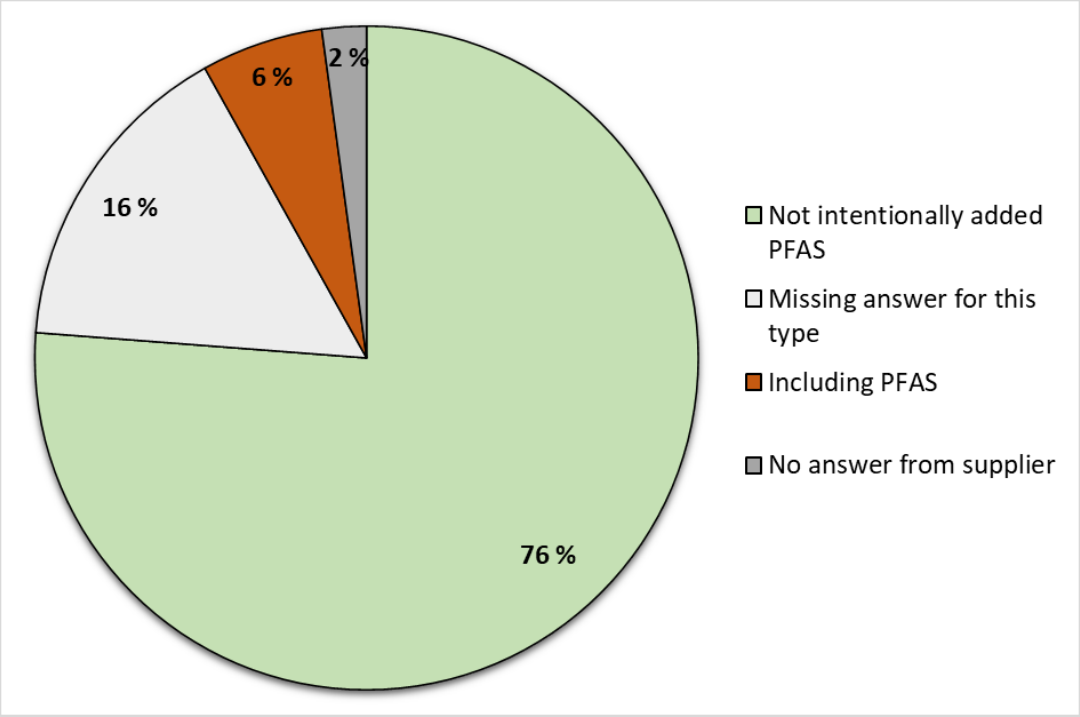
Around 30 % of the suppliers answered by filling the sent questionnaire. 60 % of the suppliers answered with sufficient own statements without filling the questionnaire. Sufficient answers were considered to contain detailed information on potential PFASs use. The table below shows two examples for a sufficient answer. (Table 3)

Table 3 Examples of sufficient answers

EXAMPLE 1	EXAMPLE 2
• *As per your request, we can confirm that in the production of our materials in ref. the following substances or class of substances, are not intentionally used:* ○ *PFAS* • *From the foregoing we can confirm that there is no reason that said substances may be found in the a.m. materials as supplied in original packaging, however we do not analyze for these spesific substances or compounds.*	• *The folllowing substances are not expected to be present in this Product. We may not specifically analyze for the presence of these substances in the Product. Therefore, we cannot guarantee the absence of level of these substances to any spescific limit or thereshold value:* ○ *Perfluoroalkyls (PFAS)* ○ *Perfluorooctane sulfonate (PFOS)* ○ *Perfluorooctanoic acid (PFOA)*

The figure below shows the outcome of the survey totally related to 185 materials supplied by 26 suppliers. (Figure 13, p. 26)

