



Identify synthetic polymers used in cosmetics and further test their biodegradation in aqueous setup in order to assess their impact on the environment

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1 Abstract

Plastics have a wide application field, where cosmetic products are one of them. Polymers which are building blocks to plastics exists in many variants, overall they can be categorized into two groups; microplastics and water soluble polymers. Both polymer types are important to study and understand since polymers in general are not covered by any legislation. To gain a more profound understanding of their impact on environment this study was conducted. In collaboration with SSNC (Naturskyddsforeningen), a database containing hundreds cosmetic products was processed. The most occurring polymers were quantified and prevalent ingredients having "poly" in their name were selected for further investigation namely Nylon 12-20 (microplast) and Acrylates C/10-30 Alkyl-crosspolymer (water soluble). A standardized analysis method OECD 301 F was performed to test the polymers biodegrading ability. Results from biodegradation method showed that, neither of the two polymers is readily biodegradable in aqueous environment, despite their different properties. In connection with the obtained results, a filtration analysis was performed, with the purpose to determine the possibility to capture the polymers using microfilters. Results mainly showed flowthrough of both polymers. Relating the results to reality implies that these polymers are not captured in waste water treatment plant due to inefficient filtration and thereby spread to the environment. In addition more research should be devoted to water-soluble polymers and their impact on nature. Based on all compiled results, it is proposed that legislation addressing microplastics should be edited and revised in such a way that water soluble polymers are included in future prohibitions (against microplastics).

Key words: *biodegradation, cosmetics, environment, microplastics, OECD, polymer, REACH, water*

Sammanfattning

Plast har många användningsområden varav kosmetiska produkter är ett av dem. I kosmetika används exempelvis naturliga ämnen, sådana som förekommer i naturen och således kan brytas ned. Sedan finns syntetiska polymerer, sådana som syntetiseras och tillverkas av människor. Det finns oerhört många varianter av syntetiska polymerer som används inom kosmetika, generellt kan de kategoriseras i två grupper; mikroplaster och vattenlösliga polymerer. Med hjälp av Naturskyddsforeningens databas som innehåller hundratals kosmetikaingredienser, söktes de komponenter som hade "poly" i sitt namn eftersom de inte täcks av lagstiftning. Bland dessa, valdes två mest förekommande polymerer för att studeras vidare, nämligen Nylon 12-20 (mikroplast) och Acrylates C/10-30 alkyl crosspolymer (vattenlös). En standardiserad analysmetod OECD 301 F tillämpades för att testa deras biologiska nedbrytbarhet. Resultatet från nedbrytbarhetstestet visade att ingen av polymertyperna, trots deras åtskiljande egenskaper, är lättnedbrytbar i vattenmiljöer. I följd av resultatet från analysen genomfördes en filtreringsanalys på KTH, för att avgöra om respektive polymer går att fånga upp i olika storlekar av mikrofilter. Resultatet visade att ingen av dem fångades upp (med den utrustning som var tillgänglig på KTH). Baserat på resultaten föreslås det att lagstiftningar som innefattar mikroplaster bör redigeras och revideras på ett sådant sätt att vattenlösliga polymerer är inkluderade i framtida förbud (mot mikroplaster). Utöver detta bör mer forskning ägnas åt vattenlösliga polymerer och deras påverkan på naturen.

Sökord: *biologisk nedbrytbarhet, kosmetika, miljö, mikroplast, OECD, polymer, REACH, vatten*

2 Introduction

In modern society, plastics are almost inevitable. They are used in everything ranging from dental material to great building blocks used in construction. The history of plastics is relatively young though. The plastic industry started developing during the 1960s. It was realized quite early that the waste of plastics would eventually threaten the environment, especially the water bodies; where most of the waste assembles (Fendall and Sewell, 2009).

Plastics are defined as man-made polymers and are also called synthetic polymers (Magnusson et al, 2016). The original purpose of developing synthetic polymers was due to their desired characteristics, mainly because of their durability and stability. Additionally they are inexpensive and are extremely easily manageable by today's society (Swift, 1993). As mentioned, plastics are made of polymers, and cosmetic industry utilizes polymers greatly in their products. There are countless of polymers and all have varying properties (Patil and Ferritto, 2013).

According to Swedish medical products agency and European parliament/Council of European Union (EU) (EG 1223/2009) a:

'cosmetic product' means any substance or mixture intended to be placed in contact with the external parts of the human body (epidermis, hair system, nails, lips and external genital organs) or with the teeth and the mucous membranes of the oral cavity with a view exclusively or mainly to cleaning them, perfuming them, changing their appearance, protecting them, keeping them in good condition or correcting body odours'.

The definition covers the extensiveness of the industry. In year 2012 it was reported that the global market value for the cosmetic industry was worth 443 billion US dollars. The annual growth is 8% worldwide, indicating that it is an enormous industry and that it is constantly growing (UNEP, 2015). In Sweden year 2014 the sales reached 16.4 billion Swedish SEK (Kosmetik- och hygienföretagen, 2017) Polymers in personal care products are used in large quantities and have therefore a significant role within the cosmetics industry (Goddard and Gruber, 1999). It has been predicted that the global market using polymers with application field for cosmetics have a net value of 3.43 billion US dollars by 2017 (Loh, 2016).

2.1 Background

Monomers are essential building blocks for the polymers. A monomer consists of one unit that can bind to other units. Polymers are built by sequential monomers in repeating units, simply repeating's of arranged monomers (European chemicals agency [ECHA], 2012). Copolymers are created by assembling different monomers into the same chain, either in a random order, or in a more structured order (UNEP, 2015). See Figure 1 for a simplified sketch of the described polymer structures. Consequently these chains are extremely large and have a high molecular weight. The degree of polymerization, meaning the number of monomer units, has an influence on the polymer property (Patil and Ferritto, 2013). Branched polymers are more stable and have higher melting temperatures, compared to linear polymers (Goddard and Gruber, 1999).

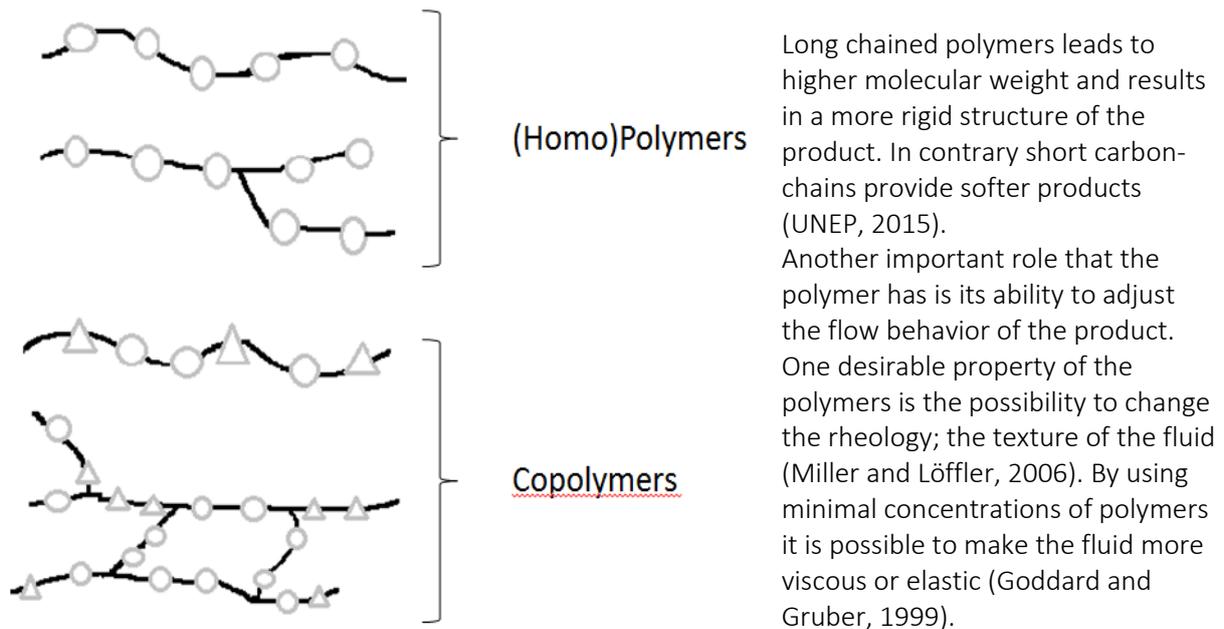


Figure 1. A simplified sketch of how different polymers can look like. Each building block represents a monomer (circles and squares).

The products can be prepared in water soluble formulations which in general have low viscosity. In most cases where soluble polymer application is utilized the main parameter that is of interest is the viscosity. The aim is to increase the viscosity so that it is possible to modify the rheology of the polymer of interest (Glass, 1986).

2.2 Degradation pathways of plastics in nature

The complete degradation of plastics into smaller parts, and furthermore biomass and carbon dioxide, often takes extremely long time, more than centuries, making them more persistent than some persistent organic pollutants (POP) (UNEP, 2015). Depending on what type of polymer it is, the plastic can maintain its shape and form for several years. The structure of the polymer complex is crucial in terms of deciding the degree of degradation (Bettencourt et al, 2010). Degradation will affect the chemistry and the molecular weight of the polymer (Andrady et al., 1993). Throughout time as the polymers decrease in size, they will turn to microplastics and later into nanoparticles. Polymers are non-degradable especially in sediments missing sunlight, oxygen and microbial communities.

