

Ida Byrkjeland

Characterisation and Identification of Plastic in Marine Environments

Pyr-GC/MS and SEM analysis of marine plastics from Svalbard and Trondheimsfjorden

Master's thesis in Chemical Engineering and Biotechnology

Supervisor: Øyvind Mikkelsen

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Faculty of Natural Sciences
Department of Chemistry

Abstract

The aim of this thesis was to contribute to the field of plastic research by developing a method for plastic beach debris identification and characterisation, in addition to investigate how different polymers weather in the marine environment.

Field work was carried out at four different beaches located at the Arctic archipelago Svalbard. Plastic beach debris was collected and visually described by type and appearance. The majority of the samples were fragments (65%) and ropes (23%). The most common colours were white (27%), green (21%) and blue (18%). In addition, sampling of microplastics from the nearby beach was carried out, sieving sand from several random spots on the beaches. No microplastic was found using this method.

28 of the in total 169 plastic samples were further analysed using pyr-GC/MS, where 21 of the 28 samples were identified as high-density polyethylene and the remaining seven as polypropylene. In addition, the surface morphology was studied using SEM. SEM pictures revealed degradation signs such as cracks, fractures, grooves, pits and flaking. Due to few plastic samples, it is difficult to say if there is a connection between polymer type and degradation process. More samples should be analysed to say anything certain regarding this.

SEM was also used to study the surface of known plastic samples which had been placed in the Trondheimfjord for 19 weeks. These pictures showed high presence of biofilm. The use of pyr-GC/MS and SEM was found to be a promising combination of techniques for studying plastic beach debris. Pyr-GC/MS successfully identified all samples at a pyrolysis temperature of 700°C. In addition, at a lower pyrolysis temperature (350°C), the technique allowed for investigation of additives and adsorbed environmental pollutants in the plastic. This revealed presence of diisooctyl adipate, diethyl phtalate and dichloroaniline. However, it was a time-consuming technique which destroys the sample during analysis. FTIR and Raman spectroscopy are two other non-destructive techniques for identifying polymers. TEM is another potential technique for investigating degradation of polymers, providing 2D pictures of the surface. SEM has an advantage over TEM by capturing 3D-pictures, allowing for investigation of particles on the surface.

Samandrag

Føremålet med denne masteroppgåva var å gje tilskot til forskingsfeltet innanfor plast ved å utvikle ein metode for å identifisere og karakterisere plastavfall frå strender, i tillegg til å undersøkje korleis forskjellige polymerar forvitrar i det marine miljøet.

Feltarbeid vart utført på fire forskjellige strender på den arktiske øysamlinga Svalbard. Plastavfall frå strender vart samla og visuelt skildra ved type og utsjånad. Dei fleste av prøvane var bitar (65%) og tau (23%). Dei vanlegaste fargane var kvit (27%), grøn (21%) og blå (18%). I tillegg vart det utført prøvetaking av mikroplast på strendene, ved å sile sand frå fleire tilfeldig stadar på strendene. Det vart ikkje funne noko mikroplast ved denne metoden.

28 av dei totalt 169 plastprøvane vart vidare analysert ved bruk av pyr-GC/MS, der 21 av dei 28 prøvane vart identifisert som høg-densitets polyetylen, og dei attverande sju som polypropylen. I tillegg vart overflatemorfologien studert ved bruk av SEM. SEM-bileta avdekkja nedbrytingsteikn som sprekker, brot, spor, groper og flass. Grunna få prøvar er det vanskeleg å seie noko om samanhengen mellom polymertype og nedbrytingsprosess. Fleire prøvar bør analyserast for å kunne seie noko sikkert rundt dette.

SEM vart også brukt til å studere overflata av kjende plastprøvar som har vore plassert i Trondheimsfjorden i 19 veker. Desse bileta viste høgt nærvær av biofilm. Bruken av pyr-GC/MS og SEM vart funne til å vera ein lovande kombinasjon av teknikkar for å studere plastavfall frå strender. Pyr-GC/MS lukkast med å identifisere alle prøvane ved ein pyrolysetemperatur på 700°C. I tillegg kunne teknikken undersøkje platen for additiver og adsorberte miljøgifter ved ein lågare pyrolysetemperatur (350°C). Dette avdekkja nærvær av diiso-oktyladipat, dietylftalt og dikloranilin. Likevel er dette ein tidkrevjande teknikk som bryt ned prøva under analyseringa. FTIR og Raman spektroskopi er to andre teknikkar for identifisering av polymerar, som ikkje bryt ned prøven. TEM er ein annan potensiell teknikk for undersøking av plastnedbryting, som gjev 2D-bilete av overflata. SEM har ein fordel over TEM ved at teknikken gjev 3D-bilete, noko som tillèt undersøkjing av partiklar på overflata.

Preface

The presented master's thesis was carried out at the Department of Chemistry at the Norwegian University of Science and Technology during the spring of 2020. The thesis is the concluding assessment for the 5 years master's degree programme "Chemical Engineering and Biotechnology", and is building on a specialisation project conducted the previous fall.

Ida Byrkjeland

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Abbreviations

ETD - Everhart-Thornley Detector

FTIR - Fourier-Transform Infrared Spectroscopy

GC - Gas Chromatography

HDPE - High Density Polyethylene

LDPE - Low Density Polyethylene

MS - Mass Spectrometry

NTNU - Norwegian University of Science and Technology

PAH - Polycyclic Aromatic Hydrocarbons

PCB - Polychlorinated Biphenyl

PE - Polyethylene

PET - Polyethylene Terephthalate

POPS - Persistent Organic Pollutants

PP - Polypropylene

PS - Polystyrene

PU - Polyurethane

PVC - Polyvinyl Chloride

Pyr-GC/MS - Pyrolysis-Gas Chromatography Mass Spectrometry

SEM - Scanning Electron Microscope

TBS - Trondheim Biological Station

TEM - Transmission Electron Microscope

UNIS - University Centre in Svalbard

1 Introduction

The plastic production increased rapidly right after the Second World War[9]. Today, it is hard to imagine how the daily life would be without this material. With its light weight, durability and wide range of different properties, plastic replaced materials like wood and metal in a wide range of applications. The uses and benefits of plastic are numerous, making it one of our most important materials. But when the first study of plastic in the ocean was reported in 1972, the concern about plastic impact on the ocean started to grow[10].

Estimations show that 10% of the world plastic production ends up in the ocean[11]. Being a durable material, plastic is estimated to persist in the nature for hundreds, even up to thousands of years. Ocean and wind currents transport plastic all over the world, to remote places far away from local plastic sources. The Arctic is believed to be a global sink of pollution, and plastic has been detected all the way from the sea floor to the digestive system of the northern fulmar[12][13].

While in the ocean, plastic debris is exposed to environmental factors such as sunlight, waves, and winds, changing the properties of the plastic and breaking it down to smaller pieces. These degradation processes are observed as i.e. discolouring, embrittlement, cracks, and scratches. Different polymers are prone to different degradation paths. To improve the performance of plastics and give desired properties, additives are incorporated during the forming processes. Despite the usefulness of additives, they can leach into the marine environment since they are not chemically bound to the polymer. Some of the additives are toxic, posing negative health effects on marine organisms. In addition, environmental pollutants such as persistent organic pollutants can adsorb to the surface of microplastics. If mistaken as food, marine organisms can ingest the plastic and be exposed to high concentrations of adsorbed pollutants.

Plastic debris in the ocean acts as a new habitat for microorganisms, such as diatoms. When eco-systems develop to live on the plastic particles, it is called plastispheres. The presence of microorganisms on the particles increases the weight which might lead the plastic to sink, distributing the amount of plastic in the water column. A study done by Eunomaia states that 94% of the marine plastic litter might be on the sea floor[14].

However, there are still large knowledge gaps with respect to the distribution of plastics in the water column.

Today, the research field of plastic pollution in the ocean is growing. However, standard protocols of how to conduct plastic sampling, identification and quantification are lacking, making the comparison of results from different studies challenging. More research is needed to map how plastic pollution impacts the marine environment, and the methods need standard protocols to make the research more efficient.

1.1 Study Aim and Objectives

Following study aims and objectives were made to increase the knowledge about plastic in the marine environment:

1. Study of real-life plastic samples from Svalbard
 - Use Pyr-GC/MS to identify the chemical compositions of the samples.
 - Use SEM to characterise the surface morphology.
 - Use Pyr-GC/MS to study presence of polymer-associated substances.
2. Study of known polymer types and circumstances in Trondheimsfjorden
 - Use SEM to study the impact of marine environment on samples in Trondheimsfjorden.

2 Theory

2.1 Plastic

Polymers are substances of high molecular weights which play an important role in our everyday life. The word polymer derives from the Greek words 'poly' and 'meros', translating to 'many parts'[15]. These parts are commonly known as monomers, and a repeating pattern of monomers which are covalently bonded is what constitutes a polymer[16]. Polymers are divided in two groups, natural and synthetic. Natural polymers are occurring naturally and have existed since life began. Some examples of natural polymers are cellulose, proteins and DNA. Synthetic polymers are manmade, meaning that the polymers are artificially manufactured at the laboratory. The properties of synthetic polymers are depending on the identity of its constituent, and they can be customised for the purpose of application. Synthetic polymers are commonly referred to as plastics[17]. Table 2.1 shows an overview the most common plastics after European demand, polypropylene (PP), low density polyethylene (LDPE), high density polyethylene (HDPE), polyvinyl chloride (PVC), polyurethane(PU), polyethylene terephthalate (PET) and polystyrene (PS), with some details[7].

Table 2.1: The most common synthetic polymers listed after the European demand in 2018[7].

Name	Acronym	Density [g/cm ³]	Example of use	Demand
Polypropylene	PP	0.90	Food packaging	19.3%
Low Density Polyethylene	LDPE	0.91	Reusable bags	17.5%
High Density Polyethylene	HDPE	0.94	Shampoo bottles	12.2%
Poly(Vinyl Chloride)	PVC	1.32	Cable insulator	10%
Polyurethane	PUR	1.22-1.27	Insulating foams	7.9%
Poly(Ethylene Terephthalate)	PET	1.35	Drinking bottles	7.7%
Polystyrene	PS	1.03	Building insulation	6.4%

The first completely synthetic polymer, Bakelite, was made by Leo Baekeland in the start of the 20th century[18]. 50 years later, the plastic production increased rapidly and has since then been growing exponentially, changing our way of living. Plastics have replaced materials like wood and metals in a number of places, due to its low cost and wide range of properties. Today, the global production of plastic is 359 million tons, where Asia accounts for half of the production. In Europe, the largest end-use market is packaging

(39.9%), followed by building and construction (19.8%)[7].

Synthetic polymers are usually derived from crude oil, which has to go through several processes. The two main techniques to synthesise polymers are polymerisation and polycondensation. During polymerisation, long polymer chains are formed by bonding identical monomers together in a chemical reaction, usually by the help of a catalyst. Polyethylene is formed by polymerisation of the monomer ethylene, in the presence of a catalyst[19]. This is a highly exothermic reaction, and the process is shown in Figure 2.1.

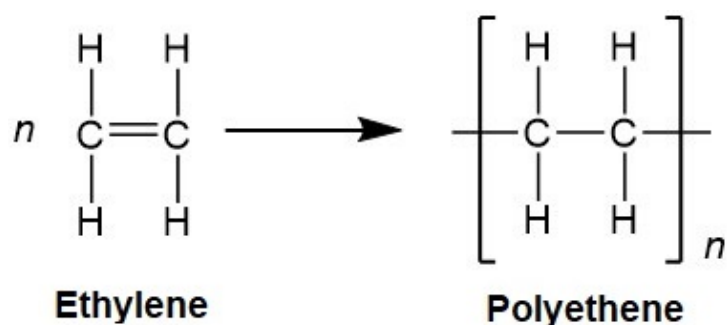


Figure 2.1: Polymerisation of ethylene to form polyethylene.

Polycondensation is the construction of long polymer chains by combining monomers with two different functional groups, eliminating small molecules such as water, alcohol or salts[20]. PET is formed by a polycondensation reaction between benzene-1,4-dicarboxylic acid and ethane-1,2-diol [21]. A hydroxy group from the carboxylic acid reacts with a hydrogen from the alcohol, releasing a water molecule and forming an ester link between the molecules. The process is shown in Figure 2.2.

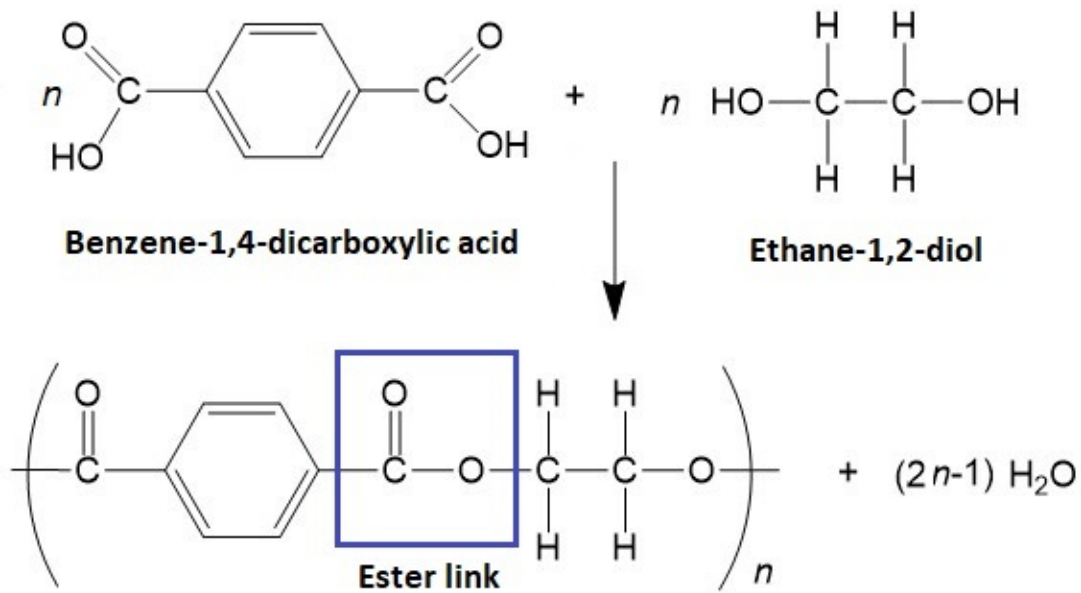


Figure 2.2: Polycondensation of a carboxylic acid and an alcohol to form PET.

Plastic can be separated in thermoplastics and thermosets, which describes how plastic acts while heated. Thermoplastics can be heated several times above their melting point without breaking down. During heating, the intermolecular forces are weakened, making it possible to reshape the plastic. After achieving the acquired shape, decreasing the temperature will strengthen the intermolecular forces again, solidifying the plastic in its new shape[22]. Example of thermoplastics are PE, PP and PS which can be found as plastic bags, bottles, and food packaging. Thermoplastic are easily recyclable, as opposed to thermosets. During the forming process of thermosets, irreversible bonds are created. If melted once more, these bonds will break, decomposing the plastic. The advantage of thermosets is that they can withstand higher temperatures and remain their strength and shape, while thermoplastics easily change during heating. An example of thermosets is car tires which are made of synthetic rubber[23].

2.1.1 Additives

Polymers themselves lack certain properties, but a wide range of chemical additives can be incorporated to the polymer to give them the desired properties and improve their

performance. Most additives are not chemically bound to the polymer but added during the polymer shaping[24]. In fact, nearly all plastics contain a certain number of additives for their purposes. Plasticisers are added to improve elasticity and durability of the plastic. UV- and heat-stabilisers are embedded to prevent degradation by UV radiation and thermal degradation, respectively. Colour is given the plastic by blending it with colourants. Fillers are used to improve the properties, but also to lower production cost. To prevent degradation by microbes, biocides are embedded to the plastic. By adding antioxidants, the overall oxidative degradation of the polymer in the presence of UV radiation is delayed[25]. Table 2.2 shows an overview of the most common additives and examples of substances[8].

Table 2.2: Different categories of additives and substance examples.[8]

Additive	Substances
Plasticiser	Diethyl esters (DEP, DIOP)
UV stabiliser	Benzotriazoles Benzophenones
Heat stabiliser	Mixed metal salt blends Organotin compounds Lead compounds
Flame retardant	Brominated flame retardants Phosphate esters
Colorants	Azocolorants Cadmium compounds Chromium compounds
Fillers	Calcium carbonate Glass fibers Carbon fibers
Biocides	Arsenic compounds Organic tin compounds
Antioxidants	Arylamines Phenolics Organophosphates

Polymers in their pure form have low toxicity since they are insoluble in water and biochemically inert. However, some of the additives that are incorporated to the plastic are toxic. Despite the usefulness of additives to enhance the plastic properties, the migration potential of additives to the environment is concerning[8]. It is documented that additives are leaching into the marine environment due to the plastic accumulation in the oceans, posing negative effects on marine organisms[26][27].

2.1.2 Presence in the marine environment

Plastic production increased rapidly in the latter half of the 20th century, at a time where the knowledge around plastic waste handling was lacking. As a result, the plastic waste has been handled improperly, leading to plastic pollution of the environment. Estimation shows that 10% of the world plastic production ends up in the ocean[11]. Plastic debris can enter the marine environment in several ways, and the major pathways are illustrated in Figure 2.3[1].

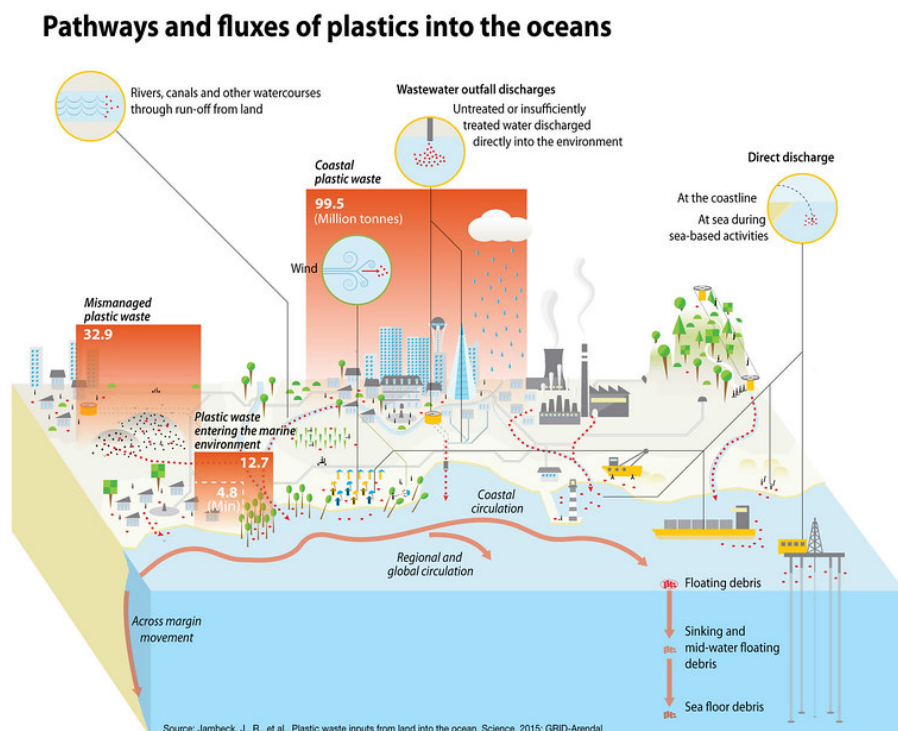


Figure 2.3: Pathways for plastic into the ocean[1].

As shown, plastic debris is dumped directly into the ocean, transported by rivers, through wastewater discharge, or blown by the wind. From there, the ocean currents can transport the plastic all over the world, and it has been found all the way from equator to the Polar circles[28]. Plastic debris is also known to get trapped in the great ocean gyres, where it accumulates over time[29]. This poses a threat on marine organisms, since plastic can circulate in the ocean for many years. In addition, plastic marine debris provides a long-lasting habitat for some algae species, some of which can be harmful to the environment, transporting them around in the ocean[30].

Some microorganisms who live on hard substances in the ocean are diatoms. Diatoms are unicellular microalgae, enclosed by a silica capsule. These microalgae can have several shapes where the two most common are radially and bilaterally symmetric[31]. Ecosystems developed to live on man-made plastic materials are called plastispheres. Benthic diatoms are microorganisms who live in the benthic zone (seabed, lakes, rivers). Plastic debris creates a new habitat for diatoms, who occur as colonies on the surfaces. Presence of diatoms on the plastic surface might cause the debris to sink, potentially decreasing the amount of plastic on ocean surface. Figure 2.4 shows SEM-pictures of the most abundant diatoms, from a study done on characterising of biodiversity of organisms on floating plastic surface[2]. These diatoms are (in most frequently observed order) *Nitzschia* (42.6%), *Amphora* (13.2%), *Licmophora* (11.8%), *Navicula* (8.8%), *Microtabella* (5.9%), *Cocconeis* (4.4%), *Thalassionema* (2.9%) and *Mindiscus* (2.9%).

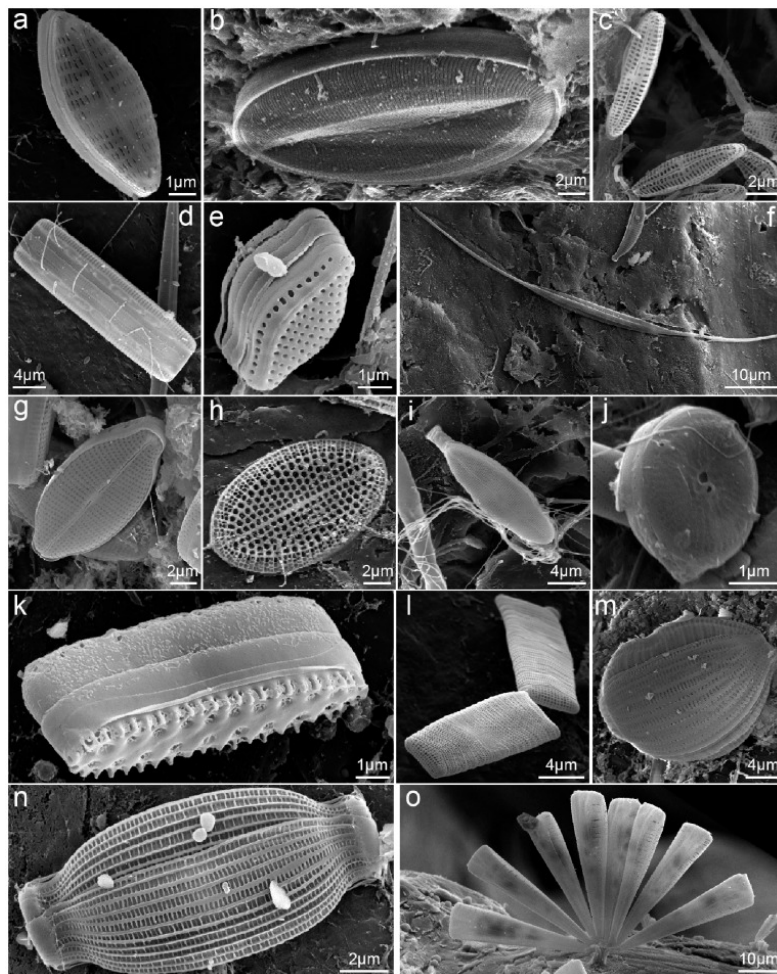


Figure 2.4: Some examples of diatoms. a: *Navicula*, b: *Mastogloia*, c: small naviculoids, d, e and f: *Nitzschia*, g and h: *Cocconeis*, i: *Achnanthes*, j and k: *Thalassionema*, l: *Microtabella*, m and n: *Amphora*, o: *Licmophora*[2].

Microplastics originates from two sources, either it is directly introduced to the environment, or it is a degradation product of meso- and macroplastic debris. According to the U.S. National Oceanic and Atmospheric Administration (NOAA), microplastic is defined as particles with a diameter less than 5 mm, and meso plastic is defined as particles with diameter above 5 mm[32]. In the marine environment, the plastic debris and the ocean are constantly interacting with each other.

Studies have observed that plastic makes up 60-80% of the marine litter[33]. On beaches, it is reported that plastic litter makes up 50-80% of the waste accumulated on beaches. Most of the plastic debris is plastic films, which are easily blown with the wind due to their light weight. Another significant source of plastic pollution is ropes and fishing equipment which are discarded from boats[34]. Plastic pollution has attracted noteworthy public attention, and beach-cleaning activities have become a popular trend to keep the beaches free from trash. Figure 2.5 shows two distribution diagrams, showing the litter composition globally and on beaches, respectively. Both diagrams reveal that plastic constitutes the majority of the marine litter. The data is collected from 1034 scientific studies done on marine litter, summarised by AWI-LITTERBASE[3].

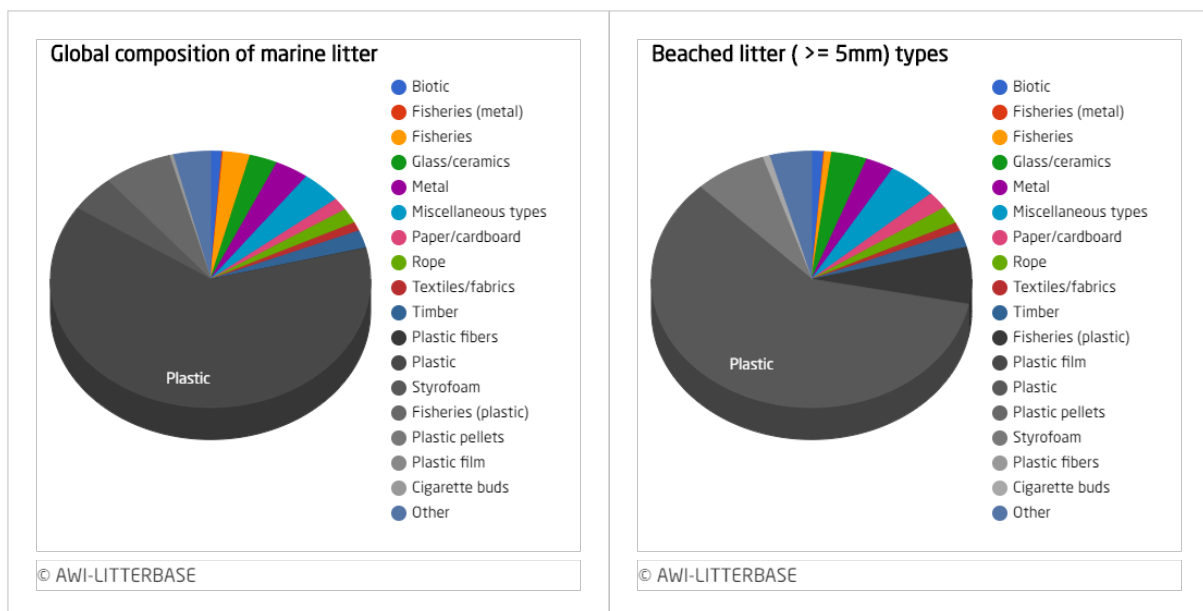


Figure 2.5: Marine litter distributions[3].

Plastic in the marine environment can be found in all parts of the water column, all the way from the surface to the ocean floor. Figure 2.6 illustrates the marine plastic

distribution in the water column, based on a study by Eunomia[4].

