

Compounding Toolbox for Polypropylene Film Recycling



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Master's Thesis

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Abstract

The recyclability of materials and plastics in general has been discussed a lot in recent years. The majority of the plastic waste ends up in landfills and is being incinerated for energy. On the other hand, the recycling rate of plastics is still quite low as the average in the EU of recycling of plastics is around 30 %. The EU has also set targets for recycling until the year 2030. The proposal is that all plastic packaging should be able to be recycled.

The aim of this thesis is to create a toolbox in which the extrusion process of how polypropylene films can be recycled is described on a pilot scale. The toolbox can then be used as a starting ground for how the recycling process can be achieved.

Two different polypropylene films have been used as the waste product: one that has been printed on and the second that has been metalized. They have then been re-extruded to determine the recyclability of these films. Different screws and methods have been used to test out the processability of the recyclates with varying results.

The films have first been compacted before shredding them into smaller pieces and then re-extruded with a 50/50 mixture of virgin pellets and recycled film flakes. The processability of the printed film has yielded good results and the product is stable enough to be recycled with minimal to no degradation to the polymer. The metalized film with the aluminum layer is more challenging to recycle since the aluminum present has caused the polymer to degrade more easily. The removal of aluminum from the film before re-extrusion should be further researched.

The purpose of the thesis is to investigate whether the printed and metalized films can withstand the extrusion process and what the effect of the re-extrusion process on the polymer itself is.

Abstrakt

Frågor om miljö och återvinning har varit ett stort samtalsämne de senaste åren. Särskilt plastskräp och vad som ska göras med det har diskuterats. En stor del av skräpet förs till avstjälningsplatser och en del bränns för energi. Andelen plast som återvinns är liten, och inom EU ligger den på 32,5%. För att motverka det här har EU gjort upp en plan som går ut på att alla plastförpackningar ska kunna återvinnas senast till 2030.

I diplomarbetet har extrudering av två olika polypropenfilmer (PP) undersökts och frågan har varit om dessa filmer går att återvinna. Utgående från resultaten har en verktygsback, som ska kunna användas i samband med plaståtervinning i framtiden, skapats. De två filmer som har undersökts är en tryckt film och en film med ett metallskikt av aluminium. Filmerna har antagits vara rena eftersom det är industriskräp som blivit kvar från tillverkningsprocessen.

Polypropen är en termoplast som används för diverse produkter, till exempel förpackningar och leksaker. Polypropen är lätt, tål starkt slitage och är genomskinlig.

En plastfilm är en benämning på plast som har en tjocklek på högst 0,254 mm. Ifall plasten är tjockare klassas den som skiva. Filmen används oftast som förpackningsmaterial för matprodukter. Den tryckta filmen ger konsumenten information om vad som finns i förpackningen, medan metallskiktet ger skydd och fungerar som en barriär mot fukt, syre och ljus. För att trycka filmer kan vattenbaserad tryckfärg eller icke-vattenbaserad tryckfärg användas. Genom att använda vakuum kan aluminiumet förångas och deponeras på filmytan.

För återvinningsprocessen användes en extruder med två skruvar, där skruvarna roterar åt samma håll inuti kanalen. En extruder kan definieras som en mekanism som pressar en massa genom en öppning. Skruvarnas uppgift är att smälta, knåda och bearbeta materialet inuti kanalen samt att föra materialet framåt till öppningen där de sedan pressar ut den smälta plasten i önskad form, i detta fall som långa band som sedan avkyls och skärs till pellets. Under den experimentella delen av den här avhandlingen har en extruder i pilotskala använts för att utföra experimenten. Proven har sedan analyserats i laboratoriet för att bestämma kvaliteten på den återvunna produkten.

Innan filmerna kunde extruderas, måste de kompakteras och skäras i mindre bitar så att de kan köras genom extrudern. Vid extruderingen gjordes en blandning av 50 % plastfilm och 50 % naturell plastpellets. Tre provkörningar gjordes under arbetet: ett förhandstest och två egentliga provkörningar. Tanken med förhandstestet var att få en startpunkt och för att se ifall det över huvud taget är möjligt att återvinna PP-plastfilm. För de olika provkörningarna användes olika skruvar för att se ifall ett byte av skruv inverkar på plastens kvalitet. Skruvbyte var också nödvändigt för att göra det möjligt att lägga fast en vakuumpump i anläggningen.

I samband med förhandsprovet kördes tre prov per material och tre kontrollprov under samma omständigheter. Provkörningen gick bra och produkterna analyserades efteråt. Den första riktiga provkörningen gjordes i slutet av mars och vakuumpumpen orsakade några problem då smältrycket gick drastiskt nedåt och polymeren gick

sönder under extruderingen. Med den valda skruven gick det inte så bra att återvinna plastfilmen i fråga.

Vid den sista provkörningen användes den första skruven med en modifikation för att användningen av en vakuumpump skulle vara möjlig. En operator utförde alla test. Dock gjordes provkörningarna utan vakuumpump då det märktes att pumpen sög upp den smälta plasten. Ett flöde av kväve tillsattes. Det här gjordes för att kvävet tar syrets plats inuti kanalen och genom det kan oxidering av polymeren undvikas. Efter återvinningen hade båda de återvunna materialen en viss färg. Där filmen med tryckfärg använts blev det återvunna materialet grönt och med den metalliserade filmen blev proven gråa eller silveraktiga. De här kan förklaras med tryckfärgen och med aluminiumet som fanns i filmerna från tidigare.

Av förhandsprovet och den sista provkörningen gjordes ytterligare en plastfilm där jag undersökte hur bra kvaliteten var på produkten vid filmtillverkning. Vid visuell inspektion av proven kunde geler och andra orenheter som tryckfärg och aluminium märkas i filmen.

Alla prover analyserades i laboratoriet och från analyserna kan jag konstatera att den tryckta filmen lämpar sig bra för att återvinnas och att det går bra att göra film på produkten. Den metalliserade filmen var dock lite svårare att återvinna och aluminiumet ser ut att orsaka degradering av polypropen.

Utgående från litteraturen som presenterats och provkörningarna kan jag dra slutsatsen att det är möjligt att återvinna polypropenplastfilm och att filmen kan användas på nytt. Vissa saker måste fortsättningsvis undersökas vidare, till exempel hur det skulle vara möjligt att neutralisera eller få bort aluminiumet ur plastfilmen samt hur tryckfärgen kan neutraliseras så att plasten skulle bli genomskinlig.

En annan fråga är huruvida det blir färg kvar inuti extrudern efter extruderingen av de den tryckta filmen som i pilotanläggningen putsades bort med hjälp av att mata in obearbetad pellets tills plasten vid utflödet var genomskinlig igen.

Som slutsats är det möjligt att åtminstone i en mindre skala återvinna polypropenplastfilm och en någorlunda bra filmprodukt kan uppnås.

Preface

This Master's thesis has been written at Borealis Polymers Oy in Kilpilahti, Porvoo from January to July of 2021. The thesis work has been part of the PlastIN project and has been a separate project from Borealis' side.

Firstly, I would like to thank my supervisor Carl-Eric Wilén from Åbo Akademi University.

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Literature Part

1. Introduction

There has been much discussion about the increased amount of plastics produced, the usage of fossil feedstock, and littering of plastics. Many think we should start to minimize the amount of plastics used and start thinking about using other raw materials instead, since large amounts of plastic products are thrown into landfills or energy recovery. Many of the products that go to landfills end up in the water supplies. This causes environmental problems in the form of pollution (Tiseo, 2020).

The yearly global production of plastics is at 359 m metric tons (Tiseo, 2020). A possible solution to minimize the amount of plastic products in landfills and burned for energy would be to recycle these products at the end of their lifecycle. This would be better for the environment in the sense that less and less plastics are thrown away and the raw material could be reused to make new products instead.

In this thesis, an extrusion toolbox for the recycling of post-industrial polypropylene (PP) films has been presented based on literature research as well as in a laboratory setting, in order to verify the results of the theoretical framework. The toolbox will support further work on developing recycling of polypropylene flexible packaging.

The recycling process is mimicked by shredding the films and then extruding. Re-granulates are further tested and extruded into film as well. The films that have been used in the experiments are considered clean and free of contaminants due to them not being used as packaging materials, and because of that, the cleaning stages of the recycling process have been left out of scope of this thesis.

Two different raw materials are used in the recycling experiments: One that has been printed on, and one that has been metalized with aluminum. The printed films are co-extruded polypropylene films with a surface print. The metalized film is also a co-extruded polypropylene film with the metalized layer on the surface.

The purpose of the thesis is to investigate whether the printed and metalized films can withstand the extrusion process and what the effect of the re-extrusion process on the polymer itself is.

2. Plastics recycling

With the growing demand for a more sustainable and cleaner world, it is of interest to minimize the waste produced from end of use plastics even when the main raw material in the production of polymers is not oil. The depleting amount of oil is also a future problem with several implications in many fields. Littering, the amount of CO₂ emitted when burning plastic waste, and climate change are problems we are facing today. Today only about 14% of plastics are recycled worldwide and in Europe the number of 32.5% is higher than the total global recycling (Sanchez, et al., 2020). This means that if plastics could be recycled instead of being dumped in landfills, it would be of interest to many companies.

Polymers can be derived from many fossil or renewable sources, for example cellulose, coal, natural gas, and salt. Two main types of chemical reactions are used to produce polymers: polymerization and polycondensation. In the polymerization process, monomers (for example propylene, ethylene) are linked together to form longer chains. (Plastics Europe, 2021)

The fact that plastics do not corrode and decompose at a slow rate is one of the problems associated with plastic waste. The fact that plastics are widely used and durable is causing challenges with the waste management of plastics as well. A great solution would be to recycle them. The variety of different polymers, as well as the additives and composites used, makes it more difficult than it would seem to recycle polymers. (Shen & Worrell, 2014)

2.1 Circular economy

The European Union is currently looking into a circular economy strategy and it has started to gain attention from manufacturers. This would change the current strategy of a linear economy which depletes the natural resources, is harmful to the environment, generates copious amounts of waste, and is a non-sustainable economy by evaluating how plastic recycling can be made into a viable stream of the plastic value chain. An upcycling and down-cycling of the recyclable plastics as a raw material has been discussed as well, meaning that the plastics can get a new purpose if they are of a worse or better quality than the original. (Sanchez, et al., 2020)

The difference between circular and linear economy is that a linear economy has a straight path of manufacture, use, and dispose. A circular economy, however, makes sure that the resources will be used for as long as possible, and that the maximum value of the products will be utilized before the products are recovered and regenerated into new products or materials of products that have served their purpose. When circular economy has been utilized, it will then, as a result, improve the competitiveness and resource efficiency of Europe. A figure of how linear and circular economy differ from each other can be seen in Figure 1. (Plastics Europe, 2021)

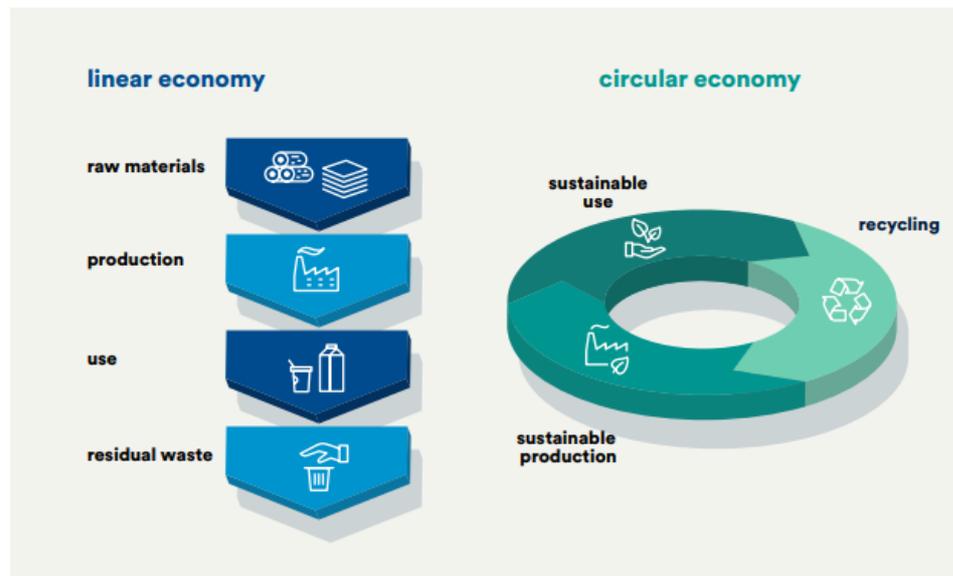


Figure 1. Linear vs. Circular economy. (Tomra, 2020)

Considering that plastics have some unique characteristics, it will enable them to play a major role in striving towards a future that is more sustainable and resource efficient. Plastics could be helpful in the saving of key resources, such as energy and water, building, and construction to name a few, this because plastics are versatile, lightweight, and durable. By applying plastics in packaging, it could help to save on food waste. For this to be possible, more and more plastic products must be recovered in order to ensure that the products will not end up in landfills or in the environment. (Plastics Europe, 2021)

2.2. EU targets for recycling

The current trend of how plastic waste is handled in Europe varies depending on the country. Statistics for Europe as a whole show that the most common way of disposing of plastics waste is energy recovery, followed by landfills. The recovery and recycling are the smallest part of about 30%. Some of the plastics end up uncollected in nature as well. Annually, 26 million tons of plastic waste is generated in the EU. In 2018, about half of the collected plastic waste for recycling was shipped to countries outside of the European Union. The reasoning behind this is the lack of capacity for recycling, as well as the technology and the financial resources being too limited to be able to recycle everything locally. (European Parliament, A, 2018; European Parliament, B, 2018)

Not having the possibility to recycle the plastics means great economic losses for the EU, since much of the value of the plastics is lost after many products are used for only a short time. The production and incineration of plastics emits around 400 million tons of CO₂ worldwide. This amount would be reduced greatly with proper recycling methods. (European Parliament, A, 2018)

In 2018, the EU backed the proposal that all plastic packaging waste should be recyclable by the year 2030. The amount of single use plastics and micro-plastics should also be limited, and these have even been banned as of the year 2021. (European Parliament, A, 2018; European Parliament, 2019)



Figure 2. How different Countries in the EU recycle plastics packaging waste. (European Parliament, A, 2018)

In Figure 2, the amount of recycling of plastics by different countries in the EU can be seen. As can be seen here, there is a big difference between the various member states. Finland does also have quite a low number of plastic recycling. The data from this figure are from 2015.