There are several types of degradation methods, some of them are; biodegradation, photo degradation, thermal degradation and chemical degradation; using alkaline and acids and last but not least in mechanical ways. In nature however, the most common way is the photo degradation and biodegradation (Andrady et al., 1993).

2.2.1 Photo –oxidation

Sunlight plays an essential role in the degradation of polymers. Calculations show that the sunlight beams, specifically the photons that reach the polymers (in the open environment) are capable of breaking chemical bonds. The sunlight beams that are exerted on the polymers are stronger than the hydro-carbon and carbon-carbon bonds, which are keeping the polymers intact. It is important to mention that this is not sufficient for complete degradation (Grassie and Scott, 1988).

2.2.2 Biodegradation

The definition of biodegradation in this report is the usage of specific microorganisms or enzymes to breakdown polymers (Premaj and Doble, 2005). Microorganisms are the earth's first inhabitants and thereby have had millions of years to evolve, subsequently they are versatile in their ability to degrade and compost various components. They can act in either aerobic environment, or in anaerobic (oxygen absent) environment. Anaerobic microorganisms can be found in locations where there is lack of oxygen for instance in soil (Swift, 2002). The equations below describe the general mechanisms that most microorganisms use.

Aerobic reaction

Polymer+O₂ →(microorganism) → CO₂+ H₂O+biomass+ residue

Anaerobic reaction

Polymer → (microorganism) →CO₂ + CH₄ + biomass + residue

Insoluble polymers in specific shapes have been found throughout several beaches suggesting breakdown through mechanical ways (Bernhard, et al., 2008). Water provides a dynamic transportation for the plastics. Fragmentation of the brittle pieces is governed by wave action, grinding and animal contact. Smaller fragments are formed and the increased surface area will increase biofouling until the particles density exceeds water and thereby sink through the water column (Kärrman, Schönlaug and Engwall, 2016). Absence of sunlight in the marine environment prevents the degradation process from occurring. It is highly unlikely that degradation occurs on the seafloor. In case photodegradation takes place in deep sea it will result in fragmentation of the plastic particles, subsequently marine organisms will ingest the particles as nutrients (Watters, Yoklavich, Love and Schroeder, 2010). Before ending up at the ultimate destination- the sea bed, there is a lag time, duration of the plastic in water.

As for now, the fragmentation and degradation rate of the microplastics in the marine system is not completely known. It can be hard to determine because of the dynamics of the waves and because of the constantly changing environment in the water. Examining the microplastics surface can help characterizing what type of degradation that it has experienced. This type of observation can help us determine whether the particles have undergone mechanical degradation (wave movement, sand interaction), biological degradation (microbes) or some type of oxidation reaction (photo-oxidation reaction) (Eerkes-Medrano, Thompson and Aldridge, 2015).

Plastic polymers found on land have different degradation kinetics than of those polymers that are found in fresh and in saline water. Even though it is not completely confirmed, it is thought that polymers on land are degraded faster than polymers in aqueous environment (Kärrman, Schönlaug and Engwall, 2016). It was reported that microplastic particles had been found ranging between 1000 particles/kg dry mass sludge to more than 4000 particles/kg dry mass sludge on agricultural land across Europe (Lwanga et al., 2016). Just like the sewage treatments have microorganisms, so does the soil in the land. Though it is still unknown what type of impact different polymers have on landfills. There are literatures stating that water soluble polymer groups such as polyacrylamides, which is a substance that can be found in cosmetics, actually benefits the soil due to its hydrating properties (Wu et al., 2012). Field studies concluded that polyacrylamides are effective in reducing agricultural contamination (Krauth et al., 2008). In fact, it is reported that they reduce toxicity levels.

2.3 Classifying synthetic polymers used in cosmetics

In this report, two types of plastics will be studied. Both of these types are abundant in cosmetic products. One is called microplastics and one water soluble plastics. One polymer type from each category will be studied further in biodegradation and a filtration test. Nylon-12 is a microplastic and Acrylates C/10-30 Alkyl Acrylate Crosspolymer is a water soluble polymer. Microplastics and water soluble plastics have different properties, which is displayed in Table 1. In general these plastics are used as film forming agents, bulking agents and viscosity controllers (UNEP, 2015).

Table 1. A comparison between the two different types of plastics.

Microplastics	Water soluble plastics
Solid structure	Is often formulated in liquid
Insoluble in water	Soluble in water
Size maximum 5 mm	No specific size or shape (no available info)

In year 2012, a total of 4360 tons of microplastics was used for cosmetic purposes across Europe, in the form of microbeads (UNEP, 2015). Recent studies show that the microbeads are to 93% composed of polyethylenes (PEs), however it can also be made of polypropylene (PP), polyethylene terephthalate (PET) and polymethyl methacrylates (PMMA) (Napper, Bakir, Rowland and Thompson, 2015). Currently, microplastics are used as exfoliating materials, it has replaced the natural ingredients such as seeds and sand grains. They can also be found in soaps, shampoos, toothpastes and many other types of cosmetic products (Natukskyddsforeningen, 2013). The Swedish chemical agency have advocated a proposition to the government for the ban of microbeads used in exfoliating product, the suggestion is currently being revised.

The properties of the water soluble polymers are that they dissolve and work as thickening agents in water, which changes the physicality of the water system. They are primarily called thickening agents and emulsifiers. These polymers have most commonly hydrophilic groups incorporated into the structures (Kadajji and Betageri, 2011). Acrylic based chemicals are often water soluble as the Acrylates/C10-30 Alkyl Acrylate Crosspolymer. Due to their favorable attributes mentioned above,

they are indeed widely used in cosmetics (Goddard and Gruber, 1999). Structure wise, hydrophilic polymers often resemble each other. Most of them include –N(amine), or –O(hydroxyl) groups which enables the polymer to interact with water. These atoms provide their lone pair for hydrogen bond formations (Glass, 1986).

There is no unifying definition of microplastics and water soluble polymers together. Water soluble polymer does not fall under the scope of microplastic definition. Microplastics are well studied and characterized, meanwhile water soluble plastics are not. Indeed further studies are needed that examines water soluble polymers and how they are associated with environmental risks.

2.4 Targeted polymers within this study

In this report, two polymer types that are common in cosmetic products will be studied, namely a Nylon-12 derivative and an acrylate compound Acrylates C/10-30 alkyl copolymer. The manufactory terminology Nylons applies to the group of polymer compounds that are established through polyamides, which originates from non-branched monomers. Nylon 12-20 is created through use of polyamide-12s, which means that there are twelve methyl groups in between the end sites of the molecule (Burnett et al., (2014). The size of the particles for the investigated Nylon, namely Tegelon 12-20, is 10 µm according to its safety sheet (Evonik Industries AG, 2008). In cosmetics, Nylon has several advantageous properties that make it convenient to use. For instance, it has bulking, adsorbing and opacifying properties. Nylon can be found in a variety of cosmetic products, for example eyeshadows, sprays and powders (Burnett et al., 2014).

Acrylates C/10-30 alkyl copolymer is an acrylic-based compound. Evonik Industries sell it by the name TEGO Carbomer 341 ER. This copolymer is in powder form and has acrylic acid as its monomer form according to its information sheet (Evonik Nutrition & Care GmbH, 2008). Acrylates C/10-30 alkyl copolymer is extremely versatile, and can be used as thickening, emulsifying and as bulking agents. Cosmetic products in which they are frequently used in are creams and lotions (Goddard and Gruber, 1999).

2.5 Bioaccumulation and toxicological effects

Many studies have shown that the plastic distribution in the environment affects the biota. One of the distributional routes for the plastics is in fact the food chain. Microplastics have been found in many organisms throughout the years. Though it is important to mention that it is not always that one can distinguish between the plastic that comes via cosmetics from plastics that came from somewhere else (UNEP, 2015). Microplastics are accumulated in animals due to ingestion. Subsequently they have also been found in larger animals, suggesting that they must have ingested them by trophic transfer while eating seafood. Eerkes-Medrano, Thompson and Aldridge (2015) reports that for seals, the magnification factor is at least 100x up through the food chain. Even though it is not fully proven, there have been reports suggesting that marine organisms that ingest microplastics have been detected having both internal and external wounds affecting their physical abilities.

Another problem that needs to be enlightened is the adsorptive and desorptive characteristics of the microplastics which affects the marine organisms. The hydrophobic surfaces of the microplastics are likely to become contaminated with waterborne hydrophobic pollutants (Kärrman, Schönlaug & Engwall, 2016). In one study, microbeads were susceptible to attach and transfer POP¹ classified chemicals. Same study showed that this event is likely to occur in seawater indicating a potential threat to the environment (Napper, Bakir, Rowland and Thompson, 2015).