Figure 13 Outcome of the survey based on materials

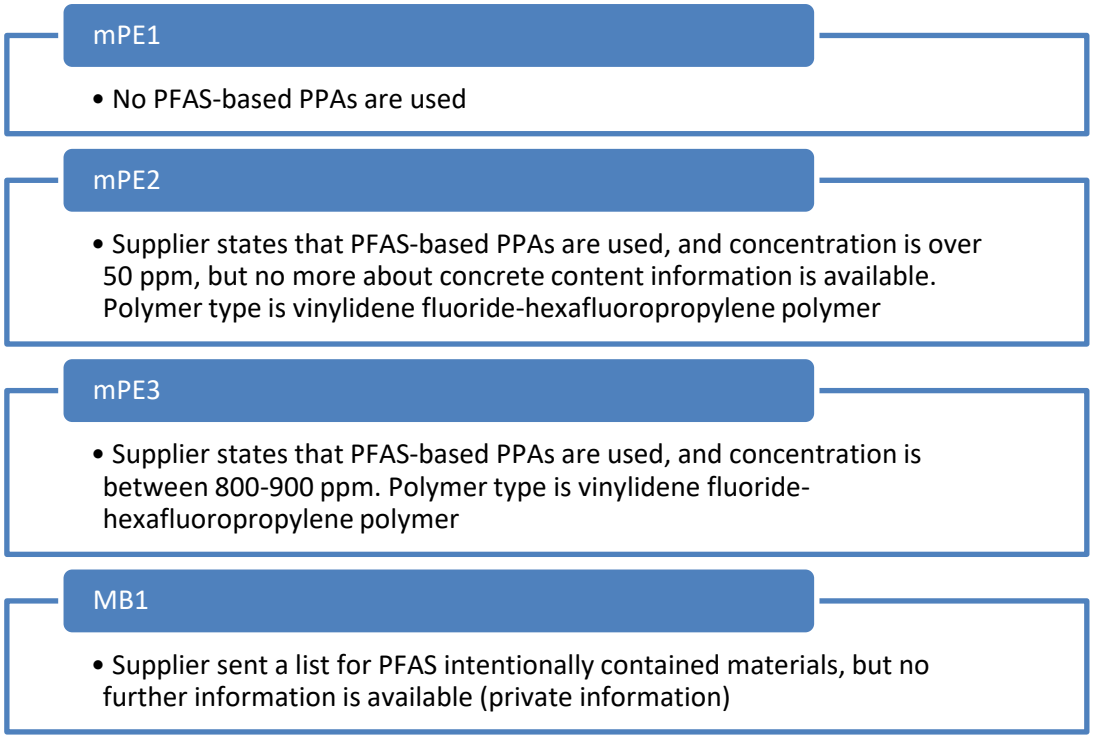


Some of the suppliers could answer for all their products without listing the material names in detail, because they do not use PFASs at all in their production. Some suppliers, who have products with PFAS in their portfolio, named the material types in their answers.

For 76 %, that is 139 out of 185 materials, there was a clear indication that PFASs are not intentionally added. However, exact the PFASs contents had not been tested so the result of this question cannot be verified. For 16 %, that is 29 out of 185 materials, the suppliers answered insufficiently. Most of these materials do not belong to the standard portfolio of the supplier at all or they are not purchased on regular basis by the company. Only 2 %, that is 4 out of 185 materials, were affected by not answering of the above mentioned two suppliers. For 6 %, that is 11 out 185 materials contain fluoropolymers according to answers of suppliers. These products are two masterbatches, eight metallocene types and one ethylene vinyl alcohol (EVOH), which is the real new information.

Figure 14 on next page extracted the answer of the suppliers for the four materials which are used for the evaluation of the TOF method (see Chapter 4.2).

Figure 14 Survey responses from suppliers whose materials included in the TOF analysis