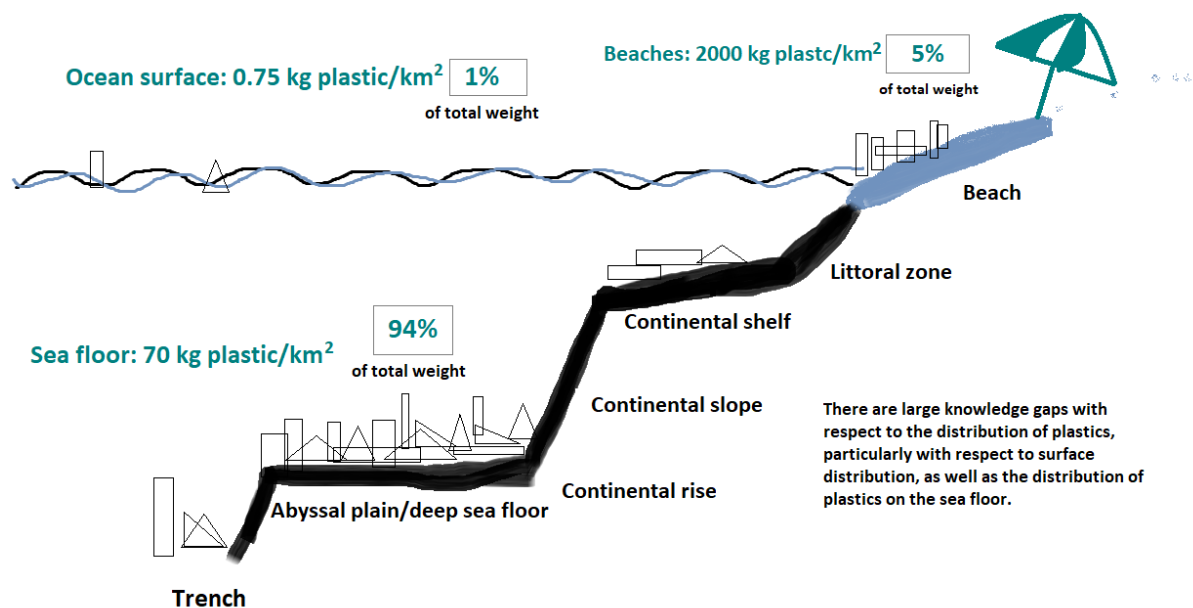


Figure 2.6: Distribution of plastics in the ocean[4].

As the figure shows, a total of 94% of the current marine plastic litter might be on the sea floor, while 5% is on the beaches, and the remaining 1% is floating on the ocean surface[14]. Plastics occurrence in the ocean column depends on the plastics density. If the density of the plastic is significantly less than the ocean water, such as PP and PE (2.1), the piece will most likely float on the ocean surface. The average ocean sea density is 1027 kg/m³ but varies with varying temperature and salinity. Plastics denser than the surrounding water will sink. However, other factors such as adsorbed particles and additives can impact the plastics and change its density[35]. Studies propose that the ocean floor is the ultimate sink for plastic debris, due to discoveries of high concentrations[36][37].

Today there are few studies done on sampling from the deep-sea sediment, since it is more difficult and expensive than studies done on the sea surfaces and beaches. More research is needed to determine the fate of marine plastic litter and its distribution in the ocean column.

2.1.3 Degradation

The advantage of plastic being durable and resistant to degradation is what makes the discharge to the environment so problematic. Plastic in the ocean is regarded to persist for hundreds of years[38]. While being transported in the ocean, the plastic weathers, changing the polymer properties and breaking them into smaller fragments. Different polymers are susceptible for different types of degradation pathways and rates. Polymers in regards of degradation can be separated into two groups, those with a pure carbon back-bone (PE, PP, PVC), and those with a back-bone containing a heteroatom (PU, PET)[39]. Degradation of plastics is observed first on the surface, which is seen as cracks, crazing, and discolouring. Cracks increases the potential of further degradation, leading to embrittlement[40]. The most common weathering processes are physical degradation, photodegradation and biological degradation, and will be further explained.

2.1.3.1 Physical degradation

During transportation in the ocean, the plastic debris weathers by several factors in the marine environment. Physical degradation happens by mechanical stress, due to energetic waves and winds. Collision with other particles such as stones and sediment will cause erosion of the plastic debris[41]. These factors cause breaking of the plastic into smaller fragments, which increases the surface to volume ratio. Physical degradation increases the plastics vulnerability for further degradation thermally and oxidative[42].

2.1.3.2 Photodegradation

Photodegradation happens when the polymer is exposed to radiation in the ultraviolet region over a longer time, weakening the bonds of the polymer. This is the primary source of polymer degradation in the outdoor environment. (Photo)oxidative degradation occurs in the presence of oxygen in addition to UV-radiation, reducing the mechanical properties of the polymer and the molecular weight. This is observed as scratches, fine cracks on the surface and discoloration[43].

An example showing the chemistry of photooxidative degradation of polyolefins is shown below[44]. In the initiation step, radiation from the sun breaks a chemical bond in the polymer back-bone (R), producing a polymer radical, shown in Equation (2.1). For this

step to occur, the polymer needs to contain an unsaturated chromophoric group which can absorb the energy. Polymers such as PE and PP do not have these, but incorporation of additives or impurities can allow for this initiation.



The formed polymer radical, R^\bullet , further reacts with oxygen in the propagation step, forming peroxy radicals, shown in Equation (2.2).



The peroxy radical, ROO^\bullet , can bond with another polymer chain, which is called cross-linking. It can also undergo chain transfer with the polymer, forming carboxylic acid and polymer radical, shown in Equation (2.3).



The carboxylic acid may undergo photolysis, giving an alkoxy radical, shown in Equation (2.4).



The produced alkoxy radical, RO^\bullet , is the key intermediate in this reaction, and can further react by different routes. One of them is reacting with the hydroxy radical, forming chain ketones.



The chain ketone can further photochemically react by Norrish type 1 or type 2 reactions, and this is where the polymer chain breaks. Type 1 reactions form carboxylic acids, esters and lactones, while vinyl unsaturation and acetone are made by the type 2 reaction[44][45]. There are many potential pathways for degradation and resulting products, and their

effectivity is shown to be depending on the type of polymer[39].

Plastic beach debris is exposed to high oxygen concentrations, sunlight, temperature, and mechanical stress compared to debris in the deep ocean or in the ocean surface. Thus, plastic on the beach is more prone to weathering processes[46]. Typical surface textures from weathered plastic can be flakes, grooves, pits, cracks and fractures[47]. Both mechanical and photo-oxidative degradation are abiotic degradations, which in general precedes biodegradation.

2.1.3.3 Biodegradation

Biodegradation is the breakdown of polymers by microorganisms and is controlled by different factors such as the plastic characteristics and type of microorganisms. A decrease in molecular weight increases the degradability by microorganisms, thus biodegradation usually occurs after other degradations. The initial step is biodeterioration, which is undesirable changes in the polymer's properties caused by microbial communities. The following step is depolymerisation, which is where the complex polymers are converted to their monomers, which are small enough to pass membranes of the microorganisms. The last step is mineralisation of the monomers, resulting in the end products CO_2 , H_2O , or CH_4 [48].

The biodegradation of polymers in the marine environment is a slow process, due to environmental factors and wild microorganisms[49]. Carbonyl groups as a result of abiotic degradation increases the polymer hydrophilicity, which improves biodegradability[50]. The rate of degradation is strongly affected by the physical properties of the plastic, such as surface area and the orientation in the ocean[51].

2.1.3.4 Studies on Degradation

Most studies done on the degradation processes of plastic are conducted in the lab without environmentally related conditions. Therefore, more studies are needed on real-life samples from the ocean surface which have been exposed to the factors of the marine environment. In addition controlled samples in the marine environment would be interesting for more realistic results.

2.1.4 Toxicity

Some of the additives incorporated to the plastic can be toxic, such as brominated flame retardants and phthalates[52][53]. Additives are usually not covalently bonded to the polymer, which means they can more easily leak out of the plastic when the plastic degrades. From here, the additives can enter the marine environment, impacting the organisms living there[54]. In addition, the released additives can be degraded to new environmental pollutants. Organic pollutants such as persistent organic pollutants (POPs) are also drawing concern. POPs are chemicals that persists in the nature and bioaccumulate in the fatty tissues of organisms, posing health risks. These pollutants can adsorb to the surface of microplastic. Due to the microplastics surface to volume ratio, the concentration of POPs is of magnitudes higher than the surrounding ocean. In one way this decreases the concentration of POPs in the ocean, but if the plastic gets ingested by an organism, they will be exposed to high concentrations which can lead to negative health effects[55].

The adsorption behaviour of microplastics is affected by increasing surface to volume ratio, temperature, and hydrophilicity. Adsorption of contaminants has been shown to increase with increasing age and degradation of the microplastic. pH and salinity are other factors influencing the adsorption conditions of contaminants. Studies show that how the different factors affect the adsorption rate depends on the contaminant and the plastic which it adsorbs to[5]. The existence of microplastics in the ocean influences the carbon cycling by increasing the dissolved organic matter (DOC). Degradation of the plastic in the marine environment makes the plastic more hydrophilic, increasing the adsorption of hydrophobic pollutants (i.e. PAHs and PCBs)[56]. Figure 2.7 shows how the role of microplastic in the ocean.

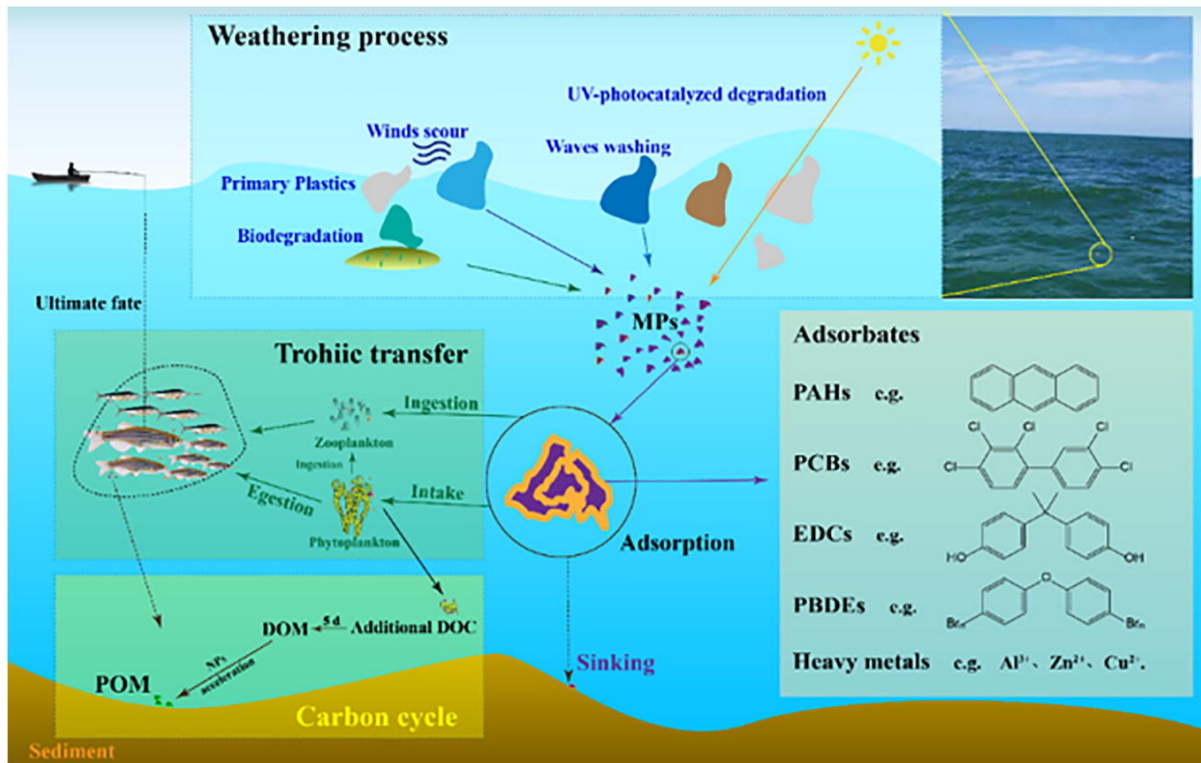


Figure 2.7: Microplastic cycle in the marine environment[5].

As shown in the figure, microplastics occurs from weathered plastic debris, increasing the surface and uptake of contaminants such as PAHs, PCBs and heavy metals. The plastic can sink to the seabed and might transfer the contaminants to the sediment. Also, microplastics have an impact on the marine carbon cycle, due to its leaching of dissolved organic carbon. Microplastics can be mistaken as food and ingested by marine organisms, leading to bioaccumulation, which is when the body absorbs the contaminant at a faster rate than the body can eliminate it.

More systematic studies should be conducted to better understand the adsorption behaviour between contaminants and plastics due to its complexity[5]. However, plastic debris is a ubiquitous pollutant in the ocean, having negative impacts on the organisms depending on the marine environment.

2.1.5 Presence in the Arctic

The wind and ocean currents transport marine plastic debris to the Arctic, to remote places far away from local plastic sources. The Gulf Stream is a large ocean current transporting plastic debris all the way from the Gulf of Mexico to the Arctic environment,

making it a global sink for pollution[57]. A study showed that the amount of plastic found on a remote beach at the Svalbard archipelago had increased with approximately 500% over a time period of 18 years, from 43 pieces in 1993 to 243 pieces in 2015[58]. Over 80% of the plastic waste originates from the fishing industry, and the pollution has deleterious effects on the wildlife in the Arctic[59]. The main source of plastic pollution in the Svalbard area is fishing vessels in the Barents Sea[60]. A study done on the northern fulmar in the Canadian high Arctic showed that 31% of the birds had at least one piece of plastic in their digestive system[13]. Large amounts of plastics have also been found at the sea floor and in the water column of Svalbard[12][61]. With increased shipping traffic and growing communities and tourism in the Arctic, the possibility of pollution is increasing[62]. Plastic pollution and its consequence for the Arctic environment and wildlife is concerning many citizens, engaging them to contribute with beach clean-ups to remove the plastic. An efficient method for monitoring marine litter is through citizen science programmes[63]. Still, the knowledge about marine plastic debris in the Arctic and how it affects the Arctic environment is scarce.

2.2 Marine Plastic Debris Research

Pollution of plastic is a globally growing concern, and the amount of published studies regarding plastic pollution in the marine environment is increasing[64]. Today there is no standard protocol of how plastic sampling, identification and quantification should be conducted, leading to difficulties when comparing results from different studies. Analytical techniques are still being developed, but a standard protocol should be defined as soon as possible[65]. The next sections will describe how plastic debris research is being done today, focusing on the marine environment.

2.2.1 Sampling of Marine Plastic Debris

The sampling of plastic debris is done in several parts of the marine environment, such as in the water, beaches, sediments and in marine biota. Marine plastic debris ranges in sizes from micrometres to meters[66]. Most plastics are buoyant and long-lasting, enabling them to float in the ocean over a long time. Sampling in the ocean can be done using trawls, filtering the water running through. The mesh size differs in studies from 50

to 3000 μm [67]. Other criteria are also varying, such as sampling depth, net size and trawling speed. For biota, various tissues and organs are investigated for plastics, and microplastics are usually found in the digestive system. Large quantities of biota samples are needed for statistical certainty, which can be challenging. For biota sampling, the strategy strongly depends on the selected organisms[68].

There is no standard protocol on how to perform plastic or microplastic beach debris sampling, and earlier studies show that the sampling on beaches has been done in various ways. The defined sample areas vary from a square of $5\text{x}5\text{cm}^2$ to $1\text{x}1\text{m}^2$. The placement of the squares differs greatly, from random spots on the beach[69], to spots depending on the tide[70]. This can either be the high or the low tidal line, where the former is the most common one. Also, the amount and distance between the sampling squares differs, from several squares close in distance, to fewer with greater distance in between. Studies show that sampling area is an important factor, but making a standard protocol is challenging since the distribution of microplastic is as dynamic as the beach itself[67]. The sampling itself is relatively easy, all the equipment needed is a spoon and a tray of a non-plastic material (to minimise contamination) for collecting the sand. Some studies use a sieve tool with different mesh sizes to sieve the sand in the sampling area, collecting the pieces suspected as plastics. In addition, the depth of the sample area varies between the studies from the top 1 cm to the top 20 cm, where sampling the top 5 cm of the sand is being the most common way[67].

2.3 Visual Identification

The first step of identifying plastics is to sort the samples visually, a relatively easy step for bigger pieces. With decreasing size of the particles, the chance of misidentification increases. When describing microplastics, it is desired to do so under a microscope[71]. To minimise the chance of misidentification, the recommended size limit of plastic particles is 1 mm. The other features described from visual inspection are size, weight, degradation stage, shape, colour and type[67].

Visual identification gives a fast description of the samples, but for identifying the chemical composition of the samples, instrumental techniques such as pyr-GC/MS, FTIR and Raman spectroscopy are desirable. For a more detailed characterisation of the degradation stages

of the plastic surfaces, instruments such as SEM and TEM are preferred.

Prior to analysis by analytical instruments, the samples should be cleaned and prepared for analysis. In this process, it is important to not use techniques or chemicals that can damage or destroy the sample. The most gentle way is to wash the samples thoroughly with clean, fresh water[72].

2.4 Identification of Chemical Composition

A proper identification is important to ensure correct results, and there are several methods suited for doing so. A technique to identify the polymer is density separation, as different polymers vary in densities[73]. First, the sample is placed in distilled water. Then, different chemicals such as ethanol or concentrated solutions of calcium or strontium chloride are added to the water. The volume of the solution added for the sample to become buoyant is weighed, and thus the density of the sample can be determined. A following C:H:N analysis can be used to identify the chemical composition, since different polymers have a characteristic elemental composition. Comparing the results from the density separation and the C:H:N analysis, the potential polymer composition can be found. The disadvantages are the time-requirement, and that small particles are hard to analyse. This technique gives only an approximation of what polymer type it could be, so to get a proper identification, more specific methods should be used[74].

Raman and Fourier-transform infrared spectroscopy (FTIR) show satisfactory performance on identifying the chemical composition of polymers and are commonly used in this application. In FTIR, infrared spectrum of the sample is obtained by measuring the amount of radiation that the sample absorbs at each wavelength. The obtained IR spectra is compared with reference IR-spectra for identification[75]. Almost the same is done in Raman spectroscopy, but instead of measuring the amount of radiation that is absorbed, the amount of radiation that is scattered is measured, providing information about the molecular vibrations[76]. Raman spectroscopy and FTIR are complementary to each other. Raman responds better to non-polar compounds, while FTIR provides a clearer identification of polar compounds[77]. Both provide fast identification of the polymer, from 20 seconds to a minute. FTIR provides spatial resolution down to 10-20 μm , while Raman spectroscopy shows spatial resolutions down to 1 μm [78]. Pyrolysis

gas chromatography-mass spectrometry (pyr-GC/MS), an emerging technique for polymer identification, is described more detailed below.

2.4.1 Pyr-GC/MS

Pyr-GC/MS is a technique consisting of a pyrolysis unit connected to a gas chromatograph, in connection with a mass spectrometer. The combination of these instruments allows for structural identification of high-molecular weight molecules, such as polymers. In the pyrolysis unit, the sample is placed on a platinum filament inside a quartz sample tube. From here the sample gets heated rapidly to a temperature between 600-1000°C in an inert atmosphere, leading to thermal decomposition of the material[79]. There are three different techniques applied for the heating process, inductive heating, isothermal furnace, and resistive heating. When heated, the sample breaks at the weakest bonds, creating smaller fragments which are more volatile. These fragments are further transported to the GC by a carrier gas for separation. The separation is resulting in a pyrogram, and the different polymers will have their characteristic pyrogram. In the end, the fragments are detected by a mass spectrometer, determining the mass/charge ratio. The identification of the sample composition is done by comparing the pyrograms of the unknown polymer with reference pyrograms of known compounds[69].

In addition to identification of polymers, this technique allows for determination of polymer-associated substances. These can be detected by thermal desorption at a lower temperature, i.e. 350°C. At lower temperatures, small and more volatile molecules can desorb without pyrolysing the polymer itself. Thermal desorption can be done in several ways, such as stepwise with fixed temperatures or by a temperature ramp[80]. Incorporated additives and environmental pollutants absorbed by the plastic are molecules which can be detected by thermal desorption. However, identifying additives are difficult due to the large amount having similar structure. For successfully determination of additives, comprehensive understanding of the additive and the polymer it is incorporated to is required, in addition to solid knowledge of the pyr-GC/MS technique[81].

Pyr-GC/MS is an emerging method for structural determination of polymers, and several studies have used this method for marine plastic identification, with successful results[79][82]. One advantage is that the technique allows for a direct analysis of the

analyte, without any pre-treatment or isolation of the analyte from the sample. In addition, pyr-GC/MS can detect polymer-associated substances, either during thermal desorption at lower temperatures or by pyrolysis of the polymer itself at high temperatures[69]. But on the other hand, it is a time-consuming technique as the samples have to be manually placed one at a time in the sample chamber. In addition, it is only possible to analyse one particle at a time, and not large sample quantities[83].

2.5 Characterisation of Surface Degradation

For investigation of sample topography and morphology such as shape, size and surface texture, microscopy techniques can be used. Optical microscopy study particles in micro- and macro sizes and is the first step in surface investigation[80]. This technique is mostly used in screening of a sample, to distinguish the plastic from other materials. It must be used with caution since it can misidentify plastic as other materials and vice versa[84]. To get more detailed information of the surface topology and morphology, electron microscopy can be used, which can study particles down to the nanometre size. Transmission electron microscopy (TEM) is an electron microscopy technique which can do so. An electron beam penetrates the sample (which needs to be thin), and the transmitted electrons are detected and converted into a 2D image. This results in high resolution images, where it is possible to image individual atoms. Some disadvantages are that the sample needs preparation before analysis, and the field of view is narrow, making it hard to capture the whole sample[85]. Scanning electron microscope (SEM), another technique for studying polymer surfaces, is described in more detail below.

2.5.1 Scanning Electron Microscope

Scanning electron microscope (SEM) is an electron microscope that can give high-resolution 3D pictures of the sample, down to 10 nm. This is done by scanning the sample surface with a beam of electrons. When the electrons interact with the atoms from the sample, signals are produced and detected, giving information about the surface topography and morphology[86]. The samples are placed on a sample holder and need to be small enough to fit it. SEM is dependent on electrically conductive samples to work. In the case of polymer analysis, the sample needs to be sputter coated with a conductive layer beforehand, usually

a very thin layer of gold[87]. Depending on the reason for analysis, different electrons are detected such as backscattered electrons and secondary electrons. Backscattered electrons are those that are reflected after interaction between the electron beam and the sample, giving information about the atomic number of the sample. Secondary electrons occur when the electron beam hits the surface, exciting electrons from the sample. When these secondary electrons get detected, an image of the sample topology is generated. A type of detector detecting the secondary electrons is an Everhart-Thornley Detector[88]. SEM is the most used imaging technique due to its serviceability and simplicity of image interpretation. Several studies have successfully used SEM to examine surface texture and degradation of polymers[47] [89]. In addition, the technique has allowed for structure investigation of microbial biofilms on marine plastics[90][2].

3 Experimental

3.1 Marine Plastic Debris at Svalbard

The plastics samples analysed in this thesis were sampled at four different places on Svalbard, Isfjord Radio, Hiorthhamna, Ny-Ålesund and Sallyhamna, during the summer of 2019. The nearby beaches were searched, and all plastic visible for the naked eye were collected in plastic bags. The sampling at Isfjord Radio and Hiorthhamna was done in connection with field work for the course AT-333, "Arctic Petroleum: Challenges for Society, Technology, and Environment" at the University Centre in Svalbard (UNIS). Sampling at Ny-Ålesund was conducted in connection with field work for the thesis. Sampling at Sallyhamna was done by Perrine Geraudie, adjunct associate professor at UNIS. In total, 169 samples were collected. Figure 3.1 shows the four sampling sites.



Figure 3.1: Location of the four sampling sites at Svalbard.

Table 3.1 gives information about the sampling areas and the amount of samples gathered.

Bigger parts such as large fishing nets were not collected due to practical difficulties.

Table 3.1: Sampling coordinates, dates and amount of samples collected at each location.

Sampling site	Coordinates	Sampling date	# Sampled
Isfjord Radio	78°03.632'N 13°38.170'Ø	03/07/19	59
Hiorthamna	78°14.929'N 15°41.842'Ø	15/07/19	42
Ny-Ålesund	78°56.293'N 11°51.846'Ø	03/08/19	24
Sallyhamna	79°49.004'N 11°35.640'Ø	08/19	44

Microplastic sampling was done in addition to the larger plastic pieces. The top five centimetres of three random spots (1x1 m square) on the beaches were investigated, shown in Figure 3.2. A sieving tool with two different mesh sizes were used to sieve the sand, to easier observe if microplastics were present. Nothing was found.

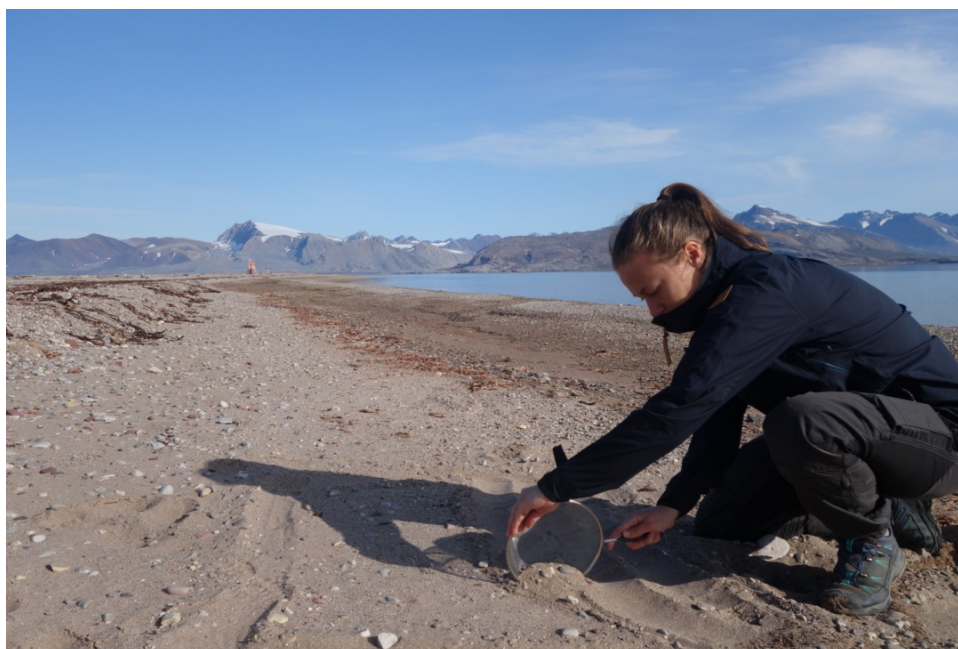


Figure 3.2: Searching for microplastics with the use of a sieving tool at the beach by Ny-Ålesund.