There have been studies showing toxicological effect of the use of microplastics in various biological organisms and human tissues. So far it is known that the toxicity of a particle depends on size and shape. It can also be dependent on the composition of the particle- what it is built of etc. Reported studies conclude that (micro)plastics have a negative impact on the studied bodies; such as mammals, nematodes and vertebrates. The uptake of the nano sized plastic particles into the mammalian systems indicates that the transported plastics can reach several organs in the body including the placentas to fetuses. UNEP (2015) report that studies on marine organisms revealed that green algae respiration system is disturbed when exposed to plastic particles such as polystyrene. It also reports mussels having several negative health effects after exposure of microplastics and marine lungworm experiencing weight loss. Long term exposure of microplastics in earthworm caused higher mortality rates (Lwanga et al., 2016). Other findings show both short term effects and long term effects that causes disturbance to the organisms (UNEP, 2015).

Variants of Nylon polymers have been tested resulting in nontoxicity on animals- with the restriction of certain limitations and concentration ranges. No data was available for the genotoxicity of the nylon polymers. The monomers of nylon have been tested in toxicological studies. The acute lethal dose among the different nylon types varied a lot. The expert panel that evaluated Nylon concluded through their assessments that Nylon-12 is nontoxic and harmless and that it can be considered as safe ranging up to at least 35% (Burnett et al., 2014).

Several types of acrylic polymers were tested on aquatic organisms, resulting in being harmless. According to Carbone and Reinert (2015), in general polymers containing nonreactive functional groups do not cause acute aquatic toxicity. Many variants of acrylates are not considered as dangerous. Studies using acrylates crosspolymers concluded that these compounds are not toxic. However there are some risks using the monomer form of the compound (Zondlo, 2002). Available literature describes the toxicity about the methyl acrylates and methyl methacrylate monomers, and that it can cause irritation to skin and mucous membranes (Autian, 1975). However it is important to keep in mind that not all the acrylic monomers share the same type of properties, subsequently not the same toxicity either.

Short term effects can sometimes be less appreciated, since it is possible to perform quick experiments and therefore detect the effect relatively fast. One should rather focus on the polymers long term threat, in order to evaluate the adverse effects that displays itself after a longer period of time (Daughton and Ternes, 1999). Long term effect of the acrylates c/10-30 alkyl crosspolymer is unclear, simply because it has not been studied. Not much information regarding the general toxicity of the acrylates C/10-30 alkyl crosspolymer was available in the literature. The found report focused on oral and dermal and ocular experiments. Oral dosages resulted in severe damages in rats; such as

¹ Persistent Organic Pollutant

tumors and inflammations, meanwhile ocular experiments showed non-toxicity (Belsito et al, 2011). Because of lack of research within this field more focus must be placed on investigating the environmental toxicity.

As soon as microplastic is released into the environment it will put tension on the eco system. Distribution of microplastics can theoretically affect abiotic aspects of the nature. It is thought that the accumulation of the microplastics can change the biogeochemical cycles through changes in aquatic environments and changes in sediment characteristics. Right type of sediment quality, with proper physical and chemical settings is essential for a balanced ecosystem (Eerkes-Medrano, Thompson and Aldridge, 2015).

2.6 Treatment plants, polymers route to nature

Microplastics found in water bodies partially originate from cosmetic products (Eerkes-Medrano et al. 2015). Today, no available removal technique has been developed to remove particles that have reached the environment. In addition it is very hard to remove such tiny particles that are as dispersed as the polymers are. Insoluble plastic polymers have been found along several beaches (Bernhard, et al., 2008). A recent investigation studied different waste water treatment plants (WWTP) in Sweden and concluded that between 70%-100% of the microlitter is retained in Swedish WWTP. Still there were significant amounts estimated to be left in the effluent (Kärrman et al., 2016). In general microbeads are not anticipated to be captured in sewage treatments because they are likely to pass through the filtration systems. This raises a concern since the effluent water reaches aquatic environments. This problem should be viewed as an international concern, since many foreign WWTP does not have the same system (Napper et al., 2015).

Unlike the microplastics, it is not possible to see the water soluble polymers washed up on beaches, making the effect harder to think of. Major problem of the water soluble polymers are that they are unseen in the waste water processes as soon as they are dissolved in the water. Improvements have been made, specifically in the detergency business, where industries have switched to biodegradable detergents instead of keeping the branched alkyl sulphonates (which can't be broken down) (Swift, 1993). Unfortunately today, no quantifying data or literature has been found, describing the abundance of specific water soluble polymer in waste water treatments plants. However it is known from literature that water soluble synthetic polymers are prepared from acrylic compounds (such as acrylic acid and methacrylic acid). Gross and Kalra (2002) reports that acrylic compounds remain in treatment plants, since they are non-degradable by sludge-cultures. This indicates their presence in aquatic environments, such as lakes and oceans. Ultimately, the environment is exposed to these substances.

2.7 Current regulations

The concern regarding the plastics' environmental impact remains. Another worrying point is the fact that there is no existent legislation that covers the potential risks of polymers associated with personal care products (Leslie et al., 2013). Legislations and laws are governed through different constitutional organs. In order to implement proposals, one needs to prove the damage that can be caused by the investigated substance. Furthermore research and analysis is needed to evaluate such questions. OECD is a collective intergovernmental organization that has developed different biodegradation methods which can be used as standardized measures to get an overview and help to determine the severity of the case. OECD methods can be seen as a first tier in this process. Their methods can be used to check if the current legislation is obtained through performing different methods (Daughton and Ternes, 1999). However there are also criteria in the form of regulations and legislations that needs to be met before selling of product to the market.

2.7.1 REACH

In 2007 European Chemical Agency (ECHA) put Registration, evaluation and authorization of chemicals (REACH) in effect, a legislation that controls and ensures that hazardous chemicals are not used (ECHA, 2007). Main aim of REACH is to improve the protection for primarily humans, and the environment from risky chemicals (ECHA, 2012). They operate by registering chemicals that are produced or imported in quantities of minimum one ton per year and company. Operating in this way enables a conspectus and provides valuable information about which chemicals that are desired and in what amounts they are consumed. REACH also requests additional information regarding the chemicals physical, chemical, ecotoxicological, and toxicological properties. The extent of the information required depends on the quantities registered. When all gathered information is completed, board-members decide and vote regarding the chemicals "harmonized classification". If the investigated chemical is ranked as dangerous certain measurements need to be taken. For example can a chemical be banned for usage in EU, or as an ingredient in any article (imported or not). Some classifications, like CMR (cancerogenic, mutagenic and toxic for reproduction) will affect specific legalization and thereby specific product types, for example toys and cosmetics where harmonized CMR-classified chemicals are banned.

2.7.2 Regulation (EG 1223/2009) on cosmetics

Regulation (EG 1223/2009) on cosmetics is also regulated under EU. Its main mission is to forbid, or restrict the usage of those chemicals which have negative health effects. For a cosmetic product to be sold on the market within the EU, it must have had fulfilled the requirements of the regulation (EG 1223/2009) on cosmetics. In summary, regulation (EG 1223/2009) on cosmetics forbids the usage of substances that are cancerogenic, mutagenic or toxic for the reproduction. However there is room for exceptions, if the expert committee decides that the usefulness outweighs the risk (Hedfors, 2016). Some requirements are listed below.

Product must contain a table of contents, where all substances > 0.1 % must be stated

Pre identified allergenic chemicals can only be used with restricted conditions
Analysis done on cosmetic product should be performed in a reliable and reproducible manner
Alternative methods to animal testing should be conducted, that are scientifically satisfactory

Even though REACH is very good for the maintenance and control of chemicals, there are still some flaws, especially related to the environmental toxicology aspect. There are many chemicals that REACH doesn't cover, more specifically polymeric materials! Also chemicals that are used below one ton per year are not necessary for registration. Therefore it is very complicated to make any risk assessments about polymers that are utilized in cosmetics. One problem is that no analysis is demanded unless the chemicals are not suspected to be hazardous. Researchers must find a correlation between the exposed chemical and the health and environmental impact in order to reach a unified decision.

Similar to REACH, the cosmetic regulations are not as extensive as it should be. Their prohibition list forbids health threatening chemicals that are cancerogenic, mutagenic and reproductively toxic substances. However it does not consider the topic of environmentally toxic substances. Keeping in mind that plastics have extremely long degradation time in nature, and that plastics have polymers as building blocks the need of regulation of polymeric material is rising. Currently polymer materials falls outside of Regulation (EG 1223/2009) on cosmetics laws.

2.8 Aim

The long term goal of this study is to identify the most common synthetic polymers that are present in cosmetic products, based on data provided by Naturskyddsforeningen, Stockholm. The specific aim is to compare two characteristically different substances, namely Nylon 12-20 and Acrylates C/10-30 Alkyl Crosspolymer and to characterize them depending on their features and use. Both mentioned compounds will be tested in a standardized degradability test OECD 301 F, thereafter, based on the results, conclusions will be drawn regarding their breakdown in water systems. The degradation test will allow a generalization which will lead to a conclusion on the breakdown of acrylic compounds in aqueous environment.

Important parameters will be identified and discussed with respect to environmental impact.