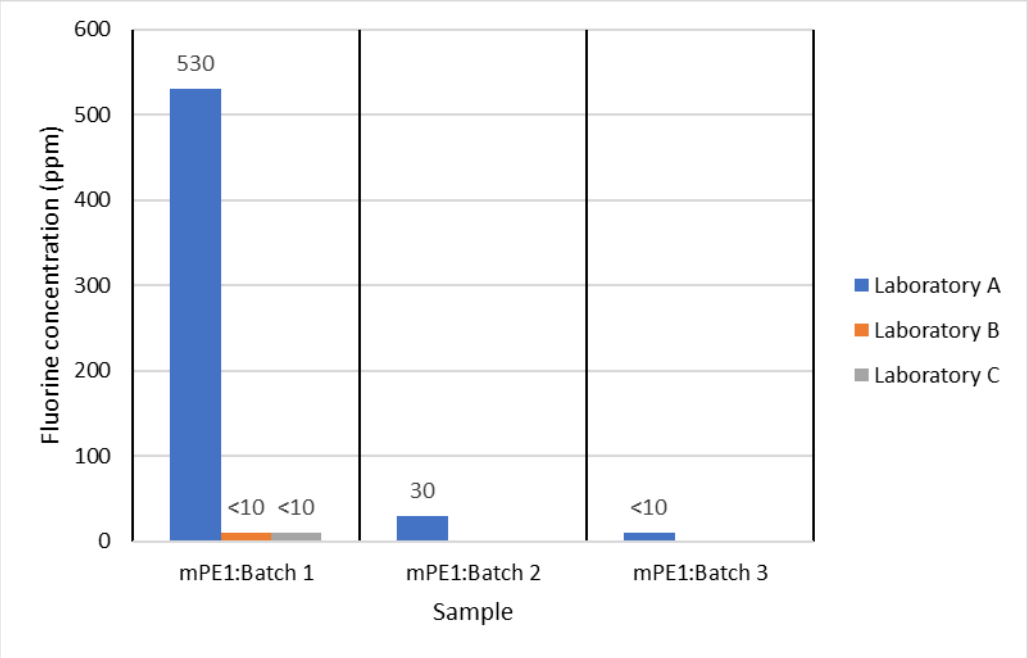


4.2 TOF analysis

The total of four samples, three metallocene types and one masterbatch, were selected for the TOF measurement. Three laboratories were used, and all of them had a detection limit of 10 ppm. The results of the TOF analysis of samples of three metallocene and one masterbatch are presented on the table in Appendix 2.

Table 4 on next page shows result for selected blank sample, or a metallocene without fluoropolymer according to supplier information. This Metallocene 1 (mPE1) was used as negative reference to exclude false positive results.

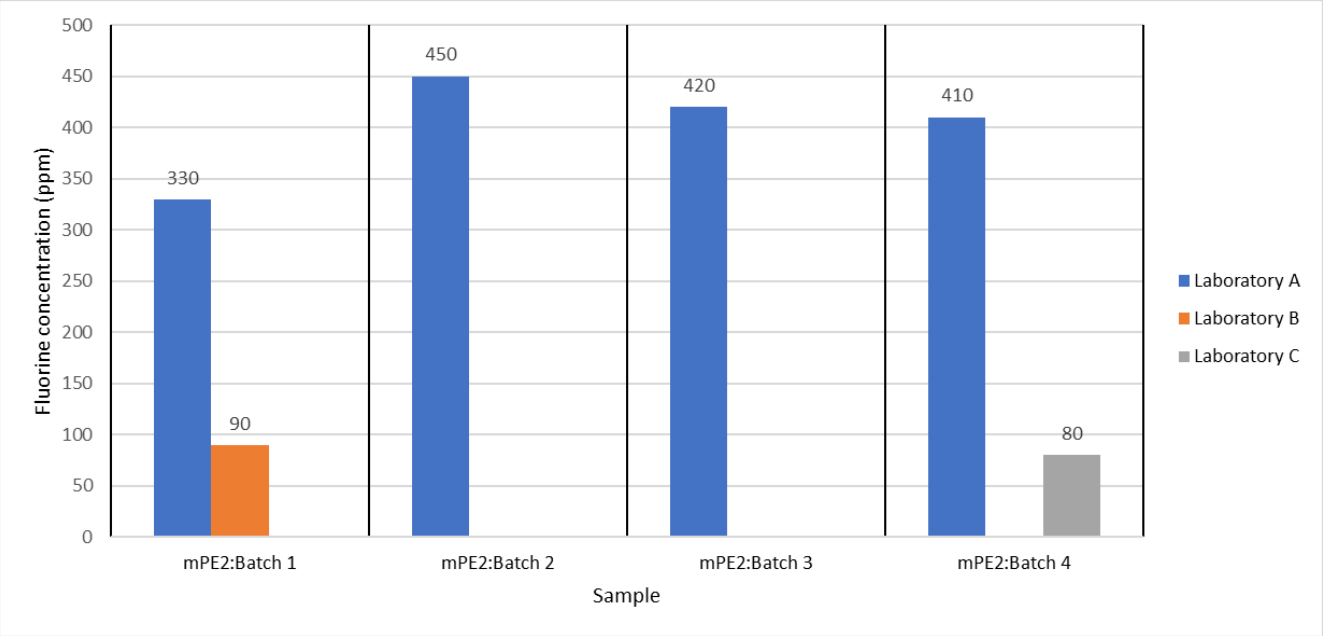
Table 4 TOF analysis result of Metallocene 1 (mPE1)



Three batches were analysed by laboratory A and one batch also at laboratories B and C. The results from these two laboratories show that fluoropolymer is not present. Laboratory A has got strongly varying results, from below detection limit, over low concentration of 30 ppm and high concentration of 530 ppm.