A law called extended producer responsibility for packaging, which is restricted to Finnish companies that have a turnover of 1 m € or more in Finland or that import packaged products to Finland, has also been implemented. The aim of the legislation is to reduce the amount of packaging waste, increase the reuse of packaging products, prevent damages to the environment, and to remove the barriers to trade. Finally, the aim is to prevent distortion and restriction of competition by having an equal treatment of materials for packaging. In short, the legislation means that it is the producer's responsibility to organize and pay for the collection of and recycling of the products used in packaging with other waste management included. These should be in accordance with the regulations agreed upon by the European Packaging waste Directive and the Finnish Waste Act. (Rinki, 2021)

2.3. Challenges with recycling of polypropylene flexible packaging

In general, the main challenge of recycling polymers is that the recycled products are usually of lower quality than those made of virgin materials. Therefore, it would be of importance to minimize or completely get rid of the color and metalized materials from the recyclable films. When those are neutralized it should, in theory, produce a better-quality product that would be quite close to the virgin material. (Strangl, et al., 2020)

The positive side of being able to recycle plastics is that the amount of plastics being dumped into landfills and then burned for energy would be minimized. This would also limit some of the emissions that come from the burning of waste. It would also extend the longevity of the plastics produced, if at least some of the plastics could be recycled and reused for new applications. This would, however, depend on how qualitative a product could be achieved during the experimental part of this thesis and whether it would be possible to make a close-to-original product.

Considering that this is a new area of recycling, the theory behind what to do and how is limited. By trial and error, it will be possible to obtain new information that could be used after the thesis is complete. Due to the limited test-runs, and therefore limited options available, there will not be a perfect formula for how to recycle polypropylene films, but it will be a step in the right direction and will be a starting point for how it would be possible to recycle different films. By having this knowledge, it will be easier to continue research in the subject.

Usually, plastics that are recycled have been recycled mechanically. Depending on the characteristics, some plastics, such as thermosets, cannot be recycled. Purity is also a factor as to why some plastics cannot be recycled mechanically. Low purity means that the plastic is a mix of multiple polymers, that it is a composite or lamination with multiple layers, and/or if there are any additives or fillers present in the polymer. (Shen & Worrell, 2014)

Feedstock recycling is another option as to how low purity plastics can be recycled. This process means that the low purity plastics are transformed into syngas or liquid fuel by pyrolysis. The new products can then be used in the steel and iron industry as a reducer in blast furnaces and to replace coke and mineral oil. (Shen & Worrell, 2014)

Another recycling process would be to chemically recycle the end-of-use plastics. In this process, the polymers are depolymerized to form monomers and then be again polymerized to form a new virgin polymer. (Shen & Worrell, 2014)

3. Polypropylene

Since the discovery of polypropylene (PP) in the 1950s, the applications have diversified over the years and the production of polypropylene has also grown. The polymer has many desirable properties, such as it being lightweight, strong, and having high heat resistance. Ease of fabrication is also a feature of polypropylene. (Spaniol, et al., 2007)

Polypropylene can easily be used to manufacture in high volumes and the plastic can be dyed different colors, if need be. (Doğan, 2012) PP is one of the most versatile polymers for different end purposes and can be found in nearly every market of plastic products (Allahvaisi, 2012).

Polypropylene is a thermoplastic and can therefore be processed with typical thermoplastic processing techniques, such as injection molding and extrusion (Doğan, 2012). In the experimental part of the thesis, the samples will be made using an extrusion process. Extrusion will be discussed further in chapter 3.

In this chapter the basics, degradation, and stabilization of polypropylene will be discussed, as well as the two types of films used in the thesis and what problems they could cause during the recycling process.

3.1. The basics of polypropylene

The molecular formula of propylene is C_3H_6 , and after ethylene it is the simplest olefin. Propylene is called an olefin in the industry, and by using a catalyst it will be polymerized into polypropylene. The used catalysts are a transition metal catalyst and a metal alkyl co-catalyst. The usage of these types of catalysts is called the Ziegler-Natta catalyst, named after Karl Ziegler and Giulio Natta. (Malpass & Band, 2012) A figure of how polypropylene is formed using a catalyst is seen in Figure 3.

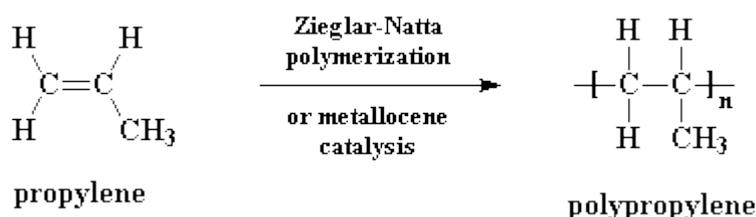


Figure 3 Polymerization of propylene. (Polymer Science Learning Center, 2021)

In PP polymerization, it is possible for the chains to form in three different manners: isotactic, atactic, and syndiotactic. This is possible seeing as the methyl group present in PP is prochiral, meaning that the molecule is not the same as its mirror image. Isotactic means the same, i.e., all the methyl groups present are oriented in the same way. An isotactic orientation is the most common in PP manufacturing. An atactic polymer means that the methyl groups in PP are randomly oriented. This is

the least desirable product seeing as how the material will be rubbery, amorphous, and tacky. The positive side of an atactic polymer is that the product can be used for example as an adhesive. The third possible orientation of polypropylene is syndiotactic, which means that the methyl group orientations are alternating from side to side in a pattern. Both isotactic and syndiotactic polypropylene have a substantial crystalline structure. In Figure 4, the three different stereoisomeric forms can be seen illustrated. (Malpass & Band, 2012; Busico & Cipullo, 2000; Merriam-Webster, 2021)

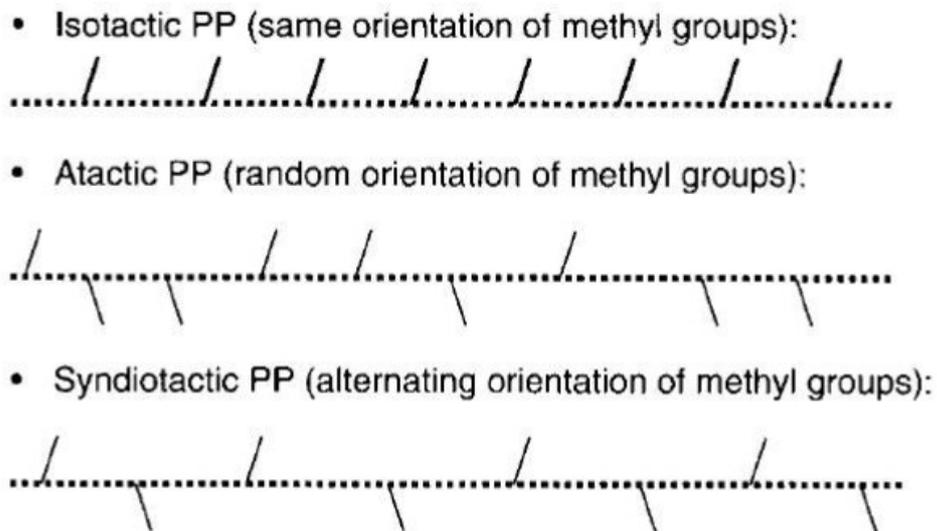


Figure 4. Different stereoisomeric forms of PP. (Malpass & Band, 2012)

After an extrusion process, the PP pellets can then be used in the making of plastic films. After the processing, the obtained films will be glossy with a high strength and a high resistance to punctures. The films will have a moderate barrier against moisture, gases, and odors as well, and the barrier properties will not be affected by a change in humidity. Examples of usage of PP films are packages for cookies, snacks, and dried foods. Other applications for PP are plastic moldings, stationary folders, plastic tubs, diapers, and so forth. (Allahvaisi, 2012) More about PP films, both printed and metalized, is discussed further in sections 2.3 and 2.4 of the thesis.

There are generally three main types of PP available: homopolymer, random copolymer, and impact copolymer (block copolymer). Homopolymer is made in a single reactor with the help of a catalyst. It is the stiffest and has the highest tensile strength at yield of the three main types. In its natural state, it is translucent and therefore has excellent see-through capacity and contact clarity with liquids. The drawback is that it has a lower impact resistance compared to the other main types, especially at temperatures below 0 °C. (Ednesajjad, 2013)

Random copolymer is made in a single reactor and has a small percentage of ethylene (<5%) added into the mixture. By adding a little bit of ethylene into the mixture, it will disrupt the crystallinity of the polymer and therefore the polymer will be the clearest and the product will be of the most flexible variant. The disadvantage of adding a small amount of ethylene is that the tensile strength will be the lowest of the three main groups. (Ednesajjad, 2013)

The third main group is impact copolymer, otherwise known as block polymer. The manufacturing process is different for the impact copolymer in the sense that manufacturing is done in two reactors. In the first reactor, the homopolymer matrix is made. In the second reactor, ethylene as well as propylene are polymerized. This leads to ethylene propylene rubber being created in the form of microscopic nodules distributed in the homopolymer matrix. This will have some improvement on the impact resistance of the final product in both ambient and lower temperatures. The end-product will then have an intermediate stiffness and tensile strength. Clarity will also be impacted, and the product will become cloudy. The more ethylene that is added, the better the impact resistance will be, but this also means that the stiffness and tensile strength will be lower. (Ednesajjad, 2013)

There is also a possible fourth type of PP available called RAHECO, which is an abbreviation of random-heterophasic polypropylene copolymer. It is a type of soft propylene-ethylene copolymer. By having a specific combination of random ethylene-propylene copolymer matrix and ethylene-propylene rubber, it allows the polymer to have a unique softness and transparency. The combination also allows for an enhanced compatibility and a reduction in particle size. (Gahleitner, et al., 2017)

3.2 Degradation and stabilization

Degradation is defined as the irreversible and detrimental changes of a polymer's molecular structure and macroscopic properties. These properties include chain length, configuration of chains, stiffness, and so forth. (Kausch, 2005)

There are several types of degradation that a polymer may be subjected to during its life cycle. These categories are chemical, thermo-chemical, photo- and/or radio-chemical, physical, mechanical, environmental, and biological. For the degradation of polymers, more than one factor can contribute to the degradation at the same time. (Kausch, 2005; Yousif & Haddad, 2013) A table showing the origins of different contributing factors to degradation can be seen in Table 1.

Table 1. Factors and causes for degradation of polypropylene. (Yousif & Haddad, 2013; Kausch, 2005)

Factor	Cause
Chemical	Hydrolysis, depolymerization, other radical reactions
Thermo-chemical	With and without oxygen present
Photo- and/or radio-chemical	UV-radiation
Physical	Through crystallization or electrical effects
Mechanical	Stress-included scission during processing or in-service life
Environmental	Including environmental stress-cracking and air pollution
Biological	Attack by enzymes and microbes

The most noticeable effects of degradation of a polypropylene on a molecular level are chain scissions, discoloration, and the introduction of functional groups. Scissioning of a polymer is defined as when a main chain breaks due to a chemical reaction. MFR can be used as a measure of chain scissioning, it is desirable to find out what and how much damage degradation has done to the polymer in all studies and applications. The easiest of tests is the analysis of discoloration, since it can be done visually. (Horie, et al., 2002)

Degradation can also occur during the polymer extrusion process. One of the possible causes of degradation besides thermal and mechanical stress during processing would be the presence of excess amount of oxygen in the molten polymer inside the barrel. This causes oxidation of the polymer and the fast breaking of the polymer in question. When the polymer starts to degrade inside the extrusion barrel, the product outflow will become unstable and run out at a faster rate than it otherwise would. Discoloration of the product will also occur. Instead of a clear stream of molten polymer strings, the degraded polymer will be discolored and exhibit from yellowish to a brownish color. If degradation occurs, it will lower the quality of the polymer and productivity will also be hindered. (Takeuchi, et al., 1997)

Typical parameters to control during extrusion is the temperature profile, retention time, and the amount of dissolved oxygen in the polymer inside the barrel in order to suppress polymer degradation. If degradation occurs, it could be time consuming to clean the extruder. Optical properties, mechanical strength, and processability, for example, will be sacrificed by polymer degradation. Prevention of degradation is vital for the productivity of the plant and steps to prevent degradation are needed from both a mechanical and a chemical point of view. (Takeuchi, et al., 1997)

From different analyses, the main cause for discoloration, and therefore polymer breakdown, seems to be the excess amount of oxygen present in the process, which then causes oxidation in the polymer melt. To prevent polymer degradation and to make the plasticized polymer stable, some steps can be taken. One option is decreasing the amount of oxygen in the molten polymer, and another is through heat history reduction. By changing the screw geometry, the problems with degradation

could be solved. (Takeuchi, et al., 1997) Other methods to reduce the dissolved oxygen inside the molten polymer would be to pump nitrogen (N₂) into the barrel during the process. The task of the nitrogen is to displace the oxygen present and it could eliminate the degradation of polymers in the extrusion process. (Maiorano, 2020)

Then how does stabilization of polymers work and how is it achieved? Much research has been done on the subject practically from the beginning of the discovery of polymers, and it is still being researched to this day. Some progress has been made, but there is still much to do. By using additives in the form of antioxidants, a more stable polymer can be achieved. Depending on the wanted properties, different antioxidants can be used. As mentioned before, less degradation can also be achieved with the help of different screw geometries, such as to change the temperature profile. (Solera, 1998)

3.3. Polypropylene printed films

PP film is the most adaptable packaging material, the reason being the low density, higher melting point, high barrier properties for gases, as well as chemical and substance resistance (diluted acids, alkalis, grease, oil, and alcohol). Water absorption is nonexistent, and decomposition is not present when in contact with fungi and bacteria. PP is also free of bisphenol A and BPA. BPA is non-suitable for food packaging, seeing as it has been discovered that it will discharge and be absorbed into food. It has been shown that BPA can have a health effect on the brain and on children's and infants' behaviors. Films from polypropylene are replacing other packaging materials, such as polyethylene and PVC. The total European plastic demand is about 51.2 million metric tons out of which around 40% is used in the packaging sector. (Ednesajjad, 2013; Packline Solutions, 2021; PlasticsEurope, 2019) An example of printed polypropylene film can be seen in Figure 5.