All the plastic samples from Svalbard were visually analysed at the laboratory at NTNU. They were described by type, colour, size, and weight. Seven pieces from each place (total of 28 pieces) were randomly chosen for further analysis.

3.1.1 Structural Identification of Polymers by Pyr-GC/MS

The chemical compositions of the unknown plastic samples were identified by using Pyrolysis Gas Chromatography Mass Spectrometry, stationed at NTNU Trondheim. The

instrument consists of three units coupled together, the pyrolysis unit (Pyrola 2000) with a platinum filament (resistive heating), GC-unit (TRACE Ultra) and the MS unit (ITQ 1100, Thermo Fisher Scientific). The capillary column was from Agilent and had a length of 30 m, inner diameter of 0.25 mm and a film thickness of 0.25 μ m. Before analysis, the Pyrola unit was calibrated for the temperatures 700°C, 800°C, 900°C, 1000°C. Calibration was done regularly, and after filament replacement. The samples were run at 700°C. Table 3.2 shows an overview of the pyr-GC/MS settings used for analysis.

Table 3.2: Pyr-GC-MS settings used for structural determination of the unknown plastic samples.

Unit	Parameter	Setting
Pyr	Chamber temperature	175°C
	Pyrolysis time	2 s
	Pyrolysis temperature	700°C
GC	Carrier gas	Helium
	Inlet temperature	320°C
	Injection flow	1.5 mL/min
	Injection mode and ratio	Split 1:60
	Temperature program	40°C for 2 min, 20°C/min for 14 min up to 320°C, hold for 14 min
MS	Interface AUX Temperature	320°C
	Ionization technique	Electron EI
	Ion source temperature	200°C
	Mass range	38-600 (m/z)
	Scan mode	Full scan

After each sample run, both the quarts and the filament were cleaned using a blow torch. 2-3 blanks were run between each sample to clean the system and minimise any carry-over. Identification of the polymers was done using NIST Mass Spectral Library and by comparing sample pyrograms and mass spectres with references from "Pyrolysis-GC/MS Data Book of Synthetic Polymers"[6].

The samples were cut to approximately 1 mm by using mm-paper, scalpel and magnifying glass. Figure 3.3 shows the samples randomly named prior to analysis. All samples were washed thoroughly with de-ionised water, and tweezers were used for sample handling.



Figure 3.3: Samples randomly named prior to analysis by pyr-GC/MS. Analysis followed alphabetical order.

The samples varied in density and width, leading to different amount of samples despite cutting them to the same size. Every sample was applied in dry form. Figure 3.4 shows an example of a plastic part after being cut and placed on the filament.



Figure 3.4: Plastic sample placed on the platinum filament.

3.1.1.1 Qualitative Analysis of Adsorbed Environmental Pollutants

Two samples from each sample spot were randomly chosen for a further qualitative analysis of possible adsorbed pollutants. The same settings were used as in section 3.1.1, except from the pyrolysis time which was changed to 5 seconds. A desorption pyrolysis at 350°C was run before pyrolysis at 700°C of each sample. This is to ensure desorption of more volatile molecules from the plastic without pyrolysing the polymer itself and makes it easier to identify possible pollutants/additives without the distribution of depolymerisation products. Present peaks were investigated using NIST Mass Spectral Library. Figure 3.5 shows the eight samples chosen for this analysis.

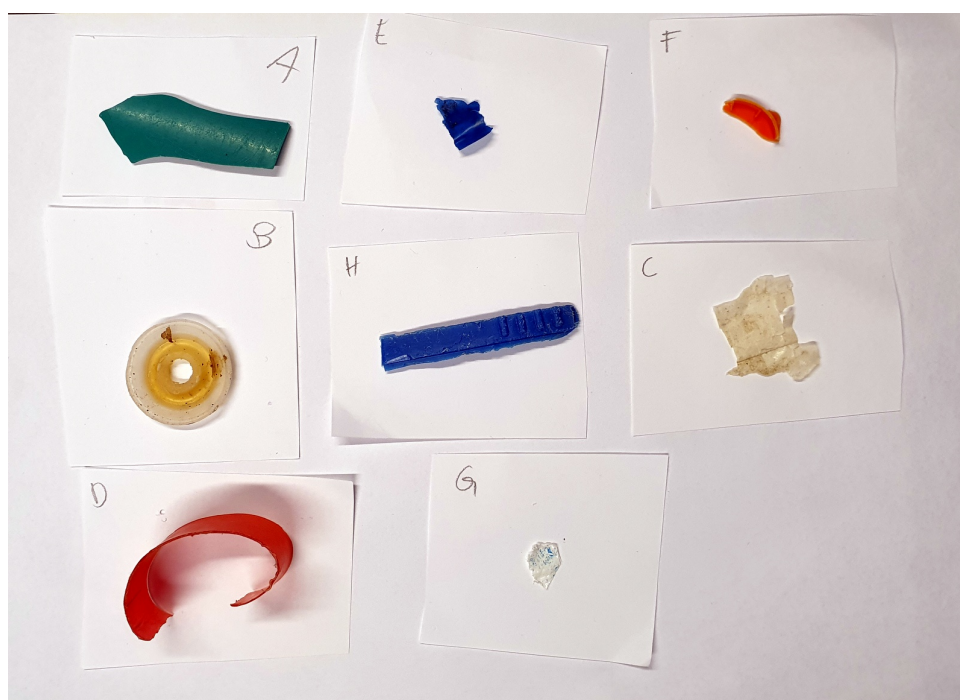


Figure 3.5: The eight plastic samples randomly named prior to analysis of environmental pollutants. Two samples from randomly chosen from each sample location.

3.1.2 Study of Surface Morphology by SEM

To investigate the surface morphology of the plastic samples, a field emission scanning electron microscope (FEI APREO) equipped with an Everhart-Thornley Detector (ETD) was used. The instrument is located at NTNU NanoLab. The seven samples from Isfjord Radio were the ones chosen for SEM analysis.

The size of the plastic samples was adjusted by cutting, to fit all pieces together on the sample holder. A piece was cut from the middle and the end of the sample, making

it a total of two pieces per sample. The final samples were cleaned thoroughly with milliQ-water, which is the gentlest preparation prior to SEM-analysis. Afterwards, the samples very carefully cleaned with isopropanol with the use of cotton swabs, to remove contaminants. This step was done cautiously to not damage the surface morphology. Lastly, the samples were dried. Figure 3.6 shows the samples after cutting and cleaning. Since plastic is a non-conductive material, the samples were coated with a thin layer of gold prior to analysis.



Figure 3.6: Samples from Isfjord Radio cleaned and cut for SEM analysis (before gold coating).

The settings used during SEM analysis were:

- Current: Mostly 0.40 nA, some pictures 0.20 nA.
- Accelerated Voltage (HV): 5.00 kV
- Mode: Secondary Electron (SE)
- Working Distance (WD): 9.3 - 13.9 mm

The pictures were taken at the magnifications 150x, 250x, 500x, 800x, 1000x and 2000x, to both get an overview of the surface and to get close-ups on details. The working distance varied from 9.6 mm to 13.9 mm, varying between the pieces, to optimise the resolution. All the samples were analysed together on the same sample holder.

3.2 Study in Trondheimsfjorden

Five different types of plastics films were placed in the Trondheim fjord for a period of 19 weeks (29/10/19 - 12/03/20), to study how the different polymers are affected by the marine environment. Table 3.3 shows some information about the plastics.

Table 3.3: Thickness, supplier and article number of the plastic films used in this experiment.

Material	Thickness [mm]	Supplier	Art nr.
PE	0.05	VWR	391-1250
PP	0.05	VWR	391-1254
PVC	0.008	VWR	KING756031
LDPE	0.03	Deqin Sunny Plastic Products Co Ltd	-
HDPE	0.014	Clas Ohlson	44-1960

Two parallels of each plastic were attached to two ropes, making it four parallels of each plastic in total. Each plastic type was cut to the size 2 x 7 cm² and were attached to the ropes by cable ties. The plastic samples had enough distance between them to avoid entangling with each other (approx. 5 cm). Figure 3.7 shows one rope with attached samples, before it was placed in the fjord. Bottles filled with stones were attached in the end of the ropes, to make them more stable after placement in the fjord.

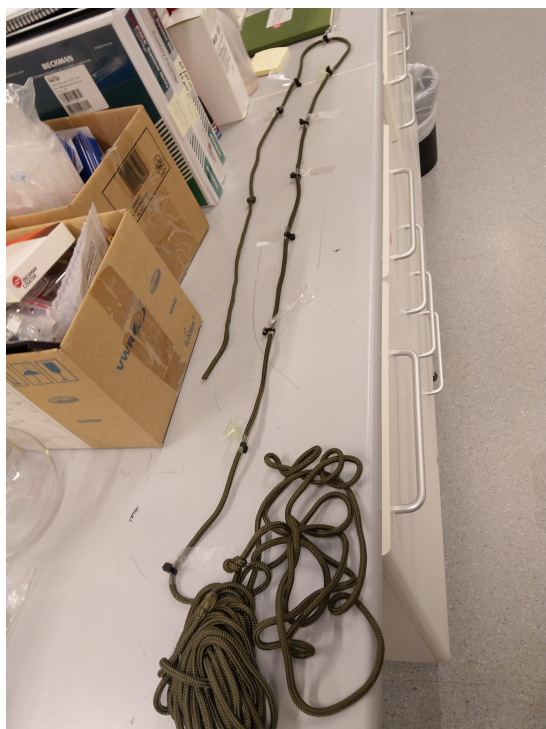


Figure 3.7: Setup of the ropes. Each plastic film was cut and attached to the rope by small cable ties, with sufficient distance in between to avoid entangled samples.

The ropes were attached to the pier at Trondheim Biological Station (TBS), shown in Figure 3.8. 19 weeks later, the samples were collected. Each sample was washed with de-ionised water, individually wrapped in marked aluminium foil and brought to the lab. From there, three small fragments of each sample were cut for further analysis by SEM.

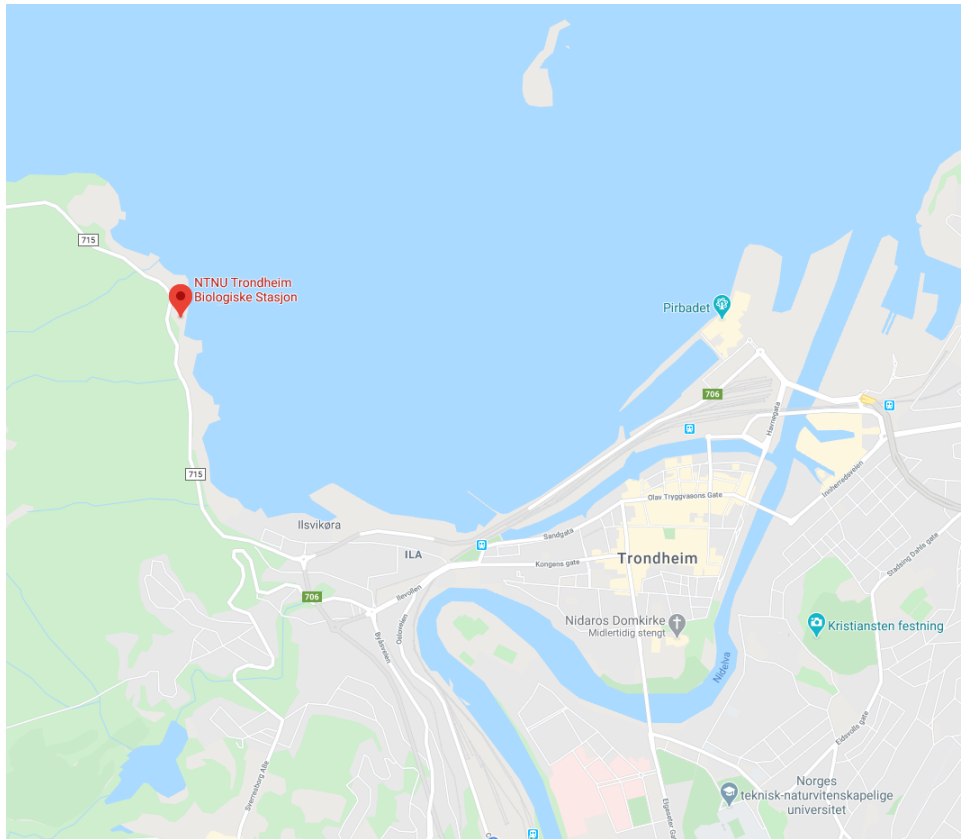


Figure 3.8: Location of the samples, at Trondheim Biological Station, $63^{\circ}26'27.4''\text{N}$ $10^{\circ}20'55.3''\text{E}$.

SEM analysis was done using the same instrument at NTNU Nanolab as described in Section 3.6. The three pieces of the same polymer were placed on the same sample holder, making it five sample holders in total. All samples were coated with a thin gold layer prior to analysis.

The settings used during SEM analysis were:

- Current: 0.25 pA.
- Accelerated Voltage (HV): 5.00 kV
- Mode: Secondary Electron (SE)
- Working Distance (WD): 9.5 - 10.3 mm

The pictures were taken at the magnifications 100x, 500x, 1000x, 2000x and 10 000x to both get an overview of the surface and close-ups on details. The working distance varied from 9.5 mm to 10.3 mm to optimise the resolution.

4 Results

Section 4.1 and 4.2 are based on analysis of the marine plastic debris collected at four beaches at Svalbard, while Section 4.3 is based on the samples from Trondheimsfjorden.

4.1 Visual Description

A total of 169 plastic pieces were collected from the four sample sites at Svalbard. All samples were brought to the lab and visually described. They were divided into three categories, fragments, films, and ropes. Table 4.1 shows an overview of the category distribution of all the samples.

Table 4.1: Category distribution of the total plastic samples.

	Fragment	Film	Rope/nets
#	109	20	40
%	65	12	23

The distribution shows that the majority of the samples were of fragments (65%) followed by ropes (23%). Figure 4.1 shows the colour distribution of all samples.

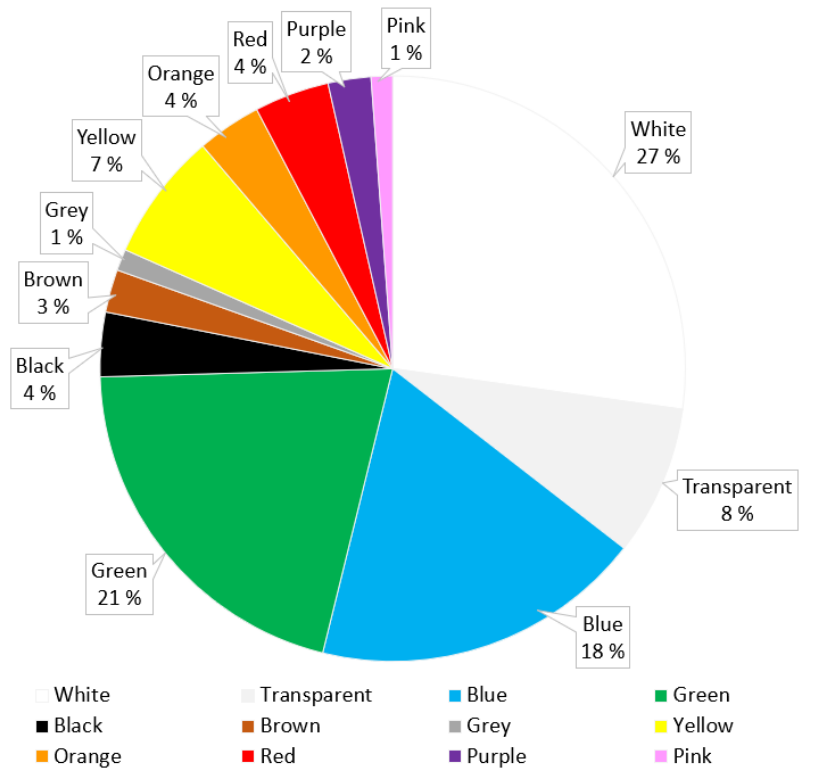


Figure 4.1: Colour distribution of all 169 samples from Svalbard.

Most samples were white (27%), followed by green (21%) and blue (18%). All samples were measured and weighed in the laboratory. Colour and category distribution of the samples from each of the sampling spots can be found in Appendix A2.1.

A description of the samples that were chosen for further analysis is shown in Table 4.2, and pictures of all samples can be seen in Figure 4.2. Seven pieces were chosen randomly from each of the four bags containing samples from each spot.

Table 4.2: Description of the samples chosen for analysis by type, colour, size and weight. # is the sample name.

Ny-Ålesund					Sallyhamna				
#	Type	Colour	Size [cm ²]	Weight [g]	#	Type	Colour	Size [cm ²]	Weight [g]
N1	Fragment	Green	12	1.2	S1	Fragment	White	7.6	2.2
N2	Fragment	Orange	20	2.8	S2	Fragment	Orange	1.7	0.2
N3	Fragment	White	8.5	5.3	S3	Fragment	Purple	18	1
N4	Fragment	Black	9.7	0.6	S4	Fragment	Transparent	21	5.6
N5	Fragment	Red	18	5.5	S5	Fragment	White	41	3.6
N6	Rope	Green	12	1.1	S6	Rope	Green	10	1
N7	Film	Blue	3	0.03	S7	Fragment	Transparent	0.9	1.3

Isfjord Radio					Hiorthhamn				
#	Type	Colour	Size [cm ²]	Weight [g]	#	Type	Colour	Size [cm ²]	Weight [g]
I1	Film	Blue	33	0.1	H1	Fragment	Blue	5	0.2
I2	Fragment	Blue	11	2.4	H2	Fragment	Red	18	1.1
I3	Rope	Green	3	0.4	H3	Film	White	8.8	0.01
I4	Fragment	Red	16	3.9	H4	Fragment	White	15	1.8
I5	Film	White	117	0.4	H5	Rope	Orange	18	2.6
I6	Fragment	Yellow	3	0.2	H6	Fragment	White	4.3	0.2
I7	Fragment	Pink	14	0.8	H7	Fragment	Black	57	8.4

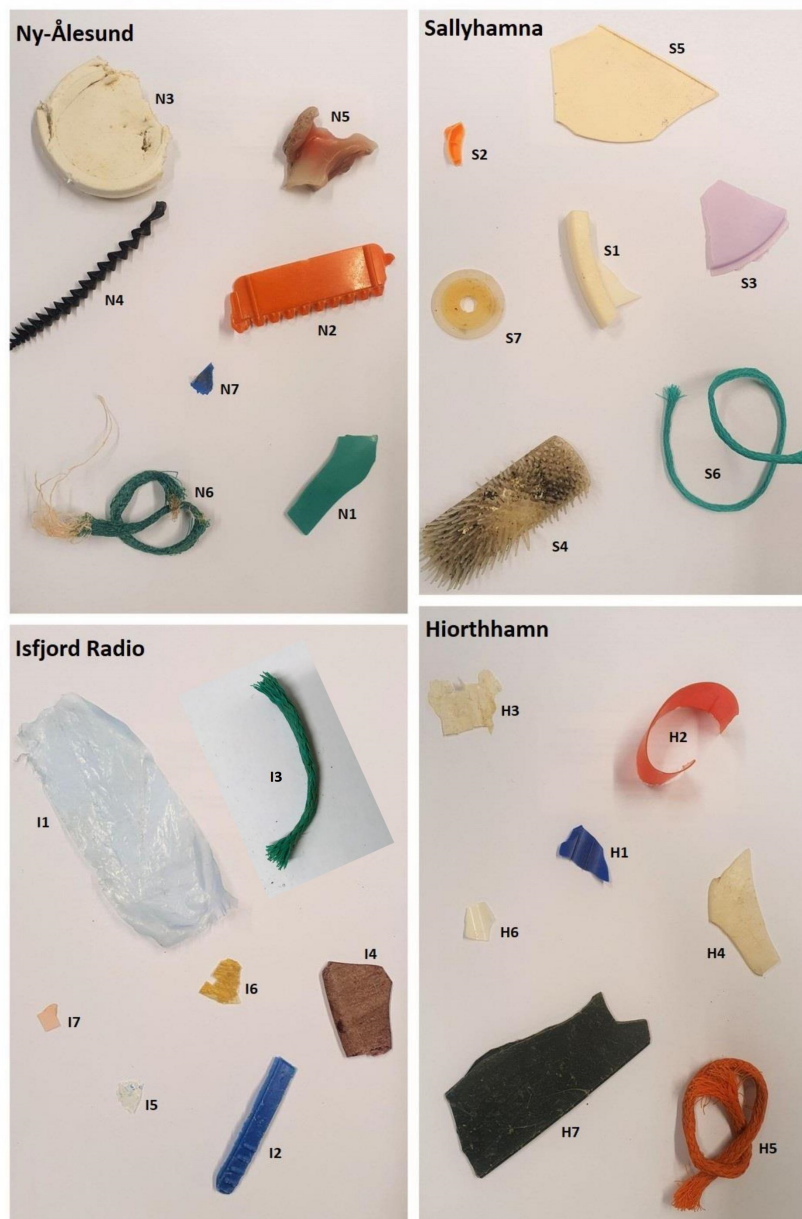


Figure 4.2: The 28 samples chosen for further analysis. Each picture represent a sample location and the seven samples collected, marked with sample names.

A list describing the rest of the samples can be found in Appendix A2.1.

4.2 Analysis of Marine Plastic Debris at Svalbard

4.2.1 Structural Identification of the Polymers by Pyr-GC/MS

To identify the chemical compositions, the sample pyrograms and their mass spectra were compared with reference pyrograms and mass spectra from literature[6]. An example showing how to identify the polymer from the pyrogram can be found in Appendix A1. Pyr-GC/MS analysis of the 28 plastic samples showed that 21 samples are composed of high-density polyethylene (PE(HDPE)) and seven samples are isotactic polypropylene (iso-PP). Table 4.3 shows an overview of the plastic samples and which polymer they are composed of. The sample names in the table are abbreviations of the sample locations; N, S, I, and H represent samples from Ny-Ålesund, Sallyhamna, Isfjord Radio, and Hiorthhamn, respectively.

Table 4.3: Overview of the samples and the found polymer type. The seven polypropylene samples are marked in blue. N, S, I, and H represent samples from Ny-Ålesund, Sallyhamna, Isfjord Radio, and Hiorthhamn, respectively.

Sample	Type	Sample	Type	Sample	Type	Sample	Type
N1	PP	S1	PE	I1	PE	H1	PP
N2	PE	S2	PP	I2	PE	H2	PE
N3	PE	S3	PE	I3	PE	H3	PE
N4	PE	S4	PE	I4	PP	H4	PE
N5	PE	S5	PP	I5	PE	H5	PE
N6	PE	S6	PE	I6	PP	H6	PE
N7	PE	S7	PE	I7	PE	H7	PP

Figure 4.3 and 4.4 show example comparison of sample and reference pyrograms for isotactic polypropylene and high-density polyethylene, respectively.

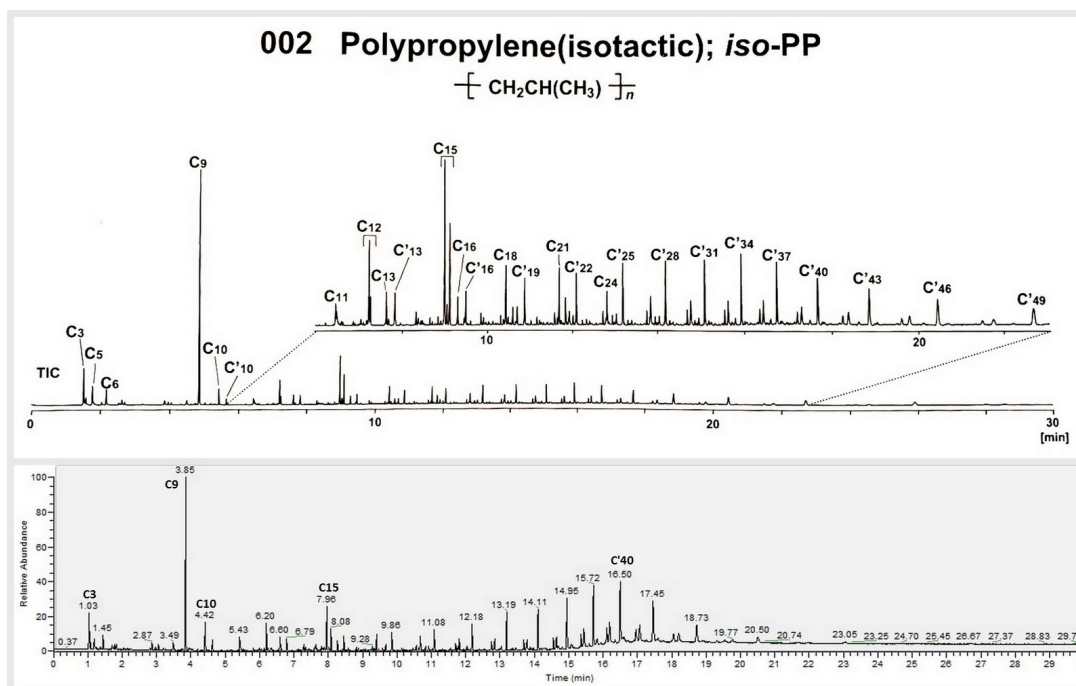


Figure 4.3: Comparison of reference and sample pyrogram of iso-PP (700°C). Some of the peaks are marked with carbon number for comparison.

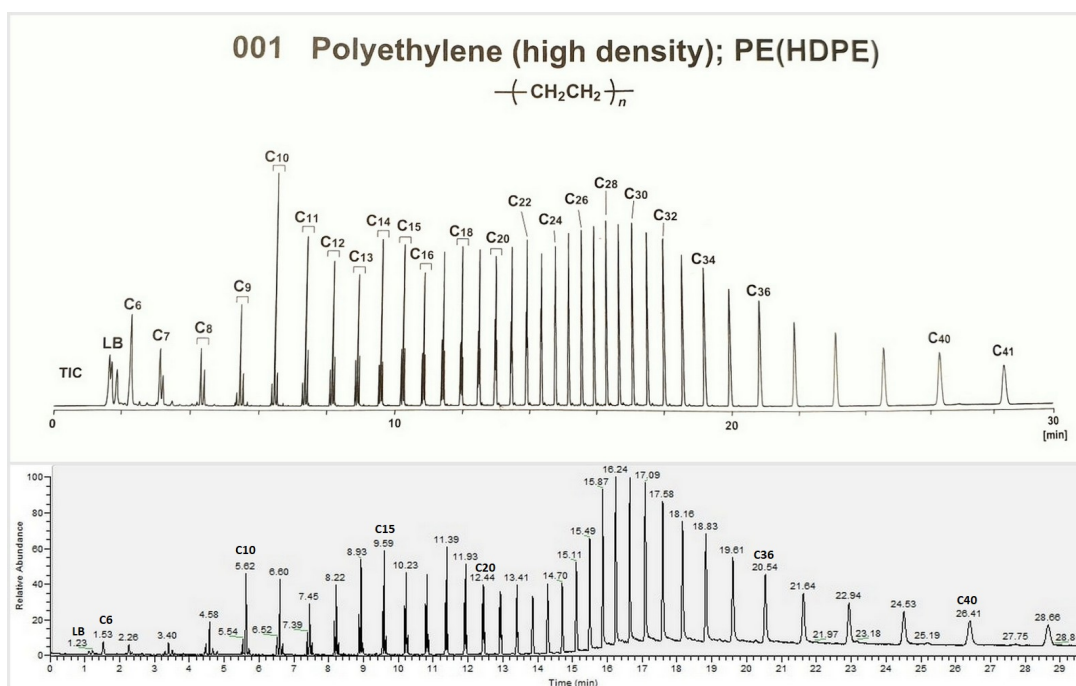


Figure 4.4: Comparison of reference and sample pyrogram of PE(HDPE) (700°C). Some of the peaks are marked with carbon number for comparison.