Table 5 on next page shows the results for Metallocene 2 (mPE2). Four different batches were analysed at laboratory A. The other laboratories analysed only one of these batches, but not the same ones. Due to time shift between the orders, batch 1 was not available anymore for laboratory C.

Table 5 TOF analysis result of Metallocene 2 (mPE2)



This stage of the analysis was planned to find out the inter-batch variance. The range between the batches is 330-450 ppm. Laboratory B analysed batch 1 and laboratory C analysed batch 4. Both laboratories found significantly lower results and the results matched better together. Difference between batch 1 and 4 at laboratory A is 80 ppm (24 %) related to batch one, only 10 ppm (11 %) based on results of laboratories B and C.

Table 6 on next page shows the results of Metallocene 3 (mPE3), for which only one batch was available, but the concentration of the processing aid was known (800-900 ppm). Difference between the batch 1 is 282 ppm (46 %) for laboratory A values and significant lower value at laboratory B.

Table 6 TOF analysis result of Metallocene 3 (mPE3)

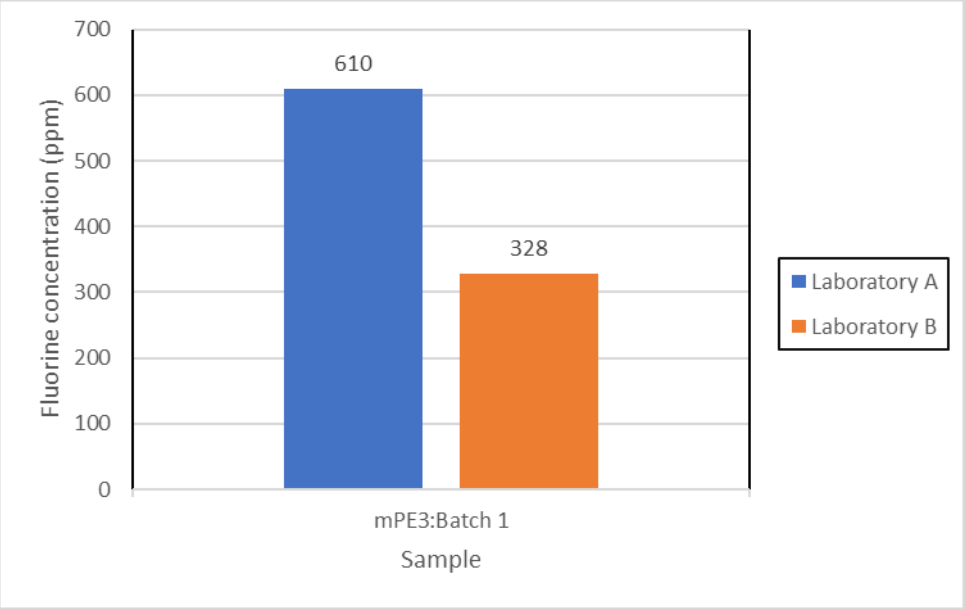
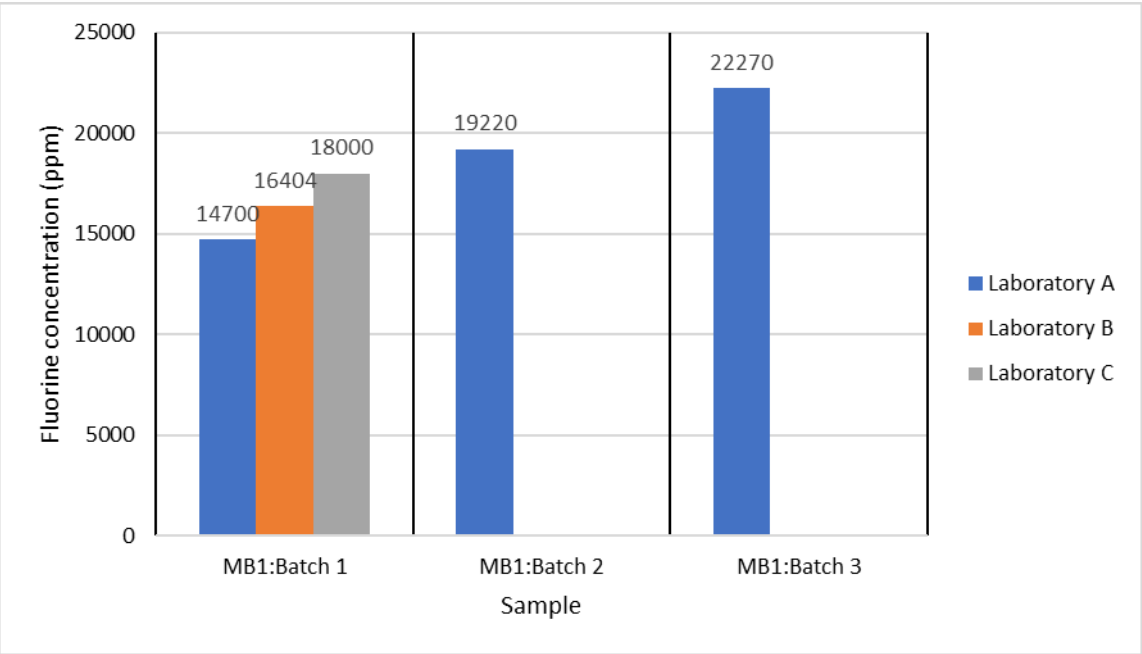