It is important to have insight to how viscosity and consistency changes when the products are formulated in cosmetic products. The aim of the practical analysis is to examine how both Nylon- 12 and Acrylates C/10-30 Alkyl crosspolymer behave in water. Second part of the experiment is to test the possibility to purify the dissolved products, using a filtration method. This will assist to validate and quantify the amount of product that is used in cosmetic products.

It is also of interest to enlighten and review the existing regulations that are stated about cosmetics (and their ingredients) in REACH and Regulation (EG 1223/2009) on cosmetics. From the environmental perspective and for more extensive and stricter regulations, suggestion for improvements will be discussed. Globally standardized methods such as OECD tests influence lawmaking, making changes possible. Results from the degradability test, will enable a clarification

whether directives are required for synthetic polymers that are used as cosmetic ingredients. In addition, that they must be tested for their environmental impact before entering the market.

2.9 Limitations

Some restrictions were requisited during the scope of this study. Since the study needed to be conducted within a certain time frame of 20 weeks, a pre-planned timeline was of priority. Everything was planned accordingly. The study only includes a generalization of those polymers that exist in the reported products present in the database provided by Naturskyddsföreningen. Because of restricted economical budget and ordering and accessing problems it was not possible to order all the mentioned polymers in Table 5. Due to lack of equipment, an external and accredited lab; AnoxKaldnes was hired to perform the OECD tests. Because the tests were expensive, replicates were dismissed since it exceeded the budget. Both microplastics and water soluble polymers that are taken into consideration in this report only refers to those originating from cosmetics and nothing else.

3 Material and method

3.1 Database search

Naturskyddsföreningen, Stockholm provided a database named "Cosmetic ingredients" that contained cosmetic products and their ingredients. The database stated a total of 874 products, in which all were reported by consumers' all over Sweden. Consumers reported various cosmetic products available on the Swedish market and each stated the ingredient from the table of contents of the chosen product. The reporting provides an overview on the distribution of the different chemicals and their frequency in cosmetic production. A second database "Synthetic polymers used in cosmetics" was also provided by Naturskyddsföreningen, where all synthetic polymeric ingredients were listed. The distribution of different cosmetic products in the database and a list of the synthetic polymers found among the ingredients can be found under section four, Results. By browsing and searching the polymer types from "Synthetic polymers used in cosmetics" in "Cosmetic ingredients" it enabled a simple quantification of how frequently they were used in the cosmetic products. Through this method, Table 5 was attained and this helped the next course of the study which was to decide which polymers that was going to be analyzed.

3.2 Ordering polymers

For this study, two polymer types, namely a polymer in microplastic form and a water soluble polymer, were to be investigated. According to data among the selected polymers the following two polymers were chosen due to convenience and frequently appearance in cosmetic products. The chemical names of the chosen ones are Nylon 12-20 and Acrylates C/10-30 Alkyl Acrylate Crosspolymer, with

the trade names Tegolon 12-20 and Tego Carbomer 341 ER, respectively. Since they are widely used within the industry, it is interesting to see how readily biodegradable they are. By conducting this study it enables an attempt to reach a conclusion and gain a profound understanding about the degradation of the polymer types in an aqueous environment.

The compounds were ordered at EVONIK INDUSTRIES with the help of Associate Professor Anna Ohlsson at KTH Royal Institute of Technology.

3.3 Biodegradation analysis

For assistance in this project, an external accredited lab, Anox Kaldnes - VEOLIA Water technologies, was contacted. They were responsible for the degradation tests that were performed. When samples arrived, they were sent to Anox Kaldnes together with their safety data sheets.

The purpose of a biodegradation test is to verify the degradation of the measured substance and furthermore, analyze the persistence of the compound in the environment based on obtained data. Organisation for Economic Co-operation and Development (OECD) tests ranging from 301 A- 301 F are screening methods that are used as a primary step to classify the degradability of the substance of interest (Thouand, 2014).

Degradability test chosen for this study is called OECD 301F and was performed on both of the synthetic polymers. It is a manometric respiratory test that measures the oxygen consumption. The principle of the test is that a known sample concentration of the polymers are dissolved in a medium containing a mixture of the following inoculants; activated sludge, sewage effluents, surface water, soil, or a mixture of these. Anox Koldnes uses activated sludge from Kävlinge WWTP. Activated sludge is responsible for handling the organic matter, the microbes in the sludge metabolise the existing organic matter. Sludge culture was added to the bottles so that the final concentration of the suspended cells in the dissolved medium was 30 mg/l. Each flask were inoculated with its polymer and medium and stirred for up to 28 days. Apart from the test sample there were also a control and an inhibitory medium, which were measured simultaneously as the polymer samples. Control is used to follow the activity of the inoculum. Meanwhile inhibitory medium is used to make sure that the test article does not inhibit the microorganisms. The consumed amount of oxygen (by the microbe) of the test sample is ordinarily expressed in ThOD and COD percentages, in which ThOD is more pleasingly. The blank is run in parallel with the sample, and the shown oxygen uptake is fixated according to the blank (Kowalczyk et al., 2015 and OECD, 1992).

3.4 Literature study

Information about cosmetic ingredients and their function was gathered mainly from scientific articles and reviewing reports. Throughout the whole literature search period KTH-library database engine was utilized to access valuable background to the subject. ChemDraw was used for creating the figures of the polymer structures.

3.5 Filtration analysis

To test the behavior of Nylon-12 and Acrylates C/10-30 alkyl crosspolymer in water and to investigate the possibility to filtrate the samples, a separate lab test was conducted at KTH AlbaNova, Division of Industrial Biotechnology, using available lab equipment and materials present in the laboratory.

1 gram of each polymer sample was transferred into a separate 100 ml glass bottle with the help of two folded paper funnels. Two different spatels were used to facilitate the transfer and to scrape down the powder into the bottle. Initially, 10 ml MilliQ-water was poured into each bottle, see Figure 4. To enable dissolution, the bottles were stirred using a table top vortex. Later, 15 ml of MilliQ-water was added into each bottle, and stirred for 1 minute on a table top vortex. Lastly 75 ml MilliQ-water was added using a measure glass and poured into both bottles. The bottles were placed on a heating/stirring plate and a magnet was added to both bottles, which provided stirring. The upcoming step was performed separately for each sample:

Nylon-12 solution was stirred and heated for 15 min.

Acrylates C/10-30 alkyl crosspolymer was stirred during 10 minutes, after that, the 100 ml solution was transferred to a 400 ml beaker and 200 ml of MilliQ-water was used to rinse as well as dilute the sample further. The beaker was placed on a heating plate together with a magnet, and stood there for 1 hour.

The following procedure, was repeated for both polymer types. To create a vacuum, the filtration setup was installed by connecting a 100 ml erlenmeyer flask to the air valve using a hose. Glass filter was fastened to the flask, and the solution containing the product was poured into the filter. Lastly, the air valve was switched on. Figure 5 shows the setup that was used during the filtration analysis. Following glass filters seen in Table 2 were used in a chronological order for both of the polymers and was applied to each solution containing each sample. In between each filter change, 5 M NaOH solution was used to clean the filter, and subsequently MilliQ-water was used for rinsing.

Table 2. Names and pore sizes of the different glass filters that were used in the lab experiment.

Filter brand	Pore size (μm)
Pyrex P4	10 – 16
Pyrex P3	16 – 40
Robu P3	16 – 40
Robu P2	40 – 100

4 Results

4.1 Identifying common polymers

The database “Cosmetic ingredients” is an excel sheet that contains a total of 874 varying cosmetic products and their table of contents. The database was created by Naturskyddsföreningen. All products and their respective ingredients have been reported by consumers from all over Sweden to Naturskyddsföreningen. See Table 3 for the reported products and their occurrence.

Table 3. Below are the product types that could be found in the “Cosmetic ingredients” database.

Product type	Occurrence in database
Aftershave	10
Face wash	48
Hair conditioner	45
Deodorant	69
Foundation	41
Lotion	153
Hairstyling product	63
Lipstick	40
Mascara	24
Shaving product	22
Schampo	103
Sunprotecting cream	24
Toothpaste	44
Soap	71
Uncategorized (make up ware in majority)	117

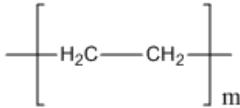
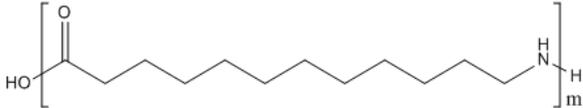
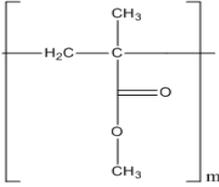
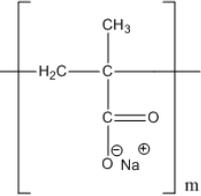
A second excel sheet, named “Synthetic polymers used in cosmetics” contained pre- selected names of polymers that are displayed in Table 4. The following chemicals in Table 4 were searched for in database “cosmetic ingredients”.

Table 4. The following 29 chemical names were given in the database “Synthetic polymers used in cosmetics”.