4.2.2 Study on Polymer-Associated Substances

Table 4.4 shows an overview with information about the samples analysed in this part. For this experiment the samples analysed have been given new names from A-H, listed in the table below. Of the eight samples, two are made of polypropylene (sample A and F) while the rest are made of polyethylene.

Table 4.4: Place, sample name and type of polymer of the eight samples chosen for environmental pollutants analysis.

Sample	Place	#	Type
A	Ny-Ålesund	N1	PP
B	Sallyhamna	S7	PE
C	Hiorthhamn	H3	PE
D	Hiorthhamn	H2	PE
E	Ny-Ålesund	N7	PE
F	Sallyhamna	S2	PP
G	Isfjord Radio	I5	PE
H	Isfjord Radio	I2	PE

Desorption pyrograms (350 °C) and pyrograms (700°C) of sample A (PP) and D (PE) are shown in Figure 4.5 and 4.6, respectively. The increasement of the baseline in the pyrograms are due to column/septum bleeding. Unlabelled peaks in the pyrograms are siloxanes from septum bleeding and ghost peaks from contamination. A big bump or/and oscillation during the first minutes of the GC-run was observed on all runs (both samples and blanks) and is explained in the discussion section.

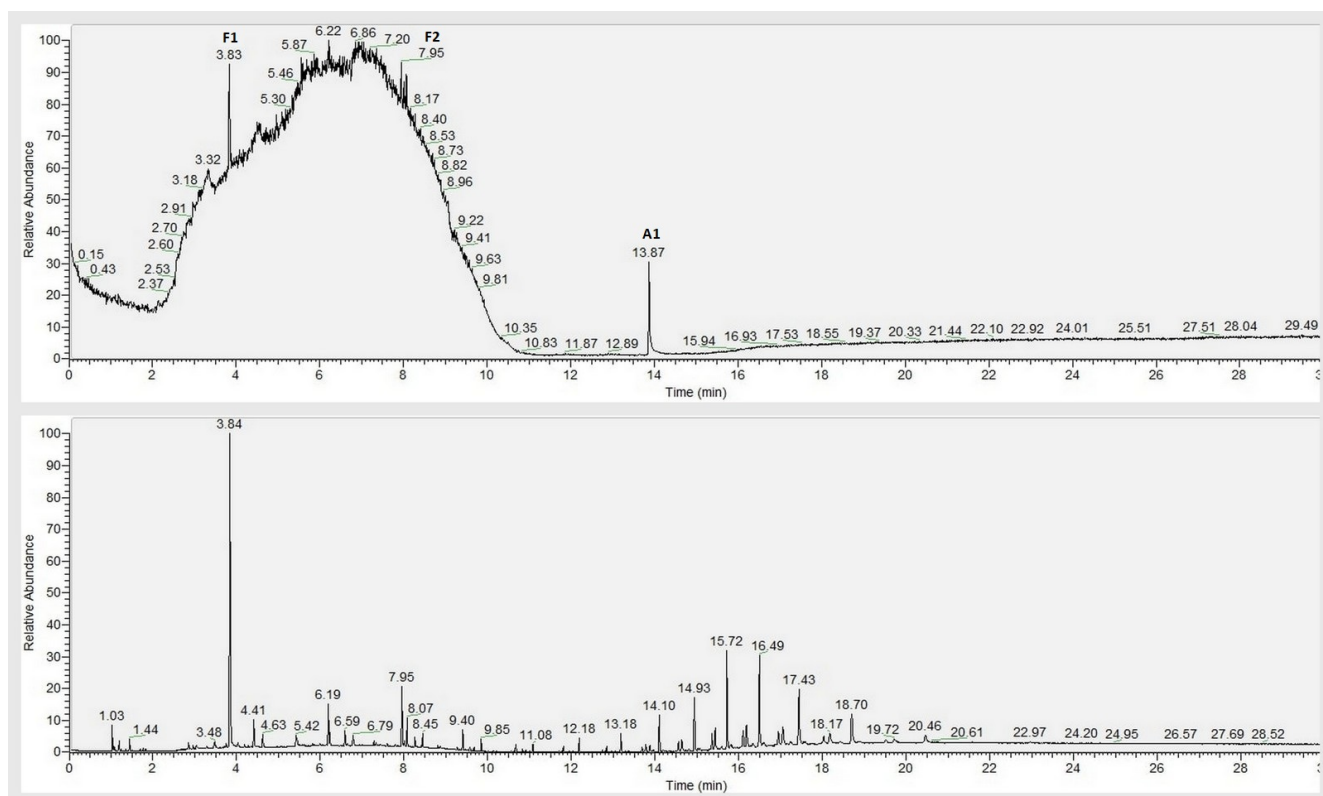


Figure 4.5: Pyrograms of plastic A (PP) 350°C and 700°C. Peaks are labelled F for polymer fragment and A for possible environmental pollutant.

Peak F1 and F2 in sample A are most likely polymer fragments, as they are also found in the high-temperature pyrogram of PP (and verified by comparing MS-spectres in NIST). Peak A1 is only detected in the desorption pyrogram, making it a potential additive. From search in NIST, it is observed that A1 potentially is the plasticise diisooctyl adipate.

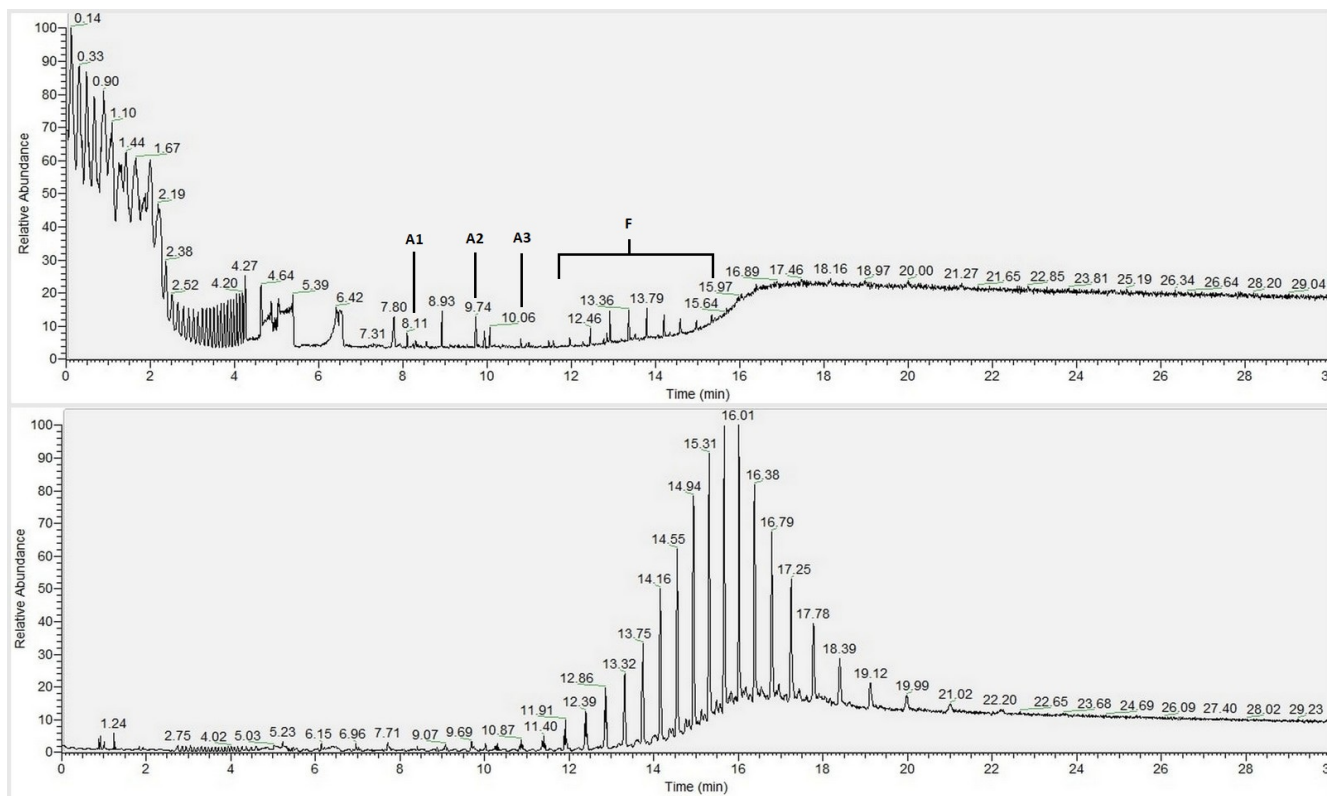


Figure 4.6: Pyrograms of plastic D (HDPE) at 350°C and 700°C. Peaks are labelled F for polymer fragment and A for possible environmental pollutant.

In sample D, the peaks (F) between 11-15 minutes most likely originate from the pyrolysis fragments of the polymer. Three potential additives/pollutants were detected by search in NIST dichloroaniline (A1), diethyl phthalate (A2) and unidentified (A3).

No peaks suspected as additives or pollutants were detected in the remaining six samples, which can be found in Appendix A2.2.1.

4.2.3 Morphology Study by SEM

Several SEM pictures of varying magnitudes were taken of the seven samples, to both get an overview of the surface and a closer look at degradation signs. Different degradation signs on the surface were identified, such as cracks/fractures, grooves, pits, and flaking. All samples were searched for these degradation signs, and the results are collected in Table 4.5. "+" and "-" represents if the degradation was or was not spotted on the sample, respectively.

Table 4.5: Overview of the samples and observations of degradations. "+" and "-" represents if the degradation was or was not spotted on the sample, respectively.

Type	Sample	Flaking	Crack	Fracture	Groove	Pit
PE	Plastic I1	-	-	-	+	+
PE	Plastic I2	-	+	+	+	+
PE	Plastic I3	+	-	-	+	-
PE	Plastic I5	+	-	-	-	-
PE	Plastic I7	+	+	+	+	-
PP	Plastic I4	+	+	+	-	+
PP	Plastic I6	+	+	+	+	-

On sample I5 and I6, there were also observed presence of biological organisms. As examples, Figure 4.7 and 4.8 show SEM pictures of sample I4 and I5, respectively. For sample I4, the photos were taken at magnitudes 100x, 150x, 500x, 1000x, while for sample I5 they were taken at magnitudes 100x, 1000x and 2000x. SEM pictures of the other samples are shown in A2.3.

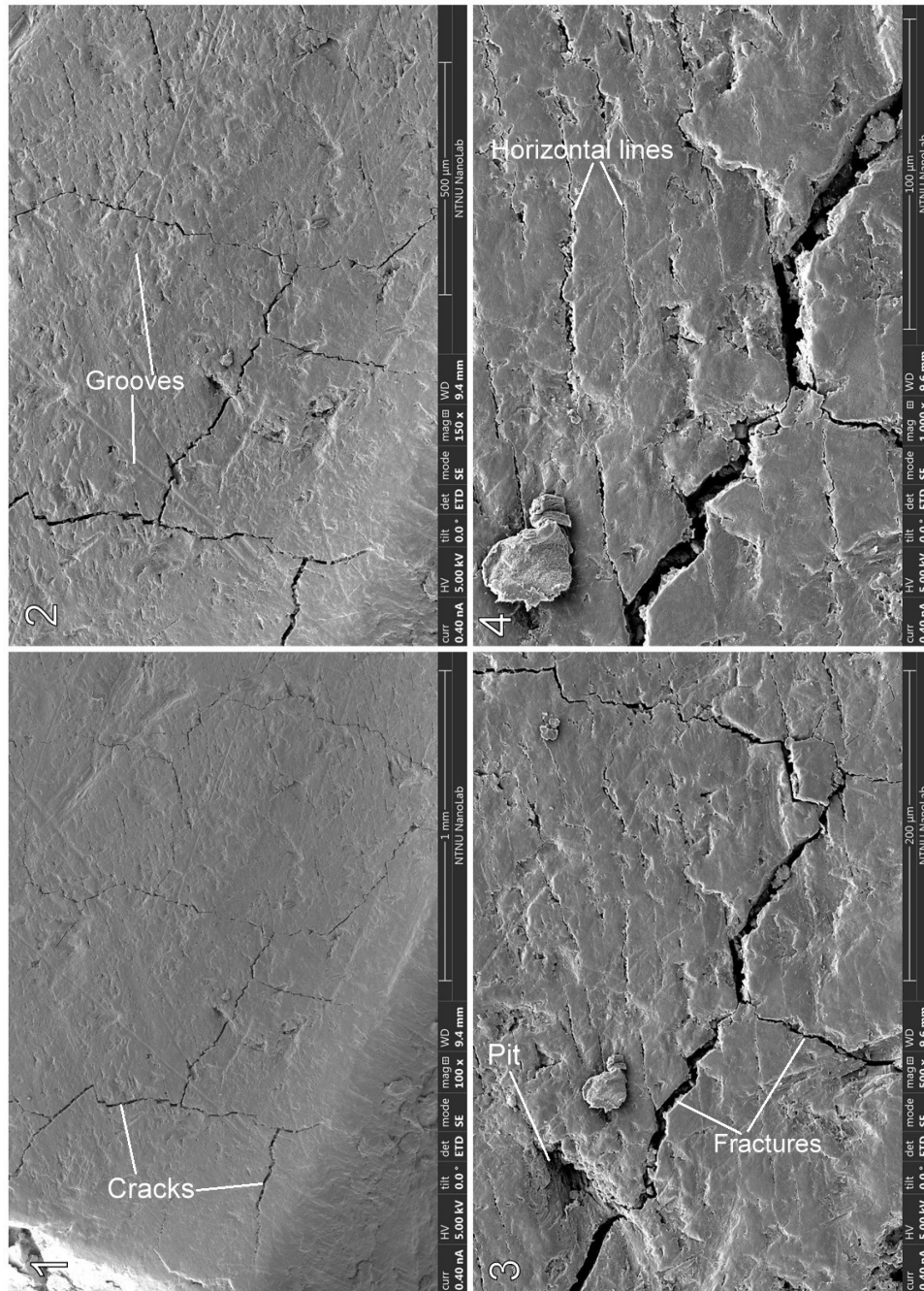


Figure 4.7: SEM pictures of sample I4, PP.

From Figure 4.7, the same spot of the plastic sample has been captured at different magnitudes. The overview picture (picture 1) shows cracks of varying degrees. In addition, grooves along the surface are observed, which can indicate that other material has been dragged against the plastic surface (picture 2). By looking closer at the surface (picture 3 and 4), the cracks look deeper, and small particles are spotted in these fractures. Symmetric horizontal lines and pits can also be observed (picture 4).

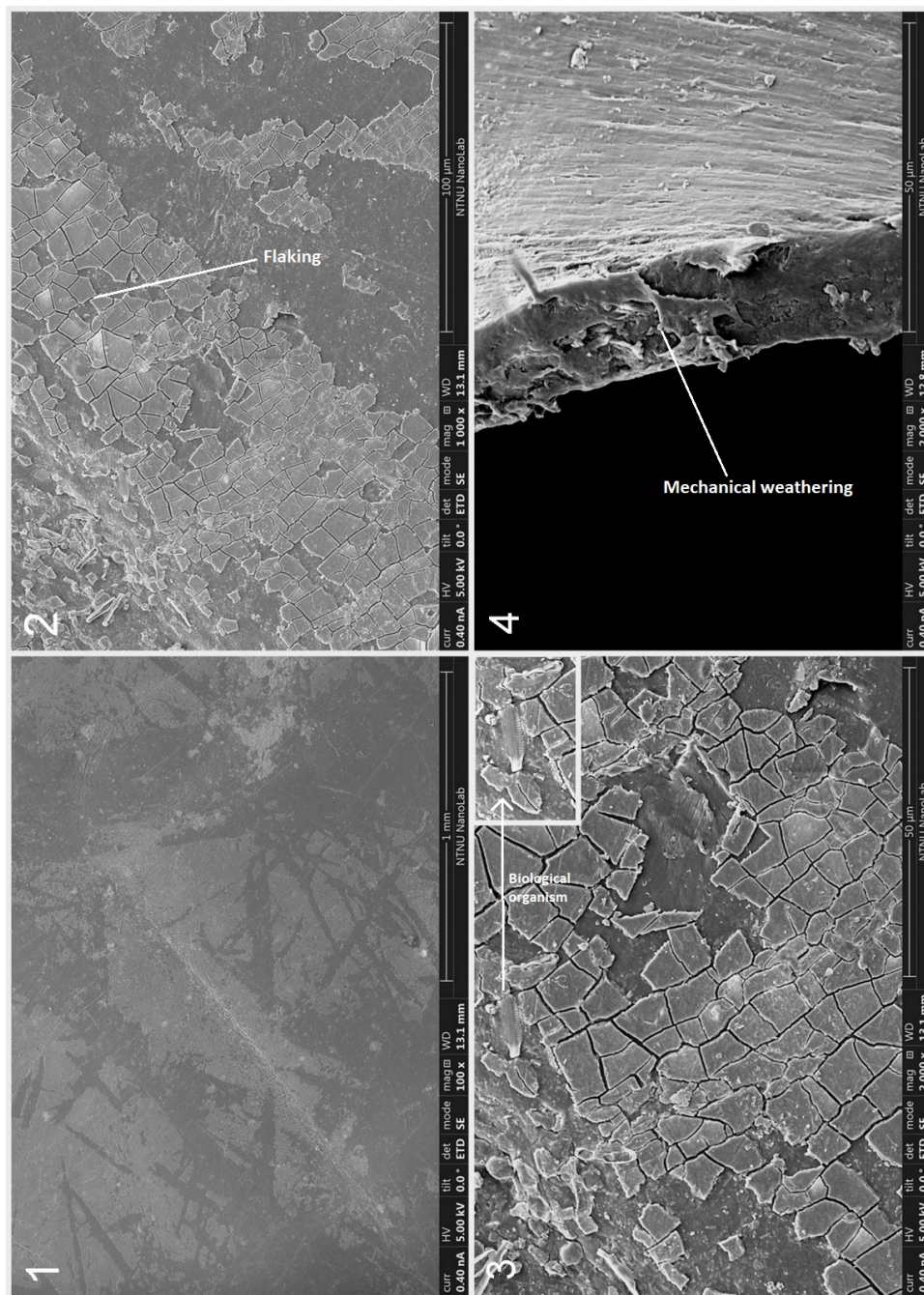


Figure 4.8: SEM pictures of sample I5, PE.

From Figure 4.8, picture 1-3 are of the same spot with different magnitudes, while picture 4 is of the edge of the sample. The overview picture (picture 1) shows no specific degradation other than surface wear. By closer inspection, it looks like the sample is constructed of two layers on top of each other, where the top layer is flaking off. Some biological organisms can also be spotted at picture 3. The sample edge (picture 4) displays little degradation, only some mechanical weathering.

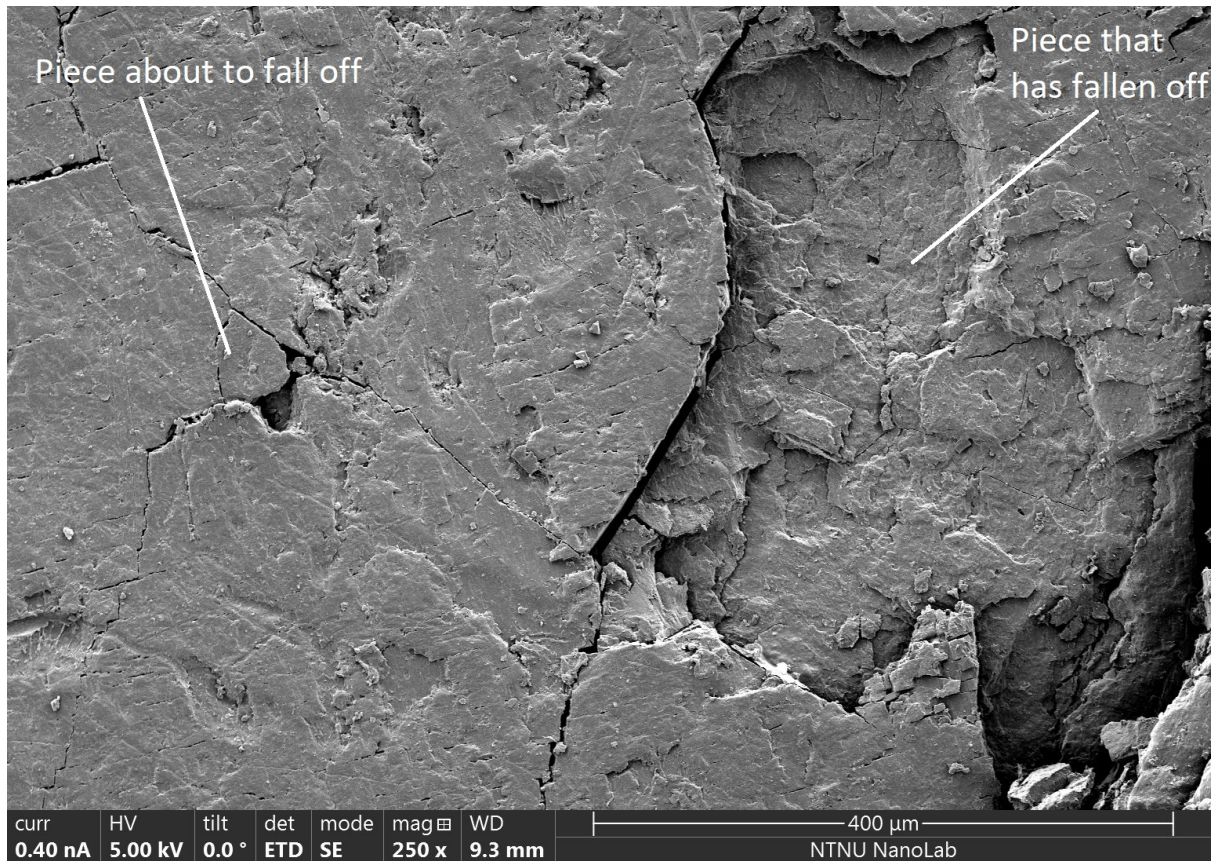


Figure 4.9: SEM picture of sample I4, iso-PP.

Figure 4.9 shows another site on sample I4, displaying other degradation signs. Here is an example of flaking, which may have arisen from cracks and fractures. In the picture, both a large piece that has fallen off and a smaller piece that is about to fall off were observed. They are both linked to cracks. By looking at the scale, these pieces have a size considerably smaller than 5 mm, meaning that they flake off as microplastics into the environment.

4.3 Study in Trondheimsfjorden

Several SEM pictures of varying magnitudes were taken of the five samples, to both get an overview of the surface and a closer look on details. Diatoms were tried identified, but note that these are assumptions. In addition, only a small part of the sample was investigated, and the amount of biofilm might vary on the plastic films. The results are shown in table 4.6, as well as marked on the pictures. "+" and "-" represents if the diatom was or was not spotted on the sample, respectively.

Table 4.6: Overview of observed diatoms on the surface of the different plastic films, and percentage present. "+" and "-" represents if the diatom was or was not spotted on the sample, respectively.

Type	Nitzschia	Amphora	Licmophora	Navicula	Cocconeis
HDPE	+	-	-	+	+
LDPE	-	-	-	-	+
PE	+	-	-	+	+
PP	+	+	+	+	+
PVC	+	+	-	+	+
Presence	80%	40%	20%	80%	100%

Degradation signs were challenging to spot on the plastic films due to large amounts of biofilms. Figure 4.10 and 4.11 show SEM pictures of the HDPE sample.

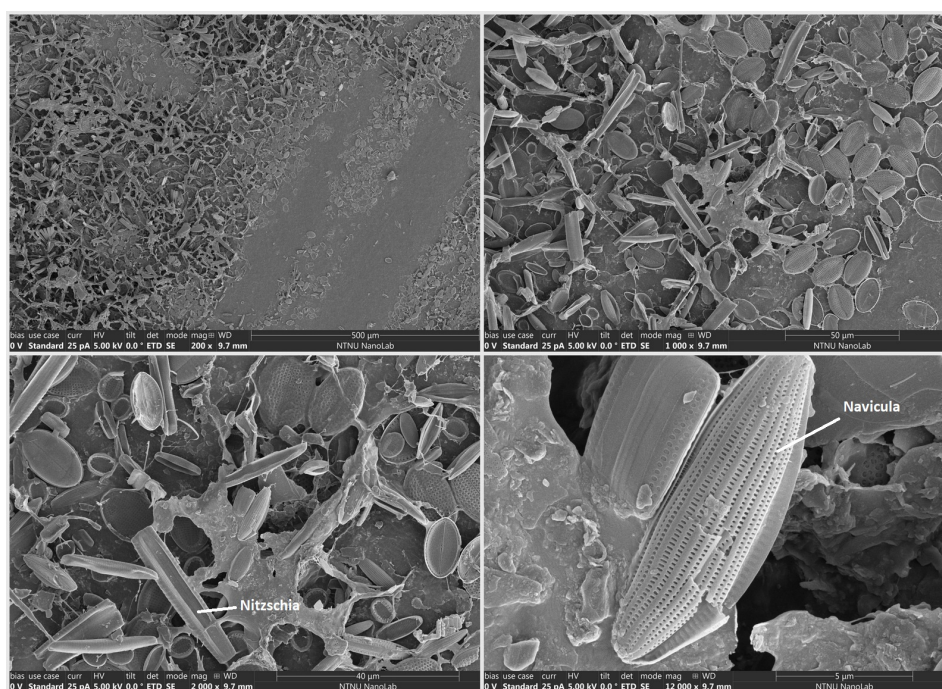


Figure 4.10: SEM pictures of HDPE at 200x, 1000x, 2000x and 12000x.