Table 7 shows results for the Masterbatch PPA 1 (MB1) containing around 50 times higher fluoropolymer concentration, which leads to new challenges at the laboratories. In case of batch 1 laboratory A measured this time lowest values. All together there are no significant differences between the values.

Table 7 TOF analysis result of Masterbatch PPA 1 (MB1)



4.3 Product development manager interview

The production development manager's interview confirmed that the use of polymer processing aid (PPA) in the extrusion process has positive effect on the optical quality of the film and, PPA perform as the so-called process lubricants when reducing shear rate between molten polymer and metal surfaces. It is known that without PPA, some polymer types have higher tendency for surface defects due to flow properties or by accumulation of carbonized polymer on die lip (die built up) which causes stripes on film surface. As mentioned, without PPA, the die lip can be more prone to build-up of degraded material, causing more frequent cleaning of the die lip, which in turn causes additional production stoppages. In addition, PPA reduces friction between the polymer and the metal of the extrusion machinery, resulting in reduced process pressure, which in turn can enable higher process output. PPA additive is normally blended into process continuously with low dosage. In some situations, like production start-ups a higher PPA amount may be feed for a short period, and the feed rate reduced later once stabilized process achieved. A lower feed rate also reduces raw material costs.

In the plastic manufacturing process, the processibility of metallocene has been found to be challenging which is why fluoropolymer is added to improve processibility it. For example, thin films are run with a reduced die lip track, which has been found to result in depredated material accumulation if mPE is used without PPA. As mentioned in the 2.2.1, masterbatches are concentrated additive granulates. They are manufactured by compounding process, where additive is blended into desired carrier material with the required concentration. The process is similar to plastic film extrusion, where the plastic granulates are melted in an extruder and then processed back into a solid form, or a plastic film.

Based on the product development interview, it can be concluded that PPA has an essential impact in extrusion, for example on film quality and production flow. With PPA, it is possible to save on material waste and labour costs. On the other hand, it also turned out that it cannot have too much PPA either. This can lead to similar problems as without it, but also to unnecessary costs. Some suppliers are developing PFAS-free PPA but testing the suitability will have to be done in trials. The interview was considered to strengthen the theoretical basis,

filling the gaps in which the interview thus provided answers. The reliability of the interview was also confirmed by the fact that the answers could also be found in official sources.

5 Discussion

5.1 Knowledge transfer through supply chain

The survey outcome has its pros and cons. Positive is in total the high response time demonstrating high awareness of the PFASs problem at stage of suppliers. All of them are familiar with the OECD definition of PFASs. Negative is, that all suppliers stating the absence of PFASs have the disclaimer, that the absence is not verified. The method survey is only accepted by 30 % of the suppliers, which is less than expected. Most of 60 % do not use the form referred to their company rules. The filling of customer forms is not allowed, due to special checked answers by lawyer and time-consuming work.

The survey indicates that suppliers avoid answering the questionnaires. The sensitivity of the topic may have influenced this, as much is going on. It is also possible that the questions were too direct, and suppliers are wary of providing too much detail. Concerning the outcome for the materials, it can be highlighted that only one material until today has got surprisingly PFAS included. It is not metallocene and no specific PPA MB, it is an EVOH type, which is used as an oxygen barrier. The high number of 29 missing materials elucidated that it would have been better if a list of relevant materials type had been integrated into the questionnaire. The mPE1 was selected as negative reference for the TOF measurement since the supplier stated that no fluoropolymers are used in processing aid.