Figure 5. Example of polypropylene printed film. (Alphapolymers, 2021)

The films can be manufactured in different ways. The films can be un-oriented, uni-axially oriented, or bi-axially oriented. A film is defined by its thickness. If the thickness is lower than 0.254 mm, the material is called a film. Anything thicker than that is defined as a sheet. The most used resins have a melt-flow index of about 2–8 g/10 min. (Ednesajjad, 2013)

Most of today's packaging films that are multilayered use between 3–12 layers joint together. By using multiple layers, and different materials for the different layers, better mechanical and physical property combinations can be achieved. These properties include puncture, heat and tear resistance, and improved moisture and oxygen barriers. By combining different polymer layers, the packed products will have an increased shelf-life. This is done by controlling the rate of oxygen, carbon dioxide, and moisture that is transmitted. The concentration of the oxygen inside the packaging is also controlled to preserve freshness of the produce longer than normally. (Polymer Properties Database, 2021)

Films that need a better mechanical strength or heat resistance than films out of high-density polyethylene (HDPE), low-density polyethylene (LDPE), and linear low-density polyethylene (LLDPE) will use polypropylene layers. PP will also provide basic strength to the packaging and act as a moisture barrier. (Polymer Properties Database, 2021)

Through printing on the films, the consumer is informed of the contents of the packaging. The importance of using the right ink is that the ink used cannot change the properties of the films. The ink also cannot be destroyed when packaging the products or when the consumer buys the product in question. (Gecol, et al., 2001)

Ink can be described as a dispersion of pigments or dyes in a liquid carrier. There are two commercially used inks: ultraviolet curing printing inks and conventional inks. Plastic containers and closures, which includes cups, tubes, and lids, use the ultraviolet curing inks. Flexographic or gravure printing processes use conventional methods to print on plastic films with conventional inks. (Gecol, et al., 2001)

Conventional inks use pigments, binders, carriers, and additives as the main ingredients. Pigments, both organic and inorganic, produce the color and opacity for the inks and impact on the fluidity of the ink. The task for the binders is that the ink can be dispersed and that the ink will be retained on the plastic film after printing. Binders are usually low molecular weight polymer resins. (Gecol, et al., 2001)

The carrier is a liquid that makes the ink flow and makes it possible for the ink to be transferred to the wanted surface. After the carrier has done its job, it should evaporate completely. Possible additives in inks include waxes, surfactants, drying agents, and antioxidant additives. (Gecol, et al., 2001)

Conventional inks are classified into two categories: solvent- and water-based. This classification is done depending on the carrier. Solvent-based inks use solvent, solvent mixtures, or water-compatible solvent as the carrier, while water-based use water as the carrier. However, the water can also be mixed with up to 20% of alcohol. The size of the pigment particles is smaller for water-based inks than inks with an oil base. (Gecol, et al., 2001)

Acidic resins, that dissolve or scatter in water when neutralized by organic bases (amines), are used as a binder in water-based inks. Acrylics are mostly used in water-based inks because of the nonfoaming properties, faster drying, better dispersion, heat resistance, level of gloss, and the longer shelf life. Water based inks have the pros of being non-flammable, giving fewer toxic vapors, and not contaminating the products inside the packages. The con with water-based inks is that there is more energy needed to dry the inks. It also produces a lower quality print than a solvent-based film. (Gecol, et al., 2001)

Because of the environmental regulations that restrict the amount of volatile organic compounds in flexographic and gravure printing emissions, the usage of water-based inks has become common. (Gecol, et al., 2001)

3.4 Polypropylene metalized film

When more demanding barrier properties are needed for packaging, the plastic films can be laminated with aluminum foil or then be combined with a metalized film. With the aluminum layer, the transmission rate of water and oxygen is greatly reduced. The aluminum also provides a glossier and more metallic look to the plastic film. It is also a good barrier against vapor and aroma as well as working as a light barrier. Recently, the use of aluminum foil has been reduced, since it is more difficult to recycle. Also, since the metalization process has been developed it has replaced the more expensive aluminum foil laminate. (Polymer Properties Database, 2021) An example of metalized polypropylene film can be seen in Figure 6.



Figure 6. Example of metalized polypropylene film. (IndiaMart, 2021)

Metalized films are formed by multiple layers of polymer as well as a single layer of aluminum. By using a vacuum, the aluminum is evaporated and attached to the plastic film. It is a common component in the composite structure of food packaging. Metalized films are also commonly used in confectionaries. The thin coats of aluminum are just some tens of nanometers thick. These films are produced by industrial roll-to-roll vacuum web coaters and are called metallizers. This is achieved by using resistively heated evaporation boats. These can coat films up to a width of 4.45 meters at a material flow of 1000 meters/min. (Struller, et al., 2014; Polymer Properties Database, 2021)

The biggest motivation for using these thin layers is to give the polymer better barrier properties that the polymer does not have on its own. One property of the film is the impermeability of different gases, such as water, oxygen, carbon dioxide, and aromas. (Struller, et al., 2014) Despite the good properties and applications, it is difficult and not profitable to separate the layers and recover them by traditional methods, such as mechanical and chemical separations like grinding and dissolution treatment. It has been discovered that it is hard to separate the layers of the metalized plastic films, since the surface area of the thinner layers is greater than that of the bulk material and is more exposed to atmospheric oxygen. This is also why most metalized films end up in landfills and are burned for energy. (Yousef, et al., 2020)

4. Extrusion

Extrusion is a process which from the outside perspective seems like an easy one. In actuality, the process is quite complex and has many parameters that need to be considered to achieve the right product and quality. One, if not the most, important part of the extruder is the online analysis instrumentation. By being able to measure the different parameters in the process, it is possible to know what is happening in the process as well as to be able to control the process. The main reason why instrumentation is so important to the process is that it is not possible to see what is happening inside the extruder. (Rauwendaal, 2010)

The most important parameters to monitor during the extrusion process are the melt pressure and temperature. Other important factors to be considered are screw speed, engine load, temperature of the barrel and die, power consumption of the various heaters, what the cooling rate is, as well as the vacuum levels if the extrusion is vented. (Rauwendaal, 2010)

Then how does the extrusion process work? Extrusion can be defined as any process that has some kind of material pressed through an opening called a die. The material is instantly going into a solid state, so that a long stream of product with a constant diameter is formed. During plastic extrusion, thermoplastics are heated up and melted before extruding. They need to be cooled down as quickly as possible after the process, so that the form of the polymer string is maintained. (Levy & Carley, 1989)

The raw material that arrives is usually powder or pellets that are kept at room temperature. When this is the case, the extruder first must melt the pellets and homogenize the melt before the melt approaches the die. The most used process equipment of the extruder is the screw extruder, which makes about 95% of the total thermoplastic extruded products. (Levy & Carley, 1989)

Usually, the extruder is made up of different parts or zones. First, a hopper where the raw material is being held. Second, the feed throat where the material enters the barrel from the hopper, followed by the heated barrel that contains the screw that is driven by an engine. The screw forces the material to the feed pipe. A breaker plate can also be fitted to filter the material and to maintain pressure. Then there is a feed pipe where the molten material exits the barrel in order to be delivered to the die. The die is the final step, in which the material is being pushed through into the desired shape of the end-product. At the exit there is a cooling system, and it helps the extruded product to be more evenly solidified. (Ye, 2021)

Onwards from that, the polymer is transported for continued processing. When the material is being processed, the mass is transformed by multiple factors: shear force, pressure, cooling rate, shaping, and residence time. (Hyvärinen, et al., 2020)

At the feed throat, the material is being added to the screw channel. The feed throat is usually fitted around the first couple of flights at the extruder screws. So that there will not be too much heating of the polymer, the feed throat area is commonly water cooled. If the temperature of the polymer is too high, the polymer will stick to the surface of the feed opening. This causes the material flow being restricted, which in turn causes additional problems in the process. By having the hoppers cross-sectional shape as circular, it will then enable a steady flow through the hopper. Also, the gradual compression at the converging zone would need to be considered. (Hyvärinen, et al., 2020)

The most important part of the extruder are the screws. The screws are rotating in tightly fitted barrels and they are the ones that transport the material from the feed to the die end. The screws also have the task of mixing, melting and compressing the ingredients. Depending on the screws' outer and root diameters, pitch, and flight width, the extruder's capacity is determined. (Senanayake & Clarke, 1999) How the screw should be put together and what to consider will be discussed in chapter 4.2.

4.1. Single screw vs twin screw extruders

Twin-screw extrusion is widely used in applications that use mixing. This type of screw can be used in applications that include mixing, compounding, and reactive extrusion. With the different system configurations, the most used nowadays are the co-rotating, self-wiping screws. The reason behind this is that they have a good balance between the efficiency of mixing and their ability to generate pressure. To be able to optimize the process, the main flow parameters are required at different parts of the screw. These are also important from the aspect of seeing how different screw geometries will affect the parameters. Other factors that also impact the main parameters are the feed rate, screw speed, and/or the temperature of the barrel. (Carneiro, et al., 2000)

The comparison of a single screw extruder and a twin-screw extruder can be seen in Figure 7. The figure shows the cross section of a single screw and twin-screw configuration, the left picture being the single screw and the right one the twin-screw extruder.

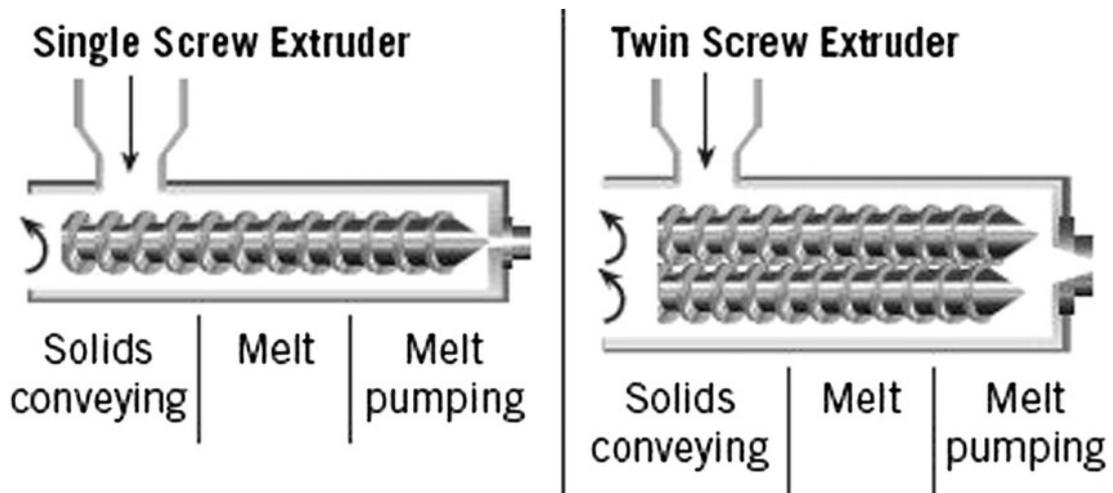


Figure 7. Cross section of a single screw and twin-screw extruder.

The single screw extruder is mostly being used in general processing of polymers, while the twin-screw extruder is mostly used for compounding different fibers, fillers, and polymer blends before they are molded into their final products. Twin-screw extruders can also be divided into two different categories, i.e., intermeshing and non-intermeshing. Of these two, the intermeshing screw type has been proven to be more effective than the non-intermeshing screw. This is due to their ability to achieve better pumping than that of non-intermeshing screws. The main reasoning behind this would be the positive displacement of the screws. (Hyvärinen, et al., 2020)

Depending on the rotation of the screws, the twin screw extruder can be co-rotating or counter-rotating. The co-rotating twin-screw extruders have their maximum velocity at the tip of the screws, while the counter-rotating ones have their maximum velocity at the intermeshing region. Since counter-rotating twin-screw extruders are reminiscent of gear pumps, it will provide the maximum amount of positive displacement. This means that it is the choice for profile extrusion, while co-rotating twin-screw extruders will be better for compounding, mixing, devolatilization, and for chemical reactions. The reasoning for using twin-screw extruders for these applications is because of how complex the flow in the intermeshing region is. This in turn provides a good mixing and good compounding characteristics. The problem with a complex flow is that it makes it more difficult to predict the performance and makes it difficult to design an extruder for a given performance requirement. (Hyvärinen, et al., 2020; Shah & Gupta, 2004)

The difference between co-rotating and counter-rotating twin-screw extruders can be seen in Figure 8.

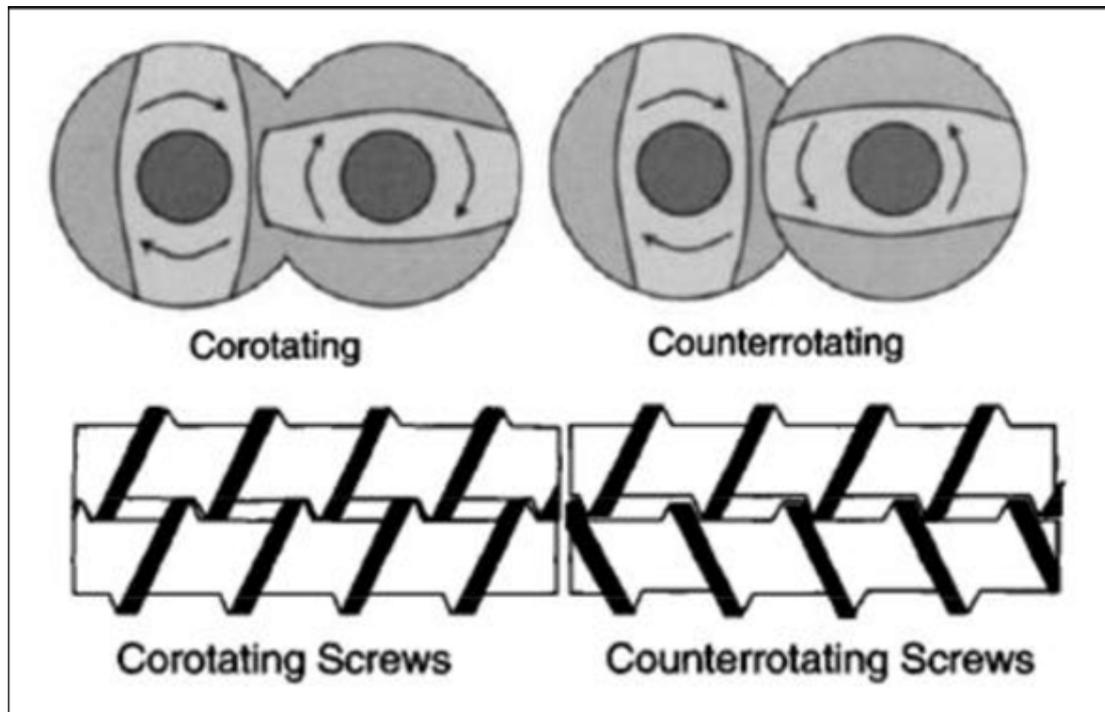


Figure 8. Co-rotating and counter rotating screws.