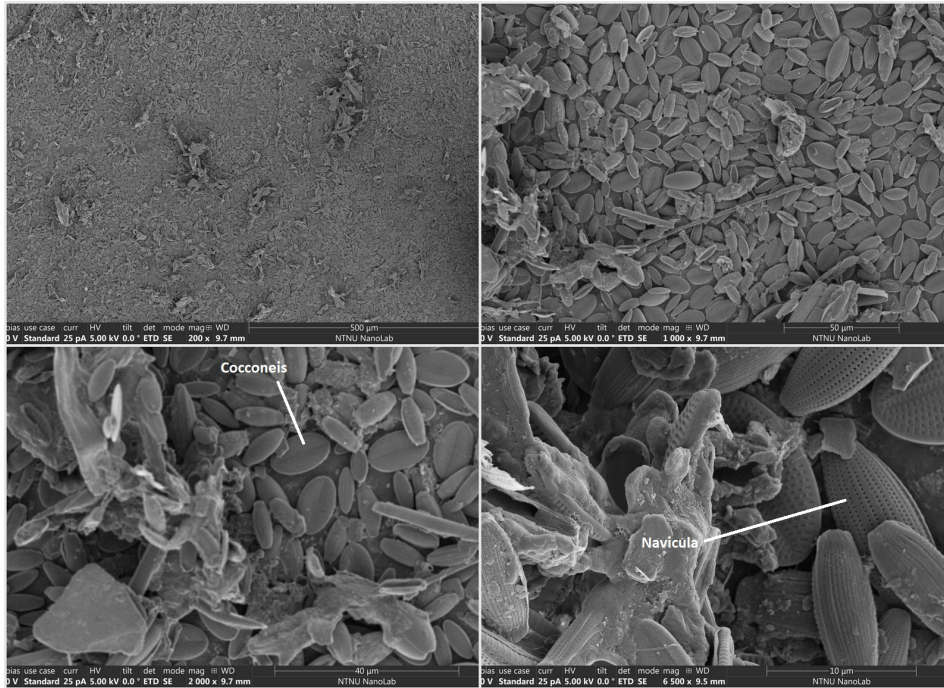


Figure 4.11: SEM pictures of HDPE at magnitudes 200x, 1000x, 2000x and 6500x.

As the figure shows, this sample is highly covered by biofilm. The plastisphere consists of mainly the diatoms *Nitzschia*, *Navicula* and *Cocconeis*. Other algae are also observed, but not identified. Figure 4.12 and 4.13 show SEM pictures of the LDPE sample.

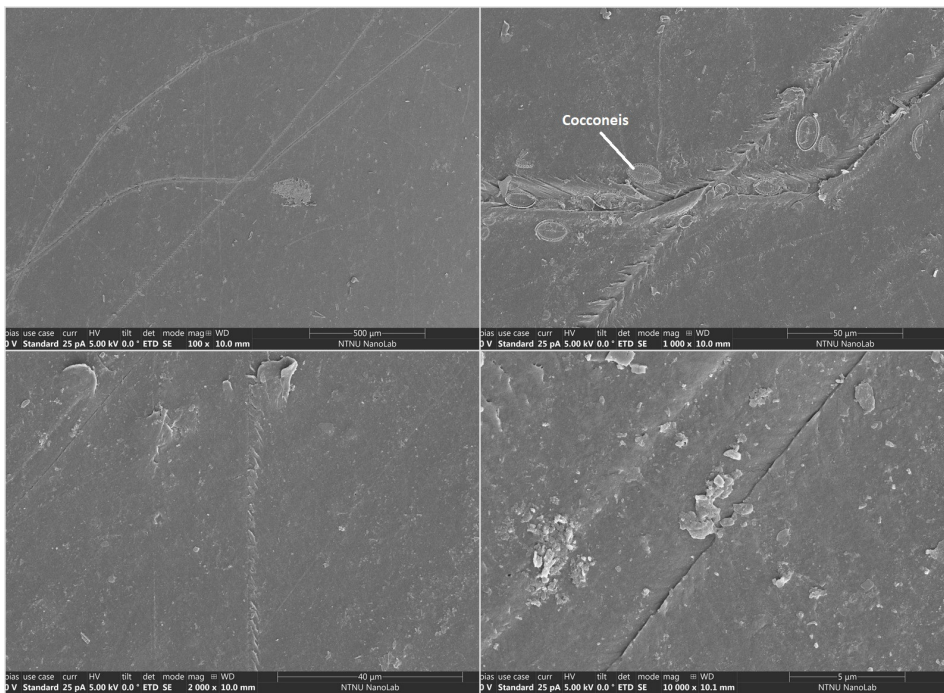


Figure 4.12: SEM pictures of LDPE at magnitudes 100x, 1000x, 2000x and 10000x.

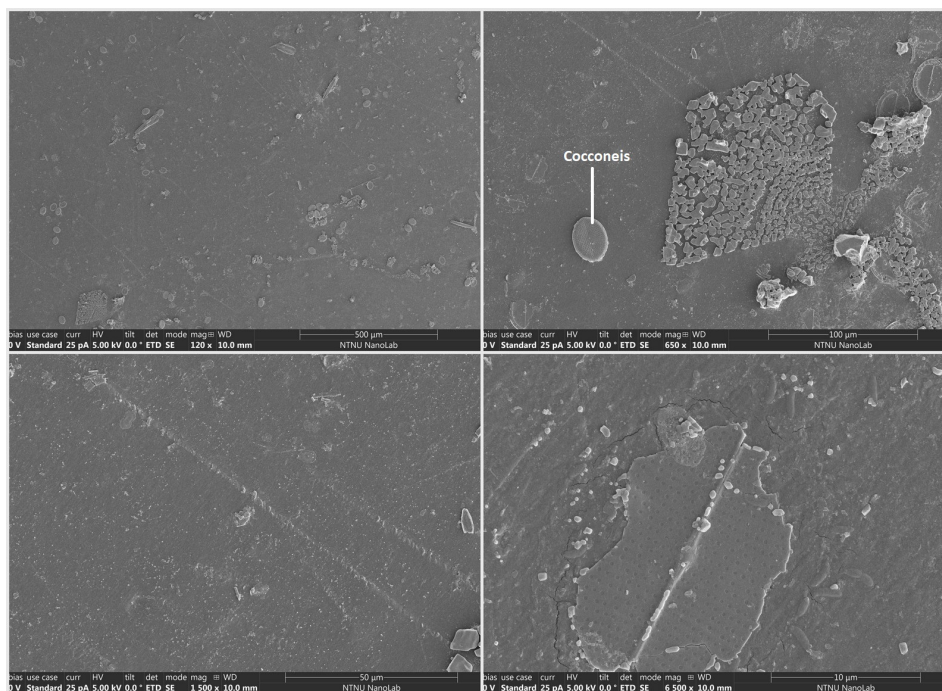


Figure 4.13: SEM pictures of LDPE at magnitudes 120x, 650x, 1500x and 6500x.

The LDPE sample shows little growth of microorganisms on the surface. Small local clusters of different algae were observed, in addition to some presence of the diatom *Cocconeis*. The little amount of biofilm made it easier to observe surface degradation signs. The figures show grooves along the surface, indicate that other material has been dragged against the plastic surface.

Figure 4.14 and 4.15 show SEM pictures of the PE sample.

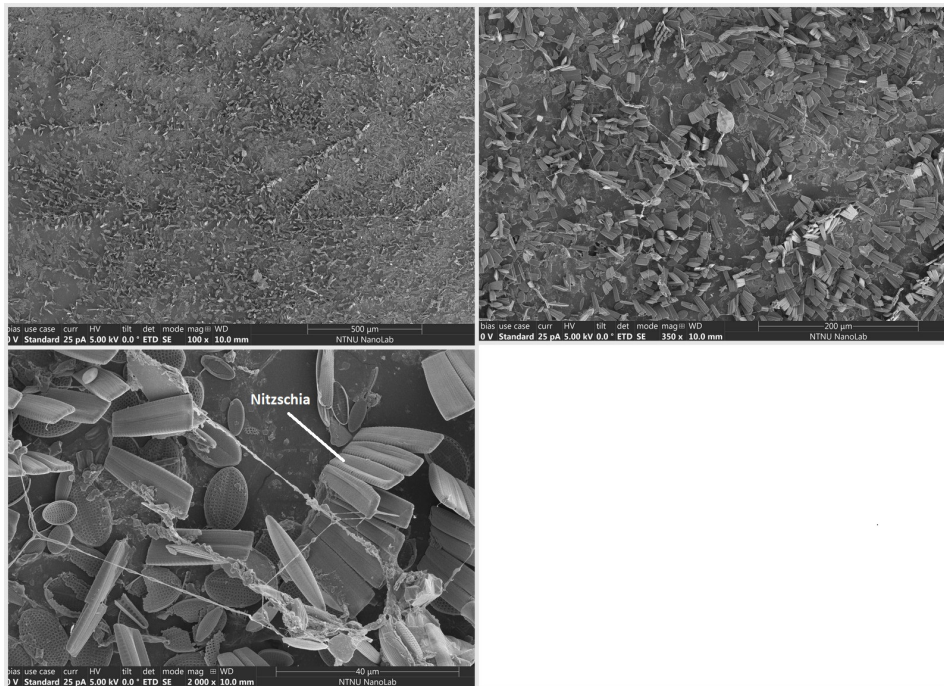


Figure 4.14: SEM pictures of PE at magnitudes 100x, 350x and 2000x.

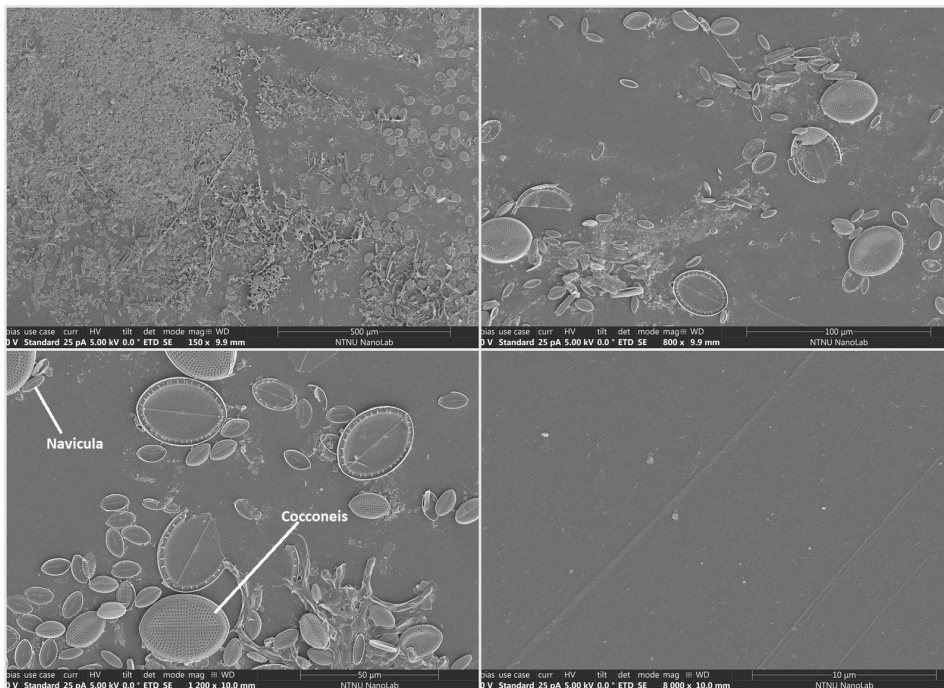


Figure 4.15: SEM pictures of PE at magnitudes 150x, 800x, 1200x and 8000x.

From the figure it is observed presence of the diatoms *Nitzschia*, *Navicula* and *Cocconeis*, in addition to other unknown algae. The uncovered parts of the plastic showed no significant degradation signs, only small signs of scratches.

Figure 4.16 and 4.17 show SEM pictures of the PP sample.

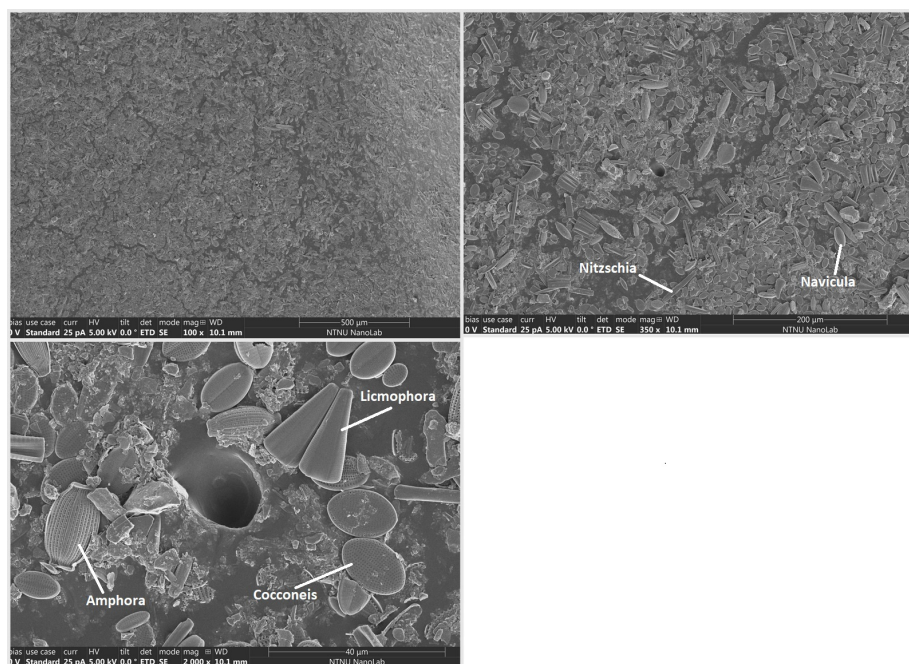


Figure 4.16: SEM pictures of PP at magnitudes 100x, 350x and 2000x.

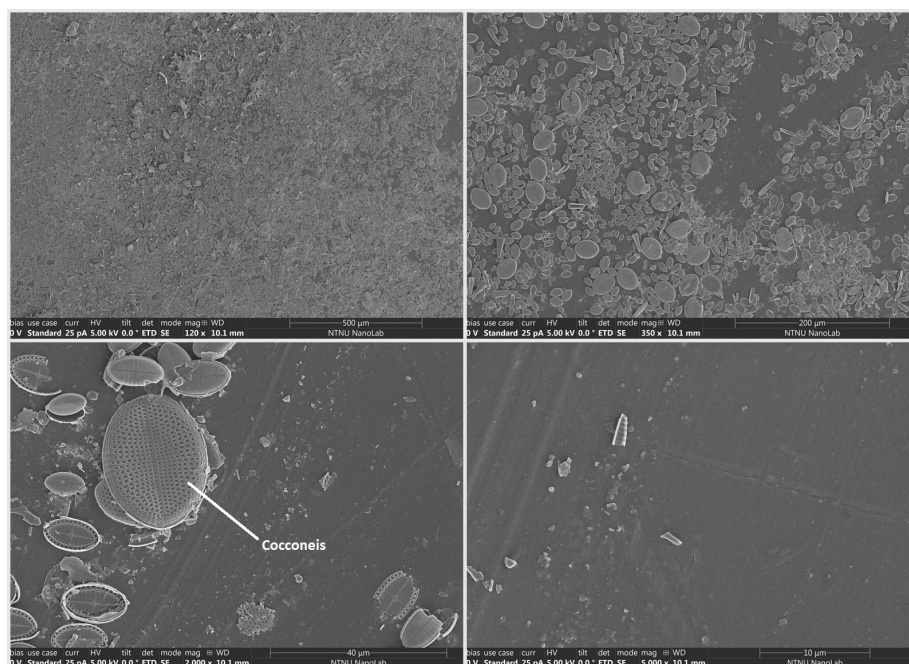


Figure 4.17: SEM picture of sample PP at magnitudes 120x, 350x, 2000x and 5000x.

The SEM pictures revealed that the plastisphere consists of all the five diatoms, Amphora, Licmophora, Cocconeis, Nitzschia and Navicula, in addition to unidentified algae. Some degradation signs were observed, such as a 20 micrometre wide pit in Figure 4.16, in addition to small scratches in Figure 4.17.

Figure 4.18 and 4.19 show SEM pictures of the PVC sample.

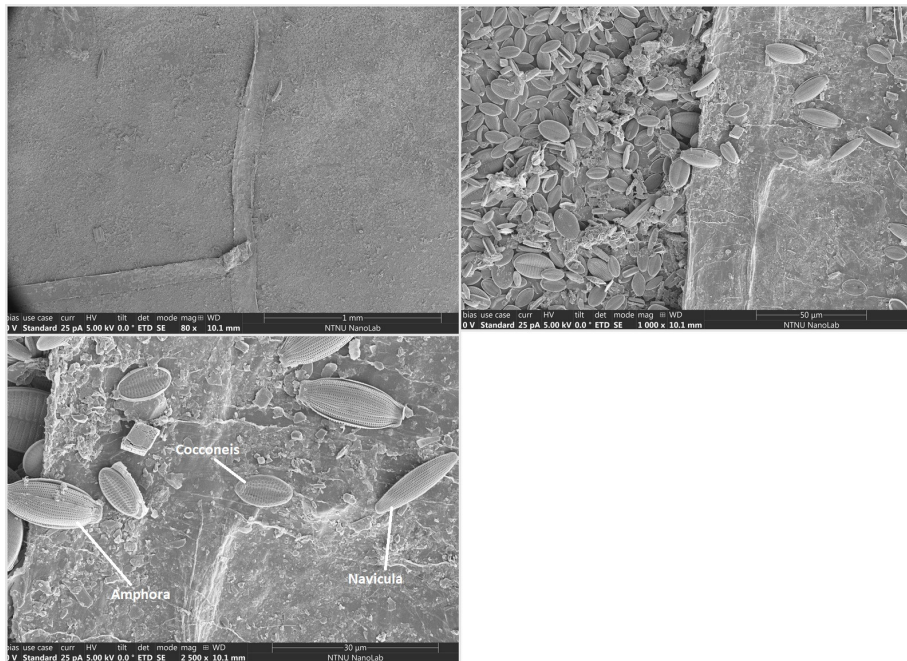


Figure 4.18: SEM pictures of PVC at magnitudes 80x, 1000x and 2500x.

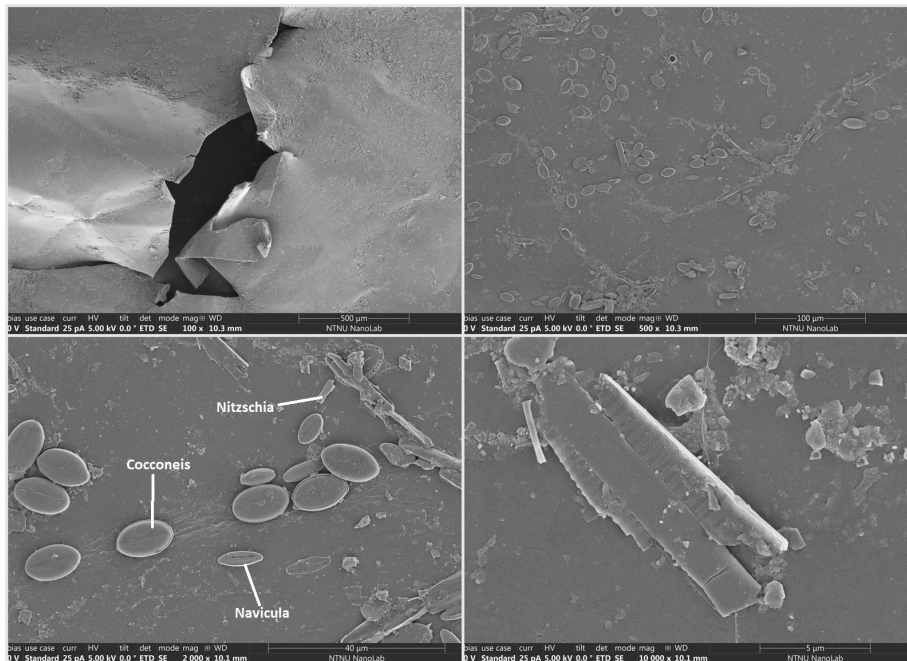


Figure 4.19: SEM pictures of PVC at magnitudes 100x, 500x, 2000x and 10000x.

As the figures show, the diatoms *Cocconeis*, *Amphora* and *Navicula* were present on the sample, in addition to other unknown particles. Small scratches on the surface was observed. Also, Figure 4.18 shows that the plastic film has been ripped, but the edge displays little degradation other than mechanical weathering.

5 Discussion

5.1 Microplast Sampling

No pieces were observed of any of the sample spots which were searched for microplastics at the four beaches at Svalbard. This could be due to the method used and the lack of a standard protocol. Because of time constraints, only a few squares were investigated. Adding more squares to the research could increase the chance of finding microplastics, since more of the beach would be covered. However, the microplastic distribution depends on the dynamic of the beach, and thus it is challenging to find optimal locations of sampling which yields for every beach. In addition, the size of the microplastic might be too small to be caught by the sieving tool used. Hence, a smaller mesh size could be used during sampling, or sand samples should be brought to the laboratory for microplastic extraction (i.e. density separation). SEM pictures reveal that the microplastic fallen off the samples have a size in the order of $100\mu\text{m}$, indicating that smaller mesh sizes might have been needed to catch the microplastic. Recent studies have found presence of microplastic on beaches at Svalbard, so it should be expected to find some concentrations of it[91]. The plastic beach debris sampling is quite easy, but the many ways to choose sampling areas makes it challenging. A standard sampling protocol would make it easier to compare the data between the studies.

5.2 Study of Marine Plastic Debris at Svalbard

From the visual inspection (Table 4.1) of the total 169 samples, the plastic was distributed as ropes, fragments, or films. The most common type was fragments with 65%, followed by fishing ropes with 23%, and the remaining 12% being films. Comparing with a recent study done at other beaches on Svalbard, it shows that fishery-related sources accounts for most of the plastic pollution[59]. The largest source is from fishing vessels in the Barents sea[60]. Fishery-related sources of pollution is in agreement with studies done on other remote beaches in the world, such as in Australia and Alaska[92][93]. Thus, it should be expected to find that the distribution was more weighted on plastic from fishery-sources. Characterisation of the colours showed that 27% of the samples were white, 21% green

and 18% blue, observed from Table 4.1. Further monitoring and research are required to get representative data from remote beaches at Svalbard and to observe the accumulation of plastic beach debris at Arctic beaches. An efficient way of doing so is to apply citizen science programs[63]. By cleaning the beaches and sea surfaces for plastic debris, this will decrease the concentration of plastics in the environment, making it less available for animals to ingest.

5.2.1 Identification by Pyr-GC/MS

Pyr-GC/MS was the method used for structural determination of the polymers, due to its successful analysis of plastic in previously studies[79][82]. It is a user-friendly method, due to its limited requirements of sample preparation prior to analysis. The sample size analysed should be kept constant to achieve the best results. For that reason, all the samples were cut to the size of about 1mm^2 . However, with the samples having different width and density, the amount might have varied even though all were cut to 1mm^2 .

Analysis by pyr-GC/MS revealed that 21 of the 28 samples were PE, while the remaining seven were PP. These are the two polymers which are of highest demand in Europe, as seen in Table 2.1. Based on other studies done on plastic debris on beaches, PE is also found to be the most abundant, followed by PP[25][94]. In this project, all the 28 samples were successfully identified. Even though impurities were present at times, they did not prevent identification. Impurities most likely caused the big bump in the pyrograms and was tried fixed by replacing the injection liner and decreasing the column by cutting. In addition, the gas flow was switched from running through the Pyrola unit to go directly into the column (S/SL mode) to minimise the noise. This noise made it difficult to observe any potential peaks with low retention time. Even though all the samples were successfully identified, another method should be executed on the samples as well for verification. FTIR has been shown in several recent studies to be the most reliable method for structural identification of plastic debris[67][95].

Samples originating from ropes were sometimes troubling. This is due to the fibres low weight, causing them to blow away by the helium gas before analysis. This made the analysis more time consuming, but a good solution was to tie the fibres before placement on the filament. Another solution to the problem could be to add a solvent, making the

fibres attach better onto the filament. A disadvantage with this method is that it is quite time consuming, taking into account that the filament needs to be cleaned between each run, and approximately 2-3 blanks had to be run to keep contamination at a minimum between every sample. In addition, the samples get destroyed during analysis, so the samples cannot be used after analysis. In this case that was not an issue because of the large number of samples. However, for studies having limited amount of samples, another method should be considered, such as FTIR or Raman spectroscopy.

Comparing with other methods, studies show that FTIR is a more developed method for analysing polymers. The method requires less analysis time, allowing quicker identification of the samples. In addition, the samples are not destroyed during analysis, so in case there is a limited amount of sample, FTIR may be a more suited method. However, a disadvantage with FTIR is that it is more easily hindered by impurities which can disturb the IR-spectres. Raman spectroscopy is another method for non-destructive identification of plastics, especially small particles ($<20\mu\text{m}$)[78]. Comparing with FTIR, Raman spectroscopy presents better spatial resolution, wider spectral coverage and narrower spectral bands[96].

5.2.2 Study of Polymer-Associated Substances

Pyr-GC/MS has successfully analysed polymer-associated substances in plastic samples in recent studies[79]. In this experiment, the desorption temperature used was 350°C . This temperature was chosen to ensure desorption of potential additives or environmental pollutants without pyrolysing the polymer itself. As observed in Figure 4.5 and 4.6, the peaks marked with F most likely originate from the polymer itself. This was also observed in the pyrograms for some of the other samples, shown in Appendix A2.2.1. The peaks were not identified as any polymer-associated substances in NIST, and the retention time is identical to the pyrolysis products of the polymer in the high-temperature pyrograms (700°C). The peaks may indicate that the polymer started to decompose at this temperature. The depolymerisation products may make it more difficult to identify any present additive or environmental pollutant. It would be interesting to optimise the pyrolysis temperature to ensure desorption of the polymer-associated substances without decomposing the polymer.

From the PP sample shown in Figure 4.5, peak A1 was possibly determined as diisooctyl adipate. This is a plasticiser used to soften the plastic and make it more flexible, so its presence in the plastic debris is possible[97]. For sample HDPE in Figure 4.6, three potential polymer-associated substances were detected (A1, A2, A3) apart from the polymer fragments (F). They were suspected due to no identical peaks in the high-temperature pyrogram. By searching in NIST, two of them were identifiable, A1 as dichloroaniline and A2 as diethyl phthalate. Dichloroaniline is shown to be a product of the biocide diuron in aerobic conditions[98]. A study showed that degradation of Diuron most likely occurs by bacteria (biodegradation), and less by photochemical degradation[99]. No information on the use of Diuron as an additive in plastic was found. HDPE is more susceptible for photo-oxidated degradation compared to biodegradation, thus Diuron is more likely adsorbed by the plastic in the ocean, than incorporated in it. Diethyl phthalate is a known plasticiser used in plastics. The peak was not found in the high-temperature program nor the blanks, thus diethyl phthalate is believed to be a leaching additive from the plastic. The last one, A3, was not identifiable in NIST.

5.2.3 Characterisation by SEM

SEM proved to be a great technique for investigating the surface of plastic samples, getting detailed pictures of both degradation signs and presence of microorganisms. Taking pictures was neither difficult nor time consuming, and no problems occurred during the analysis. Other techniques can also be applied to characterise the degradation of weathered plastic, such as TEM. TEM also provides high resolution photos and can capture samples on a closer scale. On the other hand, the field of view is narrower with TEM, making it harder to take an overview picture of the sample. The advantage of SEM is that it gives 3D pictures, compared with TEM that gives pictures in 2D. 3D pictures allow us to investigate particles on the surface. SEM also allows for imaging of a larger amount of samples at a time, and the sample preparation is easier than for TEM.