A comprehensive response was received from the supplier of mPE2 that it contains compounds identified as a fluoropolymer (a copolymer of vinylidene fluoride and hexafluoropropylene), and non-fluorine containing alternatives are being evaluated. Missing information about concentration does not enhance the evaluation of the different TOF value measured by the laboratories. The supplier of mPE3 gave most detailed information. However, identity and concentration of the fluoropolymer were disclosed. The supplier of MB1 gave an answer, which reveals PFAS intentionally contained materials, but more detailed information

belonged only to the supplier. Therefore, it is not possible to know whether alternative raw materials are being developed for fluorine containing raw materials.

In conclusion the response of this survey helps subscriber company contact their suppliers for concrete PFAS substitution discussion and provide them the basis for answers to their customers. Knowing the affected materials helps to find affected laminates in their portfolio.

5.2 Fluoropolymer concentration of granulates

TOF analysis figures show large variation between results and laboratories. Laboratory A has clearly obtained higher results for mPE1, mPE2 and mPE3. In contrast, the MB1 sample results are better aligned between different laboratories. From the blank reference, it should be noted, that laboratory A has got one very high false positive result for batch 1. It is not known in which order the samples were analysed in the laboratories. It is possible, for example, that a contamination occurred at laboratory A during the analysis after which contamination residues ended up in the following samples. Contamination is possible at sampling stage, in case there are some other granulate pieces present in the sample, so that it is not homogenic. Since laboratory A took only two to five granulate pieces per single analysis, this would have a high influence. But also, all other steps of analysis could reason for contamination like not totally cleaned glassware. The situation is being worked out with laboratory A, so no clear explanation can be given for the variation in the results.

High inter-batch and inter-lab variance of sample mPE2 is also difficult to clarify. Since the supplier do not disclose the real concentration and their expected variance, statement about correctness of the values from laboratory A could be not proven, but it seems possible. It is expected that a dosage of a processing aid during production of a granulate would lead to a deviation more than 10 %. Especially, since laboratory A is analysing individual granulates per single measurement. Both other laboratories were homogenising via cryo mill around 50 g of granulate before placing an aliquoted of this to the oxygen bomb.

Discussing the four to five times higher result between laboratory A on the one side and both other laboratories on the other side, multiple scenarios are possible. Laboratory A was correct

because a loss of analytic is more likely than finding more. But on the other hand, problems in ion chromatography like co-elution of fluoride ion with something else would lead this systematically higher values.

The situation is the same for mPE3, but not so intensively, as the multiplication factor between the values is only less than two. All measured values are reliable, they are below the disclosed concentration. A loss of fluoropolymer is expected, some PPA stick on extruder walls and the fluoropolymer contains beside F-atoms also carbon and hydrogen atoms which lowers the TOF concentration.

Based on the results of laboratory tests carried out under the guise of this thesis, the TOF analysis cannot be considered a reliable method for determining the PFAS content of plastic granulates. The validity of the TOF analysis, or its ability to measure what it was intended to measure, is valid, or it was able to determine the fluorine concentrations in the granulate samples, which in turn is related to the PFASs. (Eskelinen & Karsikas, 2012, p. 132) However, it can be decided that the reliability of the TOF analysis, or the reliability of operation and availability, is affected by random errors such as contamination and conditions of environment. (Eskelinen & Karsikas, 2012, p. 133) This conclusion can be justified by the following observations:

- variable results in TOF analysis
- differences in the operation of laboratories (on in three laboratories did not use grinding as a pre-treatment and one laboratory carried out the analyses in its subcontracted laboratory)
- more samples are needed to draw more comprehensive conclusions.

The validity of the results is weak, or they cannot be generalised outside the sample of this thesis. Factors influencing this are the small amount of available granulate batches.