The key differences between a single screw and twin-screw extruder are as follows: A twin-screw extruder has a better mixing capability than the single screw extruder. This is because of the intermeshing screws and the capability of modifying the screws to fit the wanted application. By having this capability, the mixing of the polymer can be adjusted in a more precise way than that of a single screw extruder. To achieve better mixing in a single screw extruder, flow restrictions can be applied, but are very limited. (Mayures Gears Pvt. Ltd., 2021)

Twin-screw extruders can perform many different tasks during processing, such as melting, mixing, cooking, venting, cooling, and the list goes on. For the single screw extruder, the throughput and the screw speed are dependent of each other and a screw geometry that has multiple functions in a series is much more restricted than that of a twin-screw extrusion process. The productivity in the process is also higher for a twin-screw extruder than that of a single screw extruder. (Mayures Gears Pvt. Ltd., 2021)

The price of the units is higher for a twin-screw extruder due to the complexity of the machine and the different variations in screw designs and possible tasks performed by the extruder. The single screw extruder has a much simpler design, which will lead to a lower price. (Mayures Gears Pvt. Ltd., 2021)

A twin-screw process is faster, and the plasticizing capacity is higher than that of a single screw extruder. The final difference between a single and twin-screw extruder

is that, since the process is more complex for the twin-screw extruder, there will be a need for more process control in a twin-screw extruder than in that of a single screw extruder. The single screw extruder is simpler and will be needing less control during the process and the process is easier to manipulate. When knowing all these differences, it would be beneficial to think of what kind of process the extruder will be needed for and how much customization is wanted from the extruder. (Mayures Gears Pvt. Ltd., 2021)

4.2. Changes in screw geometry and different screws

As was established in the last chapter, the positive side to the twin-screw extruders is that there is the possibility to change the screw geometry to something that is useful for the raw material at hand, and what process it needs to make the wanted product. Most of the modern extruders have a modular screw design that will help with the efficiency of mixing inside the barrel (Hyvärinen, et al., 2020). The single screw, however, is divided into three main sections, them being feeding zone, transition form, and a metering zone. The residence time is the measured material processing time. (Hyvärinen, et al., 2020)

There are different thicknesses of the flight designs, thin and thick flight designs in terms of single screw extrusion. These two can then be mixed to design and build screws, since the shear conditions are controlled with the flight and the rotational speeds. (Hyvärinen, et al., 2020)

The job of the screw is to melt the polymer, preparing the melt to be homogenized, and then moving the molten polymer to the die to be pumped out of the system. The different characteristics of the finished product depend on the quality of the melt that is delivered to the die. The basic screw design has three larger sections, and these can be seen in

Figure 9 below. Here, the feed section or conveying zone has the task of delivering the product to the transition part of the screw. At the transition section is where most of the melting is occurring. The final part is the metering section or melt conveying section. This is where the molten product is being transported to the discharge of the extruder. (Eslami, 2015)



Figure 9. Simple representation of single screw geometry. (Eslami, 2015)

In single screw extrusion, the channel depth of the screw is one of the most important aspects of the screw. Usually, it is built as having the largest value at the feed section and the lowest at the metering section. The depth of the channel is decreasing during the transition sections. By doing this, it enables the polymer to be worked more. The root diameter (i.e., the diameter between the bottom parts of the screw threads) is

constant at the feed and metering sections, and because of that the channel depth is constant during these sections. (Eslami, 2015)

For twin screw extrusion, a more detailed description of the different screw sections can be seen in

Figure 10 below. A more detailed picture of the extruder barrel and screw system is shown and how multiple different screw elements can be placed to suit the process at hand.

The first two parts are the same as before. It starts with the feed section, where the polymer is being inserted by gravity from the hopper. Here, the solid polymer is preheated and transported towards the melt section, where the polymer is melted and kneaded to form a homogenous melt. Still during the melt section, additives and filler can be added into the polymer. After the additives are fed in at a continuous flow, they are incorporated into the molten polymer. The main point of the additive is to, for example, make the end-product have some specific characteristics or to help with separating some unwanted elements that would lower the product quality. During the degassing stage of the process, the volatiles and gases are removed. The final stage is the pressure build up zone, where the pressure is increased by compressing the melt, so that a steady out-stream of polymer string can be achieved. The polymer is discharged from the process, before cooling and cutting of the polymer string is done to obtain pellets that can then be made into products. (Kholgrüber, 2021)

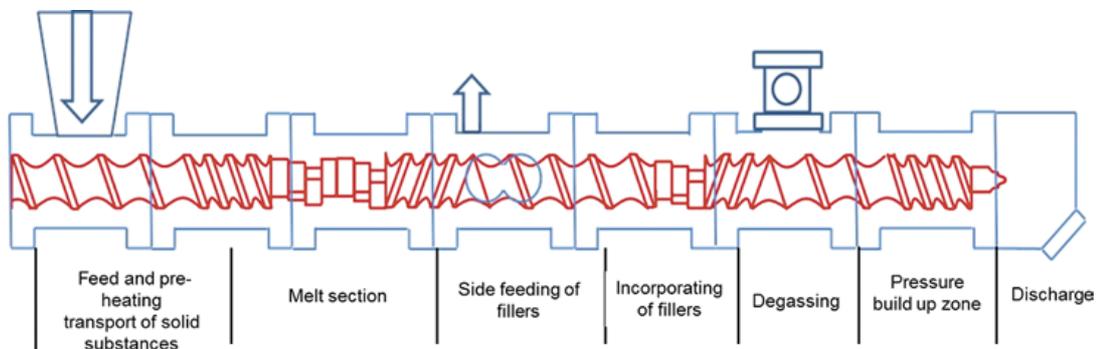


Figure 10. Detailed schematic of the different screw sections in a twin-screw extruder. (Kholgrüber, 2021)

Before starting to design a screw, one must think about many things. What are the raw materials that are going to be fed into the extruder? Are there going to be any additives added to the melt? Are there any raw materials being added downstream? And so forth. It is not as easy as it would seem. (Andersen, 2015)

The form of the polymer makes a big difference as to where the melting zone should be located in relation to the feed of the barrel and for the configuration of the conveying section. The usual size of a pellet is 3 mm, which should not cause any huge problems with the feed. If the pellets are smaller than that, there can be some problems. The melting section should be moved further down the line if the particles

are smaller. This should be done to minimize the risk of a block being caused at the feed throat. More air is going to be introduced if the particles are smaller. The air is being forced back towards the feed throat when the powder is entering the melting section. This happens because of the polymer being compressed before entering the melting section of the barrel. The excess of air then fluidizes the powder more quickly and will affect the efficiency of the conveying section. There is also a possibility for the feed throat to become clogged, which then lowers the efficiency. This would then lead to the rpm being reduced, as well as an increase in the melt temperature and mechanical energy. If this happens, the risk of the polymer or additives breaking down is increased. Other factors would also need to be considered, so that the risk of the extrusion being unsuccessful can be minimized. (Andersen, 2015)

There are different screw elements that can be used to build a screw for the applications needed. The screw design, as mentioned earlier, is an important stage before the extrusion can be done. If the design of the screw has the wrong element placed in the wrong place, it will then impact the quality of the product. In Figure 11, the different elements of the screw can be seen. (Villmow, et al., 2010) These are an example of different screw elements. There are also more with different lengths and applications.

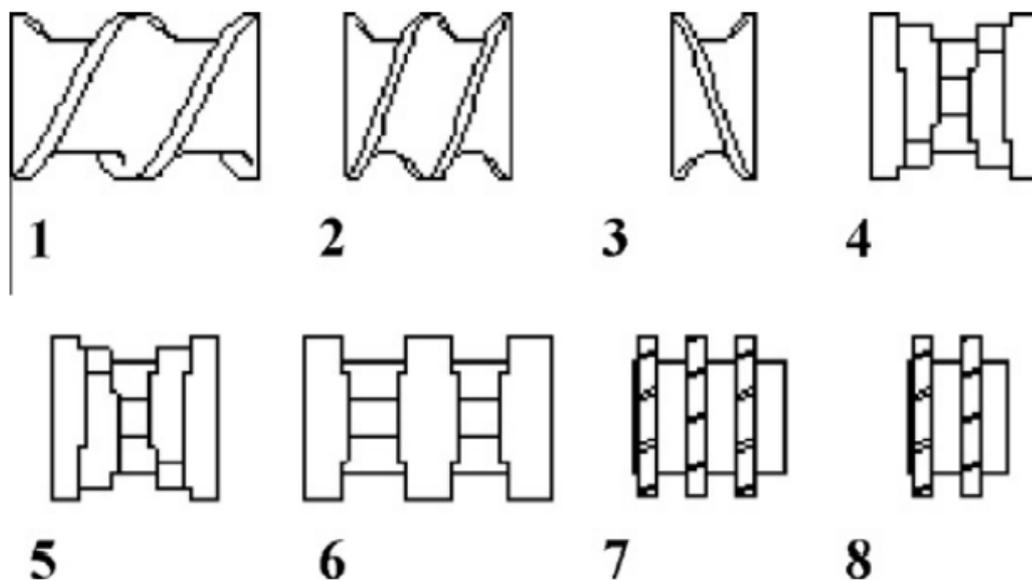


Figure 11. Different screw elements. (Villmow, et al., 2010)

Pictures one and two are two different conveying elements, the difference being the angle and depth of the channel. Element number three is a back conveying element. The back conveying element's task is to build up pressure inside the barrel. Elements four to six are different types of kneading elements. These have different configurations depending on the wanted applications. The task of the kneading elements is to achieve dispersive mixing and melting; dispersive mixing meaning that the smaller particles of the polymer break up into even smaller particles or droplets. Elements seven and eight are the mixing elements. The mixing elements'

task is the distributive mixing of the polymer; distributive mixing meaning that two different fluids are mixed, so that the physical separation is minimized and diffusion or a chemical reaction can happen. (Villmow, et al., 2010; Cong & Gupta, 2008; Bigio, 1995) The difference between dispersive and distributive mixing is that the distributive mixing increases the randomness of the dispersed phase, while the dispersive mixing provides both an increase of randomness and breaks up larger particles from the dispersed phase (Kim, 2019).

How the various screw elements are characterized is different for the various elements. Length, pitch, and number of flights are what characterize the conveying elements. Kneading elements are specified by their number of discs and staggering angles while the mixing elements are specified by their number of cogs. (Villmow, et al., 2010)

4.3. Challenges during extrusion

Due to melting, mixing, and forming, as well as making the polymer solid again, the extrusion process is quite an energy consuming process. For every kilogram of plastic, roughly 0.3 kW/kg/h of energy is needed to process the plastic. A typical extrusion process would need polymer-drying equipment, processing machinery, and units to cool down the polymer, usually with cooling water. Compressors would also be needed to convey the materials and service air. Out of this, about 50% of the energy is needed by the extrusion. (Vera-Sorroche, et al., 2013)

The barrel is heated up by two different factors, the first being electrical heating of the barrels and the second being the heating of the screw rotating. Screw heating is achieved by viscous shearing. Even though extrusion processing is an energy intense process, it is still often running at not so optimal conditions. This is because of multiple factors, one being the lack of understanding of how different process conditions affect the quality of the formed product, and how it affects energy consumption. This leads to the extrusion process being operated at conservative rates, so that the risk of disturbances is minimized. Long setup times and then downtimes are a common occurrence when there are problems with selecting the right operating conditions. Sometimes the wrong screw geometry is also being used in the extrusion process, which is because the knowledge is lacking. (Vera-Sorroche, et al., 2013)

Some difficulties faced by the processing industry are that the quality of the polymer is dependent on the homogeneity of the polymer feed. The ideal conditions of the feed would be at a constant pressure, temperature, and the throughput. Something else to actively be monitoring would be the temperature in the flowing polymer. That it should be closely monitored is more easily said than done, since it would affect the flow of the polymer. Some methods have been developed to measure the temperature of the flow in real time, but these methods are mostly for research purposes rather than used in an industrial production scale. (Vera-Sorroche, et al., 2013)

4.4. Extrusion of printed films

A problem with the recycling of plastics is that there is ink present in the film, which will then impact the overall properties of the re-extruded plastics. Depending on the temperature, there is the possibility of some volatiles evaporating, caused by the ink, and these gases will then be mixed into the plastic. This leads to the re-extruded plastics only being suitable for specific low value products. Since the flexi film is lighter in the aspect of bulk density, the process equipment also needs to be dialed in for this specific purpose, with comparison to rigid plastics. (Horodytska, et al., 2018)

The process will be easier for the mono-material than for multi-material films. This is due to the vast amount of different materials used for different layers, the difference in the processing properties, the lack of ways to identify the different layers, and the lack of a viable separation method to separate the layers. (Horodytska, et al., 2018)

There are two different types of film wastes, post-consumer and post-industrial. These two types differ from each other in a big way. The post-industrial waste film is homogenous, and the scrap is of a known polymer composition and is considered clean. About 5–12% of the production is going to become waste due to the setting up, printing, and other processes. The post-consumer waste is usually made up of multiple polymers, since the different polymer compositions are not collected in different containers but is rather dumped into a single plastic container. It is also considered dirty, with a high degree of contamination and it has been subjected to degradation during its life cycle. (Horodytska, et al., 2018) Of these two types, the post-industrial waste is the one being used in the experimental part of the thesis.