5.2.3.1 Svalbard Samples

The pictures shown in the results gave a look at two different polymers (PE and PP), and observations of different degradation signs. Table 4.5 shows the presence of degradation on the samples. Comparison of the polymers PE and PP was done to see if there were

any connection between polymer type and degradation. Based on the results, it is hard to say whether one polymer is more exposed to a degradation process compared to the other. Both polymer types contained cracks and flaking. Biological organisms are found on both PE and PP samples. This could be because plastic provides a habitat for the organisms. Figure 4.7 shows that the PP sample contains cracks and fractures, breaking the plastic to smaller particles. Pits were also observed. In addition, horizontal lines over the sample are observed, but it is difficult to say if they occurred from weathering or the production of the plastic itself.

Looking at the SEM-pictures of PE, Figure 4.8, flaking of a top layer is observed. It may seem that the original plastic sample (sample I5 from Figure 4.2) was blue, and that this blue layer has been falling off during weathering, revealing a white layer underneath. Uncertainties must be considered because some degradation signs might have been caused by sample handling and not from weathering. Figure 4.9 also shows a picture of sample I4, just another part of the sample. The picture clearly shows a bigger part that has fallen off. The missing part has cracks connected around it, which might have been the precursor for the particle loss. A little piece on the left which is about to fall off is also observed, surrounded by cracks. By looking at the scale on the picture, these parts are considered as microplastics (>5 mm), showing that cracking leads to the release of microplastics. More samples and data are needed to be able to say something concerning the correlation between degradation and polymer type. In this project, the samples were quite different in shape, thickness/hardness, and structure, which might have been a more important factor than the type of polymer.

There are some uncertainties concerning the results of this study. Since the plastic fragments were collected at the beach, it is impossible to know how long they have been in the ocean, how far they have travelled, how much radiation they have been exposed to, and how long they have been on the beach. All these factors impact the degradation of plastics, making it difficult to say something about the degradation with certainty.

5.2.3.2 Trondheimsfjorden Samples

All the five different polymer films placed in Trondheimsfjorden for a period of 19 weeks were analysed with SEM. The SEM pictures revealed major growth of biofilm on all

the samples, except from the LDPE film. The microorganisms were tried identified by comparison with Figure 2.4 from a previous study done on biodiversity of organisms on floating plastic surface[2]. Thus, the found diatoms must be considered as suggestions. From table 4.6, it is observed that the plastic having highest growth of biofilm was PP, followed by PVC, PE, HDPE and LDPE in decreasing order. Cocconeis was the most abundant diatom, being present on every of the samples. Licmophora was the least abundant diatom, only observed on the PP sample.

Degradation signs were problematic to observe due to the large presence of biofilms. Small scratches were seen on sample PP, PE, and LDPE, indicating that other material has been dragged against the plastic surface. In addition, a pit on the size of 20 μ m was observed on sample PP. The LDPE sample differed from the others by having little biofilm on the surface. However, no significant degradation sign was spotted other than scratches.

These SEM pictures confirms that plastic surfaces are creating new habitats for microorganisms in the ocean. Generally abiotic degradation precedes biodegradation, thus biodegradation is expected to occur at smaller and more weathered plastics than these films. It must be taken into account that these pictures are only of a small size of the plastic piece, and other degradation signs and microorganisms might be observed on different locations on the sample.

5.2.4 Further Work

Searching of microplastic at Svalbard resulted in no samples, even though earlier studies have found presence of microplastic at beaches of Svalbard. In addition, SEM pictures from this study revealed that microplastic fallen off the samples have a size in the order of 100 μ m. Thus, it would be interesting to decrease the mesh size of the sieves and increase sampling spots, to enhance the chance of finding microplastics.

Pyr-GC/MS successfully identified all the 28 samples analysed in this thesis. Verification by another method such as FTIR would be valuable, to check the reliability of the method. In addition to identification, quantifying the amount of polymer-associated substances in the samples would be interesting. Some of the desorption pyrograms (350°C) showed presence of polymer fragments, indicating that the polymers started to decompose at this temperature. Thus, it would be interesting to optimise the desorption temperature for the samples. This would decrease the loss of other potential peaks from polymer-associated substances.

In this study, there are too few samples to be able to say anything with certainty about the correlation between plastic type and degradation sign. This could be possible by increasing the amount of samples analysed. This also yields for the type of plastic and presence of microorganisms.

The SEM pictures of the plastic samples in Trondheimsfjorden revealed presence of different microorganisms and algae on the surface. The different microorganisms were tried identified. It would be preferable to determine the biodiversity and the specific species of the microorganisms on the different polymer films, to see if there is any difference between the polymer types.

It would be very interesting to analyse the samples from Trondheimsfjorden of polymer-associated substances, if the time had allowed it. Since this location is close to a city in opposite to the Svalbard samples, the chance of identifying any environmental pollutants is expected to be higher.

6 Conclusion

A total of 169 plastic samples were collected from four different beaches at Svalbard (Isfjord Radio, Hiorthamna, Ny-Ålesund and Sallyhamna). All samples were visually described in the lab. The major part of the samples were plastic fragments (65%), followed by ropes (23%) and the remaining samples films (12%). Most of the samples were white (27%), green (21%) and blue (18%).

Seven samples from each place were analysed by pyr-GC/MS for structural identification of the polymers. Further, two samples from each place were analysed for leaching additives or adsorbed environmental pollutants. It was found that 75% of the samples were composed of polyethylene, while the remaining 25% were composed of polypropylene. Two additives and one environmental pollutant were detected, diisooctyl adipate, diethyl phthalate and dichloroaniline. Pyr-GC/MS proved to be a promising technique in identifying the chemical composition of polymers, as well as polymer-associated substances such as additives.

Further, all seven samples from the beach of Isfjord Radio were in addition analysed by SEM, to characterise the surface morphology and study degradation signs. SEM revealed degradation such as flaking, cracks, fractures, grooves, and pits, in addition to presence of biological organisms and other adhering particles.

Five samples of different polymers which were exposed to the marine environment in Trondheimsfjorden in 19 weeks were analysed by SEM. The pictures revealed high presence of biofilm on all samples, except from LDPE. The most and the least abundant diatoms were *Cocconeis* and *Licmophora*, respectively. HDPE was the sample covered with the most biofilm, while LDPE was the least covered.

More data is needed to be able to say something specific about the correlation between polymer type, degradation processes and presence of microorganisms. The combination of pyr-GC/MS and SEM was found to be a promising method for describing the weathering of plastic beach debris. Today, there is no standard protocol on how to conduct sampling of plastics in the environment. This leads to difficulties when comparing results from studies. Thus, a standard protocol should be defined as soon as possible to reduce this limitation.

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Appendix

A1 Example of polymer identification

An example showing how to interpret pyrograms and identify the polymer type, here for sample I4 which was identified as PP. Figure A1.1 shows the acquired pyrogram for sample I4. The marked peaks are further compared with mass spectras.

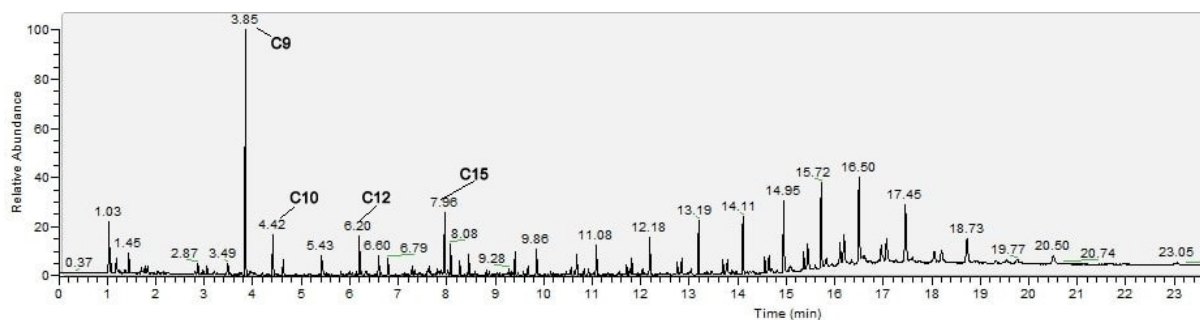


Figure A1.1: Pyrogram of sample I4.

First, the pyrogram of the sample is compared with reference pyrograms. Figure A1.2 shows the reference pyrogram for PP. The reference pyrograms were made at 600°C, compared to 700°C in this project. The 30 minute GC/MS program used was the same as the one of this project except from injection flow and injection ratio. Injecton flow used was 1.5 mL/min compared to the reference 1.0 ml/min and the injection ratio was 1:60 compared to 1:100. From this, it was expected to get the same pattern of the pyrograms, but a small displacement in elution time.

002 Polypropylene(isotactic); *iso*-PP

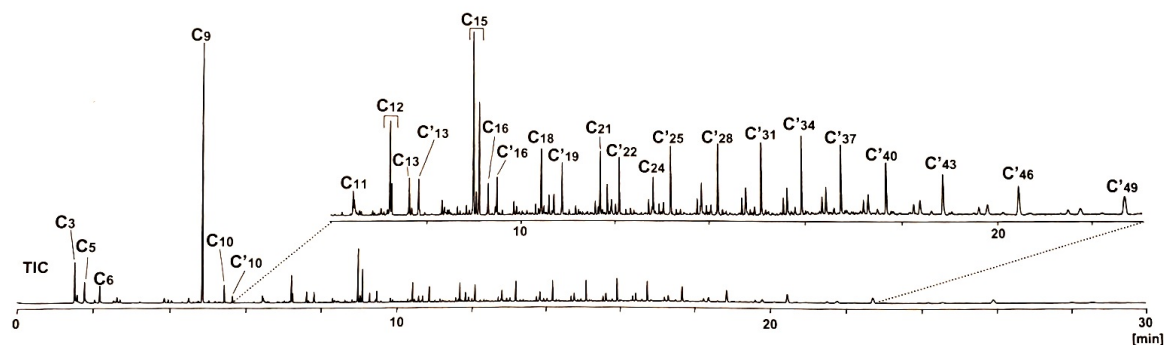
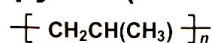


Figure A1.2: Reference pyrogram for iso-PP[6].

By comparing the pyrograms, it is observed that the sample pyrolyzates eluted a bit faster than the reference pyrolyzates, which might be due to the higher injection flow. Otherwise, the reference pyrogram for iso-PP fits well with the unknown sample.

Further on, the mass spectra of some sample pyrolyzates are compared with the reference mass spectra. This is done to verify that the pyrolyzates are the same, giving a correct identification. The peaks that are compared are given the notations C₉ (3.85 min), C₁₀ (4.42 min), C₁₂ (6.20 min) and C₁₅ (7.96 min). Figure A1.3 shows MS-spectra from the sample pyrolyzates.

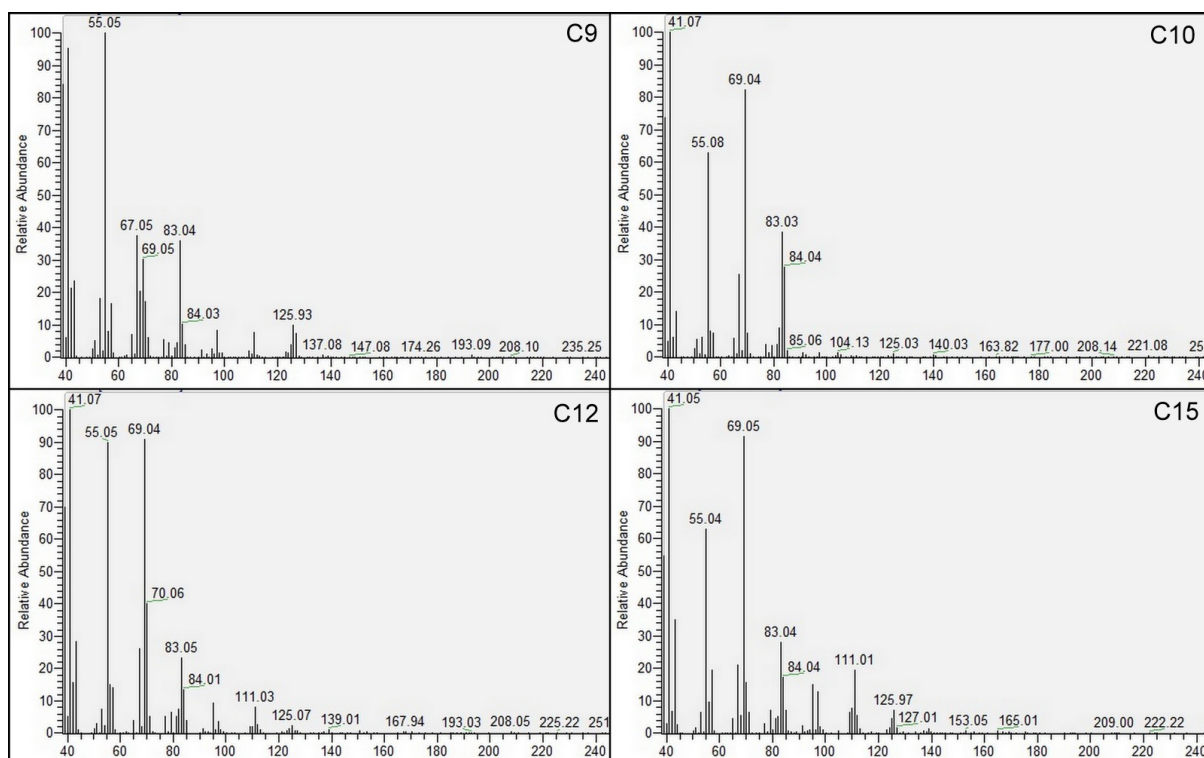


Figure A1.3: Mass spectra of pyrolyzates (C₉, C₁₀, C₁₂ and C₁₅).

The m/z range of the analysis was 38-600 amu, while the reference ranged from 29-600 amu. Therefore, m/z from 29-38 amu are not shown in the sample mass spectra. Figure A1.4 shows the reference mass spectra for the pyrolyzates of iso-PP[6].

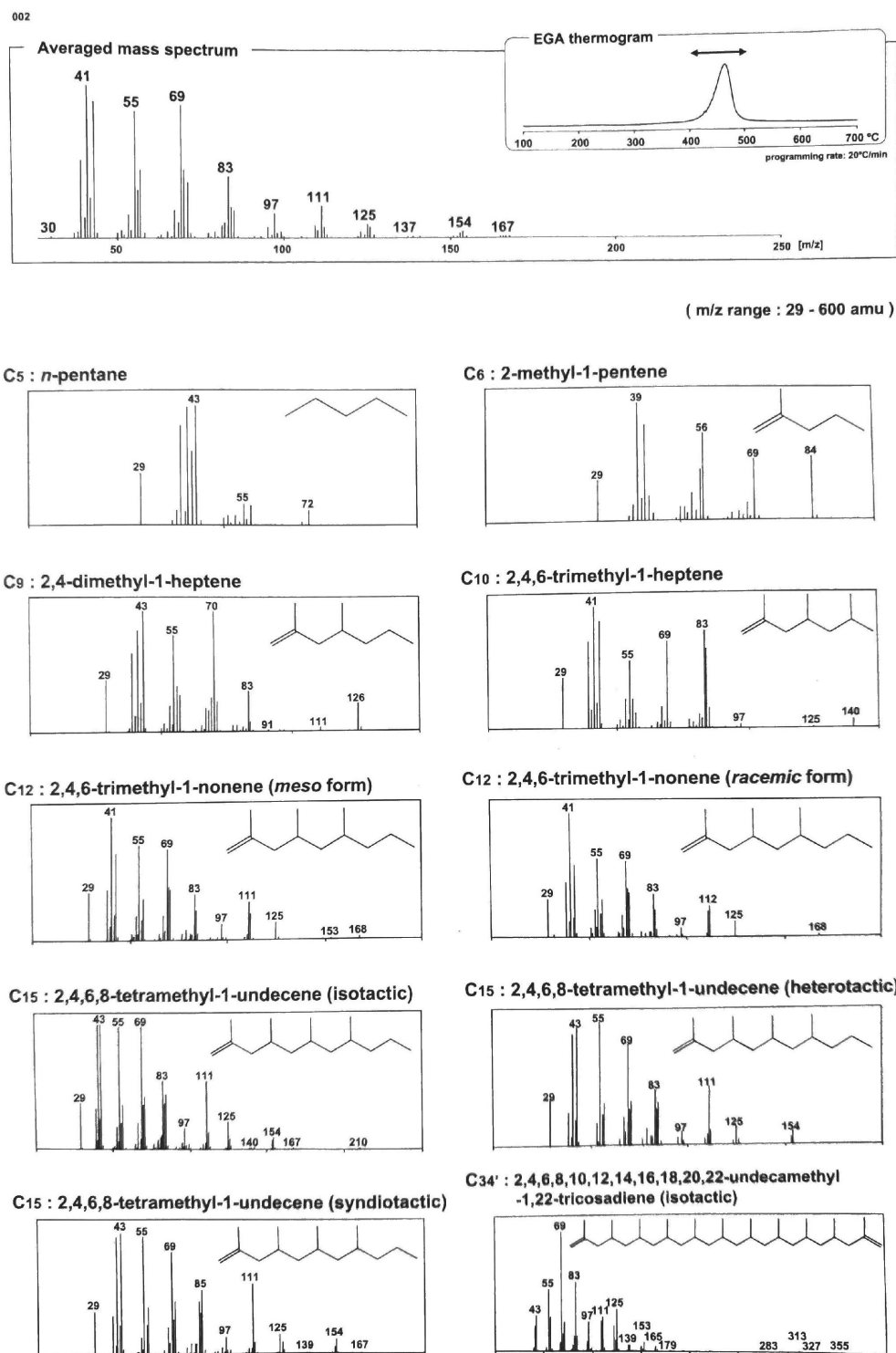


Figure A1.4: Reference mass spectra for iso-PP[6].

The comparison of pyrograms and the pyrolyzates mass spectra confirm that the sample is identified as PP. The same procedure was done for all samples.

A2 Results

A2.1 Visual identification results

A2.1.1 Isfjord Radio

Figure A2.1 shows the colour distribution of the 59 samples at Isfjord Radio.

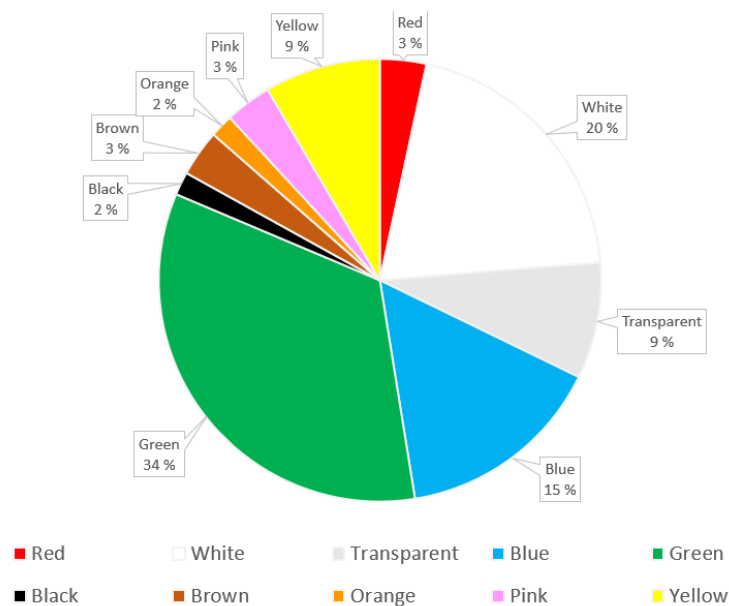


Figure A2.1: Colour distribution of the samples at Isfjord Radio.

Figure A2.8 shows the plastic type distribution of the 59 samples at Isfjord Radio.

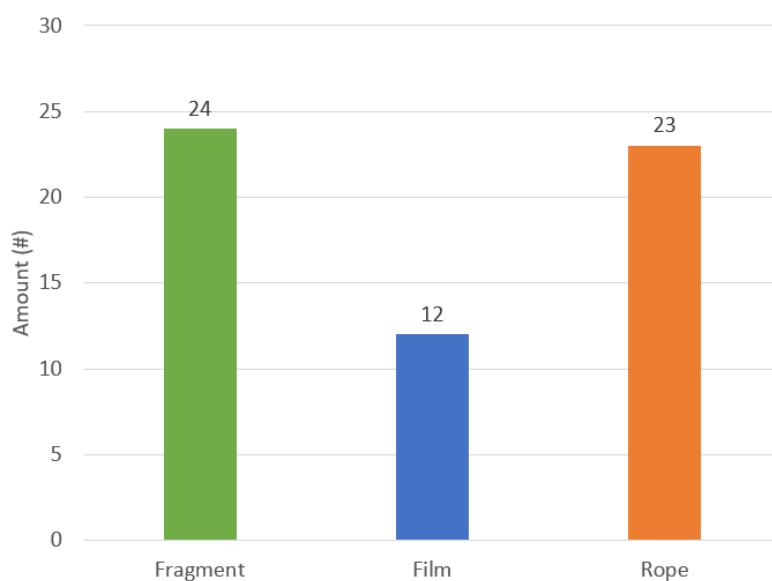


Figure A2.2: Colour distribution of the samples at Isfjord Radio.

Table A2.1 shows the description of all the samples found at Isfjord Radio.

Table A2.1: Visual description of all samples from Isfjord Radio.

#	Type	Colour	Length [cm]	Width [cm]	Weight [g]
1	Fragment	Red	3	1.8	0.9
2	Fragment	Yellow	5.2	4	1.7
3	Fragment	Transparent	7.8	7.2	2.4
4	Fragment	Yellow	5.9	3.7	1.4
5	Fragment	Yellow	3.8	3.6	0.8
6	Fragment	White	6	4	1.0
7	Fragment	Black	7.3	6.8	12
8	Fragment	Yellow	1.3	0.4	0.0
9	Fragment	Transparent	14	5.2	20
10	Fragment	Transparent	9.5	3.5	3.1
11	Fragment	White	8.2	4.7	3.4
12	Fragment	Blue	11	1	2.4
13	Fragment	Transparent	4.5	2.8	0.7
14	Fragment	Yellow	5.1	3.7	1.2
15	Fragment	White	2.6	1.2	0.3
16	Fragment	Red	6.6	2.4	3.9
17	Fragment	White	2.9	2.9	2.4
18	Fragment	Blue	11	6.2	19
19	Fragment	Green	4.8	1.8	1.2
20	Fragment	White	3.4	1.9	1.0
21	Fragment	White	2.1	1.3	0.6
22	Fragment	Blue	3.8	3.5	4.7
23	Fragment	Pink	2.5	1	0.2
24	Fragment	Green	1.6	1	0.1
25	Film	Transparent	26	4.4	0.3
26	Film	White	6.5	4.5	0,1
27	Film	White	5.7	1.8	0.0
28	Film	Blue	57	31	18
29	Film	Brown	8.2	4.7	0.4
30	Film	Blue	20	7.2	0.5

#	Type	Colour	Length [cm]	Width [cm]	Weight [g]
31	Film	Blue	8.3	4	0.1
32	Film	Blue	6.8	6.2	0.1
33	Film	White	17	6.9	0.4
34	Film	White	23	13	1.0
35	Film	White	7	2.7	0.1
36	Film	White	14	12	0.4
37	Rope	Blue	2	0.8	0.5
38	Rope	Orange	11	0.8	1.0
39	Rope	Green	6.5	0.5	0.3
40	Rope	Green	7.5	1.8	2.6
41	Rope	Brown	40	0.4	0.7
42	Rope	Pink	25	0.2	0.2
43	Rope	Green	11	0.6	1.5
44	Rope	Green	7	0.5	0.4
45	Rope	Green	5.5	1.8	1.4
46	Rope	Green	7.5	3	2.4
47	Rope	Green	4.8	0.4	0.1
48	Rope	Green	6.4	0.6	0.4
49	Rope	Green	23	0.5	0.7
50	Rope	Green	4.5	0.3	0.1
51	Rope	Green	13	3.5	1.7
52	Rope	Green	13	1.2	1.8
53	Rope	Green	5	0.4	0.1
54	Rope	Green	6.5	0.5	0.4
55	Rope	Green	4	0.5	0.1
56	Rope	Green	32	0.8	1.9
57	Rope	Green	6	0.5	0.3
58	Rope	Blue	39	0.3	3.5
59	Rope	Green	100	2.3	34

A2.1.2 Hiorthhamn

Figure A2.3 shows the colour distribution of the 42 samples at Hiorthhamn.

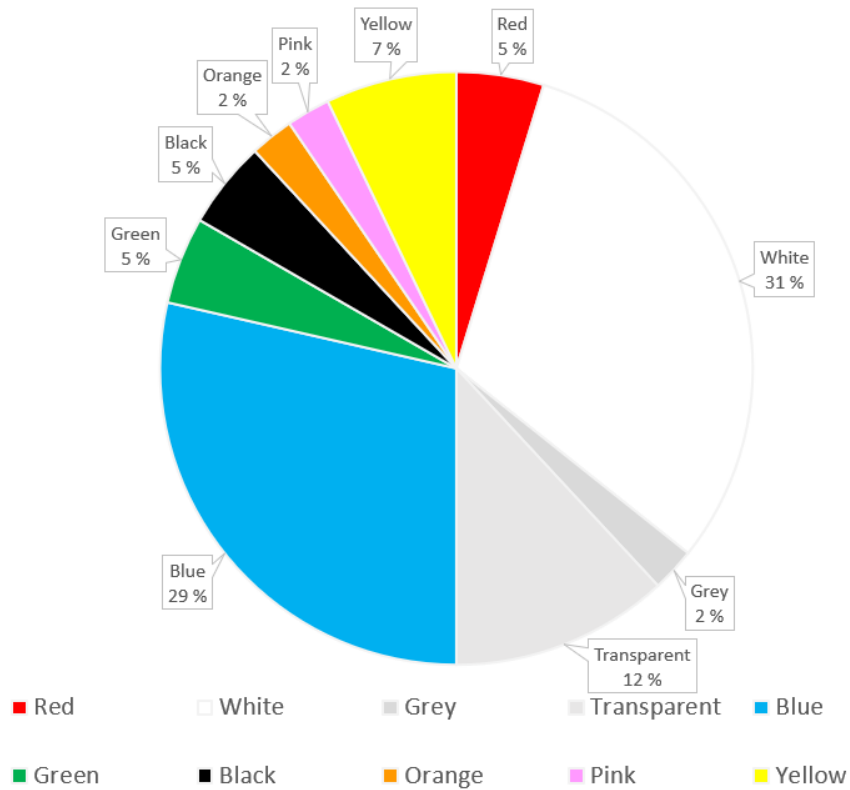


Figure A2.3: Colour distribution of the samples at Hiorthhamn.

Figure A2.8 shows the plastic type distribution of the 42 samples at Hiorthhamn.