6 Conclusions

Concluding literature and practical research of this thesis following answers can be given to the six formulated research questions:

1. What are PFASs related to chemical properties?

Per- and polyfluoroalkyl substances (PFASs) are a group of industrially manufactured chemicals, which contain at least one fully fluorinated methyl- or methylene group. They are used in many applications due to their outstanding physical properties like mechanical strength, inertness, and anti-stick function. The copolymers of vinylidene fluoride and hexafluoropropylene is the most used fluorinated processing aid in plastic packaging films. Besides the high bandwidth of positive properties man-made PFASs have also many negative effects, ahead of all persistence in environment. Several sources and extreme resistance carbon-fluor-bonding give them the name *forever chemicals.*

2. Why do PFASs exist in plastic food packaging?

PPAs based on fluoropolymers are commonly used in the production of polyolefins, as their use as a processing additive is approved by Commission Regulation (EU) 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food. The rheological properties of metallocene plastics, such as viscosity, can be controlled by a PPA, and therefore the fluoropolymer may end up in the metallocene plastic. MBs are manufactured by concentrating or adding a desired additive to a compatible carrier polymer. MB PPAs, as the name implies, contain polymer processing aids.

3. What kind of limits and bans are there in EU and US?

In January 2023, the European Chemicals Agency (ECHA) received a proposal from Denmark, the Netherlands, Germany, Sweden, and Norway for restrictions on the whole group of PFASs. The proposal is one of the widest restriction proposals in Europe and is based on issues such as the impact of PFASs on human health and the environment, and emissions from the life-cycle stages of PFASs. The proposal foresees a transitional period of 18 months from entry

into force and two exceptional transitional periods of five years and 12 years. Acceptable limit of total organic fluorine will be 50 ppm.

By July 2022, six states had passed legislation to regulate the appropriate use of PFASs in flexible food packaging. These laws were due to enter into force between the end of 2022 and the beginning of 2024. However, these laws were not intended to prohibit the total use of PFASs. From 1st January in 2023, the State of California banned the use of PFAS in plant fibre-based food packaging that contains or has been deliberately added to 100 ppm as defined by total organic fluorine (TOF). (Rackl et al., 2021) In addition, the State of Rhode Island was meant to ban the manufacture, sale, and distribution of food packaging in the state as of 1st January in 2023. The ban includes food packaging with intentionally added PFASs, which also includes polymer processing aid (PPA).

4. What are the commonly known sources of PFAS?

By spreading survey through all relevant polyolefin suppliers, a comprehensive overview about usage of PFAS in raw materials could be reached. The usage of this PPA is limited to metallocene types and special PPA masterbatches.

5. How reliable is the TOF analysis for determination PFAS?

The TOF analysis showed large variation between results and laboratories. Based on the results of laboratory tests carried out under the guise of this thesis, the TOF analysis with method EN 15408 cannot be considered a reliable method for determining the PFAS content of plastic granulates. The validity of the TOF analysis, or its ability to measure what was wanted to, was tenable. That is, it was able to determine the fluorine concentrations in the granulate samples, which in turn is related to the PFASs.

6. Are there alternatives to raw materials containing PFAS?

The interview with product development indicates that leave-out of the PPAs is not possible due to low processability of metallocene polymers (mPE). This can be justified by the relevance of the PPA, because, for example, without it some polymer types have higher tendency for

surface defects due to flow properties or by accumulation of carbonized polymer on die lip (die built up) which causes stripes on film surface. PFAS free alternatives are in development of raw material suppliers, but no market-ready versions are available at this moment.

7 Future perspectives

As noted in the discussion, a larger sample size is needed to build a more comprehensive response. In addition to granulates, it is recommended that finished plastic films should also be tested, where the analysis could possibly draw conclusions about the extrusion machinery through pPFASs-based contaminants could end up in the sample. Analysing of plastic films would make it possible to determine their pPFASs content and thus their suitability for restrictions in some US states.

Trials without polymer processing aid and metallocene polymers with PPA are recommended into investigate the effect of that on polymer flow, production efficiency and flexibility as well as quality. Secondly, alternative raw materials that do not include PFASs are recommended for trials. As mentioned earlier, according to the suppliers, non-fluorinated raw materials are under development. PFAS-free named PPA is available from various suppliers, but more specific examples were not highlighted for this thesis because without trials and more detailed research it cannot be directly determined whether alternative raw materials are suitable for the raw materials studied in this thesis.

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Appendix 1. Questionnaire form

PFAS Questionnaire

is committed to providing the best packaging for people and planet. We are analyzing the presence of **Per- and Polyfluoroalkyl Substances (PFAS)** in product purchases from you.

Please send your confirmation letter by **April 17, 2023.**

With this questionnaire, we request PFAS-information on all polyolefin products that you supply to extrusion plants (later referred as 'us'):

Questionnaire is related to the latest developments concerning restriction or ban of PFAS.

Filled in by the Supplier:

Company name	
Address	

1. Legislation of PFAS

a. Are you aware of the EU-wide PFAS restriction proposed by the European Chemicals Agency (ECHA) in February 2023?