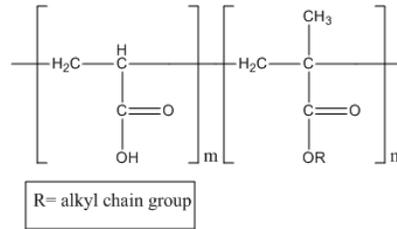
Polyethylene	Nylon-12
Polyethylene terephthalate	Nylon 66
Polymethyl methacrylate	Nylon-6
Polytetrafluoroethylene	Acrylates copolymer
Sodium polyacrylate	Styrene/Acrylates Copolymer
Acrylate/ Sodium Acrylomethyl Taurat Copolymer	VP/DMAPA Acrylates Copolymer
Dimethyl Acrylamide/Hydroxyethyl	Hydroxyethyl Acrylate/Sodium Acryloyldimethyl
Acrylate/Methoxyethyl Acrylate Copolymer	Taurate Copolymer
Acrylamide/Ammonium Acrylate Copolymer	Polyacrylate-13
Acrylates C/10-30 alkyl acrylate crosspolymer	Alkyl acrylate crosspolymer
AMP-Acrylates Copolymer	Acrylates/Octylacrylamide Copolymer
Glyceryl polyacrylate	Sodium styrene/Acrylates
vinyl caprolactam/VP/dimethylaminoethyl	AMP-Acrylates/CI-18 Alkyl Acrylate/CI-18 Alkyl
methacrylate copolymer	Acrylamide Copolymer
polyacrylate	

Among the chemicals stated in Table 4, only chemicals that were encountered more than 9 times were considered. Table 5 displays those ingredients that were the most abundant in percentage form.

Table 5. Displays names, functions and monomer structure of the most frequently occurring plastics that are found in cosmetic products, based on the selected polymers that exists in database “Synthetic polymers used in cosmetics”.

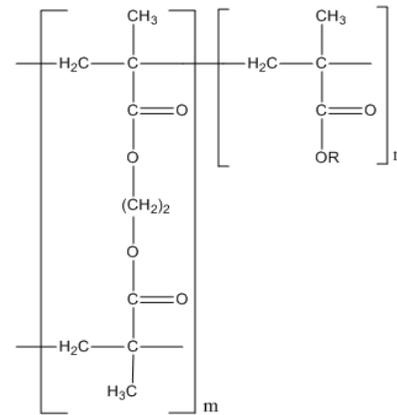
Name	Structure	Occurance in the database (%)	Function
Polyethylene (PE)		3	Grainy and film forming agent that controls viscosity and have the capability to bind product such as powders (UNEP, 2015).
Nylon- 12		2	A viscosity controlling chemical that works as a bulking agent (texture modifier) and an opacifier. It can be found in e.g anti-aging creams (UNEP, 2015).
Polymethyl methacrylate		1	Works as a sorbent that helps deliver active ingredients (Leslie 2015).
Sodium polyacrylate		1	Have several roles, such as; emulsifier and skin-conditioner which helps formation of a nicely dispersed fluid. It also works as a film former and a hair fixative agent (CID: 25188).

**Acrylates C/10-30
alkyl
crosspolymer**



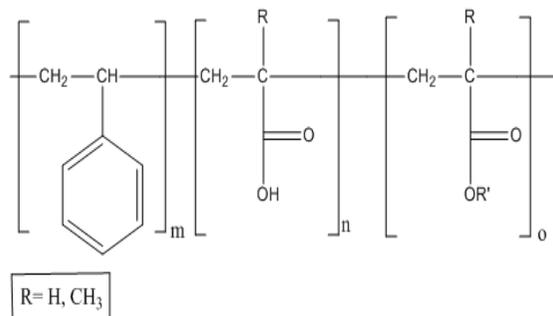
5 Is mainly used as a thickening agent that swells when exposed to solutions. Likewise the other polymers it has viscosity increasing properties (Benderly and Zolotarsky, 2013).

**Acrylates
copolymer**



2 Functions mainly as hair fixative agent and a film former (UNEP, 2015).

**Styrene/Acrylate
s Copolymer**



2 Due to their long polymer chain Styrene/acrylates copolymer tend to have a rigid structure, which is utilized in for example glitter in the form of colored microspheres (e.g. makeup) (UNEP, 2015 and Zeng et al., 2013).

4.2 OECD 301 F

After six weeks, Anox Kaldnes reported the following results that were obtained from the biodegradation method. In this time period the prefiltration, which lead to change of method is included. None of the polymer types were regarded as readily biodegradable since they did not exceed ThOD² or COD³ 60% threshold, which can be seen in Figure 2 and Figure 3.

4.2.1 Nylon-12

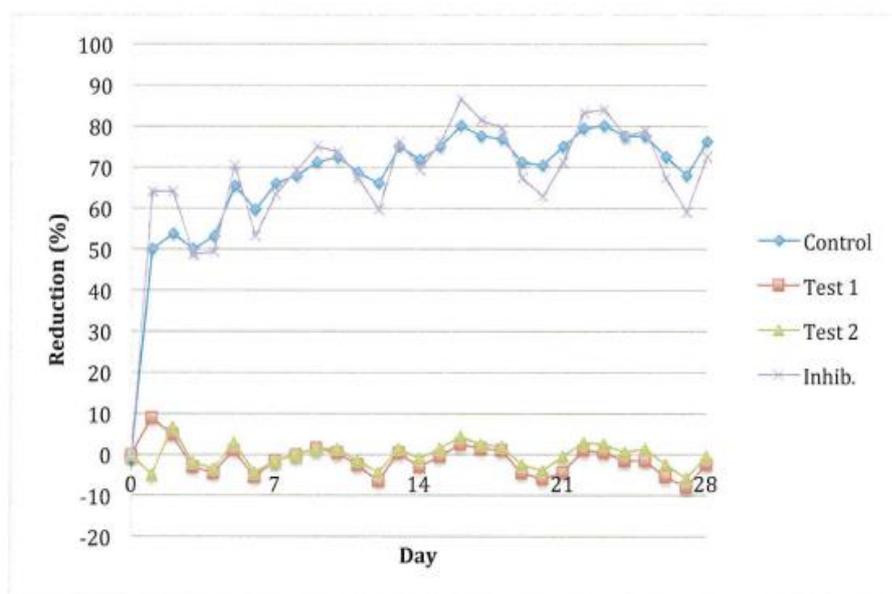


Figure 2. The figure shows the reduction of oxygen (also known as COD) over a period of time inside the enclosed bottle for sample Nylon-12, in relation to the control and inhibitory samples that were measured in the same run.

² Theoretical oxygen demand

³ Chemical oxygen demand

4.2.2 Acrylates C/10-30 Alkyl Crosspolymer

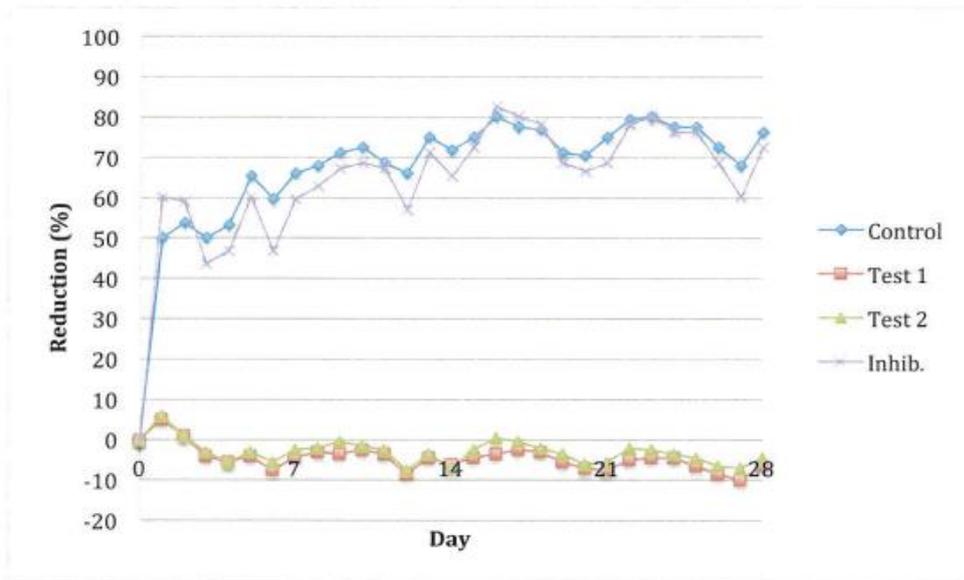


Figure 3. The figure shows the reduction of oxygen (also known as COD) over a period of time inside the enclosed bottle for sample Acrylates C/10-30 alkyl crosspolymer, in relation to the control and inhibitory samples that were measured in the same run.

4.3 Filtration analysis

The experiment that was performed at Royal Institute of technology, was divided into two sessions. First part of the lab examined the behavior of the polymers when dissolved in water. Second analysis was performed to test the filtration ability of the polymer. Following observations were notified.

4.3.1 Behavior in water

Nylon-12 tends to flocculate. When suspended into water it floats, which is due to lower density of the plastics compared to water. The entire “clump” of Nylon-12 floated on the water surface and displayed an extremely hydrophobic character. Due to this, it was insoluble in water and 0,1 g/L was not enough diluted for the Nylon-12 to dissolve despite the addition of heat and stirring.