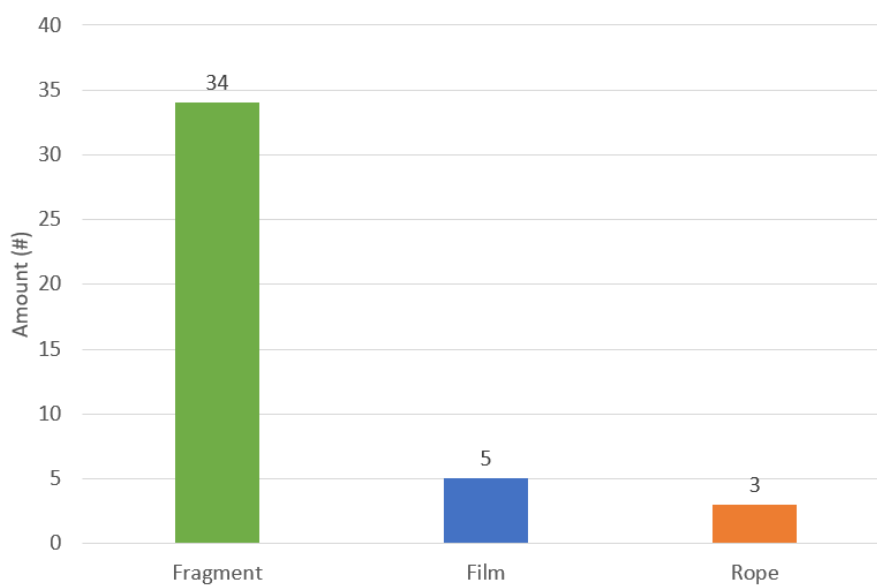


Figure A2.4: Colour distribution of the samples at Hiorthhamn.

Table A2.2 shows the description of all the samples found at Hiorthhamn.

Table A2.2: Visual description of all samples from Hiorthhamn.

#	Type	Colour	Length [cm]	Width [cm]	Weight [g]
1	Fragment	Transparent	4	2.5	2.5
2	Fragment	White	5.3	6.2	5.6
3	Fragment	White	4.7	0.7	1.5
4	Fragment	Grey	12.7	9.7	25
5	Fragment	Black	11	5.2	8.4
6	Fragment	Black	17.3	1.3	3.2
7	Fragment	Blue	6.7	2	2.8
8	Fragment	Transparent	4	0.7	0.5
9	Fragment	Yellow	60	0.3	3.3
10	Fragment	Red	9	2	1.1
11	Fragment	White	2.7	1.6	0.2
12	Fragment	White	7.4	1.9	7.4
13	Fragment	Yellow	3	1.7	0.7
14	Fragment	White	2	1.4	0.2
15	Fragment	White	5.5	3.7	5.9
16	Fragment	Blue	1.8	0.7	0.1
17	Fragment	Blue	2.2	1.7	0.3
18	Fragment	Blue	2	1	0.1
19	Fragment	Blue	5	1	0.1
20	Fragment	Blue	4.7	0.4	0.06
21	Fragment	Blue	5.6	0.8	0.1
22	Fragment	Blue	5	0.3	0.04
23	Fragment	Blue	6.5	0.3	0.2
24	Fragment	White	5.8	2.5	1.8
25	Fragment	Blue	2.6	1	0.4
26	Fragment	Pink	3.5	2.8	1.9
27	Fragment	White	7	1.5	1.9
28	Fragment	Blue	2.8	1.8	0.2
29	Fragment	White	6	3.3	0.5
30	Fragment	White	4.8	2.5	0.3
31	Fragment	White	9	7	3.9
32	Fragment	White	6.7	5.9	1.0
33	Fragment	Blue	6.8	4.5	0.4
34	Fragment	Yellow	6	4.8	3.4
35	Rope	Orange	22	0.8	2.6
36	Rope	Green	9.3	0.4	0.2
37	Rope	Green	6	0.8	0.8
38	Film	Red	3.7	2.8	3.8
39	Film	White	3.5	2.5	0.01
40	Film	Transparent	13	5	2.9
41	Film	Transparent	28	21	6.9
42	Film	Transparent	9.2	1.4	0.07

A2.1.3 Ny-Ålesund

Figure A2.5 shows the colour distribution of the 24 samples at Ny-Ålesund.

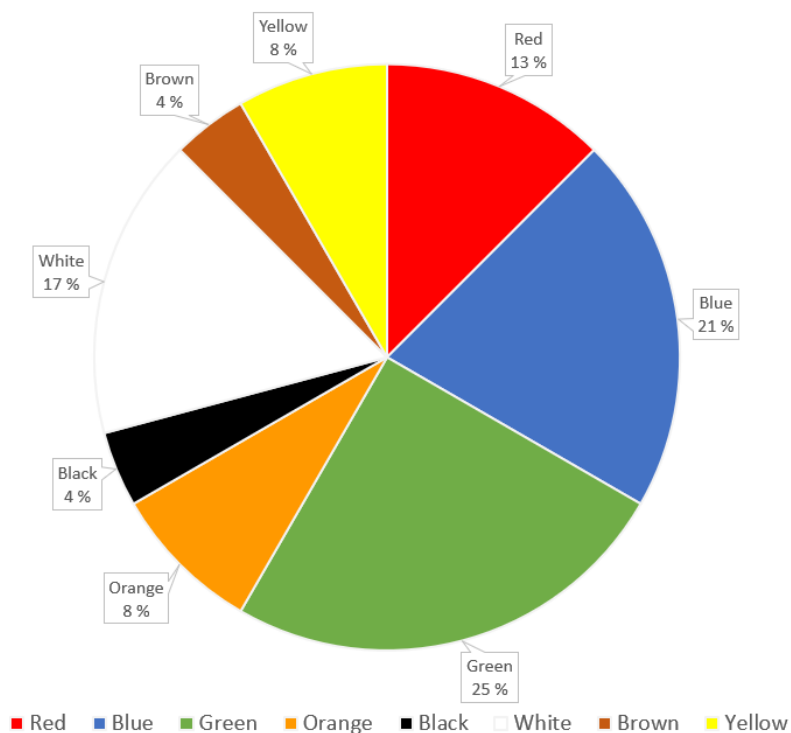


Figure A2.5: Colour distribution of the samples at Ny-Ålesund.

Figure A2.8 shows the plastic type distribution of the 24 samples at Ny-Ålesund.

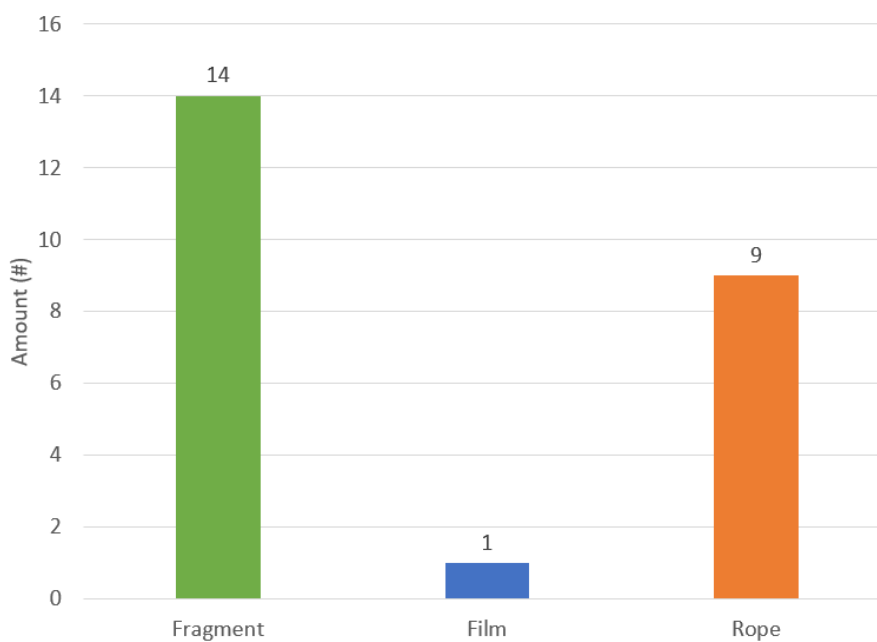


Figure A2.6: Colour distribution of the samples at Isfjord Radio.

Table A2.3 shows the description of all the samples found at Ny-Ålesund.

Table A2.3: Visual description of all samples from Ny-Ålesund.

#	Type	Colour	Length [cm]	Width [cm]	Weight [g]
1	Fragment	Red	5	3.5	5.5
2	Fragment	Blue	4	1.6	2.6
3	Fragment	Blue	1.5	0.6	0.2
4	Fragment	Green	5.6	2.1	1.2
5	Fragment	Red	3	1.5	0.9
6	Fragment	Orange	7.5	2.6	2.8
7	Fragment	Black	9.7	1	0.6
8	Fragment	White	6.5	1.3	5.3
9	Fragment	White	1.4	1	0.1
10	Fragment	Brown	20	0.3	2
11	Fragment	Red	5.5	0.4	0.3
12	Fragment	Yellow	15	5.5	1.9
13	Fragment	White	4.8	2.3	1.5
14	Fragment	White	6	5.8	1.0
15	Film	Blue	2.7	1.1	0.03
16	Rope	Green	47	0.6	3.8
17	Rope	Orange	7.5	2.5	2.8
18	Rope	Yellow	13	2.5	12
19	Rope	Green	7.5	0.6	0.4
20	Rope	Green	17	0.7	1.1
21	Rope	Green	13	0.5	0.3
22	Rope	Blue	45	0.5	1.1
23	Rope	Blue	9	0.6	0.6
24	Rope	Green	20	0.3	0.5

A2.1.4 Sallyhamna

Figure A2.7 shows the colour distribution of the 44 samples at Sallyhamna.

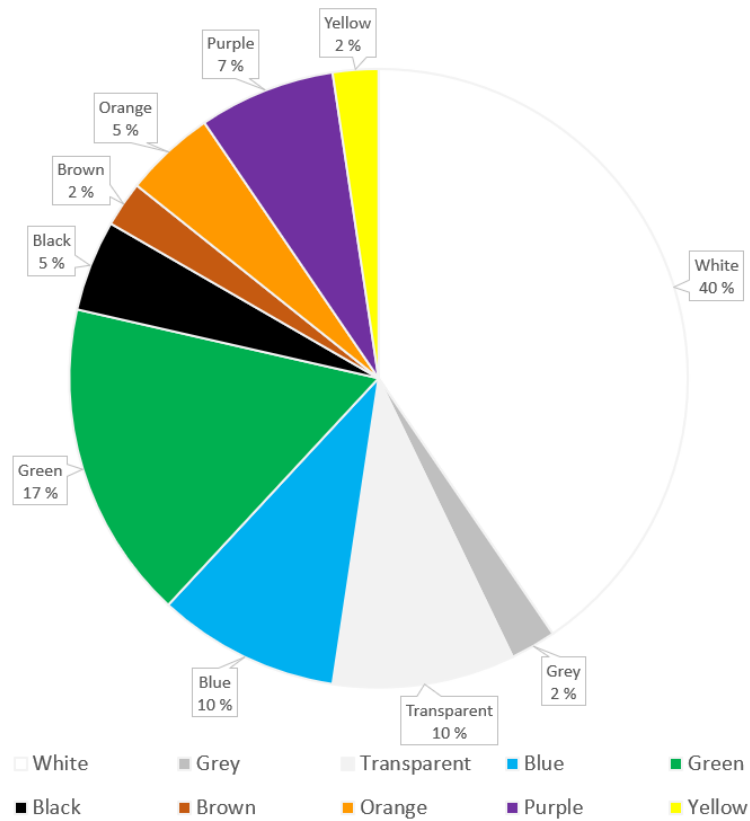


Figure A2.7: Colour distribution of the samples at Sallyhamna.

Figure A2.8 shows the plastic type distribution of the 44 samples at Sallyhamna.

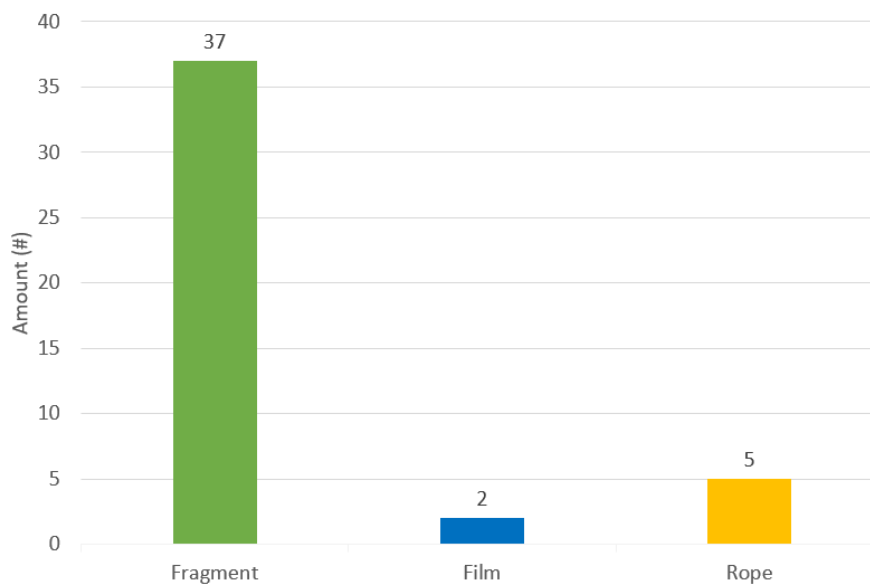


Figure A2.8: Colour distribution of the samples at Sallyhamna.

Table A2.4 shows the description of all the samples found at Sallyhamna.

Table A2.4: Visual description of all samples from Sallyhamna.

#	Type	Colour	Length [cm]	Width [cm]	Weight [g]
1	Fragment	Grey	7.2	4	3.5
2	Fragment	White	6.2	3.2	0.7
3	Fragment	Yellow	5.2	4.2	3.5
4	Fragment	White	7.8	6.5	2.3
5	Fragment	White	5.4	1.4	2.2
6	Fragment	White	7.2	1.3	0.3
7	Fragment	White	4	2.1	0.4
8	Fragment	White	3	1.1	1.7
9	Fragment	Transparent	3.4	3	7
10	Fragment	Blue	3	1.5	2.7
11	Fragment	Brown	6.8	3	6
12	Fragment	Black	4.1	4.1	11
13	Fragment	Transparent	3.1	0.3	1.3
14	Fragment	Transparent	7.5	2.8	5.6
15	Fragment	White	7.8	5.2	3.6
16	Fragment	White	2.8	1.8	2.3
17	Fragment	Transparent	2.8	2.1	0.4
18	Fragment	White	2.8	2.4	1.2
19	Fragment	White	4	1.5	0.5
20	Fragment	White	2.8	2.3	0.2
21	Fragment	White	3.1	2.1	0.2

#	Type	Colour	Length [cm]	Width [cm]	Weight [g]
22	Fragment	Purple	4.6	4	1
23	Fragment	Purple	1.6	1.5	0.2
24	Fragment	Purple	2.3	1	0.1
25	Fragment	Blue	1.9	1.2	0.2
26	Fragment	Blue	2.9	0.2	0.8
27	Fragment	Orange	1.9	0.9	0.2
28	Fragment	Orange	2.3	2.3	1.1
29	Fragment	Green	2.2	1.4	0.5
30	Fragment	Green	1.4	1.2	0.3
31	Fragment	Green	1.6	1.1	0.2
32	Fragment	Green	1.4	0.7	0.1
33	Fragment	Green	0,9	0.4	0.1
34	Fragment	Green	0.9	0.8	0.1
35	Fragment	Black	7.5	0.8	3
36	Fragment	White	3,7	1.9	0.3
37	Fragment	White	1.9	1.4	0.04
38	Rope	Green	25	0.4	1
39	Rope	Blue	4.6	0.2	0.01
40	Rope	White	46	0.6	11
41	Rope	White	41	0.6	7
42	Rope	White	85	0.6	27
43	Film	Blue	2.4	1.8	0.1
44	Film	Yellow	11	4	0.5

A2.2 Pyr-GC/MS results

A2.2.1 Qualitative Study

Figure A2.9, A2.10, A2.11, A2.12, A2.13 and A2.14 shows Desorption pyrograms (350 °C) and pyrograms (700°C) of sample B, C, E, F and G, respectively.

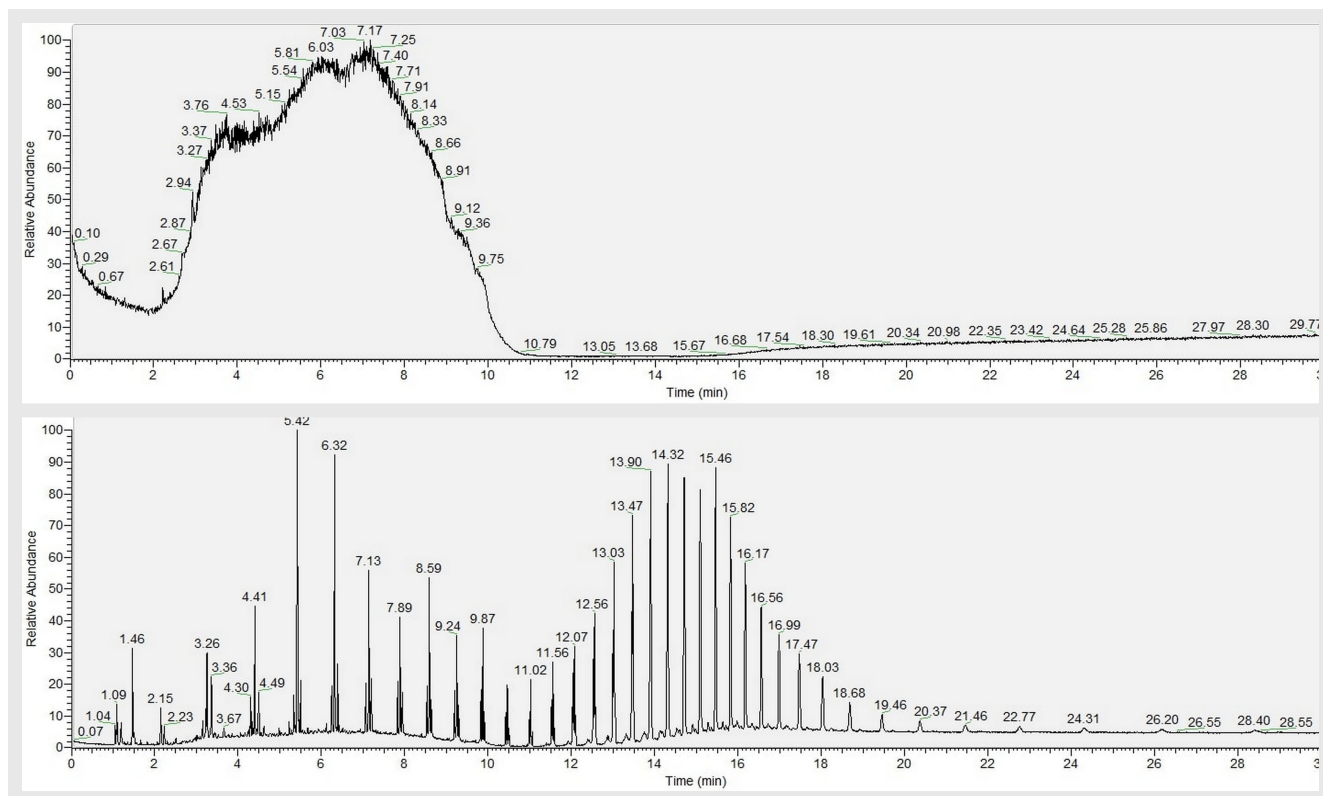


Figure A2.9: Pyrograms of plastic B (HDPE) at 350°C and 700°C.

No potential additives/pollutants were found in sample B. The peaks present most likely originates from the polymer itself.

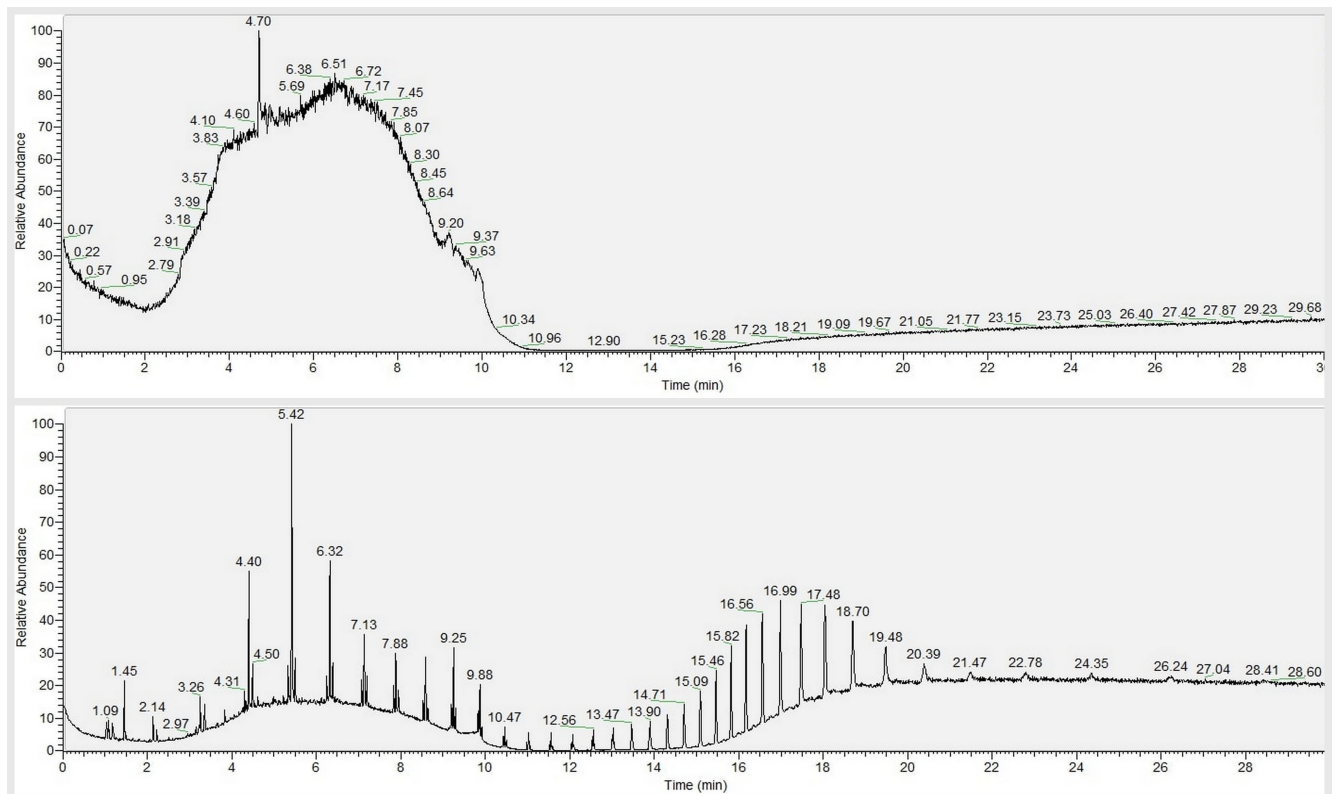


Figure A2.10: Pyrograms of plastic C (HDPE) at 350°C and 700°C.

There is one distinct peak (4.70 min) in sample C. This might be an additive or a pollutant, but it was not identified.

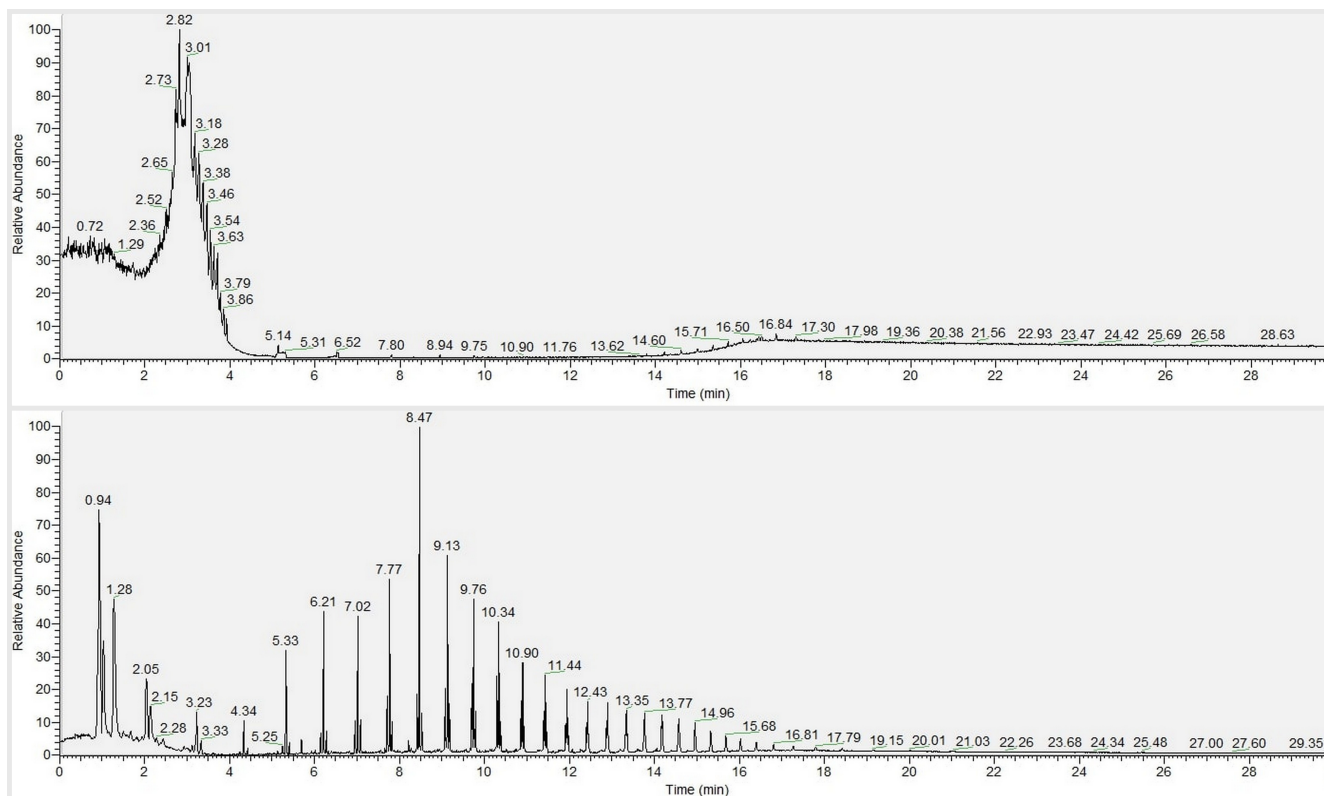


Figure A2.11: Pyrograms of plastic E (HDPE) at 350°C and 700°C.

No potential additives/pollutants were found in sample E. The peaks present most likely originates from the polymer itself.