Before printing, the surface is usually treated to increase the surface energy and to enhance ink wettability. Some of the used treatments are flame treatments, corona discharge, UV treatment, and plasma treatment. Of these treatments, the corona discharge is most common for films. The principle behind the process is that a high voltage application is done to an electrode that is located near the film. The air between the electrode and film is ionized. This ionized air does then oxidize the surface of the film. (Gecol, et al., 2003)

4.5. Neutralization of odor during extrusion

One of the problems with recycling of plastics is that there is a distinct odor present in the plastics that are recycled. Especially the plastic from post-consumer applications can have an odor. This would be because of contaminants from the products contained inside the plastic. There will be a stench when the products are ready to be recycled, since it will be a long time between when the plastics were left at the collection facility and they are recycled. One of the biggest challenges of the recycling of plastics sector is the huge amount of plastic films that are not being recycled. It is estimated that around 30–50% of the total European plastic waste comes from films. The biggest problem is the heterogeneity of the films and the challenges that come from that to recycle films in a closed loop. (Lok, et al., 2020; Roosen, et al., 2020)

Something that is being researched is how the possible odor could be removed. The aim would be to find a way to minimize the odor in the plastics, by the means of physical deodorization or by advanced washing techniques. Examples of these are the addition of hot water or some kind of chemical additive. The problem is that complete odor removal has not been achieved yet. Usually, the addition of non-environmentally friendly chemicals (detergents, absorbers, or entrainers) or a high energy input are required for that. (Lok, et al., 2020)

The odors are quite diverse by the means of origin and chemical properties. The odor is not limited only to the surface but can also be found inside the product. When the odor has been absorbed, it is a big challenge for the odor minimization process. One possible origin for the odor is residual byproducts (monomers and oligomers). These are caused by the breakdown of the polymer chain. Degradation of additives (inks) is also a culprit, as well as uptake and microbial degradation from the products inside the packages and cross-contamination from the collection of plastics. With a combination of all of these, the process can become quite complex. (Roosen, et al., 2020)

It has been showed that the odor comes from a wide range of different chemical structures, such as (un-)saturated ketones and aldehydes, phenolic compounds, fatty acids, and lactones. Other studies have shown that cosmetic fragrances and washing/cleaning agents are a culprit as well. These are absorbed by varying phenomena, such as sorption, diffusion, and migration. (Roosen, et al., 2020)

The recycling methods today include using hot or cold water with or without adding caustic soda and different detergents. These methods are quite good at removing dirt and organic contaminations from the surface of the plastics. These methods are not that good at removing every odor contributing component because of the vast range of physiochemical properties. (Roosen, et al., 2020)

Laboratory analysis of a film before and after cleaning and re-pelletizing showed that by using industrial water, washing was effective at removing a considerable portion of the most polar components but was ineffective for un-polar components. It was also revealed that the concentration of some odor causing components increased after the washing and reprocessing of the waste. (Roosen, et al., 2020)

According to Strangl et.al., today's methods of industrial mechanical recycling processes where water is used to wash the polymers with subsequent drying and extruding of the recyclates, are not very effective for odor removal. Strangl et.al. suggested that a combination of different methods would be more effective and would aid in the removal of microbial activity. It would also be of interest to develop a more advanced washing technique. (Strangl, et al., 2020) The development of these techniques for the recycling process would aid the industry to become more competitive and make the process more efficient. A possible method would be to combine today's methods with an organic solvent. (Roosen, et al., 2020)

Some new, more environmentally friendly alternatives are considered for the odor minimization process. A possible alternative would be probiotics that are usually being used in the fields of human health and food quality. There are many positives to using probiotics, including the possibility to displace other microorganisms that

would otherwise be harmful. This would be achieved, because when probiotics are added, they will take up space and eat the nutrients that would otherwise be taken up by the bacteria. There is also the possibility for the probiotics to discharge enzymes and antibiotic compounds that would keep pathogens away. (Lok, et al., 2020)

4.6. Recycling process

What the recycling process looks like after the products have been collected from the consumers can be seen in

Figure 12 below. The first step would be to separate, evaluate, and remove unwanted materials from the bulk of the raw material, followed by the grinding and washing of the waste to remove impurities. The washing process can be done either by using only water or with the addition of cleaning agents. The grounded plastics are dried to have a minimal amount of moisture present for the following steps. (Santos, et al., 2005)

After the drying is complete, the ground up materials are transported into silos for further processing. The next step of the process is compacting, meaning that films and other products that have a fine thickness are joint together. The second to last step is extrusion, which is the most interesting part of the thesis seeing as that is the technique used in the experimental part. After extrusion, the strings that come out of the outflow of the extruder, are cut into pellets for further processing. (Santos, et al., 2005)

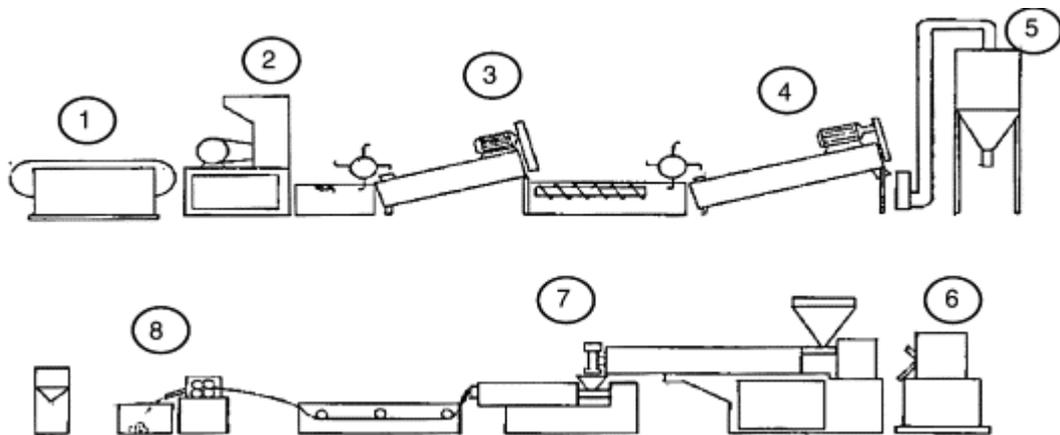


Figure 12. The complete recycling process. (Santos, et al., 2005)

Experimental part

5. Target of the experiments

In the experimental part of the thesis, the different test methods, the equipment used, and an analysis of the results from the trials will be presented and discussed. The purpose of the experiments is to obtain a clear picture of how it would be possible via extrusion to recycle polypropylene films with print or metallization. There can also be challenges with the products made from recycled plastics. Possible problems during extrusion are that the feed rate into the extruder could be lower than normally when mixing in flakes, or that the product could be of lesser quality or have some properties that would be undesirable.

In the first part of the experiments, a pre-test was done to achieve a benchmark for the following test-runs. This benchmark was designed in order to gain some insight into what the problems with the products during extrusion could be, and through that, to find a solution to solve the problems that occur.

In the second part of the experiments, a new screw was selected in order to see how the different screw geometry would process the recyclates with the addition of nitrogen feed. Here, a vacuum pump was also added in order to be able to eliminate possible volatiles present in the melt.

In the third part of the experiments yet another screw was selected, so that three different screw geometries were used during the experiments. Here, a nitrogen feed was also added in order to displace the oxygen present in the barrel and the barrel was open at position 11 to allow the volatiles to escape.

Two PP cast film reels (post industrial waste) were used as raw materials. Both films are three-layer coextruded films with PP homopolymer backbone and random copolymer as surface for print and for metallization.

A more detailed description of the tests and what equipment is used in them will be described in the following chapters.

6. Used equipment

Before the raw material could be made into new plastic pellets, it had to be processed in two stages. The first stage was to press together multiple layers of film into a compact sheet. The second stage was to shred the pressed sheets of films.

The pressing process was done using a Collin lab line P400S platen press. Before the pressing could be done, the film had to be cut into smaller pieces, so that they could fit into the mold placed on the pressing plate. To achieve the maximum thickness of the sheets, three molds were put on top of each other. Two of the molds were 1 mm thick and the third was 2 mm thick. The pressing area achieved was about 30x30 cm. About 300 g of plastic film could be pressed at a time without bigger problems. Between 5 and 7 kg material was pressed for each test-run.

The setup for the pressing machine is that there are two plates, out of which one goes on top and the other is placed at the bottom. On the bottom plate, a plastic sheet

made from PET is placed to protect the pressing plates and for it to be easier to remove the pressed sheets of PP. Next, the molds are placed on top of the protective sheet, so that the first 1 mm mold is underneath, the 2 mm mold is in the middle, and the second 1 mm mold is on top. Then, the cut pieces of plastic films are placed inside the molds. Finally, a second protective sheet is placed on top of the second plate before the metal plate is placed on top of the molds. Then the package is placed inside the presser.

For the pressing of the films, a shorter than normal program was selected. The new program runs for a total of 20 minutes instead of the normal 30 minutes. This was to make the time spent pressing shorter, and because only a partial melting of the films was needed. The program started with a 400-second heating stage for heating the films from 40 °C to 210 °C. After the heating stage, the film was not yet up to temperature, so a 120-second heating wave was done. When it reaches the right temperature, the machine is holding the temperature at 210 °C for 120 seconds at a pressure of 50 bar. After that, a final cooling stage is applied to the pressed sheets to lower the temperature down to about 40 °C. The final product of the film pressing can be seen in Figure 13.



Figure 13. Pressed printed film (left) and metalized film (right)

After the pressing process, the sheets again had to be cut into thinner pieces lengthwise, so that they could fit into the shredder and in order to achieve the flakes wanted to be used in the extrusion process. The shredder used was a Moditec low speed granulator. First, the printed film was shredded and then the metalized film was shredded. The machine was properly cleaned before and after use to ensure the risk of contamination would be less likely. The shredded material was collected into bags, again to have minimal contamination. A figure showing the printed and metalized flakes can be seen in Figure 14.



Figure 14. Printed film flakes (left) and metalized film flakes (right)

Finally, the shredded, printed, and metalized films could be extruded into pellets. The extrusion process was done using a Werner & Pfleiderer ZSK-30 twin-screw extruder. It is a type of co-rotating extruder. The screws used in the pre-test were screw #1. The plastic strings pressed out of the extruder were transported through a waterbed. By using the pool of water, proper cooling of the extruded plastic can be ensured. The strings were transported from the pool to be cut into pellets, which were collected into bags.

After each test-run, the bag was removed and properly marked, and a new bag was placed underneath to collect the next batch of pellets. In Figure 15 on the following page, the Werner & Pfleiderer ZSK-30 twin-screw extruder can be seen as a reference of the size of the extruder. After the test-runs were completed, the samples were analyzed.



Figure 15. Werner & Pfleiderer ZSK-30 twin screw extruder.

7. Test methods

After every test-run the samples must be analyzed with different methods in order to be able to compare every test point from a specific test-run and between the different test-runs. This is done to see whether the products formed with different screw geometries and additives have helped us achieve a better product compared to where we started. Two main analyses were done with every test point: melt mass-flow rate (MFR) and the volatiles measured. Various other analyses were also done.

7.1 Melt mass-flow rate

Melt mass-flow rate is used to measure the melt viscosity or flow resistance of a polymer sample at a constant load, temperature, and shear rate. The test uses a specific size of die in a heated barrel which has a piston and a weight on top of the piston. This is inserted into the barrel and pressed down on the polymer melt to force it out through the die. (Giles Jr., et al., 2005; AZO Materials, 2008)

Before the test, the barrel is clean, and the desired amount of polymer is added into the barrel. The polymer is packed inside the barrel with the piston. During a time interval, the polymer is heated into a molten stage and then the piston pushes the molten polymer through the die. After the analysis, the barrel and die are cleaned. (Giles Jr., et al., 2005)

The melt flow index is the amount of molten polymer in grams which is forced through the die during a 10-minute period (g/10min). Every resin system has its own specific length of opening and diameter, temperature in the barrel, and load by the piston. These are defined in the ISO standard of the analysis method. A lower melt mass-flow index relates to a higher viscosity of the polymer. A higher melt mass-flow index then shows that the polymer has a lower viscosity. (Giles Jr., et al., 2005; AZO Materials, 2008)

For polypropylene, the used temperature is 230 °C. There are three different tests which can be done with MFR, all with different loads to the piston: MFR₂ with a weight of 2.16 kg, MFR₅ with a weight of 5 kg and MFR₂₁ with a weight of 21.16 kg. The used test in this thesis is MFR₂ as it is the standard test for polypropylene. For polyethylene, other MFR loads are possible. (Wang, et al., 2015)

7.2 Headspace GC/MS analysis

The standard used for the analysis method of Headspace GC/MS is ASTM D4526 – 20. There is no known ISO standard for this method. (BSI group, 2021)

Headspace analysis is a technique in which a sample is analyzed by examining volatiles from a solid or liquid. Headspace is defined as the gas volume above the sample. Usually, the sample is held in an airtight container to keep the gas from escaping. The volatiles are usually the cause of an odor. (Worsfold, et al., 2019)

Once the sample has been collected, it can be analyzed with different methods, out of which it is usually done with gas chromatography or gas chromatography with mass spectroscopy detection. The simplest method is to use a gastight syringe to draw some of the headspace from a closed container. The gas is inserted into the analytical equipment. (Worsfold, et al., 2019)

7.3. Density

The ISO standard used for the measurement of density is ISO 1183-1:2019(en).

Density is an important property to know when it comes to a solid. The density can vary for example concerning the change of crystallinity, loss off plasticizers, and absorption of solvents. There can also be changes in the density of a sample. Usual causes can be, for example, the difference in crystallinity, porosity, or composition. (Bag, et al., 2003)

Knowing the exact density of a material will be helpful when determining the material, following physical changes in a sample, indicating the uniformity of different samples, determining the average density of a bigger product, and calculating the weight to cost ratio of a specific product. (Bag, et al., 2003)

The pellets had to be pressed and melted into small discs with a sample size of 7 g per disc. After obtaining the discs, the samples are first weighted in air to determine the mass of the sample. The samples are immersed into a liquid and their mass upon immersion is measured. After the immersion, the densities are calculated based upon the results. Depending on the liquid used, the standard is categorized into two different categories: Method A, in which the sample is immersed into water, and Method B where the sample is immersed into a liquid other than water. Method A is usually used when the density of a sample is expected to have a density higher than water and Method B if the expected density is lower than that of water. (Bag, et al., 2003)

By measuring the density of the samples, it can be determined how much of a difference the addition of recycled film will change the density of the polymers when metal in the form of aluminum and the print color is added to the natural polypropylene.

7.4. Color difference CIELAB

The color difference is often measured in order to analytically determine if a product meets the standards set by the manufacturer. Most analyses are made by visual inspection, but sometimes other methods are needed to ensure that the product meets industry standards. (Datacolor, 2008)

Instruments to determine color differences are used to have a quantitative measurement of how different the color truly is from the reference. The measurement equipment is CIE L*a*b*, CIE L*C*H*, CMC, and CIE94. Out of these methods, the CIE L*a*b* is used to determine the color difference between two different film samples, the first being from the pre-test and the second from test-run 2. These films are made from the pellets that were made during the different test-runs. (Datacolor, 2008) [Redacted]

The CIELAB system classifies colors based on the opponent theory of color vision. This theory implicates that colors cannot be seen as both red and green simultaneously, the same being true for yellow and blue. However, a color can be seen as a combination of red and blue, red and yellow, green and blue, and green and yellow. In the analysis, the different color coordinates are as follows:

L* is the lightness coordinate,
a* the red and green coordinate, where +a* indicates red and -a* green,
and b* the yellow and blue coordinate, where +b* indicates yellow and -b* indicates blue.

The color difference between two samples can then be determined by the difference in the distances between color locations. By using formula (1) the distance can typically be determined.

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (1)$$

Where:

ΔL^* is the light difference,
 Δa^* is the red/green difference and,
 Δb^* is the yellow/blue difference.
(Datacolor, 2008)

7.5 Yellowness index

The yellowness index is a measurement calculated from spectrophotometric data. This describes the change in color of test samples that are clear or white to yellow. It is an important property for many industries to measure. By processing multiple materials, a yellowing of the product can occur. The purity of a product can be determined by how yellow the product has become. Some environmental factors, such as UV-radiation, can cause yellowing of the products. (Puková, et al., 2021)

Yellowness index is a dimensionless number that is determined by the spectroscopic data. Usually, the index shows how the color has changed in a material due to different weather conditions. By using the same test methods as in the measurement of color difference, CIELAB is used to determine the yellowness in the color range of the axis. (Puková, et al., 2021)

The analysis in the thesis is done in order to be able to determine if one of the polymer samples obtained from the first test-run is broken down and is compared to the data of the control sample from the pre-test.