In contrary, Acrylates C/10-30 alkyl crosspolymer was dissolved more easily than the Nylon-12 sample. It increased the viscosity of solution which resulted in a thicker consistency. Another observation was that the solution started foaming immediately during stirring and shaking, which made it more difficult to analyze, since it was not a clear/transparent solution. Opposite to Nylon-12, heating and stirring of the solution facilitated the dissolving of Acrylates C/10-30 alkyl crosspolymer, see Figure 4.



Figure 4. Left hand picture demonstrates polymers behavior after have poured few mL of water into the bottle. Right side picture illustrates the different polymers behavior after have added 20 mL water.

4.3.2 Filtration results

Table 6. Observations made for each of the polymer during the filtration analysis.

Nylon-12

Filter brand	Pore size (µm)	Behaviour
Pyrex P4	10 - 16	No flowthrough, completely clogged
Pyrex P3	16 - 40	No flow through, also clogged.
Robu P3	16 - 40	Flowthrough is turbid with smaller particles, however filter retains bigger particles.
Robu P2	40 - 100	Complete flowthrough, nothing visible in filter.

Table 7. Observations made for each of the polymer during the filtration analysis.

Acrylates C/10-30
Alkyl Crosspolymer

Filter brand	Pore size (μm)	Behaviour
Pyrex P4	10 - 16	No flowthrough, filter clogged.
Pyrex P3	16 - 40	Very slow process with few visible and clean drops, almost clogged.
Robu P3	16 - 40	Complete flowthrough, nothing visible in filter
Robu P2	40 - 100	Complete flowthrough, nothing visible in filter

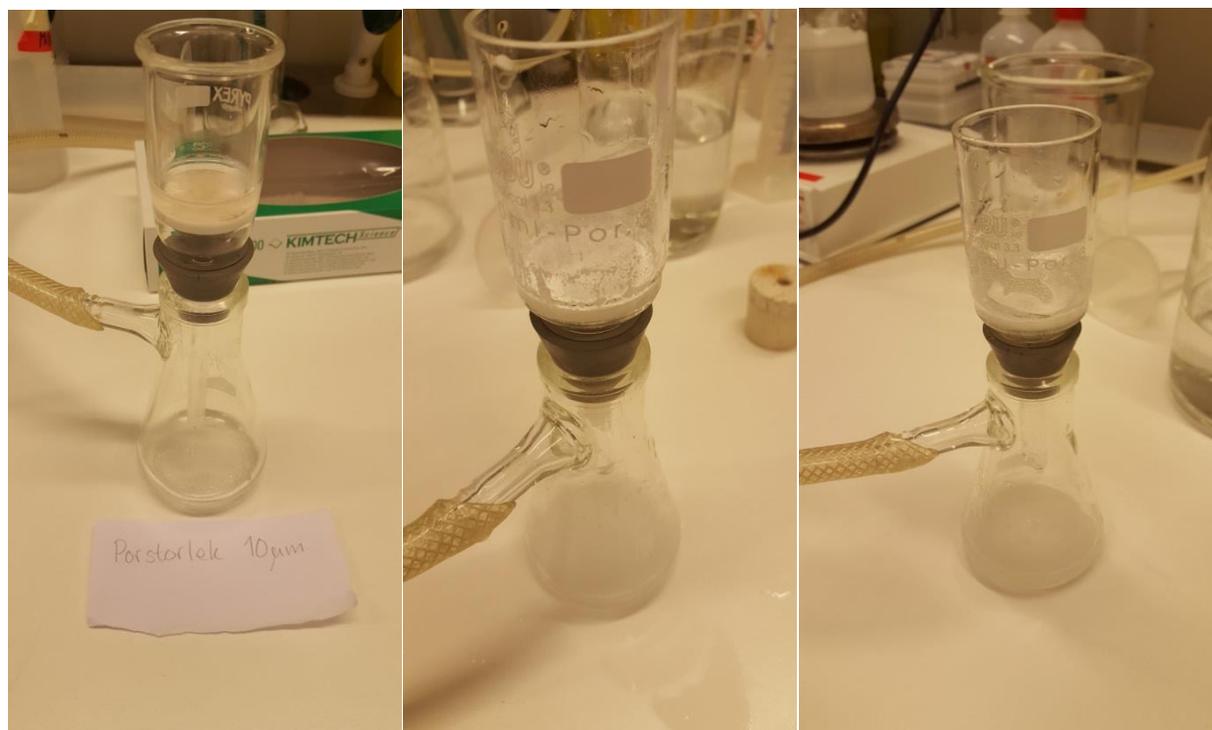


Figure 5. The experimental setup for different filters.

5 Discussion and analysis

5.1 Evaluation of results obtained from biodegradation analysis

Performing a biodegradability test, such as OECD-tests, is considered as a firsthand tier in deciding if the chemical can later be used for industrial purposes since REACH regulates chemicals based on production levels and chemical properties. OECD methods help assessing and characterizing chemicals and approximating their persistence in the environment. Another advantage is that OECD tests are used worldwide and are directed towards well-defined criteria, making sample comparisons possible. Also they give a trustworthy insight and a good approximation of how chemicals perform in controlled situations

At start of this investigation OECD 301 A was the method that was chosen because it is often a first tier and prioritized when performing biodegradation tests. OECD 301 A is die away method performed in surface water. Similar to 301 F the samples are biodegraded with the addition of activated sludge. However, 301 A uses other monitoring parameters than the ones in 301 F, namely Dissolved Organic Carbon (DOC). This method measures the organic compound present in the solution over a period of time. Before applying 301 A- analysis onto the products they needed to undergo a pre-study, where one of the steps was membrane filtration- using a 0.45 μm filter. When Nylon-12 was filtered in the pre study it was found out that 90 % of the sample was retained by the filter, meaning that only 10% was collected. When the same procedure was done on the Acrylates C/10-30 alkyl crosspolymer approximately 50 % of the sample was retained. Since the majority of Nylon-12 sample was captured, not much sample was left to work with, thus a change of method was required for the Nylon-12, and 301 F was chosen. To enable comparison between both polymer types same method was applied to both. Changing the method from 301 A to 301 F would mean that the whole sample could be used without needing to filtrate. Reuschenbach, Pagga, and Strotmann (2003) argues that using a respirometric method provides direct measurements regarding the biological degradation whereas other methods using other parameters like DOC used in 301 A does not. Same article also reports some of the advantages with the OECD 301 F method. The method is well adapted for poorly water soluble products, such as the Nylon- 12 polymer. It does not require as much dissolved sample as 301 A.

Although positive feedback about the OECD 301 F can be found in literature, there are also reviewers that think the opposite. One parameter that is used in this method is Chemical Oxygen Demand (COD). This parameter approximates the consumed oxygen in the solution together with the tested sample, during a period of time. COD is sometimes (as in this case) used as an approximation for the Theoretical Oxygen Demand (ThOD), their relationship can be described through mathematical expressions. ThOD is a rough indicator of amount of oxygen needed to oxidise a sample. With that said, ThOD is often considered as a more reliable parameter (Baker, Milke and Mihelcic (1999)). Both parameters are measured in this analysis, as seen in Figure 2 and 3. Studies demonstrate that COD is lower than ThOD, which results in a false positive outcome; meaning a higher biodegradation value than in reality. This is a common problem, supported by (Swift, 1993). As in this run with Nylon-12 and Acrylates C/10-30 alkyl crosspolymer this problem was not encountered. Figure 2 and 3 shows clear indications of relatively constant levels of both ThOD and COD.

It is generally known that OECD tests tend to produce many false negatives, which in fact is a large limitation of the method. False negatives result in non-biodegradation, nevertheless the reason behind this cause is not always the microorganism's inability to completely breakdown the studies sample. In reality it does not necessarily mean that the chemical cannot biodegrade, rather, it fails the test setup. General guidelines state that the threshold for biodegradation is at least 60% ThOD removal, values below that implies a non-biodegradable sample. However if the results were to show lower than 60 % ThOD, it could also mean that the chemical undergoes partial degradation (Kowalczyk et al., 2015).

The reason to why it exist many deviations is due to the choice of inoculum. The inoculum is suggested to have an impact on microbial kinetics according to (Kowalczyk et al., 2015). There is a high variety of microbial composition, hence, inoculum populations are not identical by any means. Microbes with specific properties are found in specific locations, microbes for hard degraded chemicals are most often found in coastal areas and river sediments (Kowalczyk et al., 2015). For the biodegradation test in this report, inoculum culture was collected from a local (Swedish) WWTP. If the same method was to be conducted in a different country or using water from another source the result could vary slightly.

Apart from the above mentioned disadvantages, it is important to know that "real life conditions" are not always easy to obtain. Therefore the external validity is not that high, since the test environment does not completely mimic or reflect the circumstances that exists in nature. Parameters such as pH, light and temperature cannot be controlled in natural environments. Meanwhile in designed tests, these parameters are often constant. Furthermore monitoring the polymer and the entire degradation process is highly limited due to several factors, such as; reduction of mass, structure changes etc. In summary most internal validity can be obtained in laboratory tests, since they are reproducible there (Müller, 2005). Absence of replicates in the biodegradation tests in the present study limits us from drawing a conclusion about the potential variability in between tests.