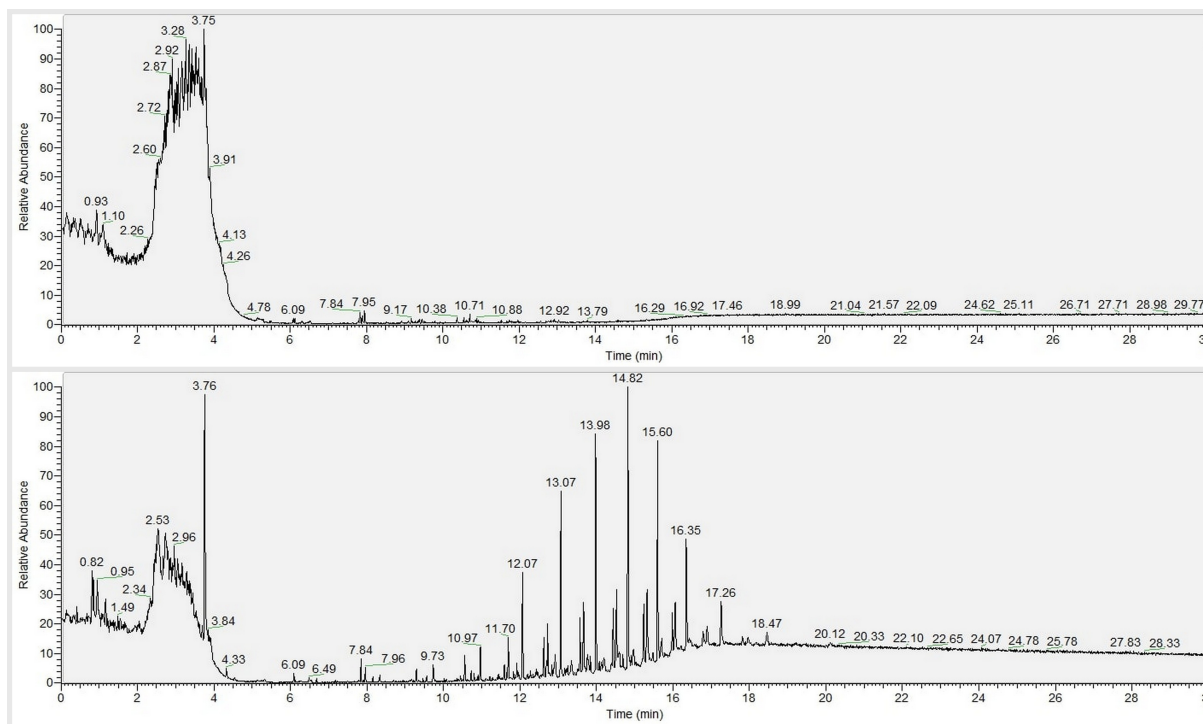


Figure A2.12: Pyrograms of plastic F (PP) at 350°C and 700°C.

No potential additive/pollutants were observed in plastic F. The peaks present most likely originates from the polymer itself.

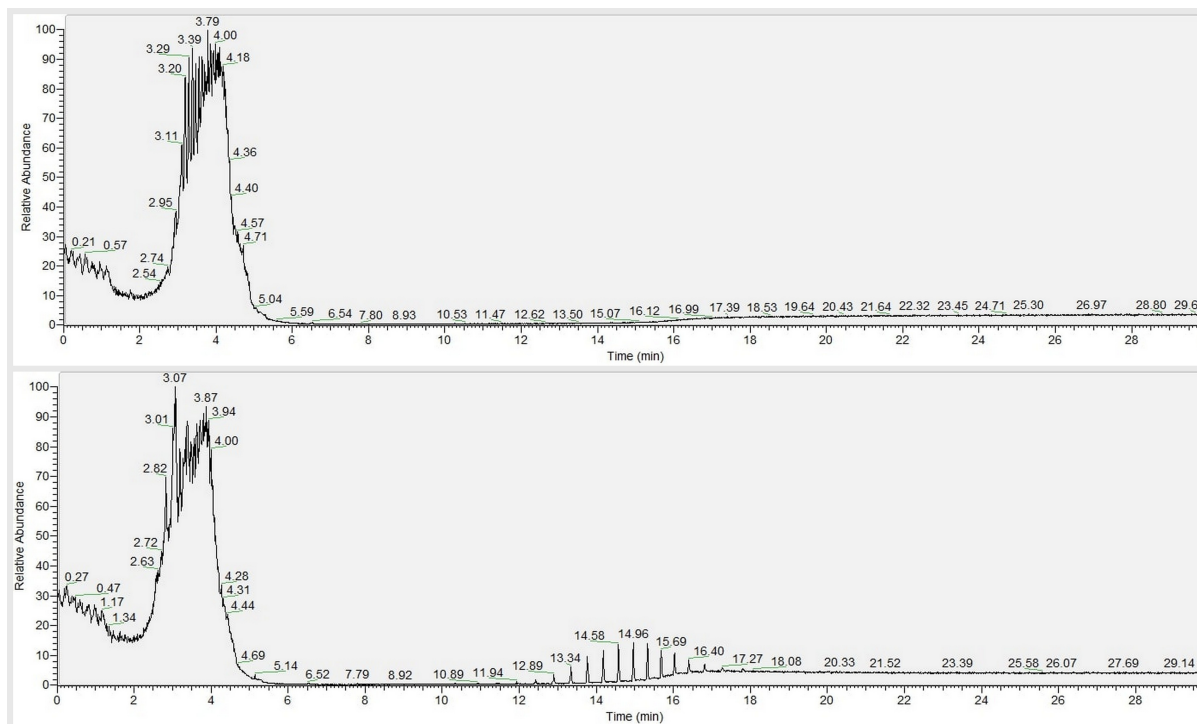


Figure A2.13: Pyrograms of plastic G (HDPE) at 350°C and 700°C.

No potential additives/pollutants were found in sample G.

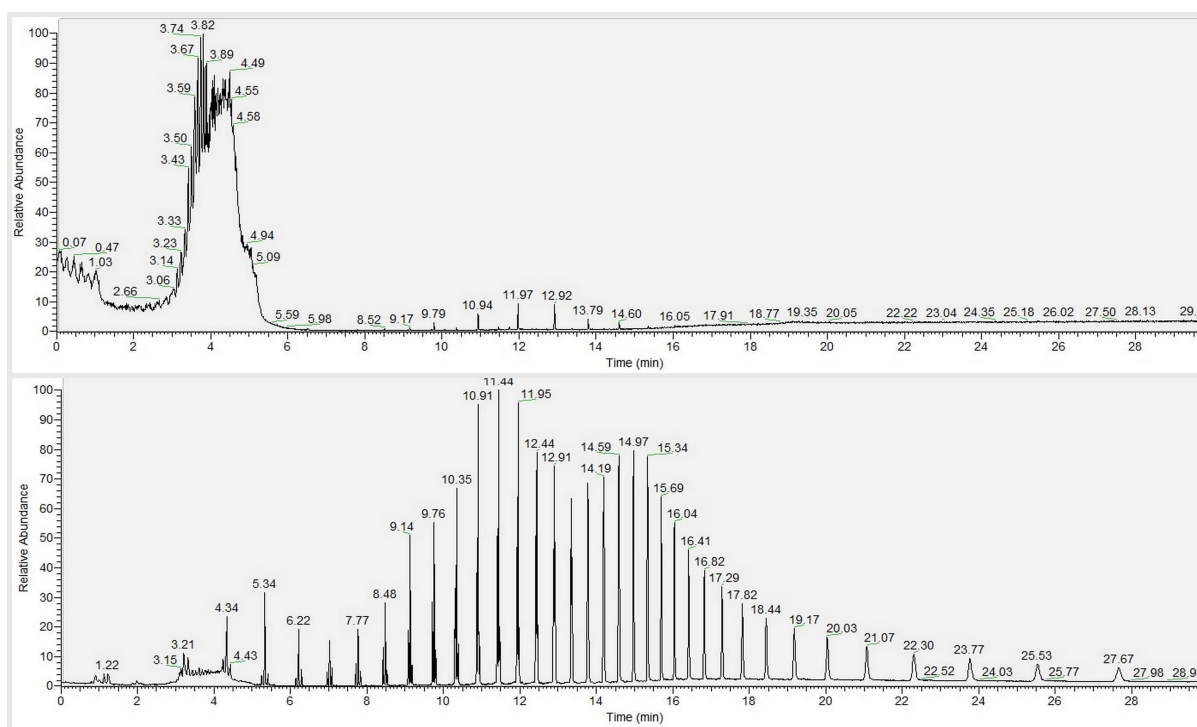


Figure A2.14: Pyrograms of plastic H (HDPE) at 350°C and 700°C.

A2.3 SEM pictures

A2.3.1 Svalbard Samples

Figure A2.15, A2.16, A2.17, A2.18 and A2.19 show SEM pictures of sample I1, I2, I3, I6 and I7, respectively.

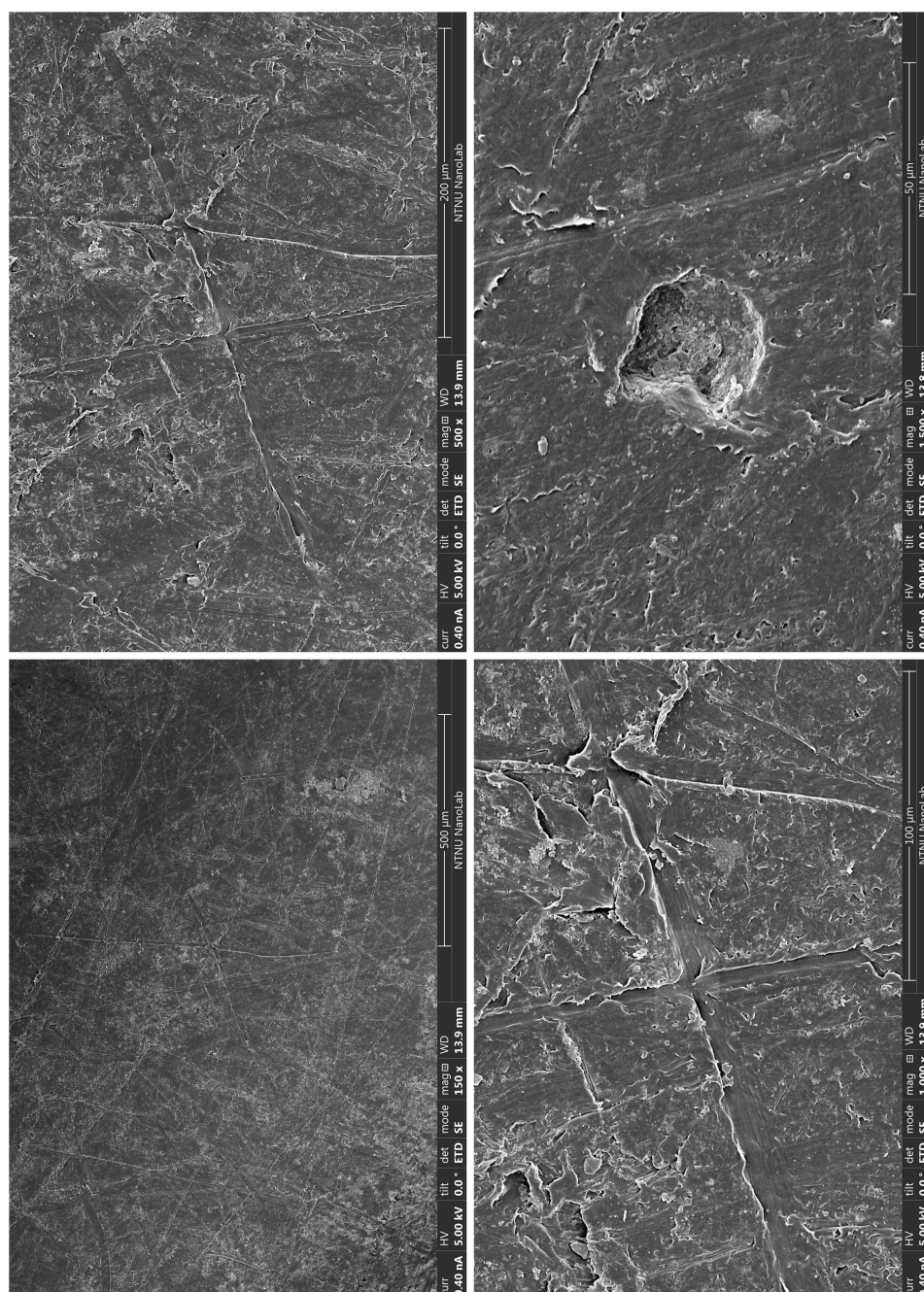


Figure A2.15: Plastic sample I1 at magnitudes 150x, 500x and 1500x.

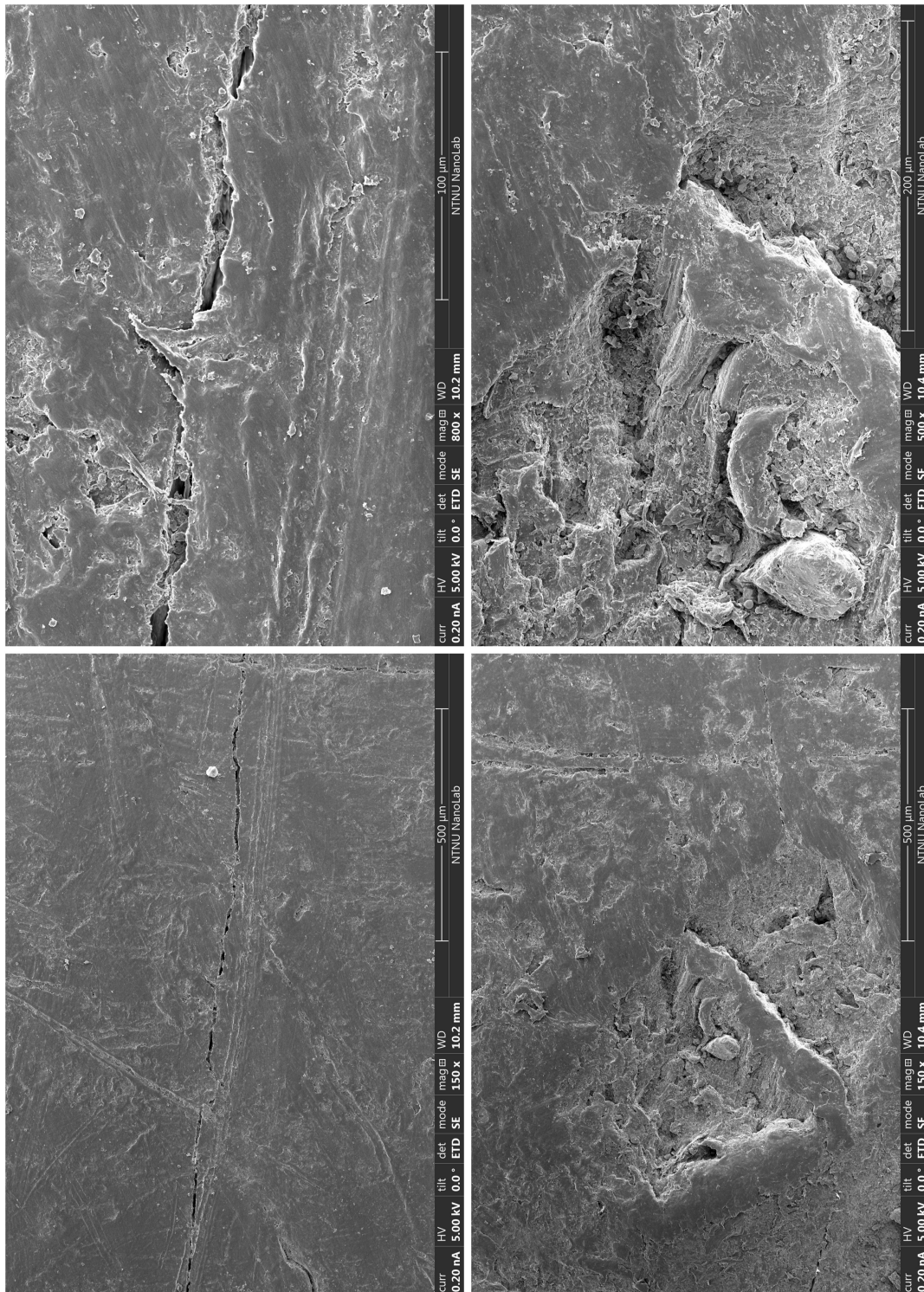


Figure A2.16: Plastic samples I2 at magnitudes 150x, 500x, 800x.

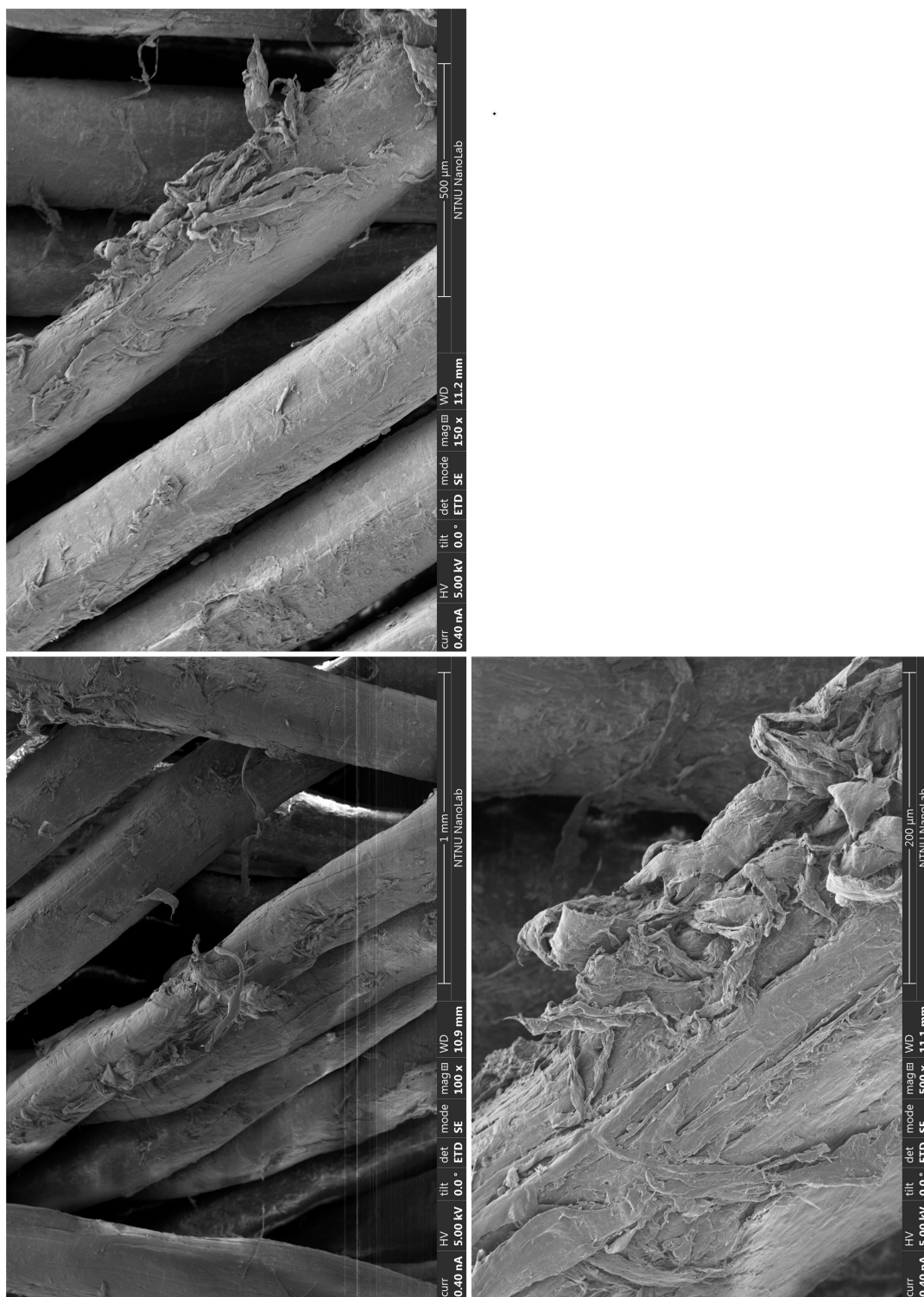


Figure A2.17: Plastic samples I3 at magnitudes 100x, 150x and 500x.

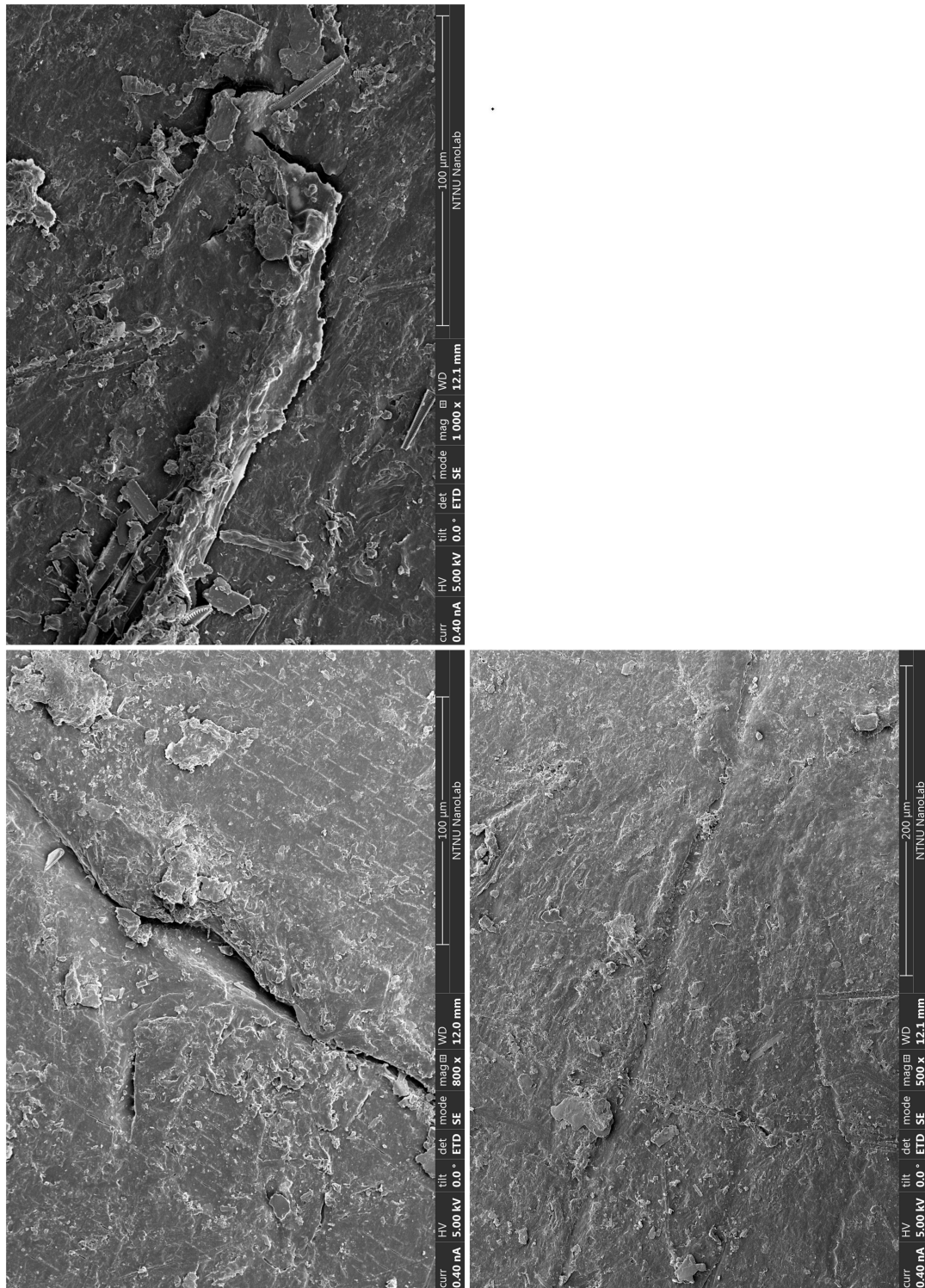


Figure A2.18: Plastic samples I6 at magnitudes 500x, 800x, 1000x.

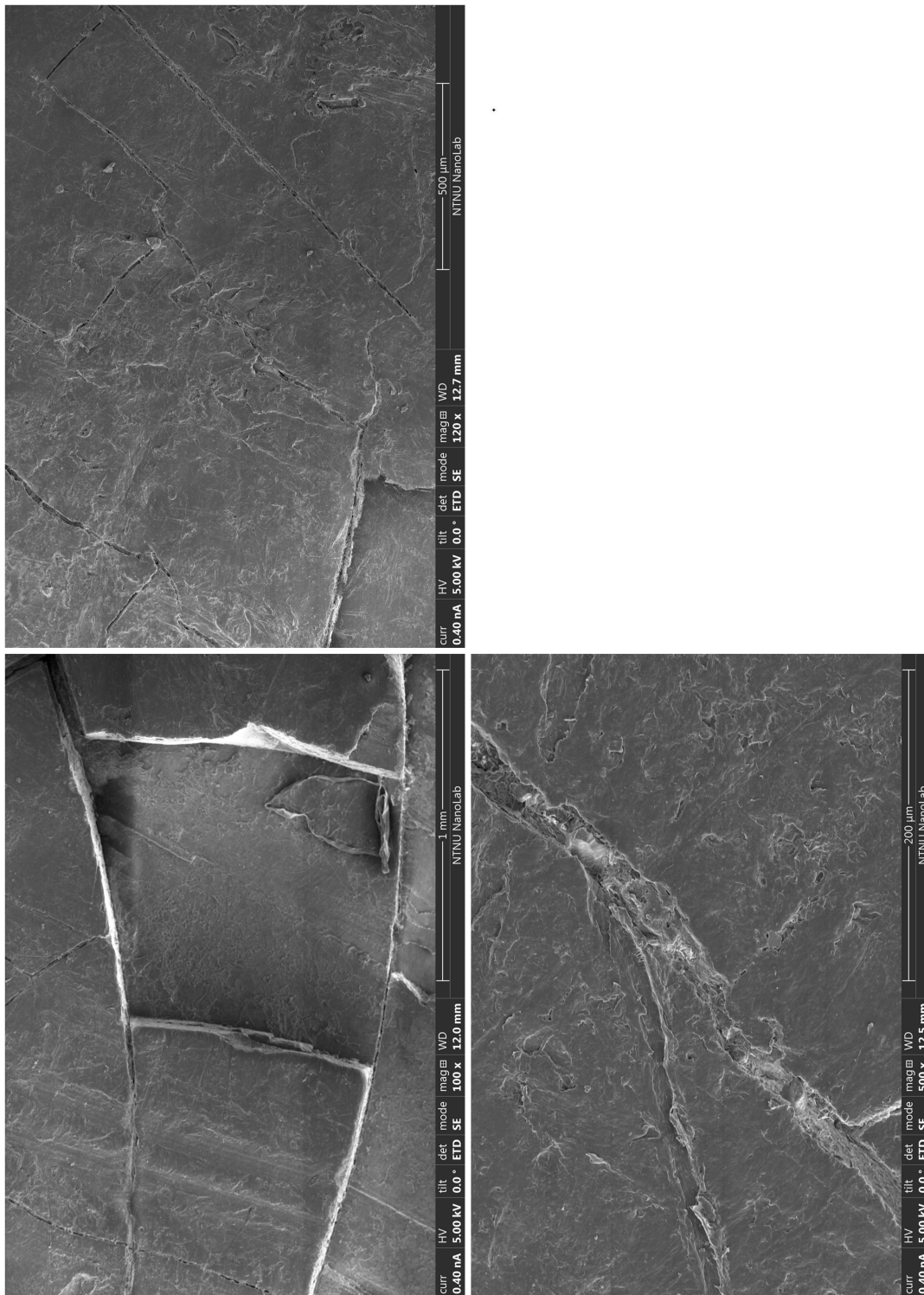


Figure A2.19: Plastic sample I7 at magnitudes 100x, 120x and 500x.