8. Test-runs

The pre-tests were done mainly to obtain an understanding of how the equipment works and for retrieving a benchmark for the following trials. By having this benchmark, there is the possibility to compare the results of the pre-test with the results from the follow-up tests in order to determine if the product from the extrusion process will be better or worse than the benchmark set by the pre-tests.

The test-runs were done by having a combination of both virgin pellets and flakes made from metalized and printed films. The ratio of virgin pellets and flakes was 50/50. Three test-runs were made with both film flakes. There was also a third sample with 100% virgin plastics driven through the extruder, which is used as a control. The virgin plastic used in the blends was a PP homopolymer cast film grade. The decision of doing test-runs with just virgin plastics was made in order to have a control sample when analyzing the recyclates, since the virgin plastics have not had as many heat cycles as the pellets made from recyclates. To be able to ensure that a constant flow of flakes enter the hopper, there had to be an agitator fitted into the feed vessel that held the flakes above the hopper. The agitator that was fitted can be seen in Figure 16.



Figure 16. The agitator used to ensure a continuous feed of polypropylene flakes.

The variables chosen during the experiments were feed rate and rpm. These variables were chosen, so that a scale-up from a pilot extruder could be made. The variables chosen were to use the normal and maximum values for both the feed rate and rpm. The values were 5 and 7kg/h feed rate and an rpm variation of 150 rpm and 220 rpm as shown in Table 2.

Table 2. Planned test-run parameters.

Test-run	Feed rate [kg/h]	rpm [1/min]	Description
1	7	150	Maximum feed rate, normal rpm
2	5	220	Normal feed rate, maximum rpm
3	5	150	Normal feed rate, normal rpm

When starting the first test-run, it was noticed that the feed was too high for the printed films at the entry of the screws and the hopper was starting to become clogged. The maximum feed rate measurement was not used for the metalized film flakes because of the problems with the printed film flakes. The cause of the problem was that flakes made out printed films have quite low density, and the screws could not keep up with the feed rate. The problem occurred for all three test-run combinations.

A decision was made to seek out the maximum and normal feed rate and rpm manually, so that the hopper would not be filled up. Based on the results from the trials, new maximum and normal values for the feed rate and rpm were chosen. The new combinations of variables after testing can be seen in Table 3.

Table 3. Actual test-run parameters.

Test-run	Feed rate [kg/h]	rpm [1/min]	Description
1	5	220	Maximum feed, maximum rpm
2	3	150	Normal feed rate, normal rpm
3	3	220	Normal feed rate, maximum rpm

To make the flakes melt inside the extruder, the different temperature zones would need to be optimized. The temperature would need to be raised slightly from the beginning of the screw to the end of the screw. In the extruder used, there are 7 different zones. The selected temperature profile can be seen in Table 4. The end temperatures were selected, so that it would be close enough to an industrial extruder. Depending on the runs, the actual temperature profile will have some small differences. In Table 3, the melt temperature was not included, since the temperature varies depending on the test-runs. Whereas in Table 4. Temperature profile for the extruder. the information from the different runs is shown.

Table 4. Temperature profile for the extruder.

Temp zones	1	2	3	4	5	6	7
Temp profile [°C]	180	200	220	220	230	230	240

Using these three combinations for both the printed and metalized film runs, as well as for the control, the tests could be run without a problem. Between the different material extrusions, the extruder needed to be flushed clean in order to get rid of components from previous test-run materials. The cleaning process was done by feeding the extruder with virgin pellets. During the cleaning process, it was noticed that it took a long time to clean the extruder after the extrusion of the printed films. The print color used seems to stick to the screws or the walls inside the extruder. For the following trials, it would be preferable to extrude the printed film last. By doing that, it should cut the time for the test-runs. After the extrusion process, new films will be made from the formed pellets.

The first real test-run was done at the end of March 2021. Before the test-runs, the screw geometry was changed in order to investigate if a better product could be achieved. The new screw to be used in the first test-runs was called screw #2. The point of this test-run was also to use nitrogen and vacuum.

Nitrogen was used, since it will replace the oxygen in the barrel. With a combination of vacuum and nitrogen, the volatiles present in the barrel could be removed and thus a more stable and better product overall could be achieved. If nitrogen and vacuum would not be used, the volatiles would just be mixed with the molten polymer instead.

Table 5. Melt index for the different test-runs from the pre-test.

Material	Test point	Melt index [g/10min]
Printed film	1	6
	2	5
	3	6
Metalized film	4	15
	5	13
	6	14
Control	7	10
	8	10
	9	10

In the second test series, there were control samples run at the same time to be able to be compared if and to know how the new screw would affect the overall quality of the recyclates. There were no problems with the control samples.

The next step was to add a vacuum pump and nitrogen. When the barrel was opened in the latter part of the extruder, the problems started occurring. The polypropylene at the outflow started to become quite runny and the polymer also got a brownish tint to it. These findings strongly indicates that the polymer had undergone thermo-oxidation with subsequent breaking of polymer chains. Reflecting on the literature part of this thesis, it seems that there was an excess of oxygen present inside the barrel which caused the problems. The addition of nitrogen and the vacuum pump did not help to solve the problem. The vacuum pump was too powerful and began sucking up the melt. A portable oxygen meter was used to measure the oxygen present at the hopper, and the lowest value measured there was around 1%.

One notable thing was that when the barrel was opened, the melt pressure dropped significantly from 9 bar to about 3 bar. This indicates that the pieces used for the screw did not generate a “polymer wall” which was needed to keep the pressure up when the barrel was open. When the barrel was closed again, the pressure increased, and the polymer oxidization was not present anymore. Different methods were used to see if the polymer degradation problem would be resolved, but they were not successful. The decision was made to stop the test-runs and revert to the previous screw (screw #1) with some small modifications to the end of the screw, so that the barrel could be run open during the final test-runs.

The final test-run was done at the end of May. The screw was modified and changed for the test-run and some more extensive testing was done before the actual test-run period.

The chosen parameters for the feed rate were 5 kg/h and the rpm was 220 rpm. These were chosen as the parameters to have the biggest possible production rate. Also, for each run there was the addition of nitrogen (N₂) to displace the oxygen inside the barrel. The input of the nitrogen feed was added to the hopper. The barrel was also open at position 11 on the barrel for all test points.

Overall, the test-run did go according to the test plan even though a small change had to be made during the running of the printed film flakes. At the selected feed rate of 5 kg/h, the hopper did start to become clogged. This problem was due to the film flakes being lighter than the metalized flakes and the natural pellets. To be able to continue with the test-run, the feed rate had to be dropped down further to 4 kg/h.

9. Results and discussion

In this chapter, the different test-runs and the results will be presented. All the analyses made for the different test samples will be presented as well and compared to each other. A discussion of the results will be had to be able to determine if polypropylene films are recyclable into some sort of quality product.

9.1. Pre-test

During the pre-tests, there were three different test-runs per raw material, which means nine test-runs in total. The runs started with the printed films, continued with the metalized films, and finalized with test-runs with 100% virgin pellets. In Table 6, the different test-runs, variables, and results can be seen.

Table 6. Pre-test test-runs with variables and values.

Material	Test point	rpm [1/min]	feed rate [kg/h]	torque [%]	Melt pressure [bar]	melt temp [°C]	residence time [s]
Printed film	1	220	5	46	9	246	80
	2	150	3	42	8	244	135
	3	220	3	40	7.4	247	118
Metalized film	4	220	5	48	7.5	245	80
	5	150	3	40	6.5	244	135
	6	220	3	40	6	246	118
control	7	220	5	49	9	246	80
	8	150	3	44	7	244	135
	9	220	3	41	7	247	118

From the table above, it can be seen that the torque, melt pressure, melt temperature, and residence time vary depending on the changes of rpm and feed rate. The residence time was measured by taking a couple of black pellets that were dropped into the hopper. By using a stopwatch, time was measured from the time the pellets were dropped into the hopper until the plastic strings that came out of the die turned black. As can be seen, the higher the feed rate and rpm, the shorter the residence time will be. In correlation, the slowest rpm and feed rate will have the longest residence time.

At the highest feed rate of 5 kg/h and rpm of 220 1/min, the pressure and torque percentage are also the highest. This would be explained by the increase in feed rate. The machine will have to work harder to keep up with the higher flow of raw material and the pressure will be higher, since there is more material pushing forward through the screw. It can also be explained by the fact that at the highest feed, the rpm was barely enough for the extruder to push the product through. At any lower rpm, the hopper would start to become clogged again.

The lowest pressure in the machine was achieved with the highest rpm and normal operating feed rate. The torque percentage was also the lowest when considering the printed film and control extrusion. The metalized film is a deviation of this observation. It could be explained by the fact that the density of the metalized flakes was higher than that of the printed films.

In all three different raw materials, the melt temperatures varied with a couple of degrees from each other. The difference in melt temperature was not big enough to be of any significance, about a 1% deviation.

In Table 7 below, the temperature profile of the different test-runs can be seen. The numbering is the same as for Table 6 on the previous page: test-runs 1–3 is the temperature profile for the printed film flake extrusion, 4–6 is for the metalized film flakes, and 7–9 for the control sample. As can be seen from the table, small deviations are noticed from the set temperatures. The deviations in temperature are again quite small from the set values for each zone. That should not have any significance in the quality of the pellets produced in extrusion.

Table 7. Temperature profile for the different test-runs by zones.

Temp profile	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7
Set	180	200	220	220	230	230	240
Testrun 1	180	201	220	220	230	230	240
Testrun 2	180	200	219	220	231	231	240
Testrun 3	178	198	218	220	231	230	240
Testrun 4	180	199	219	220	230	230	240
Testrun 5	179	200	219	220	231	230	240
Testrun 6	180	200	222	220	230	230	240
Testrun 7	180	200	219	220	230	230	240
Testrun 8	180	200	219	220	230	231	240
Testrun 9	180	198	217	220	230	231	240

After the extrusion, some of the pellets were sent to the laboratory for analysis. The melt index and the headspace volatiles were analyzed.

As was shown in the previous chapter, the melt index varied depending on the materials used. As expected, the control samples had the melt index closest to the original pellet of 8 g/10min. Some small deviations can be seen depending on the set parameters.

Melt index was also measured for the pressed films used in the test-runs. The films were first pressed together, and small pieces were cut from the sheets, so that the pieces would fit into the machine. The results from the analysis can be seen in Table 8 below.

Table 8. Melt index for the recyclates raw materials.

Material	Melt index [g/10min]
Printed pressed film	9
Metalized pressed film	6
Natural pellet	8

Notable here is the values for the melt indexes compared to the value of the melt index for the pellets made from the film recyclates. It would be expected that the values should be flipped, so that the printed film would have the lower melt index when comparing the two. The explanation for this is that the pressed films were not homogenized as they were in pellet form. If the pressed films would be melted first and would be able to be stirred, then the results could be different. Another possible cause to the differences in the melt indexes is that there would be some breakdown of the polymer with having the metalized film flakes in the mix.

The results from the volatile analysis can be seen in Table 9. All the samples are from the pre-tests.

Table 9. Results from the volatile analysis from the materials in pre-test.

[ppm]	Volatiles								
	Printed film			Metalized film			Control sample		
	Test point 1	Test point 2	Test point 3	Test point 4	Test point 5	Test point 6	Test point 7	Test point 8	Test point 9
C1	-	-	-	-	-	-	-	-	-
C2	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
C3	1.9	1.9	2.1	0.7	0.6	0.7	0.7	0.5	0.5
C4	0.7	13	14	1.7	1.8	1.9	3.7	4.5	4.7
C5	30	31	30	30	30	31	49	49	49
C6	12	13	13	17	16	18	25	24	25
C8	28	32	34	10	10	10	13	13	13
C9	15	15	17	23	23	22	29	30	29
C10	-	-	-	-	-	-	-	-	-
C12	8.7	8.2	9.4	12	12	12	13	13	13
C14	-	-	-	-	-	-	-	-	-
C15	3.1	2.7	2.8	4.1	4.2	4.3	4	4.2	4.1
C16	0	-	-	-	-	-	-	-	-
C18	-	-	-	-	-	-	-	-	-
C20	-	-	-	-	-	-	-	-	-
Total	99.9	117.3	122.8	99	98.1	100.4	137.9	138.7	138.8

From the table, it can be seen that the different materials do have slight differences between them. Listed here are the different lengths of carbon chains. An abnormality can be seen between the printed films, mainly between C₄ where the sample of test point 1 seems to have a low amount compared to the others. This abnormality could be explained as an error in the measurement.

Other deviations can be seen in C₅, where the printed film pellets and metalized film pellets have a lower amount of volatiles than that of the control. The same can be seen in C₆ and C₉ where there are less volatiles being dispersed for the recycled pellets. In C₈, there is also a difference between the different samples. Here, there is a higher percentage of volatiles in the printed pellets than for the metalized and control samples. A conclusion is that the different test-runs with different screw geometries

did not significantly affect the amount of volatiles present. The differences noted are between the different materials used during the experiments. The recyclates did not have a higher total amount of volatiles present than that of the control samples.

9.2 Test-run 1

The first test-run had six different test points, in which four were for the control sample and the other two for the recycle films. As mentioned in the previous chapter, there were some problems with breakdown of the polymer when the barrel was open and due to this the test points were limited. One of the test points was run with an open barrel. This was done to obtain a sample of the polymer to be able to analyze and determine that the polymer had broken down. The melt mass-flow index, yellowness index, as well as the headspace volatiles were measured and analyzed in order to motivate the change of screw composition for the last test-run.

It is notable that when the melt mass-flow index (MFR) was measured, the die had to be changed to a half measure to be able to achieve an accurate measurement. By changing the die to a half measure, there had to be a correction factor applied to the value which the equipment gave for the melt flow index value. For polypropylene, the correction factor is 7.7. By using formula 2, the correction for the die can be calculated.

$$MFR_{corr} = MFR_{meas} * k \quad (2)$$

where:

MFR_{corr} = the corrected melt mass-flow index,
 MFR_{meas} = the measured value of the melt mass-flow index and
 k = correction factor.

After the application of the correction factor, the measured MFR of the sample was 389 g/10min, indicating that the viscosity is low for the polymer. When comparing with the result that was measured with MFR, the polymers' attributes have changed considerably from the natural polypropylene sample that was measured before being extruded.