As a conclusion it can be stated that the OECD 301 F method provided a good approximation of how the polymers behave in a controlled aqueous environment. From this test, there were probably no false positives, since the results obtained already showed no degradation pattern. As OECD methods receive a lot of criticism by researchers, new alternative methods are demanded. Since the question about how plastic affect the environment has been a hot topic lately, robust methods that are specifically adapted for polymers should be designed.

Both of the polymer types analyzed show very similar patterns in the results which enables us to draw the conclusion that they behave similarly and are both difficult to biodegrade, despite their differing structures. The causes behind this is not completely known and cannot be specified, however literature have discussed similar issues. Müller (2005) describes that microorganisms cannot take up non soluble polymers such as microplastics (Nylon-12). Due to this reason, microorganisms undergo extracellular activity where they excrete enzymes to break down the polymers-outside the cell itself. If the molar mass of the polymers is reduced to a sufficient size with the help of the extracellular enzymes, it is possible to form water soluble polymers. In best case scenario the breakdown will generate water soluble intermediates which will facilitate microbial uptake. In this apparent case the

polymers were not metabolized, thus not broken down by the microorganisms, which resulted in no significant reduction of oxygen.

The degree of polymerization influences its degradation ability. This is valid for Acrylates C/10-30 alkyl crosspolymer since it is a copolymer. Complex polymer types such as copolymers might not have as much accessibility for the enzyme to attach and cleave, compared to a homogen polymer, leading to the conclusions that they are extremely difficult to biodegrade (Müller, 2015). It would be scientifically incorrect to assume that all other water soluble polymers behave in the same way. However parallels can be drawn to acrylic based crosspolymers, since they have the tendency to resemble and act as each other, which can be supported by (Zondlo, 2002). Generally it depends on what type of polymer it has and its functional groups.

To improve the experimental results from the external lab, we can add replicates of the samples. When conducting a scientifically correct method, it is important to have a high reliability and reproducibility, which can be reached with the addition of replicates. Furthermore, using several replicates enables the implementation of statistical methods, which generates a more reliable generalization of the obtained results (Guala, 2005). If the replicates were to show the opposite of the results that was obtained, it would not be possible to conclude anything about the biodegradation of the tested polymers.

Since both polymers are non-biodegradable they do not differ in that context. In this report it is suggested that the current definition of microplastics should be modified in such a way that it includes both microbeads and water soluble plastics. The definition of microplastics differ between different sources, therefore the definition comes across as vague. Many aspects can be thought of. Is it only governed depending on size? Or does it have to visually look like a microbead/particle in order to classify it as a microplast? Does it require it to be difficult to degrade? Water soluble polymers, such as acrylates does not guarantee biodegradability (Swift, 1993), therefore chemicals such as acrylates should be included in the microplastics definition and thereby be banned. The results of the biodegradation tests underline the fact that both polymer types have identical behavior when tested in the same environment. The similarities in behavior outweigh the differences that are described in Table 1. This should be a sufficient reason to be covered by the proposal.

5.2 Initiation to further analysis

Cosmetics are ultimately washed away in the sewage and later collected in WWTPs. The effect on the environment of the synthetic polymers is basically reliant on how well they are being handled in WWTPs. Thus, a good starting point for tackling this problem is examining the abundancy at the WWTP. As Müller (2005) states, when attempting to bring a new product to the market, it is occasionally looked at the biodegradation degree of that chemical in different environments, WWTP being one of them. Large-scale processes product developers are, sometimes, interested in seeing how the chemicals behave in WWTPs.

In media, the spotlights have been on microbeads, leaving the water soluble polymers under the

shadow and somewhat neglected. To move forward in this question, collaboration with a water institute or trade associations, such as Svenskt Vatten, IVL, or Hav-och vattenmyndigheten can be suggested. Beyond these, there are departments at diverse universities that are doing research within this field. With the help of such organizations and their expertise a technique or a process that is suitable for water soluble polymers could be developed. As seen in the results from the filtration analysis conducted at KTH, it is not easy to filter them. Therefore alternative methods need to be investigated. A suggestion to prohibit the distribution of water soluble polymers is to introduce a method to precipitate these polymers at the treatment plant. This would enable them to be captured in the sewage plant. U.S. Environmental Protection Agency (2000) describes the advantage of using polymer as a precipitate agent. Synthetic polymers with high molecular weight that are charged (anionic/cationic/nonionic) can be used to neutralize waste water due to their coagulant properties. Water in treatment plants involves different interactions because of the rich "medium". Ion interactions are also common, which is beneficial since charged polymers can help particles to suspend in the water. The polymers can also be utilized as filter support and as sludge conditioner. Different techniques can first be tested in lab scale and further in pilot scale before being implemented onto plants, similar to the study conducted by (Martin, 1996).

As an initial step, in order to assess the situation, a quantifying analysis can be done. A quantitative study investigating the incidence of polymers in effluent waters would be a potential basis for other future studies. High throughput liquid chromatography (HPLC)- analysis is a way to perform such an analysis. As an initial starting point, the polymer type that is of interest should be chosen, and used as a blank for the measurement. Subsequently by withdrawing water sample from the influent and the effluent water in a WWTP, it is possible to quantify and compare the persistence degree of the polymer. Today there is no available data on how well these water soluble polymers are purified in the treatment plants (unlike the microplastics), nor is it known if they have a significant impact on the environment and organisms. Parameters such as bioaccumulation need to be tested, and a deeper evaluation needs to be done on their potential risks to the aqueous environment.

5.3 Reflections about self- conducted lab

Upon the results reported by Anox Kaldnes regarding the two polymers degradation capacity, another analysis was conducted at KTH. The aim of the analysis was to investigate the possibility to filter both of the different polymers using microfilters provided by KTH.

The results from the analysis indicate that it is very difficult to filter both polymers. The glass filters that were used in the experiment had different brands. Therefore it is realistic to assume that the membranes differed between the different brands, and subsequently also affecting the filtration performance. PYREX equipment was perceived as relatively clogged, at times, not even water went through the filter. However another factor that can affect the behavior of the filter is how old it is and how much it has been used. For example brown contamination was noticed on Pyrex P4, which could have been the reason to why it did not work (in this case it did not even filter the water). Another theory that was developed during the analysis to why the filter did not work was that the acrylate might have stiffened in the filter which hampered the passage.

Two filters that were of different brands but of same pore size (16-40 μm) were compared to each other. Despite having the same size, they behaved different. As seen in Table 6 and table 7 nothing was collected by the ROBU P3 filter, while PYREX P3 did collect a little. Reason behind this can be that the ROBU P3 filter might have bigger pores reaching the 40 μm end of the spectra, which caused the flow through. Meanwhile the PYREX P3 filter might have smaller pores, reaching the 16 μm end of the spectra, which caused retention in the filter. The PYREX P3 filter did not allow fast passage for the solution during cleaning with NaOH, which suggests that the pores in the membranes have been blocked. In general, based on results and discussion from this experiment, one can conclude that the ROBU P3 filter was more reliable, even though the ultimate objective of the experiment was not reached. If it had been possible to filtrate the samples, additional tests could have been performed. For example, personal care products could have been analysed according to the polymer content, using a standard curve of the filtrates of known polymer concentrations.

Acrylates C/10-30 alkyl crosspolymer was dissolved to 0.33 %, by adding 1 gr sample into 300 ml water. According to Swedish ordinance on cosmetics companies must specify chemicals that make up 0.1 % of the product. Initially, when 1 gr Acrylates C/10-30 alkyl crosspolymer was dissolved in 100 ml (1 %), the solution was very soggy and turbid and during mixing it started foaming. The consistency resembled lotions and creams a lot. However after have diluted it in larger volumes of water, it became more clear and 'watery'. Judging based on the results from the experiment, it can be suggested that the approximate amount of Acrylates/C10-30 Alkyl Acrylate Crosspolymer used in products such as lotions and soaps is approximately 1 %. In case the experiment was repeated, the Acrylates C/10-30 alkyl crosspolymer would have been added to a much greater volume than 300 ml and thereafter filtrated again, since the products are most likely diluted when they reach WWTP.

The experiment can be improved in several ways. New glass filters would be needed. Also it would provide more reliable results, since everything would be tested using the same equipment. Nevertheless the results suggest that microfiltration on water soluble polymers would not result in retaining of the polymer. Ultimately, the entire planned experiment was not conducted, due to negative results, which prevented further investigation. Since the filtration method was proved to be unsuccessful it was not possible to approximate or quantify a market product, and thereby not determining the amount of present polymers.