☐ Yes ☐ No

b. Are you aware of the new US state PFAS regulations?

☐ Yes ☐ No

2. Presence of fluorine-based substances in products supplied to us

a. Is any kind of fluorine (organic or/and inorganic) containing substance present in the product?

☐ Yes *(Please continue to questions in section 2b)*

☐ No

If no, is the absence verified by a suitable method for measuring total fluorine content?

☐ Yes ☐ No

(Since you have stated that the products supplied to us do not contain fluorine-based substances, you can skip the rest of the questions and sign the document)

b. Are any of the substance(s) used defined as PFAS?

Definition by OECD: PFASs are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e. with a few noted exceptions, any chemical with at least a perfluorinated methyl group (-CF3) or a perfluorinated methylene group (-CF2-) is a PFAS.

☐ Yes, and the substance(s):
- ☐ are intentionally added in your production process either as pure polymers or as masterbatch
- ☐ are present in the used raw material
- ☐ are possible as incidental residues or impurities

☐ No

If yes, is the structure of the substance(s)
☐ monomeric, like PFOA? *(Please continue to questions in section 3a)*
☐ polymeric? *(Please continue to questions in section 3b)*
☐ other? *(Please continue to questions in section 3c)*

If no, what kind of non-PFAS, but fluorine containing substance is used, please identify the substance(s) (please provide CAS number) and confirm compliance with specific migration limits, if applicable:

3. Substances defined as PFAS

a. Monomeric structures, like PFOA
Please identify the substance(s) (please provide CAS number) and confirm compliance with specific migration limits, if applicable:

b. Polymeric structures

i. Are identities of the used monomers available?

☐ Yes ☐ No

If yes, please state the identities (please provide CAS number) below:

ii. Is the concentration of polymeric PFAS < 50 ppm?

☐ Yes, and it has been verified by a suitable analysis method

☐ Yes, and it has been evaluated but no further testing has been done

☐ No, the concentration level is *(please state ppm level)*: ppm

☐ Not known

c. Other structures

Please state the identities (please provide CAS number) and their concentration (ppm) below, if available:

4. PFAS removal plan

Please describe the plan for PFAS removal and the targeted removal date:

Completed by:

Name	
Job title	
Email address	
Date & Signature	

Appendix 2. TOF results table

Material number in SAP	Code name	Plant	Laboratory	Report number	Sample sent	Result arrived	TOF result (ppm)
*****	mPE1:Batch 1	*****	Laboratory A	*****	3.3.2023	17.3.2023	530
*****	mPE1:Batch 1	*****	Laboratory C	*****	31.3.2023	12.4.2023	<10
*****	mPE1:Batch 1	*****	Laboratory B	*****	28.2.2023	3.4.2023	<10
*****	mPE1:Batch 2	*****	Laboratory A	*****	31.3.2023	19.4.2023	30
*****	mPE1:Batch 3	*****	Laboratory A	*****	31.3.2023	19.4.2023	<10
*****	mPE2:Batch 1	*****	Laboratory A	*****	3.3.2023	17.3.2023	330
*****	mPE2:Batch 1	*****	Laboratory B	*****	28.2.2023	3.4.2023	90
*****	mPE2:Batch 2	*****	Laboratory A	*****	31.3.2023	19.4.2023	450
*****	mPE2:Batch 3	*****	Laboratory A	*****	31.3.2023	19.4.2023	420
*****	mPE2:Batch 4	*****	Laboratory C	*****	31.3.2023	12.4.2023	80
*****	mPE2:Batch 4	*****	Laboratory A	*****	31.3.2023	19.4.2023	410
*****	mPE3: Batch1	*****	Laboratory A	*****	3.3.2023	16.3.2023	610
*****	mPE3: Batch1	*****	Laboratory B	*****	28.2.2023	3.4.2023	328
*****	MB1:Batch 1	*****	Laboratory C	*****	31.3.2023	12.4.2023	18000
*****	MB1:Batch 1	*****	Laboratory A	*****	3.3.2023	17.3.2023	14700
*****	MB1:Batch 1	*****	Laboratory B	*****	28.2.2023	3.4.2023	16404
*****	MB1:Batch 2	*****	Laboratory A	*****	31.3.2023	19.4.2023	19220
*****	MB1:Batch 3	*****	Laboratory A	*****	31.3.2023	19.4.2023	22270