The yellowness index was then measured using CIELAB on the sample and compared to the same test conditions in the pre-test. The yellowness index comparison between both measured samples can be seen in Table 10.

Table 10. Measured yellowness index for the test samples.

Sample	Yellowness index
Pre-test control	9.07
Test-run 1 control	14.24

As can be seen from the table, the control sample from the first test-run has a higher yellowness index than that of the pre-test sample. This shows that the polymer was more yellow than the one from the pre-test. It is notable that both samples have a high yellowness to them when comparing the values with the index of natural polypropylene. Usually, the value is close to zero. This indicates that re-extruding natural PP will influence the clarity or whiteness of the samples.

Finally, the headspace volatiles were measured for the possible broken-down sample of polypropylene. The results from the analysis can be seen in .

Table 11.

Table 11. The measured volatiles of the control sample from test-run 1.

	Control
[ppm]	Test point 6
C1	-
C2	0.5
C3	1.2
C4	2.4
C5	17
C6	20
C8	17
C9	25
C10	-
C12	12
C14	-
C15	4
C16	-
C18	-
C20	-
Total	99.1

When comparing the result with the ones from the pre-test, they are quite similar to each other as far as volatiles are concerned. Some deviations can be seen though in the C₅ chains, which shows that there are less volatiles present with the carbon chain length. The other values are close enough to each other that they can be summed as deviations in the measurement.

With all the analyses done for the sample, it can be concluded that the polymer had been broken down during the process. The theory of breakdown from visual inspection during the test-run has been confirmed. With the known information of the properties of the polymer sample with having the barrel open during the extrusion process with the screw #2, it seems that the screw was not suited for the raw materials and the test-run had been stopped when the product had started to show signs of breakdown.

A possible theory of why the screw was not suited for the wanted purpose is that it did not build up enough of a pressure wall before the opening of the barrel to eliminate the oxygen ingress from the hopper. This can be seen in the summary of the test-runs, where the pressure dropped significantly when the barrel was open compared to when the barrel was closed. The polymer showing signs of breakdown was due to the excess amount of oxygen present in the barrel, which then caused the polymer to oxidize. Even with higher amounts of nitrogen added to the barrel at the hopper, it did not prevent the oxidization of the polymer. A portable oxygen-measuring device was applied at the barrel at which the oxygen percentage reached as low as 1.2%, but the outflow continued to show oxidization of the polymer.

In Table 12, the summary of the first test-run can be seen. Here the pressure drop can be seen clearly. When the barrel was closed, the pressure was around 7 bar and when the barrel was opened in test point 6 the pressure dropped down to 3 bar. Torque percentage during all test points was also about half of what it was during the pre-test. This can be explained by the fact that the screw in question is gentler with the raw material. The residence time was also lower for this specific screw when compared to screw #1 used in the pre-test. For the rest of the samples, the melt mass-flow index was measured and analyzed. These will be compared to each other and discussed later in this chapter.

Table 12. Summary of the test conditions and test-runs for the first test-run.

Material	Test point	rpm [1/min]	feed rate [kg/h]	torque [%]	Melt pressure [bar]	melt temp [°C]	residence time
Printed film	1	150	3	23	7.5	245	119
Metalized film	2	220	5	27	9	246	72
	3	220	5	27	9	248	72
Control	4	150	3	23	7.5	244	119
	5	220	3	22	7.5	248	95
	6	220	5	21	3	242	72

9.3. Test-run 2

For the final test-run, the screw was reverted to the screw configuration used in the pre-test, with some small modifications. The modifications were made to the screw for the barrel to be able to be open at position 11. The modifications were done at the end of the screw by rearranging the conveying elements to position 11 on the barrel.

The test program could be run through without any considerable difficulties. The focus of the test-run was on the nitrogen feed into the hopper and to have the barrel open for venting. One test point for each material was run.

Table 13. Summary of the test conditions and test-runs for the second test-run.

Material	rpm [1/min]	feed rate [kg/h]	torque [%]	Melt pressure [bar]	melt temp [°C]	residence time [s]	Product [kg]
Printed film	220	4	42	6	246	94	2.90
Metalized film	220	5	44	4.5	245	89	2.90
Control	220	5	46	6.5	245	89	2.90

Here it can be seen that the torque percentages had risen and were close to the same as they were in the pre-test which is expected when the same elements were used with the screws. The pressure dropped a little bit from between 7–9 bar to 4.5–6.5 bar. This can be explained by the fact that the barrel was open during all test points.

9.4. Melt mass-flow index

The different raw materials will be presented and analyzed from an MFR perspective in order to determine how much the different screw setups, the addition of additives, and conditions have affected the quality of the polymer and the viscosity. All samples from the test points were measured two times and the results shown in the graphs is the median value of both measurements.

9.4.1 Printed film test points

The melt mass-flow indexes for all three test-runs for the printed films can be seen in Figure 17. From the results, it can be concluded that the MFR differs slightly in the different test-runs. This shows that there is some difference depending on what kind of screw is being used during extrusion. It is interesting to notice that the melt mass-flow index as a combination of the raw materials is lower than that of the raw materials themselves.

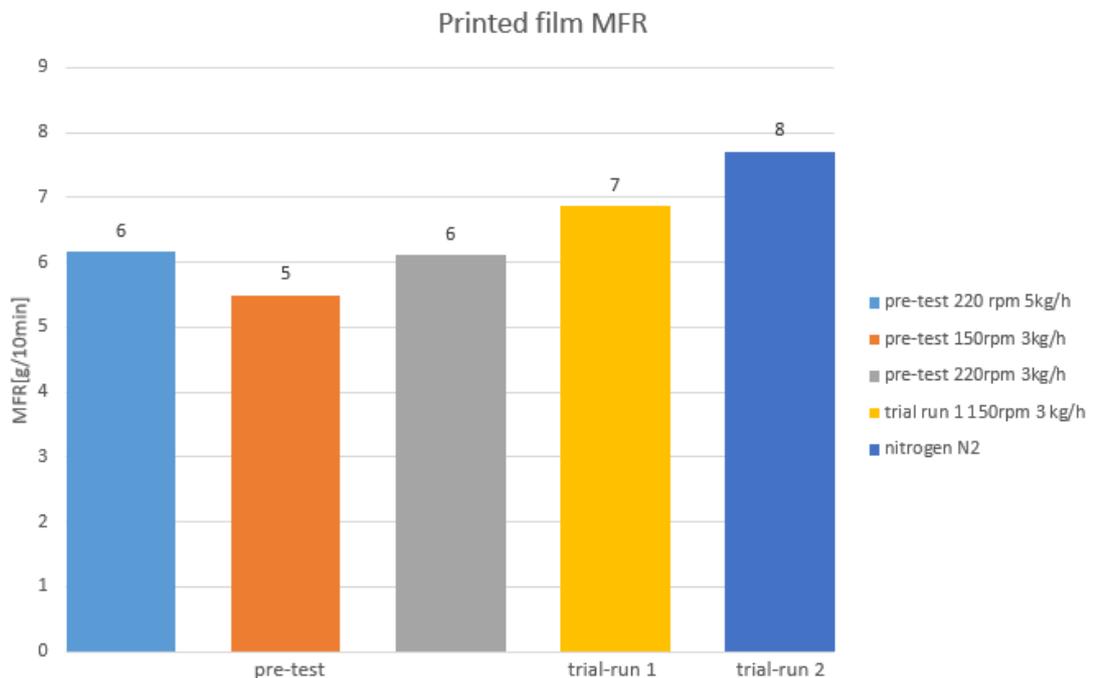


Figure 17. MFR results from all test-runs for the printed film flakes.

The melt mass-flow index for the natural polypropylene was around 8 g/10min when measured and for the pressed film flakes around 9 g/10min. Yet, a combination of the raw materials and re-extruded pellets has a lower MFR measurement.

An explanation for the results would be that the pressed films from which the MFR was measured was not homogenized, so the results are not 100% accurate. If the pressed films had first been melted down before doing the measurement, the polymer would have had a chance to become a homogenized mass and the melt mass-flow index could be different. The differences in the MFR can be related to operator variation. A conclusion is that the printed film flakes did not cause any major degradation of the polymer under the used test conditions.

From the graphs, it can be noted that the pre-test did have the values furthest from the reference and thus it could be considered the worst in quality from an MFR perspective. Based on the theory that has been discussed previously, it would be expected. The first test-run with screw #2 seems to have made the product better in terms of the MFR results with the result of the measurement being closer to 7 g/10min. The screw in question had been designed for recycled materials and has been used in previous experiments, so it would be expected that it would be better for the materials. It was also a gentler screw in terms of mixing, so it could be of interest to try to develop that screw further to be able to use it for polypropylene without it causing a breakdown of PP.

Even though there was no visible change in the color of the pellets, the final test-run seems to have been the most successful in terms of getting close to the MFR of the natural polypropylene that was used as a reference in this thesis. A combination of having modified the screws and the addition of the additives seems to have generated good results for the recyclates in the case of printed film polypropylene recycling. The MFR was close to the reference of 8 g/10min in all three different test points.

9.4.2 Metalized film test points

In Figure 18, the MFR results from all three test-runs for the metalized film flakes can be seen in graphs divided by test-run. Notable here is that there are more differences between the different test-runs than for the printed film flakes. The same natural polypropylene pellets were used. The MFR for the metalized film was measured in the same way as for the printed film.

As mentioned previously, the MFR for the metalized film flakes was around 6 g/10min, so a combination of the natural pellets and the film should be around 7 g/10min. That seems again not to be the case and the same assumption could be made here that the pressed films were not homogenized when measuring the MFR, which causes the values to shift. However, that should not make a big enough difference, so that the MFR would be close to the values obtained from the different test results.

Another possible explanation could be the aluminum that is present in the film and that it causes polypropylene to degrade more than the samples where aluminum is not present. Even though it is a small amount of metal, it could be enough to throw off the results.

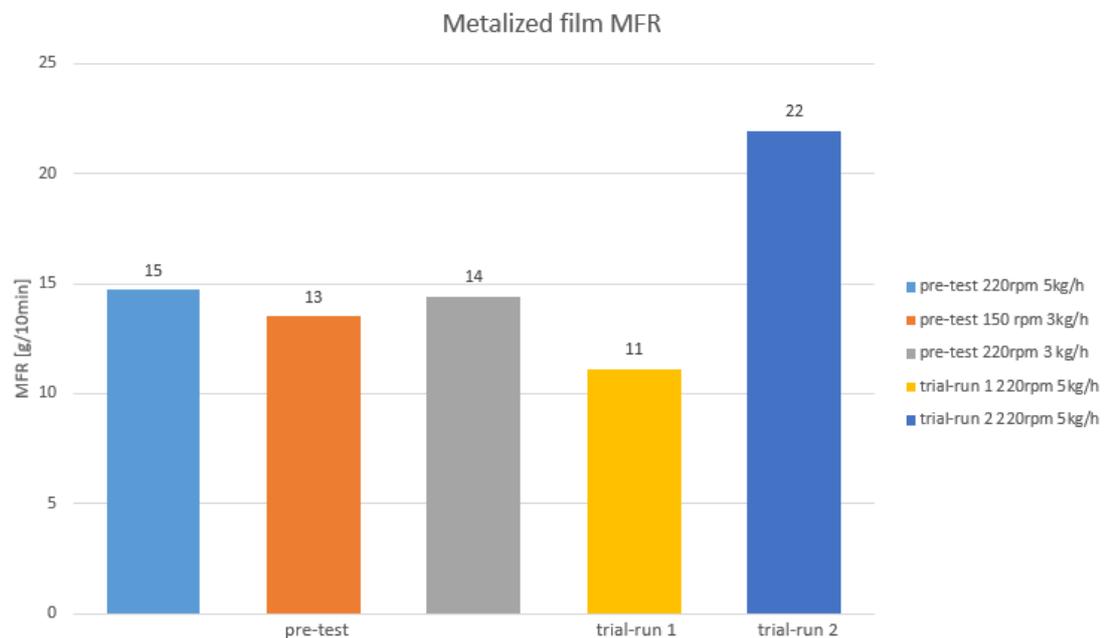


Figure 18. MFR results from all trial-runs for the metalized film flakes.

The change between the different screws seems to be quite big. The best result was achieved with the gentler screw in test-run 1 and the addition of nitrogen. In trial-run 2, the addition of nitrogen could not compensate for having an open barrel. The conclusion is made that the metalized film is more prone to degradation than the printed film. The worst results in terms of MFR was with the addition of nitrogen only. Some small breakdown of the polymer could be expected at test point 4 of test-run 2.

9.4.3 Control sample test points

The MFR results in graphs from the control test points can be seen in Figure 19 below.

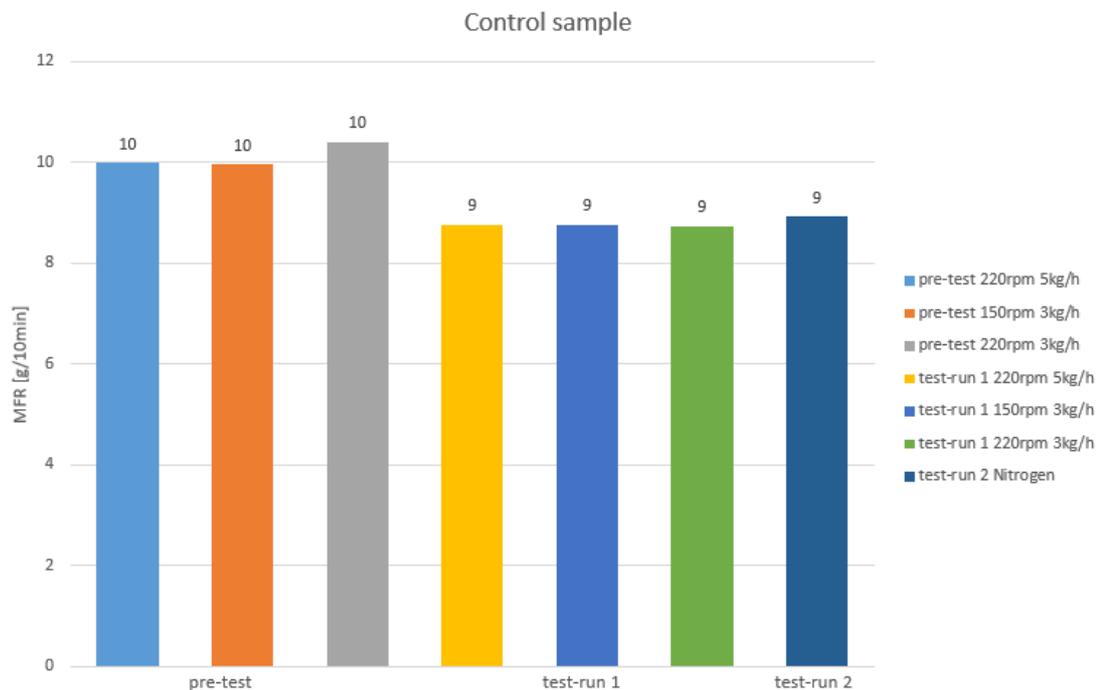


Figure 19. MFR for all test-runs for the control samples.