5.4 Industrial aspect and suggested implementations

As mentioned before the cosmetics industry is huge, therefore one cannot ignore the economical aspect of this question. If biodegradable polymers were to substitute the ones that are being used today, it would be a great relief with respect to the environmental aspect and the waste cleaning processes. In that case the biopolymers will be disposed to a bioactive environment; hence there is no need for any additional cleaning step. Gross and Kalra (2002) claims that a huge benefit using biodegradable polymers would be the facilitation of the entire waste management process. It may be considered as unnecessary and wasteful to use polymers that are specifically designed to be long-lived and stable for such short-term uses as in cosmetics. Biodegradable polymers worthy as substitutes are required. It is still too early to suggest suitable polymers that can replace every polymer that is used in

industry. However in the long run, using biodegradable polymers can be the only solution to this problem. To direct an established business towards another direction such as biodegradable polymers requires immense efforts, especially from authorities.

The resemblance of water soluble polymers to naturally occurring polymers has been discussed. Due to the resemblance between synthetic biodegradable water soluble polymers and natural biodegradable polymers it has been suggested that the synthetic water soluble polymers can indeed degrade (Swift, 1993). Biologically, this means that the microbes producing enzymes do not distinguish between the natural and synthetic polymers. With that said, next step in the industry could be to navigate the cosmetic sectors into producing polymers that are in similar shape to the ones found in nature, because that would benefit the nature accordingly. Yes, this would result in an increase of greenhouse effect as the microbes breaks down the polymers into biomass and carbon dioxide alternatively greenhouse gases. Though, for this case it can be thought that this is safer than having plastics causing unimaginable harm to the environment during several centuries. Suggestively, if the polymers were to be derived or produced from raw wood material and at the same time manufactured through energy sources such as wind power and hydroelectrical power it would create a renewable lifecycle which would benefit the environment. Ultimately net gain would be zero.

To reach this goal research within this field should expand. Research departments in universities, such as department of fibre and polymer technology, KTH could contribute to this development. Companies need to realize that there is a need to switch from oil-based production onto green production from renewable carbon material. In order for this to happen there is a demand on industrial processes that does not have a negative impact on the ecosystem balance. If dissemination of information is done correctly and if reaches the right people in the industry we will be close in approaching our target. Continuous research within the field and of course capital investments provided by foundations and authorities will speed up the process.

A typical biotechnological approach for this problem can provide a solution. Enzymes have affinity to their substrates/targets. If the polymer of interest is studied extensively, it will be possible to screen enzymes in order to find a suitable enzyme that can attach and cleave specific bonds that are present on the studied polymer. In case the enzyme manages to degrade the polymer, it would be possible to perform random mutagenesis and later find a host cell in order to produce it in a large scale bioprocess. One such well-studied microorganism is the *E.coli*, which is already utilized in several large scale bioprocesses around the world. Similar procedures have already been developed (Premaj and Mukesh, 2005 and Hayashi, Nishimura, Sakano and Tani, 1994)

Bombelli, Howe and Bertocchini, (2017) recently published her findings about wax worms/caterpillars degrading PE plastics. The organisms were found to digest the plastics that they consumed, which suggest that either enzymatic activity or the organisms own intestinal flora is responsible for breaking down the plastics. Identifying the enzyme will enable utilization of the enzyme in a large scale process. To utilize the enzymes in a large scale process a similar approach to the one described above may be a part of the solution to the problem of plastic waste management.

5.5 Propositions for improvement in regulations

As mentioned in the introduction, polymers are neither covered by REACH nor by regulation (EG 1223/2009) on cosmetics. This is because they are not considered as chemicals, rather they are classified as materials. In REACH, monomers are considered as chemical forms. Thus the regulation does not include the assembly of monomers and their potential effect. This is a huge limitation, because it implicates that thousands of components are not regulated, and can be used uncontrolled. Further this imposes a general problem, since polymers are not covered by REACH, they are not tested for their environmental persistence, nor any other relevant tests (Hedfors and Sigurjónsdóttir, 2017). OECD tests and other standardized methods, such as ISO are tools that can fulfil REACH. However they are expected to be performed by the distributor, only if it has fulfilled the criteria of being registered minimum one ton per year. In this report it is suggested that REACH must be rephrased and edited in their regulations so that polymeric materials are addressed and included. Not only for cosmetic purposes, but also for other uses, since plastics have an infinitely wide application field. Subsequently REACH should request analysis of all polymers (that are used) regardless of production volumes. Hedfors (2016) suggest that all cosmetic chemicals, including polymers, should be tested to determine whether they are cancerogenic, mutagenic, toxic for reproduction, toxic for aquatic organisms, bioaccumulative, persistent, or endocrine disruptors, before they enter the market for sale. Extra emphasis should be on potentially environmentally toxic substances, so that they are tested in the same manner as the others stated above. As a suggestion, experts should impose standardized degradability tests, so that the testing of the environmentally persistent compounds is done in routine work. By introducing this process it is possible to obtain more valid and comparable results also it would structurally help the process.

Actually regulation (EG 1223/2009) on cosmetics is older than REACH, and has been updated several times throughout the years. Still, same limitations are applied for this as in REACH. It also fails in including polymers as cosmetic ingredients. It only mentions allowed chemicals with exceptions, allowed color additives and a list of 1328 forbidden cosmetic chemicals. A common perception of regulation (EG 1223/2009) in cosmetics is that it mainly focuses on the health impact of the ingredients, since the environmental examination is covered by REACH. Majority of the risk assessments are conducted via expert review panels, and they are performed voluntarily. Unfortunately these assessments focus mainly on the health impacts, hence the environmental impacts is often disordered, as stated by (UNEP, 2015). It is nearly unprofessional to let members of the different committees such as '*Cosmetic Ingredient Review*' decides on important decisions based on their own perceptions. Also in this case, it is suggested that the upcoming directives for the updated version of regulation (EG 1223/2009) on cosmetics that polymers are incorporated.

Based on the result and on the collected information regarding the tested polymers, it can be concluded that some sort of preventing action must be taken. As discussed earlier, the easiest step would be if authorities or government improve the legislations. In 2015, president Obama signed the ban prohibiting the use of microbeads in cosmetic products (CNN, 2015). Recently Swedish chemical agency proposed that the government should ban the use of microbeads in exfoliated cosmetic

products (Kemikalieinspektionen, 2016). The proposal is currently being revised. If it is accepted it can be an inspiration to the EU as well.

6 Conclusion

In modern society plastics are inevitable since they are used in a range of products. One application field for plastics is the cosmetic industry, in which synthetic polymers have been used as ingredients, serving important features and properties for product formulation. The polymer types that are used in cosmetic products can be categorized in two: microplastics and water soluble polymers. Both polymer types have favorable properties. Interest in microplastics and their impact on marine organisms have been of great focus lately, in fact many studies have been performed on this matter. Meanwhile there is no literature on water soluble polymers (associated with cosmetic products). However the disposals of the different product and their breakdown in nature have not been studied. Do they reach the environment, are there negative impacts on the wildlife and if so, what can be done to stop the spread?

In this report the use and function of different cosmetic polymers have been elucidated. For further investigation, two specific polymers, namely Acrylates C/10-30 alkyl crosspolymer (water soluble) and Nylon- 12 (microplastic) polymers were chosen due to their frequent occurrence in cosmetic products. They were ordered from the manufacturer and later sent to an accredited laboratory to test their breakdown capability using a standardized biodegradation method called OECD 301 F. The tests showed negative results leading to the conclusion that neither of the polymers are easily biodegraded. Test results were almost identical for both polymer types suggesting that they don't differ in degrees of breakdown, under given conditions. The obtained information is valuable and can be strengthened with addition of more replicates. In the long run it can be used to inform the authorities and the public.

After receiving results from the accredited laboratory, a separate filtration analysis was conducted at KTH AlbaNova. The aim of the analysis was to test a microfiltration method for the same polymers, to see whether or not they are retained in the filter. With the equipment that was used in the laboratory, it could be concluded that neither polymer types can be collected by filtration using 16-40 μm pore size. Suggestively, acrylic based water soluble polymers cannot be trapped in filters of that size, meaning that they probably are spread through the waste water effluents to the environment. Nevertheless, it is hard to conclude the validity of the filtration analysis that was performed due to inadequate equipment.

As for microplastics/microbeads, literature sources explain that they are successfully retained in microfiltration, however a significant amount is still let out to water bodies. As a prevention action the Swedish EPA, Kemikalieinspektionen, has developed a proposal to the government, to ban microplastics that are used in exfoliating cosmetic products. The ban does not cover water soluble polymers. In this report it is suggested that the proposal should be reviewed to also include water soluble polymers in the microplastic definition. Instead of basing the definition on particle size, it can

rather be grounded on biodegradation capability. Here it is suggested that the microplastic definition should be defined in such a way so that it can unify and comprise water soluble polymers as well. As seen from the results, even though both polymer types vary in properties they tend to act identical in degree of degradation. Another suggestion for a legislation change is that for example regulation (EG 1223/2009) on cosmetics should test and analyze every synthetic polymer with respect to its environmental impact, since the regulation under REACH is not sufficient.

Today, there is no study that investigates the long term impact of water soluble polymers on the environment and organisms. More studies and experiments needs to be conducted within this field, so that we can be aware and informed of consequences that can potentially arise from spreading synthetic polymers to the environment. An overall conclusion cannot be reached regarding their environmental impact apart from the fact that the tested polymers cannot be readily biodegraded in the given condition of the OECD 301 F test.

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