From the results from the different test-runs seen above, it seems that there is not a big difference between which screw is being used in terms of re-extruding the natural polypropylene pellets. The MFR is somewhat higher than for the natural material, which is at 8 g/10min. The change in operating conditions do not have a huge effect on the polymer in question and from a viscosity standpoint it does hold up.

Comparing the results from all test-runs, and with all three materials, the conclusion that can be drawn is that the films have a considerable effect on how the MFR results differ. The metalized film does have the biggest problems in terms of achieving a product that would be close to the original natural pellets as far as the MFR is concerned.

The only substantial deviation was during test-run 1, when the barrel was open and there was a nitrogen feed. The breakdown seems to be screw-related, and oxygen was present in larger quantities somewhere in order to cause the polymer to oxidize. In Figure 20 on the following page, the MFR result can be seen for the oxidized polymer. Comparing the results from that with the graphs above, it shows that there was severe degradation of the polymer with the MFR result as high as 389 g/10min.

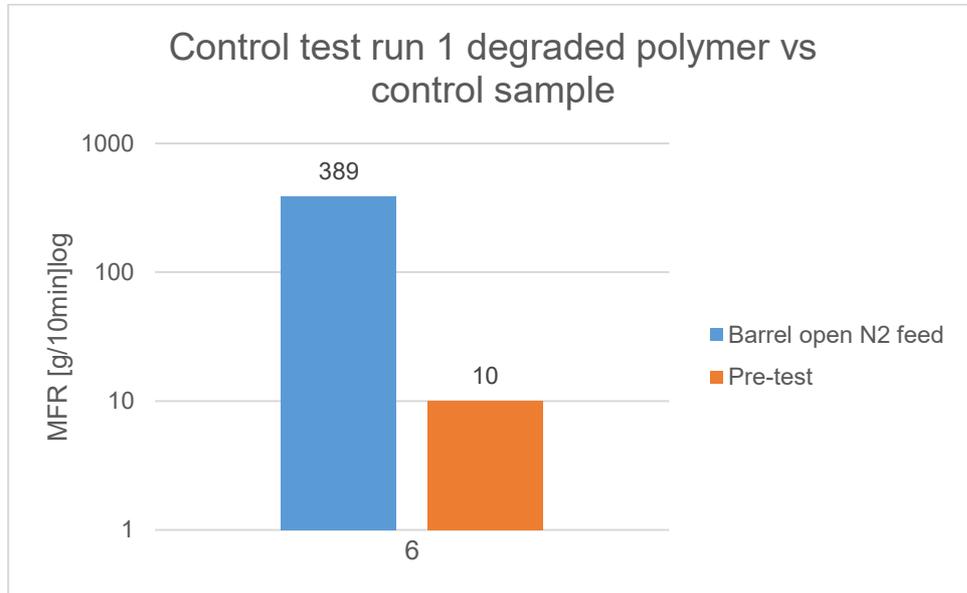


Figure 20. MFR result from test-run 1 test point 6.

9.5. Density

The density was measured on all three products from the pre-test. Three rectangle discs were pressed, and the density was measured from all three discs and an average value from the results was calculated. After pressing of the discs, it was noticed that the control sample had noticeable air pockets in the discs. This is due to the form of the re-extruded pellets. There was a hole right through the middle of each pellet. The holes appear due to the machinery used in the test-runs. When pressing the pellets into the discs, the gas in the air holes did not have anywhere to escape and it then caused the air pockets to appear in them. In Figure 21, the air pockets can be seen in the discs.



Figure 21. The pressed discs for measuring the density of the polymer with air pockets.

By having these air pockets in the discs, it was not possible to achieve an accurate reading of the density of the different polymer blends. For both the pellets made from printed and metalized film there was no visible air pockets due to the coloring of the pellets, but when measured they showed the same signs of air pockets with the density changing from measurement point to point. It can be assumed that there were air pockets present in these discs as well.

The measured densities can be seen in Figure 22 as a graph below. It is notable that the densities presented here are only approximations and do not represent the real values for the density of the different polymers.

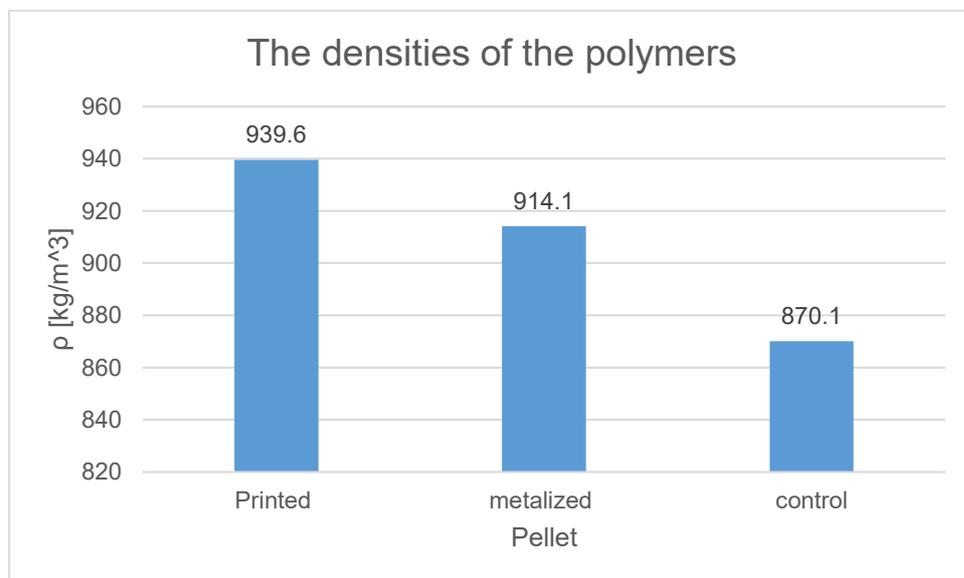


Figure 22. The densities of the different pellets from the pre-test.

As can be seen in the graph, the highest density is for the printed film followed by the metalized film pellet and the lowest is the control sample. When comparing these values with the density of a polypropylene homopolymer cast film grade with the typical density of 905 kg/m³, the control sample has a lower density than that of the raw material. This also shows that the results obtained from the density analysis are only an approximation of the density.

9.6. Cast film extrusion

For the pre-test and for test-run 2, there were films made to see if it was possible to use the pellets to make new films. For the running of the films, samples of all three materials were used from both the pre-test and test-run 2. The samples used were test point 1, 4 and 7 from the pre-test and test points 3, 6 and 7 from test-run 2.

The extrusion of the films was done by mixing the samples with 50% of the same raw material that was used in the pelletization of the recyclates. The extrusion was done using a Collin 25 cast film extruder. In Table 14, the results from the test-runs can be seen for the cast film made from the samples from the pre-test.

Table 14. Summarized cast film extrusion of the pre-test pellets.

Material	Test point	Melt temp [°C]	Pressure [bar]	Roller temp [°C]	Thickness [µm]	Processability	Gels	Appearance
Printed pellets	1	250	17-21	50	45-58	+	-	greenish tint
Metalized Pellets	4	250	17-21	59	44-60	o	-	silver/grey
Control pellets	7	250	17-21	51	45-58	++	o	clear

From the table, it can be seen that the temperature of the chill rolls varied somewhat between the different test points. The adjustments were made in order to improve the film quality. The thickness of the film was not uniform and had some variations depending on where the film had been measured. The variations in thickness could be explained by the settings of the extruder or the processability of the pellets.

The scale in the table for the processability and gels goes from best to worst: ++, +, o, - and --.

In Figure 23 on the following page, the rolls of extruded cast film made from the pellets from the pre-test can be seen, from left to right the control film, film made from printed extruded pellets, and film from metalized recycled pellets.



Figure 23. Rolls of cast film from pellets from the pre-test.

The processability of the various materials also differs from each other, with the control being the best in terms of processability and the metalized pellets the hardest to process. A decent amount of inhomogeneity could be seen in the films, mostly in the printed and metalized films as pigment agglomerates.

Table 15. Summary of the cast film extrusion of the material from test-run 2.

Material	Test point	Melt temp [°C]	Pressure [bar]	Roller temp [°C]	Thickness [µm]	Processability	Gels	Appearance
Printed pellets	3	249	17	49	45-63	+	-	greenish tint
Metalized Pellets	6	249	17	50	46-61	+	-	silver/grey
Control pellets	7	249	17	48	46-63	++	o	clear

In Table 15, a summary of the cast film extrusion process from the pellets extruded in test-run 2 can be seen. As with the previous processing, the same slight changes in roller temperature can be seen, even though the changes are not as considerable as in the extrusion prior. The thickness varies here as well, both between the different raw materials and the two different test-runs.

The processability of the metalized pellet has increased slightly, while the printed film and control have the same processability as before. The same amount of inhomogeneities can be seen in these samples as previously.

In both film extrusions, the coloring is the same as before, without any big visible changes. The films were used in color analysis to be able to determine if there were any changes in the color of the different pellets compared with each other.

In Figure 24, the rolls of polymer film made from the recycled pellet from test-run 2 can be seen, where the roll on the left is the one made from the control sample, the one in the middle from the metalized film, and the one the right from the printed film.



Figure 24. Rolls of cast film extruded films from the pellets form test-run 2.

9.6.1 Color analysis

In Table 16, the values from the CIELAB analysis of the printed and metalized re-extruded films can be seen, where L^* is the difference in darkness and lightness. If the value is positive, the sample is lighter and if it is negative, it is darker. a^* is the difference in the red/green spectrum. A positive value indicates redder and negative greener. b^* indicates the difference between yellow and blue, the positive value more yellow and negative blue.

Table 16. The results from the color analysis of the extruded films. Upper metalized film and lower printed film.

Color analysis metalized film			
Film	L^*	a^*	b^*
pre-test	13.67	-0.66	0.36
test run 2	14.17	-0.65	0.69

Color analysis printed film			
Film	L^*	a^*	b^*
pre-test	4	-20.90	11.77
test run 2	4	-21.31	11.28

From the values seen in the table for the metalized film, there seems not to be a big difference between the two samples. The variations between the two samples may be attributed to measurement error. By using formula 1 described in chapter 9.4, the color difference between two different samples can be calculated. By inserting the values into formula (1), the formula will become:

$$\Delta E^* = \sqrt{(14.17 - 13.67)^2 + (-0.65 + 0.66)^2 + (0.69 - 0.36)^2} \quad (2)$$

Calculating the formula, the value the color difference ΔE^* for the metalized film

$$\Delta E^* = 0.68$$

The value indicates a small change in the color but would still be within experimental error.

Having a look at the printed film values from the analysis, the trend continues with no huge differences between the two samples able to be seen. Using the same formula as for the metalized film, the color difference ΔE^* can be calculated by inserting the values from Table 17 into equation 1. The equation becomes:

$$\Delta E^* = \sqrt{(4 - 4)^2 + (-21.31 + 20.90)^2 + (11.28 - 11.77)^2} \quad (3)$$

Solving equation 3 gives:

$$\Delta E^* = 0.64$$

Again, a small difference in color can be seen, but not a significant one, and it can again be discussed if the deviation is from a measurement error.

9.7 Discussion of the results

Based on the test-runs and the results from the different analyses, it can be concluded that both printed and metalized polypropylene films are recyclable. The pellets can be used again to manufacture film, despite the gels and specs that can be found in the re-extruded films.

The re-extruded films have a slightly worse strength than those made from the natural pellets used as a control. As a part of the visual inspection, the strength was tested by ripping it by hand and it was able to withstand some force.

The recyclates, including the metalized film, should be further researched in the hope of finding a solution in the product quality. The metal in the film has led to some instability with the extrusion process as well as when casting the films. When ripping the film, it was noticed that the product was quite low quality, and one did not need much strength to rip the film. It seems that the aluminum in the film is degrading the polypropylene, and the removal of aluminum should be something to focus on in the future in order to be able to obtain a recyclate with better quality.

By starting the research on a small scale, the different methods can be tested before the development of a large-scale process. There is also the benefit of having less raw material going to waste if something goes wrong with the tests. Clean up is also easier to do in a small-scale process. The challenges in scaling up processes is that the parameters used in a smaller scale would somehow have to be fitted to work with a bigger system. Some graphs or formulas should be able to be adjusted in order to

find the right parameters for the process going forward, and one should also find out what the small-scale tests would correlate to on a larger extruder, for example.

A further challenge that should be discussed is the screws being contaminated by coloring and the cleaning of the screws. When these are present, the cleaning of the screws is a long process, and some raw material is going to waste during the flushing process.

10. Conclusions

The harms of polymers have been widely discussed in the media during recent years. This is due to the growing amount of polymers used and thrown away, the littering by people and, to be frank, the lack of knowledge from different sources. Recycling the polymers and making new products from the recyclates is a hot topic and is widely researched today. Being able to recycle plastics will be beneficial for the environment as well as companies and everyone else. Through recycling, a smaller amount of trash would be dumped into landfills and into the water streams.

Viable options for recycling will also have to be further researched, so that they are more economical and energy efficient. Some steps have been taken, but there is still a long way to go in order to reach the goals set by the EU, for example.

In this thesis, the goals of the EU were presented and discussed. How the raw material is made, what the challenges of recycling are, and some possible solutions to the recycling process have also been presented in the literature part of the thesis.

In the experimental part, two different films were used in the experiments. These are a printed film and a metalized film. Both films underwent the same preparation process and were extruded under similar conditions. Out of these two, the easier one to recycle is the printed film, even though the color in the print leaves contaminants in the barrel. Some good progress has been made in the quality of the product, but there is a long way to go still. Due to the huge variations in MFR, the metalized film has been deemed more difficult to recycle and the quality of the polymer as well as the film is not as good as the printed film. It should be noted that there are different kinds of ink types and only one has been used in the experiments.

The toolbox created is useful as a starting point for the recycling of the films. It has been somewhat limited due to the test-run capabilities and should be developed further. For different types of films and inks, the methods presented in this thesis can be used to determine if the same operating conditions can be applied to other films as well.

Further research would still have to be conducted for both films, in order to neutralize the color of the print and for the aluminum to be removed. However, as mentioned in the previous chapter, this will be a good starting point in the development of the toolbox for the recycling process. By continuous research and development in the field, the challenges should be solved someday soon.

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